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PROPELLANES—I

TRICYCLIC COMPOUNDS CONJOINED IN A CARBON–CARBON SINGLE BOND

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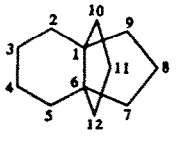
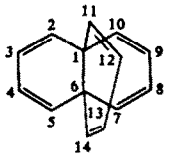
Abstract—The syntheses of a number of carbocyclic, oxa, and azapropellanes are described. Fragmentation paths of these compounds on electron impact are discussed as well as their NMR spectra and other physical properties.

ONLY very recently have concerted efforts been made to design tricyclic systems conjoined in a carbon–carbon single bond.[1,2] Although such compounds have been known, they were not prepared primarily because of interest in designing such systems.[3]

Nomenclature. The rules of nomenclature[4] used for tricyclic systems require lengthy names and as many as six numerals to define even such a simple structure as **1** which would be called tricyclo[4,3,3,$0^{1,6}$]dodecane. Based on examination of a model



1



2

of **2** the trivial name "propellane" has been suggested for such systems. If we were to extend the carbon–carbon single bond which is common to all three rings of **2** by a notional rod, we should have an object very reminiscent of a propellor. The nomenclature used herein, with the blessing of Dr. L. C. Cross,[5] would name compound **1** [4.3.3] propellane and **2** would be [4.4.4] propella-2,4,7,9,11,13-hexaene. This system gives the same locants as the tricycloalkane nomenclature. The system is numbered commencing with one of the bridgehead atoms, proceeding by the longest direct route

[1] G. Snatzke and G. Zanati, *Liebigs Ann.* **684**, 62 (1965).

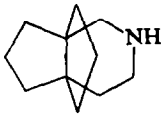
[2] F. Nerdel, K. Janowsky and D. Frank, *Tetrahedron Letters* 2979 (1965).

[3] [a]J. W. Rowe, A. Melera, D. Arigoni, O. Jeger and L. Ruzicka, *Helv. Chim. Acta* **40**, 1 (1957); [b]H. Gunther and H. Hinrichs, *Tetrahedron Letters* 787 (1966); [c]R. L. Cargill, M. E. Beckham, A. E. Siebert and J. Dorn, *J. Org. Chem.* **30**, 3647 (1965); [d]E. H. W. Böhme, Z. Valenta and K. Wiesner, *Tetrahedron Letters* 2441 (1965); [e]G. Wittig and J. Weinlich, *Chem. Ber.* **98**, 471 (1965); [f]E. Vogel, M. Maier and J. Eimer, *Tetrahedron Letters* 655 (1966); [g]J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.* **84**, 1257 (1962).

[4] *Chem. Soc. Handbook*, IUPAC rules A–32, p.76.

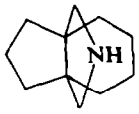
L. C. Cross, letter dated 13th April, 1966. We are grateful to Dr. Cross for his kindness in making concrete suggestions which ensure the consistency of the names used herein.

to the second bridgehead atom, returning to the first bridgehead atom by the next longest route, and finally proceeding to the second bridgehead atom by the remaining shortest route (not counting the common atom-to-atom bond). The name of a heterocyclic propellane may be formed by prefixing oxa, aza, etc., (replacement nomenclature) to that of the corresponding carbocyclic compound. If a unique numbering is not produced by following the above procedures, the lowest possible numbers, consistent with the above, will be given the hetero atoms. If a choice still exists the principles of I.U.P.A.C. rule B–1[6] will apply. Examples **3**, **4**, **5** and those in the experimental section will suffice to explain the system.



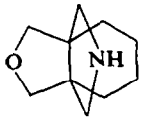
3

3-aza [4,3,3] propellane, *not* 4-aza [4,3,3] propellane



4

8-aza [4,3,3] propellane, *not* 11-aza [4,3,3] propellane



5

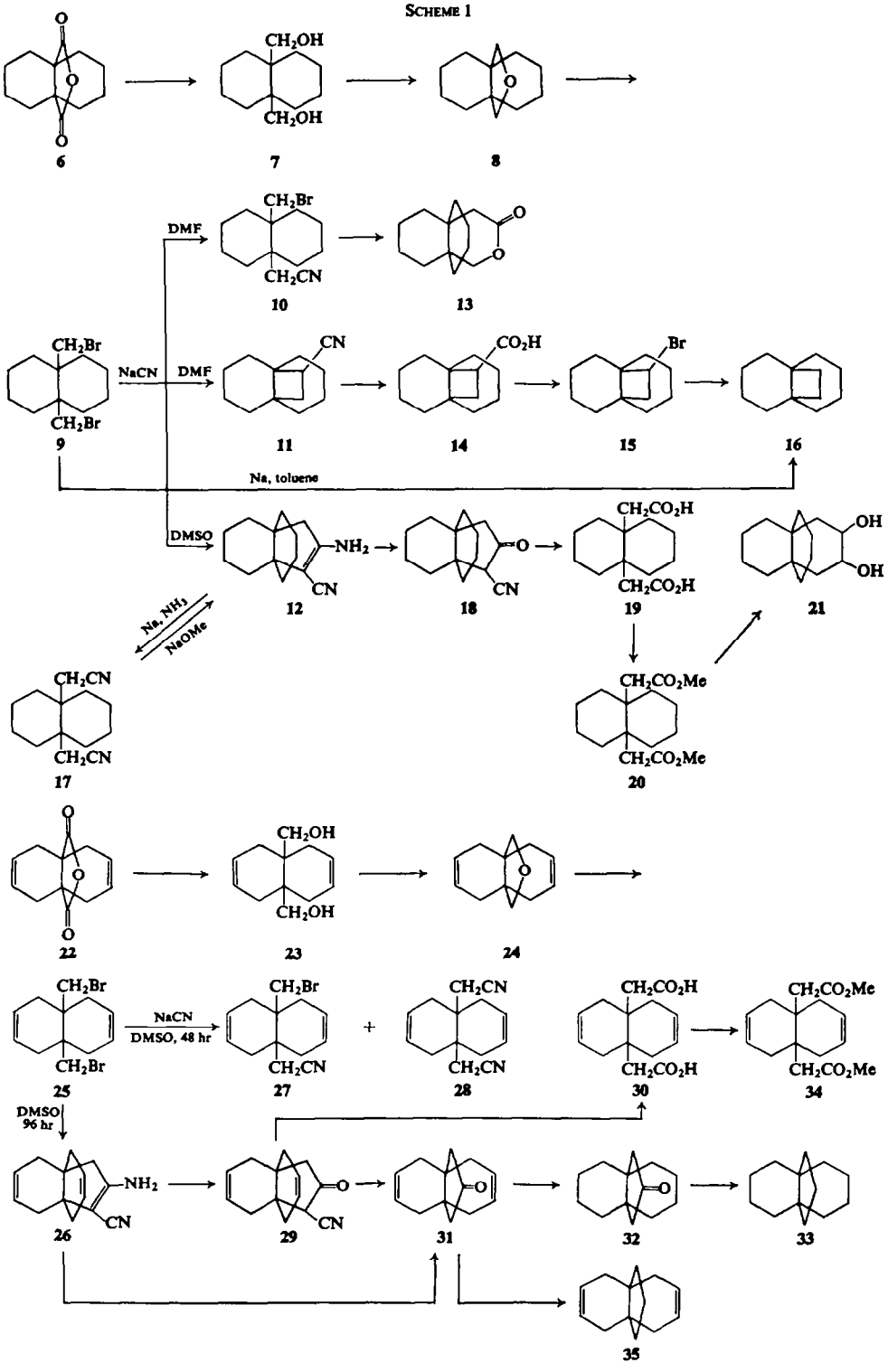
8-oxa-11-aza [4,3,3] propellane, *not* 11-oxa-8-aza [4,3,3] propellane

Synthesis of propellanes. The alicyclic propellanes studied arose from common intermediates (Scheme 1). Thus *cis*-bisbromomethyldecalin (**9**) obtained by treating 12-oxa [4,4,3] propellane **8** with triphenylphosphine dibromide served as the starting point for compounds having the [4.4.2], [4.4.3] and [4.4.4] propellane skeletons. Treatment of this dibromide with sodium cyanide in dimethylformamide led to [4,4,2] propellane **16** via the 11-cyano-derivative **11**, the 11-carboxylic acid **14**, and the 11-bromo derivative **15**. Alternatively, treatment of the dibromide with sodium in toluene gave **16** directly. However, when the same dibromide **9** was treated with sodium cyanide in dimethylsulfoxide, the aminonitrile **12** was formed. It is clear that this reaction course proceeded through the intermediacy of the dinitrile **17**, although this substance could neither be isolated along with the products **10**, **11**, **12**, nor could its coexistence be demonstrated by TLC. Yet, the formation of both **11** and **12** from **10** and **17** respectively, is readily explained (Scheme 2). These cyclizations occur under the influence of the weakly basic cyanide ion and are not directly comparable to, e.g. the Ziegler cyclization of substituted adiponitriles.[7] The aminonitrile **12** can be converted into the dinitrile **17** by treatment with sodium in liquid ammonia. The reverse course occurs when **17** is treated with sodium methoxide; cyclization leads again to **12**. Acidic hydrolysis of the vinyl amine function in **12** gives the ketonitrile **18**. Alkaline

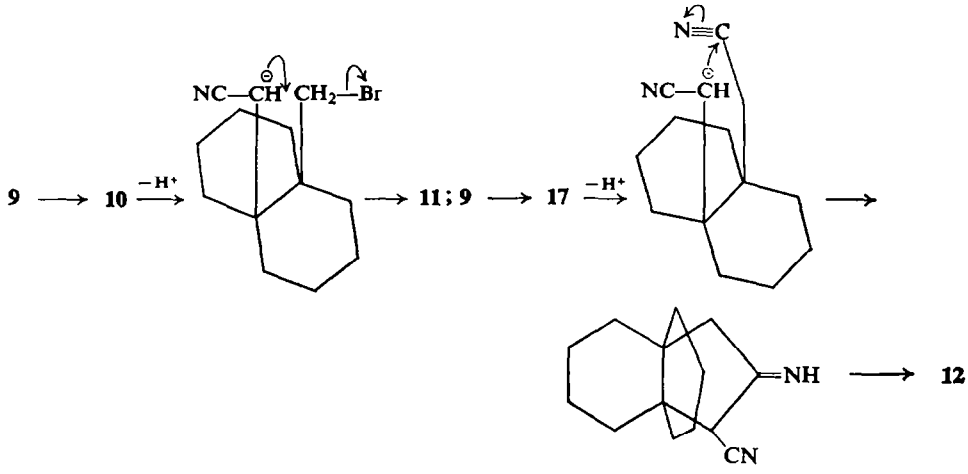
[6] Ref. 4, p. 90.

[7] J. J. Bloomfield and P. V. Fennessey, *Tetrahedron Letters* 2273 (1964).

SCHEME 1


6
7
8
DMF
10
13
NaCN
DMF
9
11
14
15
16
Na, toluene
DMSO
12
18
19
21
Na, NH3
NaOMe
17
20
22
23
24
25
NaCN
DMSO, 48 hr
27
28
30
34
DMSO
96 hr
26
29
31
32
33
35

SCHEME 2



cleavage of the α–β bond in the β-ketonitrile, with concurrent hydrolysis of the nitrile group, yields the diacid **19**, whose dimethyl ester **20** affords, under the conditions of the acyloin condensation, a derivative **21** of the [4.4.4] propellane ring system.

It turned out that the most efficacious approach to [4.4.3] propellane **33** was through the dienic analog **25**, of the dibromide **9**. In this case a higher relative yield of the dienic analog **26**, of the aminonitrile **12** was obtained. Acidic hydrolysis of the vinylamine **26** gave the β-ketonitrile **29**, which on alkaline treatment gave the diacid **30**. Stringent acidic hydrolysis of either **26** or **29** led to the dienic ketone **31**, whilst treatment of the diacid **30** with acetic anhydride led simply to the acid anhydride and not to **31** (compare **54**→**58**, scheme 4). Compound **31** led to the dienic propellane **35**.

Catalytic reduction of **31** gave the saturated ketone **32** which upon subjection to Huang-Minlon reduction gave the ultimate hydrocarbon product of this reaction sequence (Scheme 1), [4.4.3] propellane **33**.

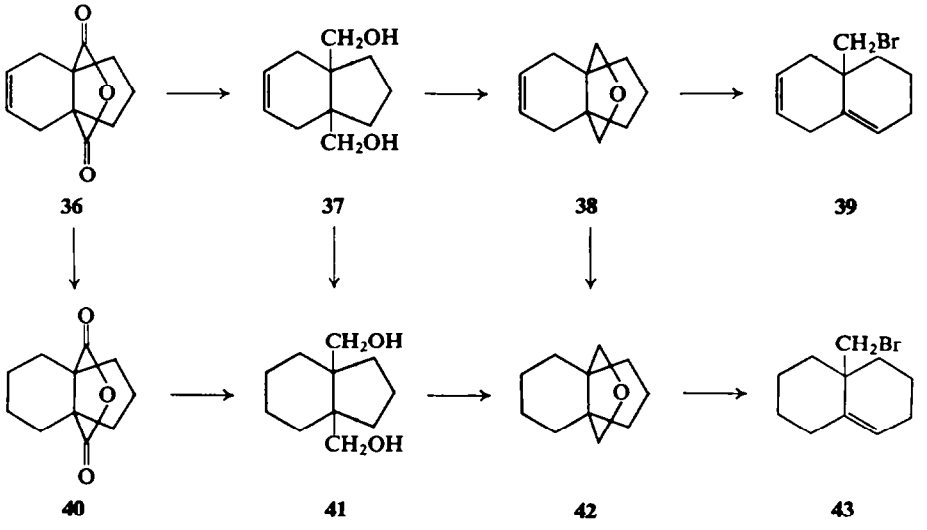
Since the dibromides **9** and **25** are the cardinal intermediates in these synthetic sequences and these were formed from the corresponding ethers **8** and **24**, respectively, it is of interest to note that both **38**, and **42**, yield on treatment with triphenylphosphine dibromide, not the corresponding dibromides but the rearranged monobromides **39** and **43**, respectively (Scheme 3).

Another point which should be stated explicitly is that compounds employed in the above synthetic sequences, e.g. **10**, **17** and **28**, contain angular groups which form part of substituted neopentyl systems. Nonetheless, these groups are sterically situated (*cis*) in a relatively inflexible environment which affords with relative ease cyclizations to yield **11**, **12** and **26** respectively.

It is therefore not at all surprising that "weird" reactions have unexpectedly been discovered[8] in similarly constituted systems.

[8] An acyloin condensation has been reported on the dimethyl ester of **22**, leading in 89–94% yield to a propellane containing the two dienic six-membered rings of the starting material and a four-membered cyclic ketol: J. J. Bloomfield and J. R. Smiley Irelan, *Abstr. of papers*, 151*st meeting Amer. Chem. Soc.*, Pittsburgh, March 28-31 (1966); *Div. of Org. Chem. abstr.* no. K57.

SCHEME 3



The routes to a number of diazapropellanes are summarized in Scheme 4. The Diels-Alder adduct **44** of butadiene and tetracyanoethylene[9] was converted by an improved procedure[10] over that reported,[9] through the use of alkali, into the *cis*-diimide **45**. Methylation gave the diimide **46** which was reduced to the substituted diaza [4,3,3] propellane **51**. When the reduction of the double bond in **46** (to give **52**) preceded LAH reduction, the saturated diaza [4,3,3] propellane **53** was obtained.

It was hoped that a successful route might be found to a number of interesting heterocyclic compounds containing the skeletal structure of **49**, substituted in both angular positions. For this reason the diene **48** was obtained from the dibromide **47**, but unfortunately ozonolysis of **48** did not lead to the hoped for isolation, even at low temperature, of a β-imidodiacid (**49**, substituted in both angular positions by CO_2H). Addition of ether to the reaction mixture immediately after ozonolysis (before the oxidative decomposition step), led to precipitation of **49** indicating that four carbon atoms were lost already during the ozonization step. An alternative synthetic sequence was therefore sought. Ozonolysis of **46** gave a diacid **54**. This was then converted into the diamine **55** which so far has not been successfully cyclized to a propellane. Nor have the dichlorodiimide **56**, not its reduction product **57** led thus far to propellanes.

The diacid **54** gave the ketonic propellane **58** upon boiling in acetic anhydride. Its thioketal **61**, upon treatment with Raney nickel gave the diimide **59** which was reduced with diborane to the diaza [3,3,3] propellane **63**. Compound **59** could alternatively be obtained by catalytic hydrogenolysis of **58** accompanied by the alcohol **60**.

UV data. Comparison of the UV data in Table 5 for various propellanes containing N-methylimide rings shows that there is reasonable interannular orbital overlap

[9] W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Amer. Chem. Soc.* **80**, 2783 (1958).
[10] S. Welner and D. Ginsburg, *Israel J. Chem.* in press.

SCHEME 4

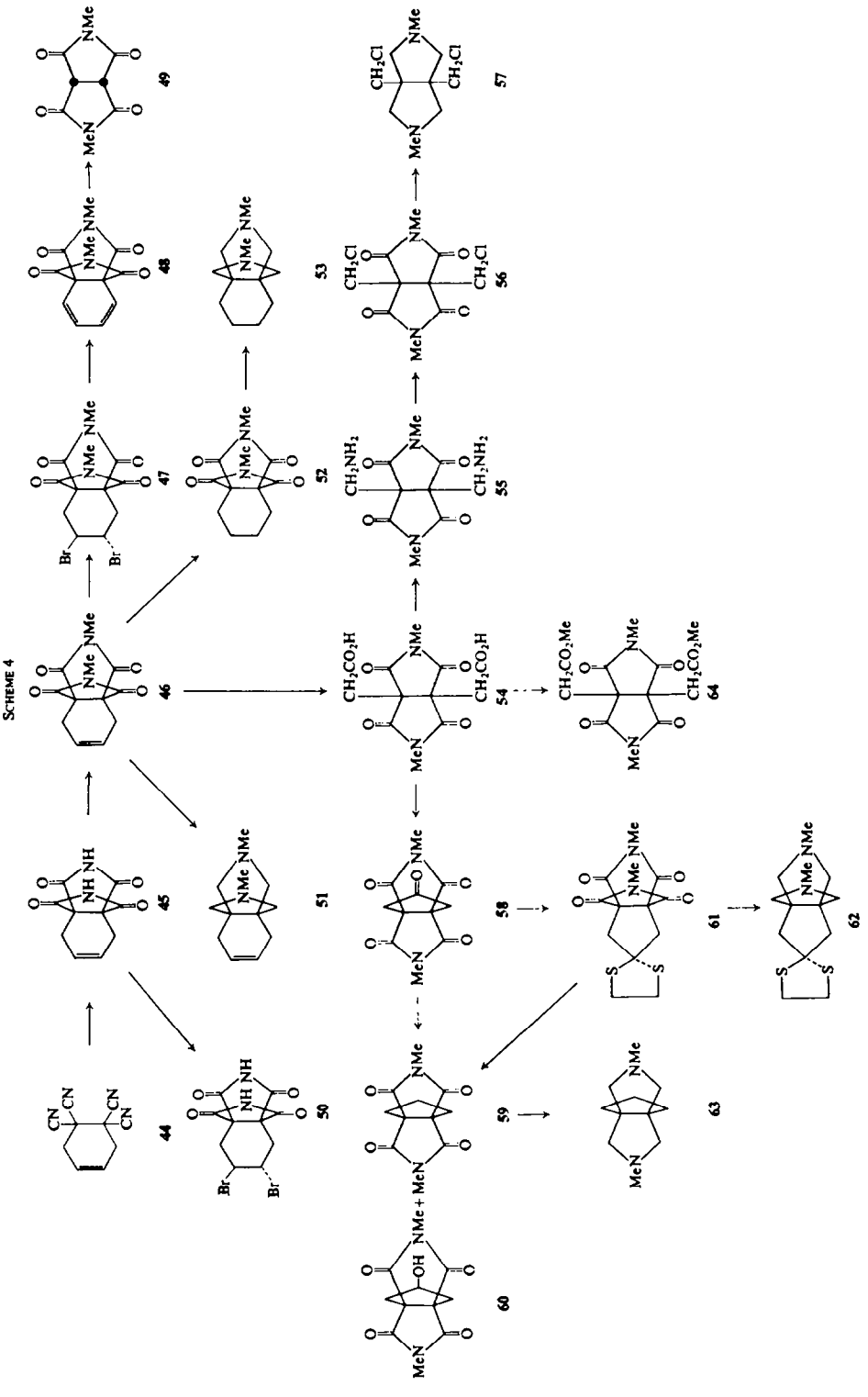


Table 5. UV ABSORPTION DATA (IN MeCN SOLUTION)

(Left hand column = λ_{max} (mμ); right hand column = ϵ_{max}).

For structural formulae see Schemes 4 and 5.

59		**74**		**52**		**70**		**46**		**69**		**58**		**73**		**48**		**49**	
246	472	250	162	246	583	248	206	246	550	248	216	246	542	250	262	243	1380	243	410
259	419	259 (sh)	106	259	450	258 (sh)	139	259	453	258 (sh)	152	259	535	260 (sh)	212	252	1920	256	418
268	422			268	464			268	490			268	570			264 (sh)	1820	265	392
												291 (sh)	11	292 (sh)	30	270	1830		
												304 (sh)	8	305 (sh)	20	286(sh)	1100		
												314 (sh)	3						

between the absorbing systems in those substances which contain two such rings.* This is obvious from a comparison of the extinction data in the pairs **59–74**, **52–70**, **46–69**, and the additional absorption maximum at 268mμ in **59**, **52**, and **46**, as well as in **58** and **48**. In **49**, a *cis*-bicyclic compound, the corresponding band appears at 265mμ, since this system is somewhat less rigid than the comparable tricyclic systems.

It is also apparent from a comparison of **59**, **52**, and **46**, that there is no interaction between the two imide rings and the double bond in **46**, whilst there is a definite interaction between these rings and the diene system in **48**, whose coplanarity leaves something to be desired.†

On the other hand, although as stated above, interaction is evident between the two imide rings in **59** (cf. **74**), there is no evidence from the UV data for interaction between the imide rings in **58** or in **73** and their respective ketonic functions.

pK Measurements. It is clear *a priori* that in propellanes having two amine functions in two different rings there will be electrostatic interaction between the two basic nitrogen atoms. This is, indeed, evident from pK measurements made by potentiometric titrations of **53**, **51** and **63**,‡ where the values for pK_{a1} and pK_{a2} were found to be 6·6 and 9·3; 5·8 and 8·5; 6·2 and 9·0 respectively. §

The routes towards monoazapropellanes are summarized in Scheme 5. When **6** was boiled with concentrated ammonium hydroxide, the imide **65** was obtained. Its methylation followed by LAH reduction gave the substituted aza [4,4,3] propellane **66**. On the other hand, the adduct **36** of cyclopentane 1,2-dicarboxylic acid anhydride with butadiene was similarly converted into the imide **67** whose double bond was reduced, yielding **68**. Methylation of **68** gave **70** which was reduced with LAH to the aza [4,3,3] propellane **71**.

Reduction of **73** with sodium borohydride afforded the intramolecularly hydrogen-bonded epimer **76** of the two theoretically possible alcoholic reduction products **76** and **77**. Since **77** could not be obtained in easy isolable form by reduction of **73** under a variety of reduction conditions (although it accompanied in one experiment the major reduction product **74** when catalytic reduction was carried out with Adams' catalyst in glacial acetic acid and accompanied **76** as a minor reduction product of lithium aluminum tri-t-butoxyhydride), this epimer was obtained pure by inversion of the tosylate of **76**.

The reduction of the ketone **73** was carried out many times. In all but one experiment complete hydrogenolysis occurred and **74** was isolated . Even when the hydrogenation was interrupted after uptake of one mole of hydrogen, only the starting material **73** and the fully hydrogenolyzed product **74** could be detected, even by TLC. Only in one case,

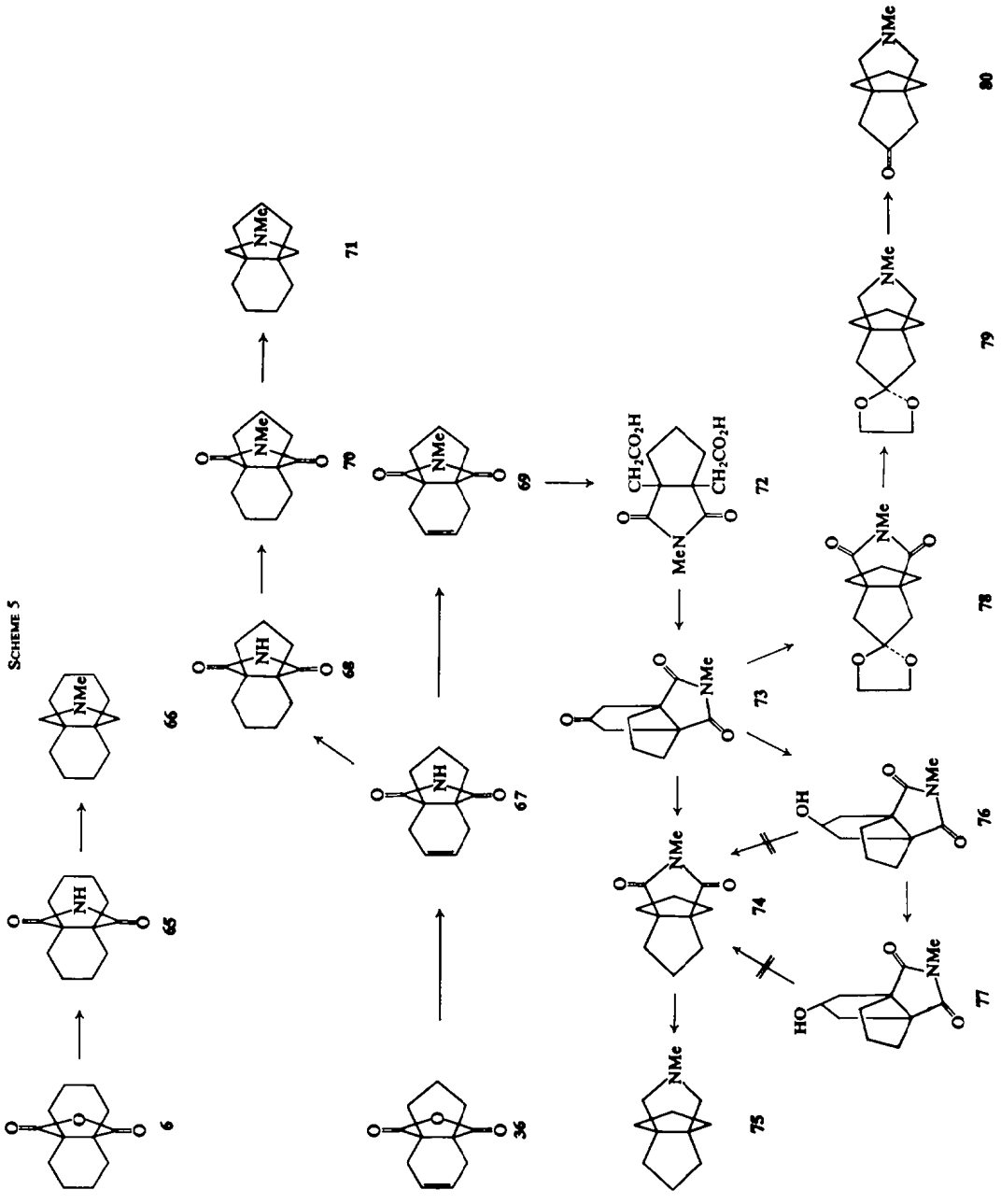
* For N-methylsuccinimide itself $\lambda\lambda_{max}$ = 222, 230-255 (sh), log $\epsilon\epsilon$ = 2·6, 2·0, in MeOH (F. Micheel and H. Albers, *Liebigs Ann.* **581**, 225 (1953)). For those substances we measured also in methanol we obtained the same maxima as found in acetonitrile. We could not observe the maximum at 222 mμ in acetonitrile but the long shoulder also appears at 230-255 mμ.

† For cyclohexadiene, λ_{max} = 256 mμ, log ϵ = 3·9, in hexane (V. Henri and L. W. Pickett, *J. Chem. Phys.* **7**, 439 (1939).

‡ The diamine (0·1 mmole) was dissolved in a 50% molar excess of 0·1N $HClO_4$ and backtitrated with 0·1N NaOH. Using this procedure for titration of glycine ethyl ester, pK_a 7·75 (A. Neuberger, *Proc. Roy. Soc.* **A158**, 68 (1937)) gave pK_a 7·4 so that the figures stated in the text are reasonably accurate.

§ For N-methylpyrrolidine, pK_a = 10·17 (L. C. Craig and R. M. Hixon, *J. Amer. Chem. Soc.* **53**, 4367 (1931).

SCHEME 5

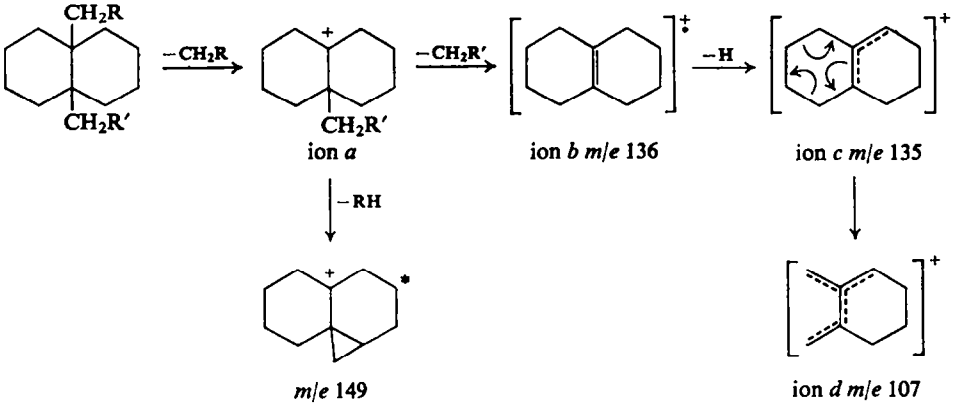

NMe
NH
O
6
65
66
68
70
71
36
67
69
72
73
74
75
76
77
78
79
80
CH2CO2H
MeN
OH
HO

after apparent uptake of two moles of hydrogen, some of the non-hydrogen-bonded alcohol **77**, was detected. On the other hand, many attempts at submitting both **76** and **77** for long periods of time to further potential hydrogenolysis under apparently the same hydrogenolytic conditions used for the interconversion **73**→**74** did not cause any observable hydrogenolysis and each of the alcohols was isolated unchanged in essentially quantitative yield.

We are at a loss to explain these facts. They bring to mind the Clemmensen reduction[11] in which many cases are known of hydrogenolysis of ketones to give hydrocarbons without the intermediacy of the alcohol oxidation state (in which zinc is the metal used), the catalytic hydrogenolysis of ketones in the α-position with respect to an aromatic ring[12] (where palladium is the metal used) and the analogous hydrogenolysis (using platinum) of ketones in the α-position to a ferrocene nucleus.[13] It may be that the correct explanation for all of these facts involves the formation of a carbonyl-metal complex followed by hydrogenolysis of a carbon-O-metal bond rather than that of a carbon-OH bond. But attractive though this explanation may be, it is an unproved hypothesis rather than proof.

Fragmentation patterns on electron impact.[14] In the bis-substituted *cis*-decalins reported in this paper, a simple fragmentation path, summarized in Scheme 6, may be discerned.

SCHEME 6



The diester **20** exhibits also the expected peaks resulting from α-cleavage[15] (Experimental section).

[4,4,2] Propellanes exhibit cleavage of the four membered ring, involving loss of ethylene, acrylonitrile and acrylic acid from **16**, **11** and **14**, respectively, leading to ion *b*, *m/e* 136 and to further fragmentation as described above.

* J. Karliner, H. Budzikiewicz and C. Djerassi, *J. Org. Chem.* **31**, 710 (1966).

[11] E. L. Martin, *Organic Reactions* Vol. 1; chap 7; p. 155. Wiley, New York (1947).

[12] W. H. Hartung, *Organic Reactions*, Vol. 7; p. 292. Wiley, New York (1953).

[13] M. Rosenblum and R. B. Woodward, *J. Amer. Chem. Soc.* **80**, 5443 (1958).

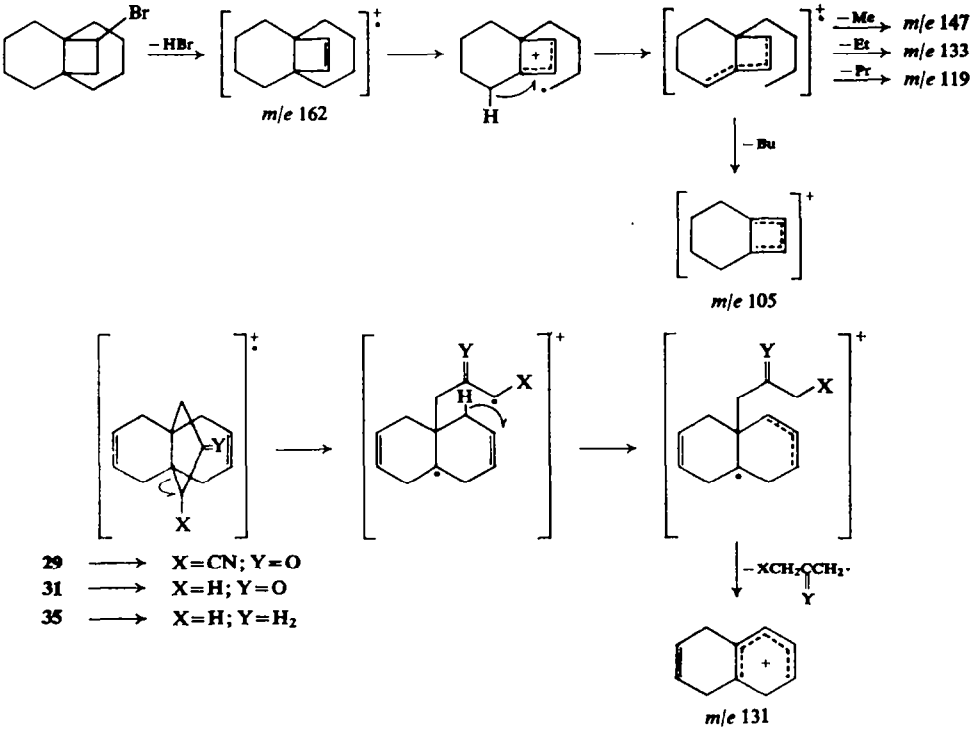
[14] We are grateful to Dr. A. Mandelbaum for the mass spectra and critical discussion.

[15] K. Biemann, *Mass Spectrometry, Organic Chemical Applications* p. 101. McGraw-Hill, New York

The unsaturated bis substituted *cis*-decalins gave ions analogous to those described in Scheme 6, except, of course, for the appropriate decrease in mass units. Their spectra, not surprisingly, also exhibit ions resulting from a retro Diels-Alder cleavage (loss of 54 mass units, equivalent to butadiene).

In propellanes containing a C=C bond or an incipient bond of this type (e.g. from dehydrobromination in **15**), cleavage of a bond α- to the bridgehead occurs as exemplified in Scheme 7.

SCHEME 7



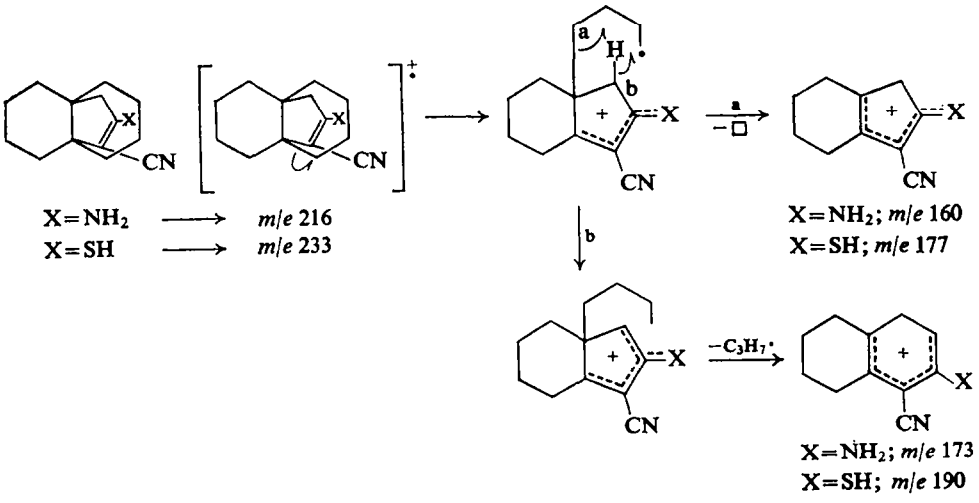
In these cases the cleavage is followed by hydrogen migration (probably that of an allylic hydrogen) and a second cleavage of the aliphatic chain occurs at the bond α- to the second bridgehead. The driving force may be the formation of a tertiary carbonium ion which is stabilized by extension of the conjugated system involved.

In addition to the path described in Scheme 7, compounds **29**, **31** and **35** undergo fragmentation via the more prosaic retro Diels-Alder path. **26** which is a (vinyl) amino nitrile, rather than an imino-nitrile does not give the ion, *m/e* 131, as above, due to its amino structure. The retro Diels-Alder path is, however, exhibited by this compound, upon electron impact.

In the compounds whose fragmentations are described in Scheme 8, the unsaturation exists in the five-membered ring, which upon the loss of an electron, it is supposed that the positive charge will reside in this region. Again, as above, the bond α- to the bridgehead in one of the saturated six-membered rings is cleaved, with extension of conjugation. But in this case, surprisingly, cleavage of the bond α- to the second bridgehead

occurs without hydrogen migration, leading to the ions, *m/e* 160 and *m/e* 177, respectively (Scheme 8, route a). An alternative path involving hydrogen transfer (route b), is, however, possible but a propyl rather than a butyl radical is lost—an unorthodox process—whose justification may be the production of the rearranged ions *m/e* 173 and *m/e* 190, respectively, both of which are found in extremely high abundance.

SCHEME 8



NMR data. For many of the compounds described herein, the corresponding NMR data is tabulated in Tables 1–4. The data for those compounds which do not lend themselves easily to formulation in tabular form, appear in the appropriate parts of the Experimental section.

TABLE 1. NMR SPECTRA OF *cis*-BICYCLIC SYSTEMS WITH TWO ANGULAR SUBSTITUENTS

Compound	Angular methylenes τ	Ring methylenes τ
7	6·6 (broad)	8·60 (broad)
9	6·4 (broad)	8·43 (broad)
10	6·5 (broad)	8·43 (broad)
	7·5 (broad)	
20	7·5 (broad)	8·4 (broad)
41	6·47 (s)	8·37 (s), 8·53 (s)
57	6·38 (s)	7·32 (s)

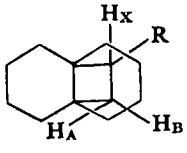
TABLE 2. UNSATURATED *cis*-BICYCLIC SYSTEMS WITH ANGULAR SUBSTITUENTS

Compound	Angular methylenes τ	Aliphatic τ	Aliphatic J	Allylic τ	Five-membered ring CH_2 τ
23	6·04 (s)	4·33 (t)	1·4 c/s	7·62 (m)	
25	6·33 (s)	4·40 (t)	1·2 c/s	7·82 (d) 1·2 c/s	
27	6·43 (s) 7·43 (s)	4·38 (t)	1·5 c/s	7·82 (m)	
28[16]	7·51 (s)	4·36 (t)	1·5 c/s	7·4–8·9 (m)	
34	7·59 (s)	4·42 (t)	1·6 c/s	7·88 (broad)	
37	6·39; 6·57 AB quartet J_{gem} = 11·4 c/s	4·38 (t)	1·5 c/s	7·96 (m)	8·36 (broad s)

[16] At 100 MHz in $CDCl_3$ the allylic protons are resolved to an AB-type quartet, J_{gem} = 17 c/s. The temp. studies (in benzene) show that the two CH_2CN are hindering each other thus giving a rather broad singlet probably due to strong solvation with the polar CN groups. The non-equivalent allylic methylene protons at higher temps show the expected additional couplings with the protons on the double bond and across the double bond (allylic and homoallylic). The non-equivalence of these ring protons does not disappear up to 140° and thus was not examined at higher temps.

We are greatly indebted to Dr. W. von Philipsborn of the University of Zürich for measuring this spectrum and for his interpretation of the results.

TABLE 3. NMR SPECTRA OF [4,4,2] PROPELLANES



R	Six-membered ring τ	Four-membered ring τ	J (c/s)
H	8·63 (s)	8·37 (s)	
CN	8·4–8·9 (m)	H_A 8·34 (quartet) H_B 7·64 (triplet) H_X 6·82 (quartet)	J_{AX} = 7·8 J_{AB} = 9·8 J_{BX} = 9·8
CO_2H	8·2–8·8 (m)	H_A collapses with six-membered ring protons H_B 7·70 (triplet) H_X 6·78 (quartet)	 J_{AB} = 10·0 J_{AX} = 7·2; J_{BX} = 10·0
Br	8·4–8·9 (m)	H_A 8·15 (quartet) H_B 7·62 (triplet) H_X 5·40 (quartet)	J_{AX} = 7·2 J_{AB} = 10·1 J_{BX} = 10·1

TABLE 4. NMR SPECTRA OF [4.4.3] AND [4.3.3] PROPELLANES

Compound	Six-membered ring τ	Five-membered ring τ	Five-membered heterocyclic ring τ
8	8·55 (s)		6·36 (s)
66	8·56 (s)		7·32 (s) 7·59 (s) (NCH_3)
32	8·5 (broad s)	7·8 (broad s)	
33	8·64 (broad)	8·38 (broad)	
42	8·53 (s)	8·34 (m)	6·42 (s)
71	8·52 (s)	8·41 (m)	7·53, 7·69 7·78 (s) (NCH_3) AB quartet J = 8·6 c/s
53	8·48 (s)		7·51, 7·61 7·71 (s) (NCH_3) AB quartet J = 8·6 c/s
75		8·50 (m)	7·76 (s) 7·85 (s) (NCH_3)
63		8·39 (s)	7·47, 7·65 7·70 (s) (NCH_3) AB quartet J = 9·0 c/s

Further reactions of propellanes including their photochemistry, the efficacy of certain members of the series as complexing agents, bridging between the three rings of various propellanes in order to design molecules of more complicated geometry, etc., will be reported elsewhere. A completely different synthetic approach for the preparation of specific alicyclic propellanes has been designed in this laboratory and will be reported independently.[17]

EXPERIMENTAL

cis-4a, 8a-*Bishydroxymethyldecalin* (7)

The anhydride 6[18] (14·9 g) was reduced with LAH (6 g) in refluxing THF (400 ml) for 6 hr. After the usual workup the *diol* was obtained (12·4 g; 87·5%), m.p. 180–182° (acetone). Lit.[1] m.p. 165–167°. (Found: C, 73·01, N, 11·03; O, 15·90. Calc. for $C_{12}H_{22}O_2$: C, 72·68; H, 11·18; O, 16·14%). IR ($CHCl_3$): 3640, 3450 cm^{-1} (OH). NMR (pyridine): τ 4·18 (v. broad) (2H,O*H*), 6·10 (broad s) (4H, CH_2O), 8·40 (v. broad s) (16H, CH_2).

12-*Oxa* [4.4.3] *propellane* (8)

The *cis*-diol 7 (33 g) and *p*-toluenesulfonic acid (0·1 g) were heated under reflux in benzene, the water formed being removed azeotropically in the required quantity during 3 hr. The solvent was removed and a soln of the residue in hexane was filtered through a column of basic alumina (Merck; 500 g). The *ether* was obtained after removal of the solvent (26·5 g, 89%), m.p. 51° (hexane). The substance has been reported as an oil, b.p. 56° (0·05 mm).[1,19] (Found: C, 79·92; H, 10·98; O, 9·12. M.W. (mass spectral): 180. Calc. for $C_{12}H_{20}O$: C, 79·94; H, 11·18; O, 8·88%. M.W. 180·28). IR ($CHCl_3$): 3000, 2930, 2880, 2870, 1042, 1058 cm^{-1}. NMR (CCl_4): τ 6·38 (s) (4H, CH_2O), 8·55 (s) (16H, CH_2).

cis-4*a*, 8*a*-*Bisbromomethyldecalin* (9)

To a soln of triphenylphosphine (6·8 g; 0·026 mole) in dry chlorobenzene (20 ml), Br (4·15 g; 0·026 mole) was added, under N, at 0°. The bromide pptd. The temp was raised to 120° and a soln

[17] D. Becker and H. J. E. Loewenthal, unpublished results.

[18] K. Alder and K. H. Backendorf, *Ber. Dtsch. Chem. Ges.* **71**, 2199 (1938).

[19] Prof. V. Prelog has informed us that he has prepared this and similar compounds with Dale, some years ago.

of **8** (4·2 g) in chlorobenzene (10 ml) was added dropwise with magnetic stirring during 10 min. The reaction mixture was kept at 120–130° for 15 hr. The chlorobenzene was removed in a vacuum and the crude dibromide distilled with a small quantity of triphenylphosphine at a bath temp of 150–160° (0·05 mm). The distillate was taken up in hot hexane and chromatographed on basic alumina (Merck, 300 g). Elution with hexane affords traces of starting material. The pure *dibromide* (3·7 g; 50% yield) is eluted with benzene–hexane (1 : 10), m.p. 112° (hexane chilled to −10°). (Found: C, 44·92; H, 6·10; Br, 48·80. M.W. (mass spectral): 324 (with the characteristic isotopic lines at 322, 326). $C_{12}H_{20}Br_2$ requires: C, 44·46; H, 6·21; Br, 49·30%. M.W. 324·12). IR($CHCl_3$): 2950, 2880 cm^{-1}. NMR(CCl_4): τ 6·42 (v. broad) (4H, CH_2Br), 8·45 (broad) (16H, CH_2).

Reaction of **9** *with sodium cyanide*

(a) A mixture of **9** (4 g; 0·012 mole), NaCN (10 g; 0·2 mole) and dimethyl formamide was heated under N at 120–130° for 48 hr. The mixture was cooled and poured into water (1 l.). This was extracted thrice with AcOEt–ether (250 ml portions), the organic phase was washed with water and dried (s. Na_2SO_4). After treatment with active carbon, removal of the solvents and trituration with hexane, cis-*4a-bromomethyl-8a-cyanomethyldecalin* **10** was obtained (0·74 g, 22·5%), m.p. 101–102° (hexane). (Found: C, 58·48; H, 7·55, Br, 28·89, N, 5·40. $C_{13}H_{20}BrN$ requires C, 57·79; H, 7·49; Br, 29·54; N, 5·18%). IR ($CHCl_3$): 2955, 2880, (CH) 2260 cm^{-1} (C≡N). NMR ($CDCl_3$): τ 6·5 (very broad) (2H, CH_2Br), 7·5 (v. broad) (2H, CH_2CN), 8·43 (broad singlet) (16H, CH_2). The above hexane mother liquor was passed through a column of neutral alumina (Merck; 50 g). Elution with benzene–hexane (1 : 4) gave 11-*cyano* [4.4.2] *propellane* **11** (0·93 g; 40%), which was purified by sublimation at 50° (0·05 mm), m.p. 73–74°. (Found: C, 82·60; H, 9·97; N, 7·52. M.W. (mass spectral): 189. $C_{13}H_{19}N$ requires: C, 82·48; H, 10·12; N, 7·40%. M.W. 189·29). IR ($CHCl_3$): 2985, 2940, 2810, 2850 (CH), 2240 cm^{-1} (CN). NMR ($CDCl_3$): see Table 3. Continued elution with benzene–hexane (2 : 3) yields a further quantity of **10** (0·48 g; total yield 37%).

There is no reaction at 100°. A longer reaction time at 120–130° raises the yield of **11** and lowers that of **10**. At 150°, for 96 hr **11** is obtained in 40% yield and **12** (see procedure b) in 10% yield.

(b) A mixture of the dibromide **9** (5 g; 0·015 mole), NaCN (12 g; 0·24 mole) and DMSO (80 ml) was heated under N at 120–130° for 4 days. After a similar workup (emulsions during extraction broken with NaCl), trituration of the residue with hexane gives the *aminonitrile* **12** (48·5 mg; 15%), m.p. 191° (hexane–benzene). (Found: C, 77·92; H, 9·35; N, 12·95. M.W. 216. $C_{14}H_{20}N_2$ requires: C, 77·73; H, 9·32; N, 12·95%. M.W. 216·31). IR ($CHCl_3$): 3520 (m), 3420 (m) (NH stretch); 3000 (w), 2940 (s), 2870 (s) (CH stretch); 2190 (C≡N), 1650 (C=C); 1610 cm^{-1} (NH bend). NMR ($CDCl_3$): τ 5·4 (broad) (2H, NH_2), 7·77 (s) (2H, CH_2—C(NH_2)=C), 8·57 (s) (16H, CH_2).

17 cannot be detected in the reaction mixture even when TLC was used.

[4.4.2] *Propellane* (**16**)

(a) *Via Wurtz reaction.* To an emulsion of Na (0·60 g) in boiling toluene (150 ml) was added dropwise a soln of **9** (0·63 g) in toluene (150 ml) during 4 hr. Refluxing was continued for an additional 24 hr. After cooling, MeOH was added to decompose the Na and after the usual workup the *hydrocarbon* **16** (0·23 g; 72%) was obtained, b.p. 102–104° (24 mm). n_D^{24} 1·4958. Lit.[3f] n_D^{20} 1·4938. (Found: C, 87·05; H, 12·72. Calc. for $C_{12}H_{20}$: C, 87·73; H, 12·27%). IR ($CHCl_3$): 2980, 2950, 2880, 2850 cm^{-1}. NMR (CCl_4): τ 8·37 (s) (4H), 8·63 (s) (16H).

(b) *From* 11-*cyano* [4.4.2] *propellane*. A mixture of **11** (0·75 g) in AcOH (5 ml), H_2SO_4 (5 ml) and water (5 ml) was heated at 150° for 1 hr. After cooling to 60°, small portions of $NaNO_2$ (0·5 g) were added during 15 min. The mixture was poured into ice water. After the usual workup, 11-*carboxy* [4,4,2] *propellane* was obtained (0·61 g; 74%), m.p. 133° EtOH aq or by sublimation at 80° 0·01 mm). (Found: C, 75·06; H, 9·68; O, 15·27. M.W. 208. $C_{13}H_{20}O_2$ requires: C, 74·96; H, 9·68; O, 15·36%. M.W. 208·30). IR($CHCl_3$): 2990, 2940, 2870, 2850; 1750 (m, sh), 1715 cm^{-1} (C=O). NMR ($CDCl_3$): see Table 3.

A mixture of the carboxylic acid (0·62 g; 3 mmoles), red HgO (0·58 g; 2·7 mmoles). and dry CCl_4 (20 ml) was heated under reflux in a N atm and Br (0·46 g) was added. The Br color disappeared after 10 min and after 15 min CO_2 evolution commenced. After 1 hr the mixture was cooled and the solvent as well as solid were removed. The residue was taken up in ether, washed with water, dil. K_2CO_3 aq and water. After drying (Na_2SO_4) and removal of the ether, the 11-*bromo* [4.4.2] *propellane* **15** was

distilled, b.p. 58° (0·1 mm) n_D^{24} 1·5308 (0·68 g; 92%). (Found: C, 59·12; H, 7·56; Br, 33·53. $C_{12}H_{19}Br$ requires: C, 59·36; H, 7·87; Br, 32·86%). IR (CS_2): 2980, 2940, 2850, 2830 cm^{-1} (CH). NMR(CCl_4): see Table 3.

A mixture of the bromide (0·2 g), LAH (0·15 g) in ether (25 ml) was heated under reflux for 5 hr. The hydrocarbon was obtained (134 mg, 98%), b.p. 102–104° (24 mm) identical in all respects to the product obtained by procedure a.

Preparation of the lactone **13**

A mixture of **10** (0·33 g), AcOH (2·5 ml), H_2SO_4 (2·5 ml) and water (2·5 ml) was heated at 150° for 1 hr. After cooling to 60° $NaNO_2$ (0·2 g) was added in portions. The *lactone* **13** (0·2 g, 78%) was isolated, m.p. 144° (hexane). (Found: C, 74·89; 14, 10·02; O, 15·15. M.W. 208. $C_{13}H_{20}O_2$ requires: C, 74·99; H, 9·66; O, 15·35%. M.W. 208·30). IR ($CHCl_3$): 2950, 2930, 2880, 1730 cm^{-1} (δ-lactone). NMR ($CDCl_3$): τ 5·78 (s) (2H, CH_2O), 7·58 (s) (2H, CH_2CO), 8·46 (s) (16H, CH_2).

Equilibration of **12** *with* cis-4a,8a-*Biscyanomethyldecalin* **(17)**

To a soln of Na (100 mg) in liquid ammonia (60 ml) under N, was added a soln of **12** (108 mg) in THF (5 ml). After stirring for 1 hr the ammonia was evaporated and water added. After ether extraction, washing with water and drying (Na_2SO_4), the ether was removed. The residue of the dinitrile showed no NH_2 and the C≡N band shifted to 2250 cm^{-1} (unconjugated CN). Treatment of the dinitrile in methanolic solution with MeONa converts it quantitatively to **12**. Since the route **12** → **18** → **19** was available, it was found unnecessary to stabilize the dinitrile **17** in its open form and it was not characterized further.

11-*Cyano* [4,4,3] *propellan*-12-*one* **(18)**

A mixture of **12** (0·3 g), AcOH (5 ml) and conc HCl (5 ml) was boiled for 3 hr. Water (10 ml) was added, the mixture cooled and the *ketonitrile* **18** was removed by filtration (0·3 g; 100%), m.p. 150–152° (benzene–hexane or sublimation at 100°, 0·05 mm). (Found: C, 76·49; H, 8·86; N, 6·84. M.W. 217. $C_{14}H_{19}NO$ requires: C, 77·38; H, 8·81; N, 6·45%. M.W. 217·27). IR ($CHCl_3$): 2950, 2875, 2250 (C≡N); 1770 cm^{-1} (C=O).

The 2,4-*dinitrophenylhydrazone* had m.p. 210° (dec, from aq. EtOH). (Found: N, 17·15. $C_{20}H_{23}O_4N_5$ requires: N, 17·62%).

11-*Cyano*-12-*mercapto* [4.4.3] *propell*-11-*ene*. A mixture of **18** (0·1 g), ethanedithiol (0·4 ml), BF_3 in ether (0·2 ml) was set aside at room temp for 4 hr and then 10% KOH aq (15 ml) was added. The whole was extracted with ether, then washed with water and dried (Na_2SO_4). Removal of the solvent left a residue of the crude thioketal (quant. yield). The crude compound was dissolved in ethylene glycol (2 ml) and to the soln hydrazine (95%; 0·2 g) and solid KOH (0·3 g) were added and the whole refluxed for 15 hr. The residue of the *mercaptonitrile* (47 mg; 44%), had m.p. 156° (hexane). (Found: C, 72·21; H, 7·55; S, 13·70. M.W. 233. $C_{14}H_{19}NS$ requires: C, 72·07, H, 8·21, S, 13·72%. M.W. 233·30). IR ($CHCl_3$): 3000, 2940, 2860 (CH), 2580, 2560 (SH), 2205 (CN), 1585 cm^{-1} (C=C).

cis-4a, 8a-*Biscarboxymethyldecalin* **(19)**

A mixture of **18** (4·3 g), KOH (8 g), ethylene glycol (30 ml) and water (10 ml) was refluxed for 15 hr. After cooling and acidification with conc HCl the whole was extracted with AcOEt–ether, the extract was washed with water and dried (Na_2SO_4). Removal of the solvent gave the *dicarboxylic acid*, m.p. 256° (dec, from aq EtOH) (4·5 g; 90%). (Found: C, 66·41; H, 8·55; O, 24·90. $C_{14}H_{22}O_4$ requires: C, 66·11; H, 8.72; O, 24·90%). IR (KBr): 2950, 2930, 2880, 1720 (s, sh), 1695 cm^{-1} (s). NMR (pyridine): τ −1·72 (broad singlet) (CO_2H), 7·5–8·6 (broad) (aliph. H).

cis-4a, 8a-*Biscarbomethoxymethyldecalin* **(20)**

The *dimethyl ester* was formed (170 mg; 95%) by methylation of **19** (160 mg) with excess diazomethane in ether-THF. It had b.p. 80–90° (0·05 mm), n_D^{24} 1·4386. (Found: C, 68·05; H, 9·62; O, 22·35. $C_{16}H_{26}O_4$ requires: C, 68·05; H, 9·28; O, 22·67%) IR ($CHCl_3$): 2990, 2940, 2875; 1730 cm^{-1} (ester CO). NMR (CCl_4): τ 6·43 (s) (6H, OCH_3), 8·46 (very broad) (20H, CH_2). Fragmentation pattern on electron impact:

M^+ for **20** (*m/e* 282) $\xrightarrow{-OMe}$ *m/e* 251 $\xrightarrow{-MeOH}$ *m/e* 219; *m/e* 251 $\xrightarrow{-ketene}$ *m/e* 209 $\xrightarrow{m^*}$ *m/e* 177.

3,4-*Dihydroxy* [4.4.4] *propellane* (**21**)

A soln of **20** (0·42 g; 1·5 mmole) in THF (20 ml) was added dropwise to a soln of Na (276 mg; 12 mmoles) in liquid ammonia (80 ml) and THF (20 ml). The ammonia was evaporated and MeOH (2 ml), water (50 ml) and ether (50 ml) were added. The organic phase was washed with water, dil. HCl aq, water, dil. $NaHCO_3$ aq, water and dried (Na_2SO_4). Removal of the solvents and trituration with chf gave the *diol* (110 mg; 33%), m.p. 158° (benzene). (Found: C, 74·89; H, 10·63; O, 14·86. M.W. 224. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·78; O, 14·26%. M.W. 224·33). IR (KBr): 3400–3250 cm^{-1} (OH). The chf mother liquor after trituration contains acyloin and the corresponding diketone. Evaporation of the chf, followed by $NaBH_4$ reduction of the residue in MeOH–THF gives more of the diol (100 mg; total yield 62%).

cis-4a, 8a-*Bishydroxymethyldecalin*-2,6-*diene* (**23**)

The anhydride **22**[18] was reduced in 90% yield as described above for the reduction of **6** to **7**. The *diol* had m.p. 165–168° (acetone). Lit.[1] m.p. 125–127°. We cannot explain the large discrepancy in m.p.'s but since the NMR data and analyses of compounds stemming from **29** are in accord with its structure, perhaps the German authors[1] were dealing with a polymorphic form. NMR (pyridine): τ 4·34 (t at X part of ABX spectrum; $J_{AX} = J_{BX} = 1·4$ c/s) (4 olefinic H), 6·05 (s) (4H, CH_2OH), 7·63, 7·78 (8H, CH_2, $J_{AB} = 18·4$ c/s).

12-*Oxa* [4,4,3] *propella*-3,8-*diene* (**24**)

A soln of **23** (25 g) in toluene was heated under reflux in the presence of *p*-toluenesulfonic acid (0·2 g). The required water (2·3 ml) was removed azeotropically during 15 hr. After the usual workup the *ether* was obtained (20·5 g; 90%), b.p. 126° (24 mm). n_D^{24} 1·5167. (Found: C, 81·41, H, 9·07; O, 9·40. M.W. 176. $C_{12}H_{16}O$ requires: C, 81·77; H, 9·15; O, 9·08%. M.W. 176·25). IR ($CHCl_3$): 2980–2835 (CH), 1661, 1630 (C=C), 1029, 1008 cm^{-1} (C—O). NMR (CCl_4): τ 4·50 (t) (4 olefinic H), 6·40 (s) (4H, CH_2O), 7·96 (complex multiplet) (8 allylic H).

cis-4a, 8a-*Bisbromomethyldecalin*-2,6-*diene* (**25**)

This was prepared as described for **9**, from triphenylphosphine (28·8 g), chlorobenzene (120 ml), Br (17·6 g) and **24** (17·6 g). The *dibromide* (20·8 g; 65%), had b.p. 150–160° (0·5 mm), m.p. 79° (EtOH). (Found: C, 45·34; H, 5·08; Br, 48·88. M.W. 320. With isotopic lines 318, 322. $C_{12}H_{16}Br_2$ requires: C, 45·06; H, 5·03; Br, 49·92%. M.W. 320·09). IR ($CHCl_3$): 3000–2845 (CH), 1660 cm^{-1} (C=C). NMR ($CDCl_3$): τ 4·40 (t) (4 olefinic H), 6·33 (s) (4H, CH_2Br), 7·82 (d) (8 allylic H).

Reaction of **25** *with sodium cyanide*

When **25** (60 g) was heated with NaCN (98 g) in dry methylsulfoxide (500 ml) for 96 hr at 130° as described above for **9**, similar workup gave in this case 11-*cyano*-12-*amino* [4.4.3] *propella*-3,8,11-*triene* **26** (31 g; 78%), m.p. 160° (benzene). (Found: C, 79·18; H, 7·71; N, 13·35. M.W. 212. $C_{14}H_{16}N_2$ requires: C, 79·21; H, 7·60, N, 13·20%. M.W. 212·28). IR ($CHCl_3$): 3518, 3410 (NH_2), 2998–2838 (CH), 2182 (CN), 1660, 1650, 1640 (C=C), 1599 cm^{-1} (NH bend). NMR ($CDCl_3$): τ 4·28 (m) (4 olefinic H), 5·39 (broad) (2H, NH_2), 7·67 (s) (2H, CH_2), 7·78–8·00 (sharp multiplets) (8 allylic H).

When this preparation is carried out for only 48 hr and by the same workup, the aminonitrile (1·2 g from 7·6 g dibromide) is formed in 24% yield. Concentration of the benzene mother liquor and its chromatography over neutral alumina (Merck; 300 g) gives upon elution with benzene traces of starting material. Elution with chf–benzene (1:4) gives the corresponding 4a-*bromomethyl*-8a-*cyanomethyl* derivative **27**, (0·69 g; 10·8%), m.p. 104° (hexane). (Found: C, 58·79; H, 5·74; Br. 30·61; N, 5·20. M.W. 265 with characteristic isotopic lines 265, 267. $C_{13}H_{16}BrN$ requires: C, 58·65; H, 6·05; Br, 30·02; N, 5·25%. M.W. 266·17). IR ($CHCl_3$): 2974–2842 (CH), 2250 (CN), 1660, 1630, 1695 cm^{-1} (w) (C=C). NMR ($CDCl_3$): τ 4·38 (t) (4 olefinic H), 6·43 (s) (2H, CH_2Br), 7·47 (s) (2H, CH_2CN), 7·82 (quartet) (8 allylic H). Continued elution gives fractions with decreasing quantities of the bromonitrile and increasing quantities of the dinitrile. Fractional crystallization permits isolation of the pure cis-4a,8a-*biscyanomethyldecalin*-2,6-*diene* **28** (1·2 g, 24%), m.p. 154° (benzene–hexane). (Found: C, 79·46; H, 7·36; N, 13·00. M.W. 212. $C_{14}H_{16}N_2$ requires: C, 79·21; H, 7·60; N, 13·20%. M.W. 212·28). IR ($CHCl_3$): 2980–2845 (CH), 2250 (CN), 1659 (w), 1630, 1600 cm^{-1} (C=C). NMR ($CDCl_3$): τ 4·36 (t) (4 olefinic H), 7·51 (s) (4H, CH_2CN), 7·4–8·9 (multiplets) (8 allylic H).

Further elution with chf–benzene (2:3) affords more of the aminonitrile (571 mg), m.p. 160°, identical to product described above.

11-*Cyano* [4.4.3] *propella*-3,8-*diene*-12-*one* (**29**)

A mixture of **26** (28 g), EtOH (70 ml), water (40 ml) and conc. HCl (40 ml) was heated under reflux for 3 hr. After cooling the *cyanoketone* **29** pptd quantitatively (28 g), m.p. 104° (aq EtOH). (Found: C, 78·76; H, 7·14, N, 6·83. M.W. 213. $C_{14}H_{15}ON$ requires C, 78·84; H, 7·09; N, 6·57%. M.W. 213·27). IR ($CHCl_3$): 2980–2845 (CH), 2250 (CN), 1765 (CO), 1680, 1665, 1640 cm^{-1} (vw) (C=C). NMR ($CDCl_3$): τ 4·36 (t) (4 olefinic H), 6·47 (s) (C*H* CN), 7·7–8·9 (multiplets) (10H, CH_2).

cis-4a,8a-*Biscarboxymethyldecalin*-2,6-*diene* (**30**)

A mixture of **29** (13 g), hydrazine (10 g), KOH (30 g), water (60 ml) and ethylene glycol (150 ml) was refluxed overnight. After the usual workup the *diacid* was obtained (14·1 g; 92·5%), m.p. 235° (dec, aq EtOH). (Found: C, 67·26; H, 7·53; O, 25·00. $C_{14}H_{18}O_4$ requires: C, 67·18; H, 7·25; O, 25·57%). IR (KBr): 1720 (sh), 1700 cm^{-1} (CO). NMR (pyridine): τ −2·92 (broad) (2H, CO_2H), 4·45 (broad) (4 olefinic H), 7·27 (s) (4H CH_2CO_2H), 7·54 (broad singlet) (8 allylic H).

The *dimethyl ester* **34** was obtained by methylation with diazomethane in ether–THF, b.p. 124° (0·5 mm). n_D^{24} 1·5069. (Found: C, 69·05; H, 7·98; O, 23·00. M.W. 278. $C_{16}H_{22}O_4$ requires: C, 69·04; H, 7·97; O, 22·99%. M.W. 278·34). IR($CHCl_3$): 1730 (CO), 1658 cm^{-1} (w) (C=C). NMR ($CDCl_3$): τ 4·42 (t) (4 olefinic H), 634 (s) (6H, OCH_3), 7·59 (s) (4H, CH_2CO), 7·88 (broad singlet) (8 allylic H).

Treatment of the diacid **30** with boiling Ac_2O gave the seven-membered anhydride of **30**, in 78% yield, m.p. 169–171° (hexane). (Found: M.W. 232. $C_{14}H_{16}O_3$ requires: M.W. 232·27). IR ($CHCl_3$): 1797, 1750 cm^{-1} (CO). NMR ($CDCl_3$): τ 4·42 (t) (4 olefinic H), 7·24 (s) (4H, CH_2CO), 7·77–7·92 (m) (8 allylic H).

[4.4.3] *Propella*-3,8-*dien*-12-*one* (**31**)

The aminonitrile **26** (2·1 g) was heated with 20% HCl (16 ml) in a sealed tube at 175° for 5 hr. After the usual workup, and chromatography in benzene over basic alumina (Merck; 80 g), elution with chf–benzene (3:7) gave the *dienic ketone* (800 mg; 45%), b.p. 42° (0·5 mm). n_D^{24} 1·5358. (Found: M.W. 188. $C_{13}H_{16}O$ requires: 188·26). The ketone is unstable on standing, becomes viscous and then does not afford proper microanalytical results. IR ($CHCl_3$): 1740 cm^{-1} (CO). UV (CH_3CN): $\lambda\lambda$(mμ); 262 (min), 285 (sh), 297 (max), 307 (sh), 318 (sh). $\epsilon\epsilon$: 16·8, 23·1, 25·2, 21·1, 10·5. NMR (CCl_4): τ 4·42 (m) (4 olefinic H), 7·67–8·50 (sharp multiplet) (12H).

The ketone **31** may be obtained under identical experimental conditions also from **29**.

[4.4.3] *Propellan*-12-*one* **32**

Catalytic reduction of freshly prepared **31** (280 mg) in AcOH, using Adams' catalyst (20 mg) at room temp and atm press was completed, for uptake of 2 moles H, after 1 hr. After removal of the catalyst and solvent, the sat *ketone* (260 mg) had m.p. 97–99° (aq EtOH). (Found: C, 81·26; H, 10·47; O, 8·49. M.W. 192. $C_{13}H_{20}O$ requires: C, 81·20; H, 10·48; O, 8·32%. M.W. 192·29). IR ($CHCl_3$): 1730 (CO). UV (CH_3CN): $\lambda\lambda$ (mμ): 250 (min), 288 (sh), 295 (max), 307 (sh), 318 (sh). $\epsilon\epsilon$: 11·5, 17·3, 19·3, 15·3, 7·7. NMR ($CDCl_3$): τ 7·80 (broad) (4H, CH_2CO), 8·50 (broad) (16H).

[4.4.3] *Propella*-3,8-*diene* (**35**)

A mixture of freshly prepared **31** (200 mg), hydrazine (0·4 ml), KOH (0·5 g), and ethylene glycol (10 ml) was heated at 140° for 3 hr, then heated at 190° for an additional 5 hr. After cooling and extraction with pentane, washing with water, drying (Na_2SO_2), concentration and chromatography over basic alumina (Merck; 15 g), the *diene* **35** was eluted with hexane and distilled, b.p. 140° (24 mm) n_D^{24} 1·5205 (105 mg) 57%). (Found: C, 89·45; H, 10·31. M.W. 174. $C_{13}H_{18}$ requires: C, 89·59; H, 10·41%. M.W. 174·27). NMR (CCl_4): τ 4·58 (broad) (4 olefinic H), 8·12 (broad), 8·40 (broad).

[4.4.3] *Propellane* (**33**)

A mixture of **32** (300 mg), hydrazine (0·6 ml), KOH (0·6 g) and ethylene glycol (10 ml) was treated exactly as described above for the dienic ketone. The sat propellane, b.p. 146° (24 mm) was obtained (120 mg; 43%), m.p. 76–78°. Lit.[2] m.p. 80°. (Found: M.W. 178. $C_{13}H_{22}$ requires: M.W. 178·31). NMR (CCl_4): τ 8·38, 8·64 (broad multiplets).

7,9-*Dioxo*-8-*oxa* [4.3.3] *propell*-3-*ene* (**36**)

1-Cyclopentene-1,2-dicarboxylic acid anhydride[20] (3·5 g), butadiene (10 ml) and dioxan (10 ml) were heated in a sealed tube at 110° for 12 hr. After cooling, the *anhydride* **36** separated as needles (4·6 g; 96%), m.p. 122° (hexane). (Found: C, 68·83; H, 6·52. M.W. 192. $C_{11}H_{12}O_3$ requires: C, 68·73; H, 6·29%. M.W. 192·21). IR ($CHCl_3$): 1853, 1780 (CO), 1638 cm^{-1} (C=C). NMR ($CDCl_3$): τ 3·98 (quintet) (2 olefinic H), 7·08, 7·32 (m) (4 allylic H), 7·5–8·3 (m) (6H, CH_2).

cis-3a, 7a-*Bishydroxymethylhydrind*-5-*ene* (**37**)

Reduction of **36** (10 g) with LAH in THF as described above for **6**→**7** gave the *diol* (7·9 g; 83%), m.p. 158·160° (hexane or benzene). (Found: C, 72·83; H, 9·46. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%). IR ($CHCl_3$): 3620, 3400 (OH), 1660 cm^{-1} (C=C). NMR ($CDCl_3$): τ 4·48 (t) (J = 1·8 c/s; 2 olefinic H), 5·48 (s) (2H, OH), 6,39· 6·57 (AB quartet; J_{AB} = 11·4 c/s) (4H, CH_2O), 7·86, 8·07 (AB quartet, J_{AB} = 18·0 c/s) (4 allylic H), 8·36 (broad s) (6H, CH_2). The OH peak moves to τ 2·57 in the presence of CF_3CO_2H.

8-*Oxa* [4.3.3] *propell*-3-*ene* (**38**)

A mixture of **37**, (4 g), *p*-toluenesulfonic acid (150 mg) and toluene (50 ml) was heated under reflux for 1 hr during which time the theoretical quantity of water (0·4 ml) was removed azeotropically. The usual workup afforded the *ether* (3·2 g; 89%), b.p. 106° (26 mm), m.p. 83°. (Found: M.W. 164. $C_{11}H_{16}O$ requires: M.W. 164·24. NMR (CCl_4): τ 4·18 (t), (J = 3 c/s) (2 olefinic H), 6·52 (s) (4H, CH_2O), 8·02 (d, J = 3 c/s) (4 allylic H), 8·43 (broad s) (6H, CH_2).

4a-*Bromomethyldecalin*-2,8-*diene* (**39**)

A soln of **38** (5·5 g; 0·034 mole) in MeCN (10 ml) was added to a refluxing soln in MeCN (20 ml) of triphenylphosphine (10·5 g; 0·04 mole) and Br (6·4 g; 0·04 mole) under N and boiling was continued overnight. The solvent was removed in a vacuum and the crude residue was distilled from an oil bath at 150°. The distillate was washed with water, $NaHCO_3$ and water and redistilled. The pure bromide **39** (4·2 g; 56%) had b.p. 58° (0·08 mm). (Found: C, 58·18; H, 6·59; Br, 35·14. M.W. 226 with isotopic bromine peaks at 226 and 228. $C_{11}H_{15}Br$ requires: C, 58·16; H, 6·65; Br, 35·18%. M.W. 227·15). UV (hexane): λ_{max} 228–232 mμ; ϵ_{max} 1600. NMR (CCl_4): τ 4·1–4·6 (m) (3 olefinic H), 6·56 (m) (2H, CH_2Br), 7·7–8·4 (m) (8H, CH_2 including allylic H).

7,9-*Dioxo*-8-*oxa* [4.3.3] *propellane* (**40**)

The anhydride **36** (4·5 g) was reduced catalytically at atm press and room temp in the presence of PdC (30%; 40 mg) and glacial AcOH (50 ml), during 5 hr. After removal of catalyst and solvent, the product was distilled, (3·8 g; 84%), b.p. 96° (0·2 mm), m.p. 84° (hexane). (Found: C, 67·93; H, 7·36; O, 24·95. $C_{11}H_{14}O_3$ requires: C, 68·02; H, 7·27; O, 24·71%). IR ($CHCl_3$): 1860, 1840, 1780 cm^{-1} (CO). NMR (CCl_4): τ 7·6–8·6 (m) (CH_2).

cis-3a,7a-*Bishydroxymethylhydrindan* (**41**)

This diol was obtained either by LAH reduction of **40** or by catalytic reduction of **37** in glacial AcOH in the presence of 30% Pd-C as described for **36** → **40**, in 85% and 98% yield, respectively. The *diol* had m.p. 203° (hexane). (Found: C, 71·69; H, 10·94; O, 17·04. $C_{11}H_{20}O_2$ requires: C, 71·69; H, 10·94; O, 17·37%). IR ($CHCl_3$): 3600, 3420 cm^{-1} (OH). NMR ($CDCl_3$): τ 5·65 (s) (2H, OH), 6·47 (s) (4H, CH_2O), 8·37 (s) (8H, CH_2), 8·53 (s) (6H, CH_2).

8-*Oxa* [4.3.3] *propellane* (**42**)

This ether was prepared from **41** in 80% yield as described for **37** → **38**. The *ether* had m.p. 101–103° (by sublimation at 80°, 25 mm). It may also be prepared quantitatively by catalytic reduction of **38** in glacial AcOH in the presence of 30% Pd-C or Adams' catalyst, as described for **36** → **40**. (Found: C, 78·82; H, 10·85; O, 10·22. M.W. 166. $C_{11}H_{18}O$ requires: C, 79·46; H, 10·92; O, 9·63%. M.W. 166·25). IR ($CHCl_3$); 1067, 1045 cm^{-1}. NMR (CCl_4): τ 6·42 (s) (4H, CH_2O), 8·32 (broad s) (6H, CH_2), 8·54 (s) (8H, CH_2).

[20] S. C. Sen-Gupta, *J. Ind. Chem. Soc.* **17**, 183 (1940). This method was not reproducible unless at all of the synthetic stages of preparing 2-carbethoxycyclopentanone cyanohydrin an acid pH was maintained to prevent decomposition.

4a-*Bromomethyldecalin*-8-*ene* (**43**)

The ether **42** was treated with triphenylphosphine dibromide as described for **38** → **39**. The *bromide* was obtained in 50% yield, b.p. 58–60° (0·08 mm). (Found: M.W. 228 with isotopic bromine peaks at 228 and 230. $C_{11}H_{17}Br$ requires: M.W. 229·16). UV (hexane): λ_{max} 228–232 mμ, ϵ_{max} 1200. NMR (CCl_4): τ 4·55 (m) (1 olefinic H), 6·42 (m) (2H, CH_2Br), 7·7–8·8 (m) (14H, CH_2 including allylic H).

7,9,10,12-*Tetraoxo*-8,11-*diaza* [4.3.3] *propell*-3-*ene* (**45**)

Compound **44** was prepared from tetracyanoethylene and butadiene. A soln of this tetranitrile (1·46 g; 0·008 mole) in 25% aq methanolic KOH (20 ml) was heated under reflux for 3 hr. Most of the solvents were removed at the water pump and 10% HCl was added to pH 3. The soln was warmed on the steam bath for 30 min whereupon a colorless ppt was formed. It was obtained by filtration (0·95–1·1 g; 53–60%), m.p. 340° (dec begins at 320°). The same compound was obtained by acid hydrolysis of the Diels-Alder adduct, in unstated yield, m.p. > 300°.[9] Carrying out the acid hydrolysis we obtained the *cis*-diimide in only 10% yield. IR (KBr): 3300–3000 (NH); 1810, 1760–1720, 1710 cm^{-1} (imide CO).

3,4-*Dibromo*-7,9,10,12-*tetraoxo*-8,11-*diaza* [4.3.3] *propellane* (**50**)

To a soln of **45** (220 mg.; 0·001 mole) in glacial AcOH (10 ml) Br (0·051 ml, 0·001 mole) was added with stirring which was continued overnight at room temp. The ppt was collected (220 mg, 58%), m.p. 290–295° (dec; acetone or water). (Found: C, 31·89; H, 2·23; N, 6·74. M.W. 380 (with isotopic Br peaks at 378 and 382. $C_{10}H_8N_2O_4Br_2$ requires: C, 31·59; H, 2·11; N, 7·37%. M.W. 379·91). IR (KBr): 3300–3000 (br) (NH), 1820, 1780, 1750, 1720 (sh) cm^{-1} (imide CO). NMR: No suitable solvent was found.

8,11-*Dimethyl*-7,9,10,12-*tetraoxo*-8,11-diaza [4.3.3] *propell*-3-*ene* (**46**)

The *cis*- diimide **45** (1 g) was dissolved in boiling abs MeOH (125 ml), and to the cooled soln was added excess ethereal diazomethane. A colorless solid precipitated during 2 hr. The solvents were removed and the residue was triturated with MeOH and the *methylated diimide* was obtained by filtration (0·9 g; 79%), m.p. (with sublimation) 248–251° (MeOH). (Found: C, 58·15; H, 4·90; N, 11·10. M.W. 248. $C_{12}H_{12}N_2O_4$ requires: C, 58·06; H, 4·87; N, 11·29%. M.W. 248·23). IR (KBr): 3060 (=CH), 2970, 2930, 2860 (CH), 1820, 1780, 1740, 1710 (imide CO), the bands at 1450, 1390, 1320 cm^{-1} appear here and in all of the spectra of the methylimides reported in the paper. NMR ($CDCl_3$): τ 4·02 (t, fine struc.; J = 3 c/s) (2H, C*H*), 6·96 (s) (6H, NCH_3), 7·2 (d, J = 3 c/s) (4H, CH_2). From the methanolic mother liquor was isolated a product which appears to be that of methylation and addition of an extra mole of diazomethane to the C=C double bond, m.p. 160° (dec, gas evolution). It was not characterized further.

3,4-*Dibromo*-8,11-*dimethyl*-7,9,10,12-*tetraoxo*-8,11-*diaza*[4.3.3]*propellane* (**47**)

To a soln of **46** (1·24 g; 0·005 mole) in glacial AcOH (30 ml), Br (0·28 ml; 0·005 mole) was added with stirring and the stirring was continued at room temp for 20 hr. The ppt was removed by filtration and the solvent at the water pump whereupon more *dibromide* was obtained; m.p. 274·5–276° (AcOEt–hexane) (1·6–1·75 g; 79–85%). (Found: C, 35·24; H, 3·10; Br, 39·32; N, 6·62. M.W. 408 (with isotopic Br peaks at 406 and 410. $C_{12}H_{12}Br_2N_2O_4$ requires: C, 35·30; H, 2·96; Br, 39·18; N, 6·81%. M.W. 407·94). IR (KBr): 3020, 2970, 2950 (CH), 1820, 1780, 1750, 1720 (imide CO), 1450, 1380, 1310 cm^{-1}. NMR: no solvent was found.

8,11-*Dimethyl*-7,9,10,12-*tetraoxo*-8,11-*diaza*[4.3.3]*propellane* (**52**)

To a soln of **46** (0·5 g) in glacial AcOH (60 ml), Adams' catalyst (30 mg) was added. The theoretical uptake of H (1 mole) ceased after 0·5 hr. After removal of the catalyst and solvent, the *diimide* was obtained (0·44 g; 87%), m.p. 204–205° (benzene–hexane, or MeOH). (Found: C, 57·40; H, 5·59; N, 11·40; O, 25·55. M.W. 250. $C_{12}H_{14}N_2O_4$ requires: C, 57·59; H, 5·64; N, 11·20; O, 25·58%. M.W. 250·25). IR (KBr): 1810, 1780, 1740, 1720 (imide CO), 1450, 1380, 1310 cm^{-1}. NMR $CHCl_3$): τ 6·95 (s) (6*H*, NCH_3), 7·8 (m) (4H, CH_2), 8·45 (m) (4H, CH_2).

8,11-*Dimethyl*-8,11-*diaza*[4.3.3]*propellane* (**53**)

A mixture of **52** (3·8 g), LAH (6 g) and THF (150 ml) was heated under reflux for 8 days. After the usual workup, extraction of the crude product with AcOEt and removal of the solvent, the crude product still exhibited a slight carbonyl absorption (IR). Chromatography over neutral alumina (Merck; 100 g) followed by elution with benzene, gave the amine. (There appears to be oxidation on the column as other fractions have a much greater carbonyl absorption (IR) than can be expected from the composition of the crude product.) Distillation gave the pure *amine* (1 g; 34%), b.p. 120° (25 mm). (Found: M.W. 194. $C_{12}H_{23}N_2$ requires: 194·31). IR ($CHCl_3$): 2940–2800 cm^{-1} (CH). NMR ($CDCl_3$): τ 7·51, 7·61 (AB quartet; J = 8·9 c/s) (8H, NCH_2), 7·71 (s) (6H, NCH_3), 8·48 (s) (8H, CH_2). The yellow *picrate* had m.p. 210–213° (MeOH). (Found: C, 44·54; H, 4·16; N, 17·00. $C_{24}H_{28}N_8O_{14}$ requires: C, 44·17; H, 4·33; N, 17·17%). The *mono-methiodide* had m.p. 190·5–191·5° from dry acetone). (Found: C, 46·56; H, 7·60; I, 37·45; N, 8·40. $C_{13}H_{25}IN_2$ requires: C, 46·48;, (H, 7·49; I, 37·76; N, 8·33%). NMR (methanol-d_4): τ 6·20 (s) (4H, $\overset{+}{N}CH_2$), 6·41 (s) (3H, $\overset{+}{N}CH_3$) 6·61 (3H, $\overset{+}{N}CH_3$), 7·01, 7·62 (quartet; J = 11 c/s) (4H, NCH_2), 7·60 (s) (3H, NCH_3) 8·30 (s) (8H, $CH)_2$.

8,11-*Dimethyl*-8,11-*diaza*[4.3.3]*propell*-3-*ene* (**51**)

A mixture of **46** (0·25 g), LAH (0·38 g) and THF (55 ml) was heated under reflux for 6 days. After workup as described above and purification via the picrate, the pure *amine* was obtained (95 mg; 50%). (Found: M.W. 192. $C_{12}H_{20}N_2$ requires: 192·30). IR ($CHCl_3$): 2940–2780 cm^{-1} (CH). NMR ($CDCl_3$): τ 4·12 (t) (2 vinyl H; J = 3·2 c/s), 7·46, 7·61, (AB quartet, J = 9 c/s) (8H, NCH_2), 7·73 (s) (6H, NCH_3), 7·90 (d, J = 3·2 c/s) (4H, CH_2). The *picrate* had m.p. 208–210° (from acetone–EtOH). (Found: C, 44·42; H, 4·10; N, 17·31; O, 34·38. $C_{24}H_{26}N_8O_{14}$ requires: C, 44·31; H, 4·03; N, 17·43; O, 34·43%).

8,11-*Dimethyl*-7,9,10,12-*tetraoxo*-8,11-*diaza*[4.3.3]*propella*-2,4-*diene* (**48**)

A soln of **47** (1·26 g) in dimethylformamide (75 ml) containing LiCl (0·99 g) was heated under N at 130° for 4 hr. After cooling to room temp water was added and the pptd *diene* was collected (0·43–0·47 g; 60–65%), m.p. 289–290° (from AcOEt–hexane). (Found: C, 58·60; H, 4·29; N, 11·39; O, 26·02. M.W. 246. $C_{12}H_{10}N_2O_4$ requires: C, 58·53; H, 4·09; N, 11·38; O, 25·99%. M.W. 246·22). IR (KBr): 3080, 3060 (=CH), 2960 (CH_3), 1820, 1780, 1750, 1720 (imide CO), 1650, 1620 (diene), 1450, 1380, 1320 cm^{-1}. NMR (DMSO-d_6): τ 3·75 (m) (4H, CH), 7·08 (s) (6H, NCH_3).

Ozonolysis of **48**

Ozone was passed through a soln of **48** (4·4 g) in AcOH (200 ml) during 4 hr at 20°. The solvent was removed in a high vacuum. Formic acid (150 ml) and 30% H_2O_2 (65 ml) were added to the residue and the whole was set aside for 24 hr. The solvents were removed in a high vacuum and the residue was sublimed, yielding the cis-*diimide* **49** (3·16 g; 91%), m.p. 315 (dec). (Found: C, 49·05; H, 4·25; N, 14·14; O, 32·80. M.W. 196. $C_8H_8N_2O_4$ requires: C, 48·98; H, 4·11; N, 14·28; O, 32·63%. M.W. 196·16). IR (KBr): 3000, 2970 (CH), 1850–1820, 1780, 1720 (br) (imide CO), 1450, 1390, 1310 cm^{-1}. NMR (DMSO-d_6): τ 5·88 (s) (2H, CH), 7·20 (s) (6H, NCH_3). The best conditions were the above. Ozonolysis in CH_2Cl_2, AcOEt, or MeOH gave a poorer yield. It was clear from the pptn of **49** by adding ether to a methanolic aliquot of the ozonolysis reaction mixture, that loss of four carbons had already occurred to a considerable extent during the earlier stage of the above procedure.

Ozonolysis of **46**

Ozone was passed through a suspension of **46** (4 g) in glacial AcOH (60 ml) during 2 hr at 20°. As the reaction proceeds the substrate is dissolved followed by pptn of the ozonide. The solvent was removed in a high vacuum. To the residue of ozonide (6·5 g) were added formic acid (4·5 ml) and 30% H_2O_2 (27 ml) and the whole is carefully warmed on a water bath (70°). As soon as the exothermic reaction starts, cooling is necessary. Finally, the soln is heated under reflux for 2 hr and then set aside at room temp for 24 hr. The diacid **54** which crystallized from the reaction mixture was collected. More diacid was obtained from the mother liquor, m.p. 257–260° (water) (4·5; 85%). The analytical sample contains 1 mole of water of hydration which cannot be removed at 200° (0·01 mm). (Found: C, 43·66; H, 4·34; N, 8·48; O, 43·00. $C_{12}H_{12}N_2O_8$. H_2O requires: C, 43·64; H, 4·27; N,

8·48; O, 43·60%). IR (KBr): 3450–3430 (OH), 3300–3000 (strong H bond), 1820, 1780–1700 (imide and carboxyl CO), 1450, 1380, 1320 cm^{-1}. NMR (acetone-d_6): τ 4·70 (s) (4H, O*H*), 6·68 (s) (4H, CH_2) 7·08 (s) (6H, NCH_3). The position of the τ 4·70 peak is affected by addition of water in varying concentration.

The *dimethyl ester* **64** was obtained by methylation of the diacid (0·33 g) in abs MeOH (10 ml) with excess diazomethane during 2 hr. Removal of the solvents gave the product (0·3 g; 88%), m.p. 219–220° (acetone–MeOH). (Found: C, 49·52; H, 4·86; N, 8·24; O, 37·55. M.W. 340. $C_{14}H_{16}N_2O_8$ requires: C, 49·41; H, 4·74; N, 8·23; O, 37·62%. M.W. 340·28). IR (KBr): 2960, 2940, 2860 (CH), 1820, 1780, 1760–1720 (imide and ester CO), 1450, 1380, 1320 cm^{-1}. NMR (acetone-d_6): τ 6·32 (s) (6H, OCH_3), 6·65 (s) (4H, CH_2), 7·02 (s) (6H, NCH_3).

7,10-*Dimethyl*-6,8,9,11-*tetraoxo*-7,10-*diaza*[3.3.3]*propellan*-3-*one* (**58**)

A soln of **54** (2·2 g) in Ac_2O (35 ml) was heated in a N atm at 110–120°; the CO_2 evolved was collected in $Ba(OH)_2$ aq. The reaction was stopped when no more CO_2 was evolved (48 hr; the theoretical amount of $BaCO_3$ was formed). The solvent was removed, the residue was washed with ether, collected and dried. The residue was dissolved in acetone and neutral alumina (Merck; 20 g) was added with vigorous stirring. The product is adsorbed in the alumina; the acetone is removed in a vacuum. The ketone adsorbing alumina was placed above a layer of additional neutral alumina (130 g) in a chromatographic column. The pure *ketone* **58** was eluted with MeOH–chf (1:9) (1·35 g; 82%), m.p. ~335° (dec begins at 310°) (acetone–hexane). (Found: C, 52·67; H, 3·95; N, 11·15; O, 31·82. M.W. 250. $C_{11}H_{10}N_2O_5$ requires: C, 52·80; H, 4·03; N, 11·20; O, 31·97%. M.W. 250·21). IR (KBr): 1820, 1770, 1750–1730 (imide and ketone CO), 1440, 1380, 1310 cm^{-1}. NMR (DMSO-d_6): τ 7·18 (s), 7·20 (m). The *2,4-dinitrophenylhydrazone was obtained* from a suspension of the ketone in MeOH after standing with the soln of the reagent for 72 hr. The ketone disappeared and the crystalline yellow derivative appeared, m.p. 301° (dec; from nitromethane). (Found: C, 47·22; H, 3·65; N, 19·59; O, 29·92. $C_{17}H_{14}N_6O_8$ requires: C, 47·44; H, 3·28; N, 19·53; O, 29·74%).

The *oxime* was prepared by refluxing a mixture of the ketone (3 g), hydroxylamine hydrochloride (3 g), dry MeOH (15 ml) and dry pyridine (15 ml) for 2·5 hr. After removal of the solvents in a vacuum and addition of cold water, the ppt was collected (2·8 g; 88%), m.p. 284° (dec, from water). (Found: C, 50·28; H, 4·66; N, 15·50; O, 29·58. M.W. 265. $C_{11}H_{11}N_3O_5$ requires: C, 49·81; H, 4·18; N, 15·84; O, 30·16%, M.W. 265·22). IR (KBr): 3500–3100 (br) (OH), 1820, 1780, 1760–1720 (imide CO) 1440, 1370, 1300 cm^{-1}. NMR (pyridine): τ −3·20 (s) (1H, NO*H*), 6·20 (s) (2H, CH_2), 6·35 (2H, CH_2), 7·17 (s) (6H, NCH_3).

The *thioketal* **61** was prepared by cooling a mixture of the ketone (2 g) which dissolved as the reaction progressed, BF_3–etherate (2 ml) and ethanedithiol (2 ml) overnight. Cold MeOH (10 ml) was added and the thioketal was collected. More product could be isolated from the mother liquor. Elution from a column of neutral alumina (100 g) with chf–benzene (3:7) afforded the pure thioketal (2 g, 78%), m.p. 283·5° (from chf–hexane). (Found: C, 47·78; H, 4·34; O, 19·75. M.W. 326. $C_{13}H_{14}O_4S_2$ requires: C, 47·81; H, 4·33; O, 19·62%. M.W. 326·26). IR ($CHCl_3$): 1820, 1780, 1750, 1720 (imide CO), 1450, 1380, 1300 cm^{-1}. NMR ($CDCl_3$): τ 6·62 (s) (4H, SCH_2), 6·95 (s) (6H, NCH_3), 7·09 (s) (4H, CH_2).

7,10-*Dimethyl*-6,8,9,11-*tetraoxo*-7,10-*diaza*[3.3.3]*propellane* (**59**)

A mixture of **61** (350 mg), Raney Ni (3 g) and dry EtOH (30 ml) was heated under reflux for 22 hr. The catalyst was collected, washed with dry EtOH, the solvent removed from the combined ethanolic solns. The *diimide* (200 mg; 79%) had m.p. 201–202° (chf–hexane). (Found: C, 54·98; H, 5·35; N, 11·60; M.W. 236. $C_{11}H_{12}N_2O_4$ requires: C, 55·93; H, 5·12; N, 11·86%. M.W. 236·22). IR ($CHCl_3$): 1820, 1780, 1750, 1720 (imide CO), 1450, 1380, 1300 cm^{-1}. NMR ($CDCl_3$): τ 6·98 (s) (6H, NCH_3), 7·62 (m) (4H, CH_2), 7·90–8·25 (m) (2H, CH_2).

3-*Ethanedithio*-7,10-*dimethyl*-7,10-*diaza*[3.3.3]*propellane* (**62**)

A soln of **61** (1 g) in dry THF (30 ml) was added dropwise with stirring to a cold soln of diborane in dry THF (2N; 50 ml). Stirring was continued for 90 hr. Aqueous HCl (1:1; 42·5 ml) was added with cooling. The whole was heated under reflux for 1·5 hr, the solvent was removed and the soln was basified with NaOH aq and extracted with AcOEt. The extract was dried (Na_2SO_4), the solvent

was removed and the crude residue was converted into the yellow *picrate* (0·41 g), m.p. 225–228° (acetone). (Found: C, 42·84; H, 4·40; N, 14·81. $C_{25}H_{28}N_8O_{14}S_2.CH_3COCH_3$ requires: C, 42·72; H, 4·35; N, 14·81%). IR (KBr) showed C=O absorption of the acetone (solvent of crystallization) in the analytical sample at 1720 cm^{-1}. The picrate was converted into the free base with NaOH aq and this was extracted with AcOEt. After drying and removing the solvent, the *thioamine* was distilled (150 mg; 18%), b.p. 94° (0·5 mm). IR ($CHCl_3$): 2940–2780 cm^{-1} (CH). NMR ($CDCl_3$): τ 6·73 (s) (4H, S–CH_2), 7·67 (s), 7·68 (s) (10H, NCH_3 and CH_2), 7·24, 7·53 (AB quartet; J = 9·2 c/s) (8H, NCH_2).

3,7-*Diaza*[3.3.3]*propellane* (**63**)

A soln of **59** (2·7 g) in dry THF was added with cooling to a soln of diborane in THF (2N; 150 ml). After heating under reflux for 60 hr and the usual workup the crude oil was distilled giving the pure *amine* **63** (0·3 g; 14%), b.p. 94° (35 mm). IR ($CHCl_3$): 2940–2800 cm^{-1} (CH). NMR ($CDCl_3$): see Table 4. The yellow *picrate* had m.p. 240° (dec begins at 220°) (from EtOH–acetone). (Found: C, 43·71; H, 4·10; N, 17·59; O, 34·60. $C_{23}H_{26}N_8O_{14}$ requires: C, 43·24; H, 4·11; N, 17·56; O, 35·09%).

Catalytic reduction of **58**

A suspension of **58** (3·5 g) and Adams' catalyst (200 mg) in glacial AcOH (400 ml) was reduced at room temp during 1 week. After removal of the catalyst and solvent, the colorless solid residue was treated with boiling chf and the undissolved *alcohol* **60** was removed by filtration (320 mg; 8%), m.p. 267–268° (from AcOEt–hexane). (Found: C, 52·85; H, 4·56; N, 11·23; O, 31·58, M.W. 252. $C_{11}H_{12}N_2O_5$ requires: C, 52·38; H, 4·80; N, 11·11; O, 31·72%. M.W. 252·22). IR (KBr): 3530, 3480 (OH), 2950, 2920 (CH), 1810, 1770, 1740–1720 (imide CO), 1440, 1380, 1300 cm^{-1}. NMR (DMSO-d_6): τ 4·86 (m) (IH, OH), 6·70 (m) (IH, C*H*OH), 7·20 (s) (6H, NCH_3) 7·73 (broad s) (4H, CH_2). Hexane was added to the hot chf filtrate. The *diimide* **59** was obtained as colorless crystals (2·72 g; 81%), m.p. 201–202° (chf–hexane). It was identical in all respects with the product obtained from **61** (see above).

Conversion of **54** *into the corresponding diamine* **55**

A soln of **54** (2·8 g) in excess $SOCl_2$ (60 ml) was heated under reflux until all of the solid had dissolved (12 hr). The excess $SOCl_2$ was removed in a vacuum. Trituration of the residue with dry ether gave the diacid chloride (2·94 g; 100%), which was collected and dissolved in acetone (12·5 ml). To this cold soln was added with stirring a soln of sodium azide (1·9 g) in water (20 ml). A colorless ppt was obtained after additional stirring (15 min), the ppt was collected, washed with water and dried in a vacuum at room temp. The IR spectrum indicated that this was a mixture of the azide (2170 cm^{-1}) and the isocyanate (2280 cm^{-1}) (1·6 g). To this was added dry toluene (30 ml) and the mixture was heated under reflux for 2·5 hr. Most of the solid dissolved concurrently with gas being evolved. The undissolved ppt was removed by filtering the hot soln. The solvent was removed and the solid residue of the diisocyanate was dried (1·24 g; 48% based on diacid). This was heated under reflux with conc. HCl (10 ml) for 2 hr. The acid was removed in a vacuum and the residual *diamine dihydrochloride* (0·9 g; 33% based on diacid) had m.p. 250–254° (aq EtOH). (Found: C, 36·58; H, 4·70; Cl, 21·49; N, 16·95. $C_{10}H_{16}Cl_2N_4O_4$ requires: C, 36·69; H, 4·74; Cl, 21·68; N, 17·13%). IR (KBr): 3200–2700 (NH_3^+), 1820, 1780, 1750, 1720 (imide CO), 1570, 1520 (NH_3 bending), 1460, 1380, 1320 cm^{-1}. NMR (D_2O): τ 5·30 (s) (6H, $\overset{+}{N}H_3$), 6·20 (s) (4H, CH_2), 6·98 (s) (6H, CH_2).

Conversion of **55** *into the dichloride* **56**

To a soln of **55** (1·2 g) in conc. HCl (10 ml) was added dropwise with cooling a soln of $NaNO_2$ (1 g) in water (20 ml). The colorless ppt was collected (1·02 g; 95%), m.p. 207–208° (AcOEt–hexane). (Found: C, 40·77; H, 3·48; Cl, 23·39; N, 9·51. M.W. 294 (with isotopic chlorine peaks at 292 and 296). $C_{10}H_{10}Cl_2N_2O_4$ requires: C, 40·95; H, 3·44; Cl, 24·21; N, 9·56%. M.W. 293·01). IR ($CHCl_3$): 1820, 1780, 1750, 1720 (imide CO), 1450, 1380, 1310 cm^{-1}. NMR ($CDCl_3$): τ 5·55 (s) (4H, CH_2), 6·93 (s) (6H, NCH_3).

Attempted cyclization of the third ring by treating with methylamine failed. Even at room temp the methylimide rings are opened by this reagent both in aq and in methanolic soln.

Reduction of **56** *with diborane*

The methylimide rings can be reduced to the tertiary amine rings without affecting the Cl atoms. A soln of **56** (2·5 g) in dry THF (50 ml) was added dropwise with cooling and stirring to an ice cold soln of diborane in THF (2N; 200 ml), in an atm of N. The mixture was then heated under reflux for 60 hr. After the usual workup (described above) the oily product was molecularly distilled twice at 70° (1·5 mm). The pure *diamine* **57** (900 mg; 45%) had m.p. 88–90° and must be kept in the dark under N. (Found: C, 50·84; H, 7·47; N, 12·03. M.W. 238 (with isotopic Cl peaks at 236 and 240). $C_{10}H_{18}Cl_2N_2$ requires: C, 50·62; H, 7·65; N, 11·82%. M.W. 237·07). IR ($CHCl_3$): 2940–2780 cm^{-1}. NMR ($CDCl_3$): τ 6·38 (s) (4H, CH_2), 7·35 (s) (8H, NCH_2), 7·70 (s) (6H, NCH_3).

11,13-*Dioxo*-12-*aza*[4.4.3]*propellane* (**65**)

A soln of **6** (5·7 g) in conc NH_4OH (28%; 300 ml) was boiled for 4 hr. After cooling, the ppt was collected. AcOEt extraction gave a further portion of the *imide* (5·3 g; total yield 91%), m.p. 150–151° (benzene–hexane or aqueous isopropanol). (Found: C, 70·26; H, 8·28; N, 6·18. $C_{12}H_{17}NO_2$ requires: C, 69·54; H, 8·27; N, 6·76%). IR ($CHCl_3$): 2940, 2860, 1775, 1690–1720 cm^{-1}. NMR ($CDCl_3$): τ 2·3 (1H NH); 9·2–9·7 (m) (16H CH_2).

12-*Methyl*-12-*aza*[4.4.3]*propellane* **66**

The methanolic (150 ml) soln of **65** (3·1 g) was treated with excess diazomethane in ether. The crude methylated product (3 g; 90%) was subjected to LAH (1·9 g) reduction in ether (150 ml) under reflux for 8 days. The *amine* was obtained as an oil, b.p. 139°/19 mm (2·1 g; 78%). (Found: C, 80·05; H, 11·72; N, 7·02. M.W. 193. $C_{13}H_{23}N$ requires: C, 80·76; H, 11·99; N, 7·25%. M.W. 193·32). IR ($CHCl_3$): 2940–2910, 2860 cm^{-1}. NMR(CCl_4): τ 7·32 (s) (4H CH_2N) 7·59 (s) (3H, NCH_3) 8·56 (s) (16H CH_2). The yellow *picrate* had m.p. 206–208° (dec from EtOH). (Found: C, 54·10; H, 6·18; N, 13·12; O, 26·65. $C_{19}H_{26}N_4O_7$ requires: C, 54·02; H, 6·20; N, 13·26; O, 26·51%).

7,9-*Dioxo*-8-*aza*[4.3.3]*propell*-3-*ene* (**67**)

The anhydride **36** (26 g) was boiled in conc NH_4OH (28%; 500 ml) for 1 hr. More NH_4OH was added (50 ml) and boiling was continued for 4 hr. After cooling the pptd crude imide **67** was collected (13·8 g). Extraction of the mother liquor gave more imide (8·7 g; total yield 87%), m.p. 156–158° (water). (Found: C, 68·84; H, 7·01; N, 7·53; O, 16·95%. M.W. 191. $C_{11}H_{13}NO_2$ requires: C, 69·09; H, 6·85; N, 7·33; O, 16·73%. M.W. 191·22). IR ($CHCl_3$): 3410 (NH), 2970–2950, 2880–2850 (CH), 1785, 1750–1700 (br) (imide CO), 1580 cm^{-1} (C=C). NMR ($CDCl_3$): τ 4·1 (quintet) (2 olefinic H), 7·17–8·50 (m) 10H, CH_2 including allylic H).

7,9-*Dioxo*-8-*methyl*-8-*aza*[4.3.3]*propell*-3-*ene* (**69**)

To a methanolic (300 ml) soln of **67** (22·2 g) was added ethereal diazomethane. After the usual workup the *methylated imide* (19 g; 80%) was obtained, m.p. 85–87° (water). (Found: C, 70·14; H, 6·94; N, 7·24; O, 15·68%. M.W. 205. $C_{12}H_{15}NO_2$ requires: C, 70·22; H, 7·37; N, 6·82; O, 15·59%. M.W. 202·25). IR ($CHCl_3$): 2960–2940, 2870–2840 (CH), 1775, 1715–1690 (br) (imide CO), 1575 cm^{-1} (C=C). NMR ($CDCl_3$): τ 4·1 (quintet) (2 olefinic H), 7·05 (s) (3H, NCH_3), 7·3–8·5 (10H, CH_2 including allylic H).

7,9-*Dioxo*-8-*methyl*-8-*aza*[4.3.3]*propellane* (**70**)

The theoretical volume of H was taken up by **69** (0·5 g) in glacial AcOH (25 ml) in the presence of Adams' catalyst (50 mg) at room temp and atm press during 35 min. After removal of catalyst and solvent, the residue was distilled, b.p. 70° (0·3 mm) giving the *saturated imide* **70** (0·26 g; 51%). (Found: C, 68·93; H, 8·08; N, 6·64; O, 16·27. M.W. 207. $C_{12}H_{17}NO_2$ requires: C, 69·54; H, 8·27; N, 6·76; O, 15·44%. M.W. 207·26). IR ($CHCl_3$): 2950, 2870 (CH), 1770, 1705–1690 cm^{-1} (imide CO). NMR (CCl_4): τ 7·1 (s) (3H, NCH_3); 7·6–9·0 (m) (14H, CH_2).

8-*Methyl*-8-*aza*[4.3.3]*propellane* (**71**)

A mixture of **70** (1·8 g), LAH (2 g) and ether (150 ml) was heated under reflux for 7 days. After the usual workup the *amine* **71** was obtained as an oil (1·05 g; 70%), b.p. 89° (19 mm). (Found: C,

79·92; H, 11·81; N, 8·03. M.W. 179. $C_{12}H_{21}N$ requires: C, 80·38; H, 11·81; N, 7·83%. M.W, 179·30). The picrate had m.p. 218° (dec, from EtOH). (Found: C, 52·89; H, 5·76; N, 13·16; O, 28·10, $C_{18}H_{24}N_4O_7$ requires: C, 52·93; H, 5·92; N, 13·72; O, 27·42%).

7,9-Dioxo-8-aza[4.3.3]*propellane* (**68**)

The imide **67** (3·46 g) was catalytically reduced in glacial AcOH (250 ml) in the presence of Adams' catalyst (0·3 g) during 3 hr. After removal of the catalyst and solvent the imide **68** was obtained (3·2 g; 92%), m.p. 135–137° (hexane). (Found: C, 68·68; H, 7·82; N, 7·28; O, 16·27. M.W. 193. $C_{11}H_{15}NO_2$ requires: C, 68·37; H, 7·82; N, 7·25; O, 16·56%. M.W. 193·24). IR ($CHCl_3$): 3400, 3260 (NH), 2950, 2880 (CH), 1780, 1750–1700 cm^{-1} (imide CO). NMR ($CDCl_3$): τ 5·2 (broad) (IH, N*H*), 8·82–9·4 (m) (14*H*, CH_2).

Ozonolysis of **69**

Ozone was passed through a soln of the methylated imide (17 g) in glacial AcOH (300 ml) for 5 hr at room temp. The solvent was removed in a vacuum and to the ozonide residue was added H_2O_2 (30%; 190 ml) and formic acid (114 ml). The mixture was warmed until the exothermic reaction set in, then cooled and set aside overnight at room temp. The solvents were removed in a vacuum and the resulting oil was triturated with chf. The diacid **72** (20 g; 91%), had m.p. 105–107° (chf). (Found: C, 53·35; H, 5·80; N, 5·18; O, 35·55. $C_{12}H_{15}NO_6$ requires: C, 53·53; H, 5·62; N, 5·20; O, 35·65%). IR (KBr): 3500–3100 (OH), 2980–2960 (CH), 1780, 1705–1670 (imide CO), 1730 cm^{-1}, (carboxyl CO). NMR acetone-d_6: τ 6·12 (s) (2H, CO_2H), 7·06 (s) (7H, CH_2CO and NCH_3) 7·7–8·1 (m) (6H, CH_2).

2,4-Dioxo-3-methyl-3-aza[3.3.3]*propellan-7-one* (**73**)

A soln of the diacid (12 g) in AcO (200 ml) was heated at 120° in an atm of N for 36 hr. 90% of the theoretical amount of CO_2 evolved was collected as $BaCO_3$. The solvent was removed in a high vacuum. The residual brown oil in benzene was chromatographed on neutral alumina (500 g) and eluted with chf–benzene (2:8). The *ketone* **73** (7·5 g; 81%), had m.p. 125° (hexane). (Found: C, 63·87; H, 5·99; N, 6·68; O, 23·29. M.W. 207. $C_{11}H_{13}NO_3$ requires: C, 63·75; H, 6·32; N, 6·76; O, 23·16%. M.W. 207·22). IR ($CHCl_3$): 2980–2960 (CH), 1785, 1710 (imide CO), 1760 cm^{-1} (ketone CO). NMR ($CDCl_3$): τ 7·00 (s) (3H, NCH_3) 7·16, 7·47 (AB quartet, J_{AB} = 19 c/s) (4H, CH_2), 7·7–8·5 (m) (6H, CH_2).

The *thioketal* was obtained from the ketone (0·22 g), ethanedithiol (0·5 ml) and BF_3–etherate (0·5 ml) refrigerated overnight. After the usual workup the crude product was obtained (0·21 g; 71%). It was recrystallized thrice, m.p. 86–88·5° (hexane). (Found: C, 54·95; H, 6·08; N, 5·02; S, 22·20. $C_{13}H_{17}NO_2S_2$ requires: C, 55·12; H, 6·00; N, 4·95; O, 11·29; S, 22·64%). IR ($CHCl_3$); 2970–2940, 2870 (CH), 1775, 1710–1690 cm^{-1} (imide CO). NMR ($CDCl_3$): τ 6·70 (s) (4H CH_2S); 7·02 (s) (3H, NCH_3); 7·14, 7·70 (AB quartet; J_{AB} = 13·6 c/s). (4H, CH_2), 8·0–8·1 (m) (6H, CH_2).

2,4-Dioxo-3-methyl-3-aza[3.3.3]*propellane* (**74**)

A soln of **73** (0·42 g) in glacial AcOH (25 ml) in the presence of Adams' catalyst (40 mg) took up 2 *moles* H during 5 hr at room temp and atm press. After removal of the catalyst and solvent the *imide* with no further functional groups was obtained (0·32 g; 81%), m.p. 56–57° (hexane). (Found: C, 68·19; H, 7·86; N, 7·41; O, 16·84. M.W. 193. $C_{11}H_{15}NO_2$ requires: C, 68·37; H, 7·82; N, 7·25; O, 16·56%. M.W. 193·24. IR ($CHCl_3$): 2960–2940, 2870 (CH), 1770, 1720–1680 cm^{-1} (imide CO). NMR ($CHCl_3$): τ 7·05 (s) (3H, NCH_3), 7·5–8·5 (m) (12H, CH_2).

3-Methyl-3-aza[3.3.3]*propellane* (**75**)

A mixture of **74** (0·8 g), LAH (1·5 g) and ether (100 ml) was heated under reflux for 1 week. After the usual workup the *amine* was distilled, b.p. 98–103° (18 mm). (0·25 g; 35%). (Found: M.W. 165. $C_{11}H_{19}N$ requires: M.W. 165·27). The yellow *picrate* had m.p. 212° (dec, from EtOH). (Found: C, 51·65; H, 5·59; N, 14·32; O, 28·47. $C_{17}H_{22}N_4O_7$ requires: C, 51·77; H, 5·62; N, 14·21; O, 28·40%).

The two epimeric 2,4-dioxo-3-Methyl-3-aza[3.3.3]*propellan-7-ols* (**76**, **77**)

(a) Reduction of **73** (0·5 g) dissolved in MeOH (15 ml) with $NaBH_4$ (0·15 g) during 24 hr gave the intramolecularly hydrogen-bonded *alcohol* **76** (0·42 g; 80%), m.p. 87–89° (hexane). (Found:

C, 63·05; H, 7·22; N, 6·87; O, 22·87. M.W. 209. $C_{11}H_{15}NO_3$ requires: C, 63·14; H, 7·23; N, 6·69; O, 22·94%. M.W. 209·24). IR ($CHCl_3$): 3620, 3550–3400 (OH); 2960–2940, 2870 (CH) 1770, 1720–1680 (imide CO) 1008, 1028 cm^{-1}. NMR (pyridine): τ 3·6 (broad) (1H O*H*), 5·55 (quintet C*H*OH), 7·05 (s) (3H, NCH_3), 7·25–8·40 (m) (10H CH_2).

Reduction of **73** with lithium aluminum tri-t-butoxyhydride gave some of the other epimer but it was difficult to isolate it from the reaction mixture. Therefore, the epimer was prepared by inversion of the tosylate of the hydrogen-bonded epimer.

(b) The alcohol **76** (0·24 g) was treated with *p*-toluenesulfonyl chloride (0·50 g) in dry pyridine (3 ml) and the crude tosylate thus formed (0·38 g; 85%), was dissolved in CH_2Cl_2 (2 ml) and the soln was passed through a column of basic alumina (Merck; 30 g). Elution with MeOH–chf (1 : 9) gave **77** (0·1 g; 42%), m.p. 142–145° (hexane–benzene). (Found: C, 63·60; H, 6·94. M.W. 209. $C_{11}H_{15}NO_3$ requires: C, 63·14; H, 7·23%. M.W. 209·24). IR ($CHCl_3$): 3610, 3550–3400 (OH); 2960–2940, 2870; (CH) 1770, 1710–1680 (imide CO), 995, 1032 cm^{-1}. NMR (pyridine): τ 4·25 (broad) (1H, O*H*), 5·45 (broad) (1H, C*H*OH), 7·02 (broad) (3H, NCH_3), 7·25–8·50 (10H, CH_2).

Attempted catalytic hydrogenolysis of the epimeric alcohols

Each of the alcohols in glacial AcOH in the presence of Adams' catalyst, under the same conditions employed for the hydrogenolysis of the ketone **73** (see above), failed to take up any H even during long periods (1 week). Each of the alcohols was recovered unchanged. To make sure that the catalyst had not been poisoned, cyclohexene was added at the end of the experiment and it absorbed the theoretical amount of hydrogen.

2,4-*Dioxo*-3-*methyl*-7-*ethanedioxy*-3-*aza*[3.3.3]*propellane* (**78**)

A mixture of **73** (0·48 g), *p*-toluenesulfonic acid (0·25 g), ethylene glycol (0·25 ml) and dry benzene (50 ml) was heated under reflux for 24 hr, the water formed being removed azeotropically. After washing with $NaHCO_3$ aq and evaporation of the solvent, the *ketal* was obtained (0·5 g; 88%), m.p. 102–103° (hexane). (Found: C, 62·53; H, 7·19. $C_{13}H_{17}NO_4$ requires: C, 62·14; H, 6·82%). IR ($CHCl_3$): 2960–2940, 2890–2880 (CH), 1775, 1710–1690 cm^{-1} (imide CO).

7-*Ethanedioxy*-3-*methyl*-3-*aza*[3.3.3]*propellane* (**79**)

A mixture of the ketal (0·82 g) LAH (1 g) and ether (150 ml) was heated under reflux for 1 week. After the usual workup the *ketal-amine* was obtained, (0·52 g; 70%), b.p. 152° (19 mm). IR ($CHCl_3$): 2940–2920, 2860, 2830, 2780 cm^{-1} (CH). The *picrate* had m.p. 189–191° (dec, from EtOH–acetone). (Found: C, 50·52; H, 5·49; N, 12·76. $C_{19}H_{24}N_4O_9$ requires: C, 50·42; H, 5·35; N, 12·39%).

3-*Methyl*-3-*aza*[3.3.3]*propellane*-7-*one* (**80**)

Treatment of **79** (5 g) in boiling acetone (600 ml) containing *p*-toluenesulfonic acid (13 g) for 20 hr gave, after removal of the solvent a crude residue. The soln of the residue in ether was extracted with 10% HCl and the acid soln was adjusted to pH 10 by addition of 10% NaOH aq. The *aminoketone* was extracted into ether and removal of the solvent gave pure material (2·9 g; 72%), m.p. 45–47°. (Found: M.W. 179. $C_{11}H_{17}NO$ requires: 179·25). IR ($CHCl_3$): 1740 cm^{-1} (CO). NMR ($CDCl_3$): τ 7·20–7·65 (m) (8H, CH_2CO and CH_2N), 7·72 (s) (3H, NCH_3), 8·0–8·7 (m) (6H, CH_2).