PROPELLANES—I
TRICYCLIC COMPOUNDS CONJOINED
IN A CARBON—CARBON SINGLE BOND

J. ALTMAN, E. BABA, J. ITZCHAKI and D. GINSBURG
Department of Chemistry, Israel Institute of Technology, Haifa, Israel

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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. Although such compounds have been known, they were not prepared primarily because of interest in designing such systems.

Nomenclature. The rules of nomenclature used for tricyclic systems require lengthy names and as many as six numerals to define even such a simple structure as which would be called tricyclo[4,3,3,0'2]dodecane. Based on examination of a model of 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 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, would name compound [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

5. 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.

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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-16 will apply. Examples 3, 4, 5 and those in the experimental section will suffice to explain the system.

3-aza \([4,3,3]\) propellane, not 4-aza \([4,3,3]\) propellane

8-aza \([4,3,3]\) propellane, not 11-aza \([4,3,3]\) propellane

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-cyanide 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. 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

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6 Ref. 4, p. 90.

cleavage of the $\alpha$-$\beta$ bond in the $\beta$-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 $\beta$-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 subject 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 in similarly constituted systems.

\* 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, Ireland, Abstr. of papers, 51st meeting Amer. Chem. Soc., Pittsburgh, March 28–31 (1966); Div. of Org. Chem. abstr. no. K57.
The routes to a number of diazapropropellanes are summarized in Scheme 4. The Diels-Alder adduct 44 of butadiene and tetracyanoethylene was converted by an improved procedure over that reported, 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 CO₂H). 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 thiokeatal 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.

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Table 5. UV absorption data (in MeCN solution)

(Left hand column = $\lambda_{\text{max}}$ (m$\mu$); right hand column = $\varepsilon_{\text{max}}$).

For structural formulae see Schemes 4 and 5.

<table>
<thead>
<tr>
<th></th>
<th>59</th>
<th>74</th>
<th>52</th>
<th>70</th>
<th>46</th>
<th>69</th>
<th>58</th>
<th>73</th>
<th>48</th>
<th>49</th>
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<tr>
<td>246</td>
<td>472</td>
<td>250</td>
<td>162</td>
<td>246</td>
<td>583</td>
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<td>248</td>
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<tr>
<td>259</td>
<td>419</td>
<td>259 (sh)</td>
<td>106</td>
<td>259</td>
<td>450</td>
<td>258 (sh)</td>
<td>139</td>
<td>259</td>
<td>453</td>
<td>258 (sh)</td>
</tr>
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<td>268</td>
<td>422</td>
<td>268</td>
<td>464</td>
<td>268</td>
<td>490</td>
<td>268</td>
<td>490</td>
<td>268</td>
<td>570</td>
<td>268</td>
</tr>
<tr>
<td></td>
<td></td>
<td>304 (sh)</td>
<td>8</td>
<td>305 (sh)</td>
<td>20</td>
<td>286 (sh)</td>
<td>1100</td>
<td>314 (sh)</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
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 268 m\(\mu\) in 59, 52, and 46, as well as in 58 and 48. In 49, a cis-bicyclic compound, the corresponding band appears at 265 m\(\mu\), 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 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,
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.

\[\text{SCHEME 6}\]

\[
\begin{align*}
\text{ion a} & \quad \text{m/e 149} \\
\text{ion b} & \quad \text{m/e 136} \\
\text{ion c} & \quad \text{m/e 135} \\
\text{ion d} & \quad \text{m/e 107}
\end{align*}
\]

The diester 20 exhibits also the expected peaks resulting from α-cleavage\(^ {15}\) (Experimental section).

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


\(^{14}\) We are grateful to Dr. A. Mandelbaum for the mass spectra and critical discussion.

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.

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.

\[
\begin{align*}
\text{Scheme 8} \\
\text{X=NH}_2 & \quad \rightarrow \quad \text{m/e 216} \\
\text{X=SH} & \quad \rightarrow \quad \text{m/e 233} \\
\end{align*}
\]

\[
\begin{align*}
\text{X=NH}_2; \text{m/e 160} \\
\text{X=SH; m/e 177} \\
\end{align*}
\]

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 | Ring methylenes |
|          | \( \tau \)       | \( \tau \)       |
| 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angiular methylenes</th>
<th>Aliphatic</th>
<th>Allylic</th>
<th>Five-membered ring CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ</td>
<td>τ</td>
<td>J</td>
<td>τ</td>
</tr>
<tr>
<td>23</td>
<td>6.04 (s)</td>
<td>4.33 (t)</td>
<td>1.4 c/s</td>
<td>7.62 (m)</td>
</tr>
<tr>
<td>25</td>
<td>6.33 (s)</td>
<td>4.40 (t)</td>
<td>1.2 c/s</td>
<td>7.82 (d) 1.2 c/s</td>
</tr>
<tr>
<td>27</td>
<td>6.43 (s)</td>
<td>4.38 (t)</td>
<td>1.5 c/s</td>
<td>7.82 (m)</td>
</tr>
<tr>
<td>28</td>
<td>7.51 (s)</td>
<td>4.36 (t)</td>
<td>1.5 c/s</td>
<td>7.4-8.9 (m)</td>
</tr>
<tr>
<td>34</td>
<td>7.59 (s)</td>
<td>4.42 (t)</td>
<td>1.6 c/s</td>
<td>7.88 (broad)</td>
</tr>
<tr>
<td>37</td>
<td>6.39; 6.57</td>
<td>4.38 (t)</td>
<td>1.5 c/s</td>
<td>7.96 (m)</td>
</tr>
</tbody>
</table>
\[ J_{gem} = 11.4 \text{ c/s} \]

16 At 100 MHz in CDCl₃ the allylic protons are resolved to an AB-type quartet, $J_{gem} = 17$ c/s. The temp. studies (in benzene) show that the two CH₂CN 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

<table>
<thead>
<tr>
<th>R</th>
<th>Six-membered ring</th>
<th>Four-membered ring</th>
<th>J (c/s)</th>
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<tr>
<td></td>
<td>τ</td>
<td>τ</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>8.63 (s)</td>
<td>8.37 (s)</td>
<td></td>
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<tr>
<td>CN</td>
<td>8.4-8.9 (m)</td>
<td>Hₐ 8.34 (quartet)</td>
<td>$J_{AX} = 7.8$</td>
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<tr>
<td></td>
<td></td>
<td>Hₐ 7.64 (triplet)</td>
<td>$J_{AB} = 9.8$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hₐ 6.82 (quartet)</td>
<td>$J_{BX} = 9.8$</td>
</tr>
<tr>
<td>CO₂H</td>
<td>8.2-8.8 (m)</td>
<td>Hₐ collapses with six-membered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ring protons</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hₐ 7.70 (triplet)</td>
<td>$J_{AB} = 10.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hₐ 6.78 (quartet)</td>
<td>$J_{AX} = 7.2$; $J_{BX} = 10.0$</td>
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<tr>
<td>Br</td>
<td>8.4-8.9 (m)</td>
<td>Hₐ 8.15 (quartet)</td>
<td>$J_{AX} = 7.2$</td>
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<tr>
<td></td>
<td></td>
<td>Hₐ 7.62 (triplet)</td>
<td>$J_{AB} = 10.1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hₐ 5.60 (quartet)</td>
<td>$J_{BX} = 10.1$</td>
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TABLE 4. NMR SPECTRA OF [4.4.3] AND [4.3.3] PROPELLANES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Six-membered ring</th>
<th>Five-membered ring</th>
<th>Five-membered heterocyclic ring</th>
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<tr>
<td></td>
<td>( \tau )</td>
<td>( \tau )</td>
<td>( \tau )</td>
</tr>
<tr>
<td>8</td>
<td>8.55 (s)</td>
<td>6.36 (s)</td>
<td>7.32 (s) 7.59 (s) (NCH(_3))</td>
</tr>
<tr>
<td>66</td>
<td>8.56 (s)</td>
<td>8.38 (broad)</td>
<td>8.53 (s)</td>
</tr>
<tr>
<td>32</td>
<td>8.5 (broad s)</td>
<td>7.8 (broad s)</td>
<td>8.52 (s)</td>
</tr>
<tr>
<td>33</td>
<td>8.64 (broad)</td>
<td>8.34 (m)</td>
<td>8.41 (m)</td>
</tr>
<tr>
<td>42</td>
<td>8.53 (s)</td>
<td>6.42 (s)</td>
<td>7.51, 7.61 7.71 (s) (NCH(_3))</td>
</tr>
<tr>
<td>71</td>
<td>8.52 (s)</td>
<td>7.53, 7.69 7.78 (s) (NCH(_3))</td>
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</tr>
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<td>53</td>
<td>8.48 (s)</td>
<td>7.51, 7.61 7.71 (s) (NCH(_3))</td>
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</tr>
<tr>
<td>75</td>
<td>8.50 (m)</td>
<td>7.76 (s) 7.85 (s) (NCH(_3))</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>8.39 (s)</td>
<td>7.47, 7.65 7.70 (s) (NCH(_3)) AB quartet J = 9.0 c/s</td>
<td></td>
</tr>
</tbody>
</table>

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 \(^6\) (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): \( \delta 4.18 \) (v. broad) (2H, OH), \( \delta 6.10 \) (broad s) (4H, C&O), 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\(_{22}\)O\(_2\): 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\(_4\)): \( \delta 6.38 \) (4H, CH\(_2\)O), 8.40 (v. broad s) (16H, CH\(_2\)).

**cis-4a, 8a-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.


\(^{19}\) Prof. V. Prelog has informed us that he has prepared this and similar compounds with Dale, some years ago.
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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). C12H20Br2 requires: C, 44.46; H, 6.21; Br, 49.30%. M.W. 324.12). IR(CHCl3): 2950, 2880 cm⁻¹. NMR (CDCl₃): τ 6.42 (v. broad) (4H, C&Br), 8.45 (broad) (16H, CHr).

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. Na₂SO₄). After treatment with active carbon, removal of the solvents and trituration with hexane, cis-4a-bromomethyl-8α-cyanomethylaxalin 10 was obtained (0.74 g, 22.5%), m.p. 101–102° (hexane). (Found: C, 58.48; H, 7.97; N, 7.52. M.W. (mass spectral): 189. C13H19N requires: C, 57.79; H, 7.49; N, 12.95%. M.W. 189.29). IR (CHCl₃): 2955, 2880, (CH) 2260 cm⁻¹ (GN). NMR (CDCl₃): τ 6.5 (very broad) (2H, CHrBr), 7.5 (v. broad) (2H, CH₂CN), 8.43 (broad singlet) (16H, CHd. The above hexane mother liquor was passed through a column of neutral alumina (Merck; 50 g). Elution with benzene–hexane (1:4) gave 1 I-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. C13H19O requires: C, 82.48; H, 10.12; N, 7.40%. M.W. 189.29). IR (CHCl₃): 2985, 2940, 2810, 2850 (CH), 2190 (C=N), 1650 (C==C); 1610 cm⁻¹ (NH bend). NMR (CDCl₃): 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. C14H17NO requires: C, 77.73; H, 9.32; N, 12.95 %. M.W. 216.31). IR (CHCl₃): 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 (CDCl₃): see Table 3. Continued elution with benzene–hexane (2:3) yields a further quantity of 10 (0.48 g; total yield 37%).

11 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 solution 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 (0.19 g, 72%) was obtained, b.p. 102–104° (24mm). nD²⁰ 1.4958. Lit.3²² 1.4938. (Found: C, 87.05; H, 12.72. Calc. for C₁₂H₂₀: C, 87.73; H, 12.27%). IR (CHCl₃): 2980, 2950, 2880, 2850 cm⁻¹. NMR (CDCl₃): τ 8.07 (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), H₂SO₄ (5 ml) and water (5 ml) was heated at 150° for 1 hr. After cooling to 60°, small portions of NaNO₂ (0.5 g) were added during extraction broken with NaCl, trituration of the residue with hexane gives theaminonitrile 12 (48.5 mg, 15%), m.p. 191° (hexane–benzene). (Found: C, 77.92; H, 9.35; N, 12.95. M.W. 216. C₁₄H₁₇NO requires: C, 77.73; H, 9.32; N, 12.95 %. M.W. 216.31). IR (CHCl₃): 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 (CDCl₃): τ 5.4 (broad) (2H, NH₂), 7.77 (s) (2H, CH₂NH+C), 8.57 (s) (16H, CHd.

A mixture of the carboxylic acid (0.62 g; 3 mmoles), red HgO (0.58 g; 2.7 mmoles), and dry CCl₄ (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 CO₂ 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. K₂CO₃aq and water. After drying (Na₂SO₄) and removal of the ether, the 11-bromo [4.4.2] propellane 15 was
distilled, b.p. 58° (0·1 mm) nD25 1·5308 (0·68 g; 92%). (Found: C, 59·12; H, 7·56; Br, 33·86. C12H18Br requires: C, 59·36; H, 7·87; Br, 32·86%). IR (CS2): 2980, 2940, 2850, 2830 cm⁻¹ (CH). NMR (CCl₃): 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), H₂SO₄ (2·5 ml) and water (2·5 ml) was heated at 150° for 1 hr. After cooling to 60° NaNO₂ (0·2 g) was added in portions. The lactone 13 (0·2 g, 78%) was isolated, m.p. 144° (hexane). (Found: C, 74·89; H, 8·10; O, 15·15. M.W. 208. C₂H₂O₂ requires: C, 74·99; H, 8·88; O, 15·15%. M.W. 208·30). IR (CHCl₃): 2950, 2875, 2250 (C=O); 1770 cm⁻¹ (C=O). NMR (CDCl₃): δ 5·78 (s) (2H, C=O), 7·58 (s) (2H, C=O), 8·46 (s) (16H, C₆H₄).

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

To a soln of Na (100 mg) in liquid ammonia (60 ml) under N₂ 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 (Na₂SO₄), the ether was removed. The residue of the dinitrile showed no NH₂ 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. C₄H₆N₂O requires: C, 77·38; H, 8·81; N, 6·45%. M.W. 217·27). IR (CHCl₃): 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. C₂₀H₁₄N₄O₅ 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), BF₃ 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 (Na₂SO₄). Removal of the solvent left a residue of the crude thioketal (quant. yield). The crude compound was dissolved in ethylene glycol (2 ml) and the soln was heated to 95° (5 min; 0·2 g) and solid KOH (0·3 g) was added and the whole refluxed for 15 hr. The residue of the mercaptotricarbonyl (47 mg; 44%) had m.p. 156° (hexane). (Found: C, 72·21; H, 7·55; S, 13·70. M.W. 233. C₁₄H₁₄NS requires: C, 72·07; H, 8·21; S, 13·72%. M.W. 233·30). IR (CHCl₃): 3000, 2940, 2860 (CH), 2580, 2560 (SH), 2205 (CN), 1585 cm⁻¹ (C≡C).

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

A mixture of 18 (0·3 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 (Na₂SO₄). 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. C₁₄H₂₂O₄ requires: C, 66·11; H, 8·72; O, 24·90%). IR (KBr): 2950, 2930, 2870, 1720 (s), 1695 cm⁻¹ (s). NMR (pyridine): δ 1·72 (broad singlet) (CO₂H), 7·5–8·6 (broad) (aliph. H).

**cis-4a, 8a-Biscarbomethoxymethyldecaline (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), nD25 1·4386. (Found: C, 68·05; H, 9·62; O, 22·35. C₁₆H₂₆O₄ requires: C, 67·98; H, 8·88; O, 22·14%). IR (CHCl₃): 2950, 2940, 2875, 1730 cm⁻¹ (ester CO). NMR (CDCl₃): δ 6·43 (s) (6H, OCH₃), 8·46 (very broad) (20H, CH₂). Fragmentation pattern on electron impact:

M⁺ for 20 (m/e 282) → m/e 251 → m/e 219; m/e 251 → ketene → m/e 209 → 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 mmole) in liquid ammonia (80 ml) and THF (20 ml). The ammonia was evaporated and MeGH (2 ml), water (50 ml) and ether (50 ml) were added. The organic phase was washed with water, dil. HCl aq, water, dil. NaHCO₃ aq, water and dried (Na₂SO₄). Removal of the solvents and trituration with chf gave the dial (110 mg; 33%), m.p. 158° (benzene). (Found: C, 74.89; H, 10.63; O, 14.86. M.W. 224. C₁₁H₂₄O₂ requires: C, 74.95; H, 10.78; O, 14.26%). 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 NaBH₄ reduction of the residue in MeGH-THF gives more of the dial (100 mg; total yield 62%).

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

The anhydride 22 cis was reduced in 90% yield as described above for the reduction of 6 to 7. The dial had m.p. 165-168° (acetone). Lit. 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 were dealing with a polymorphic form. NMR (pyridine): δ 4.34 (t at X part of ABX spectrum; Jₓₓ = Jₓₓ = 1.4 c/s) (4 olefinic H), 6.05 (s) (4H, CH₂OH), 7.63, 7.78 (8H, CH₂, Jₓₓ = 18.4 c/s).

d12-0 [4.4,3] propellane-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). (Found: C, 81.41; H, 9.07; O, 9.40. M.W. 176). C₁₂H₁₈O requires: C, 81.77; H, 9.15; O, 9.08%. M.W. 176.25). IR (CHCl₃): 298&2835 (CH), 1661.1630 (C=C), 1029,1008 cm⁻¹ (C=O). NMR (CCl₄): δ 4.50 (t) (4 olefinic 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 (208 g; 65%), had b.p. 150-160° (0.5 mm), m.p. 79° (EtOH). (Found: C, 45.34; H, 5.08; Br, 49.92%. M.W. 320). IR (CHCl₃): 3000-2845 (CH), 1660 cm⁻¹ (C==), 1599 cm⁻¹ (NH bend). NMR (CDCl₃): δ 4.40 (t) (4 olefinic H), 6.33 (s) (4H, CH₂Br), 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 48 hr at 130° as described above for 9, similar workup gave in this case 11-cyano-12-aminu [4.4.3] propellana-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. C₁₄H₁₆N₂ requires: C, 79-21; H, 7-60, N, 13-20%. M.W. 212.28). IR (CHCl₃): 3518, 3410 (NH), 2998-2838 (CH), 2182 (CN), 1660, 1650, 1640 (C==C), 1599 cm⁻¹ (NH bend). NMR (CDCl₃): δ 4.36 (t) (4 olefinic H), 7.51 (s) (4H, CH₂CN), 7.4-8.9 (multiplets) (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. 54° (benzene–hexane). (Found: C, 79-46; H, 7-36; N, 13-00. M.W. 212. C₁₄H₁₈N₂ requires: C, 79-21; H, 7-60, N, 13-20%. M.W. 212.28). IR (CHCl₃): 2980-2845 (CH), 2250 (CN), 1659, 1630, 1695 cm⁻¹ (w) (C==C). NMR (CDCl₃): δ 4.36 (t) (4 olefinic H), 7.51 (s) (4H, CH₂CN), 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. 160°. (Found: C, 78.76; H, 7.14; N, 6.83. M.W. 213. IR (CHCl₃): 2980, 2845 (CH), 2250 (CN), 1765 (CO), 1680, 1665, 1640 cm⁻¹ (νν(C≡C)). NMR (CDCl₃): τ 4.36 (t) (4 olefinic H), 6.47 (s) (CH CN), 7.7-8.9 (multiplets) (10H, CH₅).

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. C₁₄H₁₈O₄ 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, CH₂COH), 4.45 (broad) (4 olefinic H), 7.27 (s) (4H CH₂CO), 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). (Found: C, 69.05; H, 7.98; O, 23.00. C₁₅H₂₀O₂ requires: C, 68.97; H, 8.01; O, 23.02%). IR (CHCl₃): 1730 (CO). NMR (CDCl₃): τ 4.42 (t) (4 olefinic H), 7.24 (s) (4H CH₂CO), 7.77-7.92 (m) (8 allylic H).

Treatment of the diacid 30 with boiling AcrO gave the seven-membered anhydride of 30, in 78 %

[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

[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

[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 (Na₂SO₄), concentration and chromatography
over basic alumina (Merck; 15 g), the diene 35 was eluted with hexane and distilled, b.p. 140°

[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. C₁₃H₂₂ requires: M.W. 178.31). NMR (CDCl₃): 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 anhydride29 (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. C11H12O2 requires: C, 68.73; H, 6.29%. M.W. 192.21). IR (CHCl₃): 1853, 1780 (C=O), 1638 cm⁻¹ (C=C). NMR (CDCl₃): \( \tau \) 3.98 (quintet) (2 olefinic H), 7.08, 7.32 (m) (4 allylic H), 7.5-8.3 (m) (6H, CH₃).

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. C₁₁H₁₄O₂ requires: C, 72.49; H, 9.96%). IR (CH₅CN): 3620, 3400 (OH), 1660 cm⁻¹ (C=O). NMR (CDCl₃): \( \tau \) 4.48 (1) (J= 1.8 c/s; 2 olefinic H), 5.48 (s) (2H, OH), 6.39, 6.57 (AB quartet; Jₐ₋ₐ = 11.4 c/s) (4H, CH₂O), 7.86, 8.07 (AB quartet, Jₐ₋ₐ = 18.0 c/s) (4 allylic H), 8.36 (broad s) (6H, CH₃). The OH peak moves to \( \tau \) 2.57 in the presence of CF₃COOH.

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. C₁₁H₁₄O requires: M.W. 164.24. NMR (CDCl₃): \( \tau \) 4.18 (t), (J=3 c/s) (2 olefinic H), 6.52 (s) (4H, CH₂O), 8.02 (d, J = 3 c/s) (4 allylic H), 8.43 (broad s) (6H, CH₃).

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, NaHCO₃ 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. C₁₁H₁₄Br requires: C, 58.16; H, 6.65; Br, 35.18%. M.W. 227.15). UV (hexane): \( \lambda_{max} \) 228-232 mμ; \( \epsilon_{max} \) 1600. NMR (CDCl₃): \( \tau \) 4.146 (m) (3 olefinic H), 6.56 (m) (2H, CH₂Br), 7.7-8.4 (m) (8H, CH₂ 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. 168° (0.2 mm), m.p. 84° (hexane). (Found: C, 67.93; H, 7.36; O, 24.95. C₁₁H₁₄O₂ requires: C, 68.02; H, 7.27; O, 24.71%). IR (CHCl₃): 1860, 1840, 1780 cm⁻¹ (C=O). NMR (CDCl₃): \( \tau \) 7.6-8.6 (m) (CH₂).

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. C₁₁H₁₄O₂ requires: C, 71-69; H, 10-94; O, 17-37%). IR (CHCl₃): 3600, 3420 cm⁻¹ (OH). NMR (CDCl₃): \( \tau \) 6-65 (s) (2H, OH), 6-47 (s) (4H, CH₂O), 8-37 (s) (8H, CH₃), 8-53 (s) (6H, CH₂).

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. C₁₁H₁₄O₂ requires: C, 79-46; H, 10-92; O, 9-63%. M.W. 166-25). IR (CHCl₃): 1067, 1045 cm⁻¹. NMR (CDCl₃): \( \tau \) 6-62 (s) (4H, CH₂O), 8-32 (broad s) (6H, CH₃), 8-54 (s) (8H, CH₂).

29 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.

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4a-Bromomethyldecalin-8-ene (43)

The ether 42 was treated with triphenyl phosphine 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_{12}Br requires: M.W. 229.16). UV (hexane): λ_{max} 228-232 μm, ε_{max} 1200. NMR (CCl_{4}): τ 4.55 (m) (1 olefinic H), 6.42 (m) (2H, CH_{2}Br), 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°. 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 (46)

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, 50%), m.p. 290-295° (dec; acetone or water). (Found: C, 51.89; H, 2.23; N, 6.74. M.W. 380 (with isotopic Br peaks at 378 and 382. C_{10}H_{12}N_{2}O_{4}Br_{2} requires: C, 31.59; H, 2.11; N, 7.37%. M.W. 379.91). 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, CH), 6.96 (s) (6H, NCH&), 7.2 (d, J = 3 c/s) (4H, CH₂). 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.

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

To a soln of 46 (1 g) in glacial AcOH (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. 248-251° (MeOH). (Found: C, 58.15; H, 4.87; N, 11.29. M.W. 248. C_{12}H_{14}N_{2}O_{4} requires: C, 58.15; H, 4.87; N, 11.29%. M.W. 248.23). IR (KBr): 3060 (=CH), 2970, 2930, 2860 (CH), 1820, 1780, 1750, 1720 (imide CO).
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. C₁₂H₂₂N₄ requires: C, 44.17; H, 4.33; N, 17.17%). IR (CHCl₃): 2940-2800 cm⁻¹ (CH). NMR (CDCl₃): δ 7.51, 7.61 (AB quartet; J = 8.9 c/s) (8H, NC₆H), 7.71 (s) (6H, NCH₃), 8.48 (s) (8H, CH₂). The yellow picrate had m.p. 210-213° (MeOH). (Found: C, 44.54; H, 4.16; N, 17.00. C₂₀H₂₆N₄O₄ requires: C, 44.30; H, 4.30; N, 17.40%).

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. C₁₂H₂₀N₂ requires: 192.30). IR (CHCl₃): 2940-2780 cm⁻¹ (CH). NMR (CDCl₃): δ 4.12 (t) (2 vinyl H; J = 3.2 c/s), 7.46, 7.61, (AB quartet, J = 9 c/s) (8H, NCH₂), 7.73 (s) (6H, NCH₃ 7.80 (d, J = 3.2 c/s) (4H, CH₂). The picrate had m.p. 208-210° (from acetone-EtOH). (Found: C, 44.42; H, 4.10; N, 17.31; O, 34.38. C₁₂H₂₆N₄O₄ requires: C, 44.30; H, 4.30; N, 17.40; O, 34.43%).

8,11-Dimethyl-7,9,10,12-tetraoxo-8,11-diaza[4.3.3]propelä-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; 66%), m.p. 289-290° (from AcOEt-hexane). (Found: C, 58.60; H, 4.29; N, 11.39; O, 26.02. M.W. 246. C₁₂H₁₀N₂O₈ requires: C, 58.53; H, 4.09; N, 11.38; O, 25.99%). M.W. 246.22). IR (KBr): 3080, 3060 (=CH), 2960 (CH₂), 1820, 1780, 1720 (imide CO), 1650, 1620 (diene), 1450, 1380, 1320 cm⁻¹. NMR (DMSO-d₆): δ 3.75 (m) (4H, CH), 7.08 (s) (6H, NCH₂). The best conditions were the above. Ozonolysis of 48

Ozone was passed through a soln of 48 (4.4 g) in AcOII (200 ml) during 4 h at 20°. The solvent was removed in a high vacuum. Formic acid (150 ml) and 30% H₂O₂ (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. C₁₂H₁₆N₂O₈ 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), 1650, 1620 (diene), 1450, 1380, 1320 cm⁻¹. NMR (DMSO-d₆): δ 3-75 (m) (4H, CH), 7-08 (s) (6H, NCH₂). The best conditions were the above. Ozonolysis in CH₂Cl₂, 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% H₂O₂ (27 ml) and the whole was 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 uₐo° (0.01 mm). (Found: C, 43.66; H, 4.34; N, 8.48; O, 43.00. C₁₂H₁₂N₂O₆. H₂O requires: C, 43.64; H, 4.27; N,
IR (KBr): 3450-3430 (OH), 3300-3200 (strong H bond), 1820, 1780-1700 (imide and carboxyl-CO), 1450, 1380, 1320 cm\(^{-1}\). NMR (acetone-\(d_6\)): \(\tau\) 4.70 (s) (4H, \(\text{OH}\)), 6.68 (s) (4H, \(\text{CH}_2\)), 7.08 (s) (6H, \(\text{NCH}_3\)). The position of the \(\tau\) 4-70 peak is affected by addition of water in varying concentration.

The dimerhyl 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. \(\text{C}_4\text{H}_{10}\text{N}_2\text{O}_5\) requires: C, 49.41; H, 4.74; N, 8.23; O, 37.62\%). IR (KBr): 2960, 2940, 2930 (CH), 1820, 1780, 1760-1720 (imide and ester-CO), 1450, 1380, 1320 cm\(^{-1}\). NMR (acetone-\(d_6\)): \(\tau\) 6.32 (s) (6H, \(\text{OCH}_3\)), 6.65 (s) (4H, \(\text{CH}_2\)), 7.02 (s) (6H, \(\text{NCH}_3\)).

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

A soln of 54 (2.2 g) in \(\text{Ac}_2\text{O}\) (35 ml) was heated in a N atm at 110-120\°; the CO\(_2\) evolved was collected in \(\text{Ba(OH)}_2\) 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, 52.87; H, 3.95; N, 11.15; O, 31.67. M.W. 250. \(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\) requires: C, 52.80; H, 4.03; N, 11.20; O, 31.97\%). IR (KBr): 1820, 1770, 1750-1730 (imide and ketone CO), 1440, 1380, 1310 cm\(^{-1}\). NMR (DMSO-\(d_6\)): \(\tau\) 7.18 (s), 7.20 (m).

The 2,4-dinitrophenylhydrazone \(\text{W}(\text{L})\) 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. \(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5\) 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 2-3 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; O, 19.59; N, 29.92. \(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\) requires: C, 47.44; H, 4.18; N, 15.84; O, 29.74\%).

The thioketal 61 was prepared by cooling a mixture of the ketone (2 g) which dissolved as the reaction progressed \(\text{BF}_3\)-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 \(\text{CHCl}_3\)-benzene (3:7) afforded the pure thioketal (2 g, 78\%), m.p. 283-295\° (from \(\text{CHCl}_3\)-hexane). (Found: C, 50.28; H, 4.66; O, 19.59; N, 19.59; 29.92. \(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\) requires: C, 47.48; H, 4.18; N, 19.53; O, 29.74\%).

3-Ethanedithio-7,10-dimethyl-7,10-diazah[3.3.3]propellan (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 (\(\text{Na}_2\text{SO}_4\)), 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$_6$O$_{14}$S$_2$.CH$_3$COCH$_3$ 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 treated with AcOEt. The yellow picrate had m.p. 225-228° (acetone). (Found: 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$_3$): see Table 4.

3,7-Diazao3,3,3-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. 225-228° (acetone). (Found: C, 43.71; H, 4.10; N, 17.59; O, 34.60. C$_{23}$H$_{28}$N$_6$O$_{14}$ requires: C, 43.24; H, 4.11; N, 17.56; O, 34.60%). 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, 17.15; O, 31.58, M.W. 252. C$_{19}$H$_{18}$N$_6$O$_4$ requires: C, 52.38; H, 4.80; N, 17.11; O, 31.75%). IR (KBr): 3530, 3480 (OH), 2950, 2920 (CH), 1810, 1770, 1740-1720 (imide CO), 1440, 1380 cm$^{-1}$. NMR (DMSO-de): 6 4.86 (m) (IH, OH), 6.70 (m) (IH, CHOH), 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 (272 g; 91%), 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 (2710 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$_{16}$H$_{16}$Cl$_2$N$_4$O$_4$ 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, bending), 1460, 1380, 1320 cm$^{-1}$. NMR (D$_2$O): $\tau$ 5.30 (s) (6H, NCH$_3$), 6.20 (s) (4H, CH$_2$), 6.98 (s) (6H, NCH$_3$) 7.73 (broad s) (4H, 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 NaNOr (1 g) in water (20 ml). A colorless ppt was collected (1.92 g; 95%), m.p. 207–208° (AcOEt–hexane). (Found: C, 36.58; H, 4.70; Cl, 21.49; N, 16.95. C$_{10}$H$_{18}$Cl$_2$N$_4$O$_4$ 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$^{-1}$.

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 NaNOr (1 g) in water (20 ml). The colorless ppt was collected (1.02 g; 95%), m.p. 207–208° (AcOEt–hexane). (Found: C, 36.58; H, 4.70; Cl, 21.49; N, 16.95. C$_{10}$H$_{18}$Cl$_2$N$_4$O$_4$ 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$^{-1}$.
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°C (1-5 mm). The pure dianime 57 (900 mg; 45%) had m.p. 88-90°C 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). CuH15C12N2 requires: C, 50.62; H, 7.65; N, 11.82%. M.W. 237.07). IR (CHC13): 2940-2780 cm⁻¹. NMR (CDCl3): τ 6.38 (s) (4H, CH2), 7.35 (s) (8H, NCH2), 7.70 (s) (6H, NCH3).

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

A soln of 6 (5.7 g) in cone NH4OH (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°C (benzene-hexane or aqueous isopropanol). (Found: C, 70.26; H, 8.28; N, 6.18. C12H13NO2 requires: C, 69.54; H, 8.27; N, 7.67%). IR (CHC13): 2940, 2860, 1775, 1690-1720 cm⁻¹. NMR (CDCl3): τ 2.3 (1H NH); 9.2-9.7 (m) (16H CH2). The yellow picrate had m.p. 206-208°C (dec from EtOH). (Found: C, 54.10; H, 6.18; N, 13.12; O, 26.65). IR (CHCl3): 3410 (NH), 2970-2950, 2860-2850 (CH), 1785, 1750-1700 (br) (imide CO), 1580 cm⁻¹ (C==N). NMR (CDCl3): τ 4.1 (quintet) (2 olefinic H), 7.17-8.50 (m) (10H, CH2 including allylic H).

7,9-Dioxo-8-aza[4.4.3]propellane (66)

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°C (water). (Found: C, 70.14; H, 6.94; N, 7.24; O, 15.68%. M.W. 205. C12H15NO2 requires: C, 69.09; H, 6.85; N, 7.33; O, 16.73%). M.W. 191.22). IR (CHCl3): 2940-2910, 2860 cm⁻¹. NMR(CDCl3): τ 7.32 (s) (4H CH2N) 7.59 (s) (3H, NCH3) 8.56 (s) (16H CH2). The yellow picrate had m.p. 206-208°C (dec from EtOH). (Found: C, 54.10; H, 6.18; N, 13.12; O, 26.65). IR (CHCl3): 2960-2940, 2870-2840 (0), 1775, 1715-1690 (br) (imide CO). 1575 cm⁻¹ (C==N). NMR (CDCl3): τ 4.1 (quintet) (2 olefinic H), 7.17-8.50 (m) (10H, CH2 including allylic H).

7,9-Dioxo-8-methyl-8-aza[4.4.3]propell-3-ene (67)

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°C (19 mm). (Found: C,
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, 52.89; H, 7.28; O, 16.27. M.W. 193.24). IR (CHCl₃): 3400, 3260 (NH), 2950, 2880 (CH), 1780, 1750-1700 cm⁻¹ (imide CO). NMR (CDCl₃): δ 5.2 (broad) (IH, NH), 8.82-9.4 (m) (14H, CH). 

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 H₂O₂ (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. C₉H₇NO₄ 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-d₆: δ 6.12 (s) (2H, CO₂H), 7.6 (s) (7H, CH₂CO and NCH₂) 7.7-8.1 (m) (6H, CH₂). 

2,4-Dioxo-3-methyl-3-aza[3.3.3]propellane (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 CO₂ evolved was collected as BaCO₃. 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, 23.16%. M.W. 207.22). IR (CHCl₃): 2980-2960 (CH), 1785, 1710 (imide CO), 1760 cm⁻¹ (ketone CO). NMR (CDCl₃): δ 7.05 (s) (3H, NCH₂), 7.5-8.5 (m) (12H, CH₂). 

The thioketal was obtained from the ketone (0.22 g), ethanedithiol (0.5 ml) and BF₃-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. C₁₇H₁₉NO₂S₂ requires: C, 55.12; H, 6.00; N, 4.95; O, 22.64%). IR (CHCl₃): 2970-2940, 2870 (CH), 1775, 1710-1690 cm⁻¹ (imide CO). NMR (CDCl₃): δ 7.00 (s) (3H, CH₂CH₂S), 7.16, 7.47 (AB quartet, JAB = 19 c/s) (4H, CH₂), 7.7-8.5 (m) (6H, CH₂). 

2,4-Dioxo-3-methyl-3-aza[3.3.3]propellan-7-one (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. 193.24. C₁₇H₁₅NO₂ requires: C, 68.37; H, 7.82; N, 7.25; O, 16.56%. M.W. 193.24). IR (CHCl₃): 2980-2940, 2870 (CH), 1770, 1720-1680 cm⁻¹ (imide CO). NMR (CDCl₃): δ 7.05 (s) (3H, NCH₂S), 7.5-8.5 (m) (6H, CH₂). 

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. C₁₇H₁₇N 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. C₁₇H₁₁₂N₄O₇ 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]propellane-7-ols (76, 77)

(a) Reduction of 73 (0.5 g) dissolved in MeOH (15 ml) with NaBH₄ (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. \( \text{C}_{13}\text{H}_{12}\text{N}_{3} \) requires: C, 63.14; H, 7.23; N, 6.89; O, 22.67%. M.W. 209-210. IR (CHCl₃): 3620, 3550-3400 (OH); 2960-2940, 2870 (CH) 1770, 1720-1680 (imide CO) 1008, 1028 cm⁻¹. NMR (pyridine): \( \tau \) 3.6 (broad) (1H OH), 5.55 (quintet CHOH), 7.05 (s) (3H, NCH₃), 7.25-8.40 (m) (10H CH₂).

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 CH₂Cl₂ (2 ml) and the soln was passed through a column of basic alumina (Merek; 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. \( \text{C}_{13}\text{H}_{12}\text{N}_{3} \) requires: C, 63.14; H, 6.89%). IR (CHCl₃): 3620, 3550-3400 (OH); 2960-2940, 2870 (CH) 1770, 1710-1680 (imide CO), 995, 1032 cm⁻¹. NMR (pyridine): \( \tau \) 4.25 (broad) (1H, OH), 5.45 (broad) (1H, CHOH), 7.02 (broad) (3H, NCH₃), 7.25-8.50 (1OH, CH₂).

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-azapropellane (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 NaHCO₃ 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. \( \text{C}_{13}\text{H}_{17}\text{N}_{4} \) requires: C, 62.14; H, 7.82%). IR (CHCl₃): 2960-2940, 2890-2880 (CH), 1775, 1710-1690 cm⁻¹ (imide CO).

7-Ethanedioxy-3-methyl-3-azapropellane (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 (CHCl₃): 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. \( \text{C}_{19}\text{H}_{27}\text{N}_{4} \) requires: C, 50.42; H, 5.35; N, 12.39%).

3-Methyl-3-aza[3.3.3]propellone-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. \( \text{C}_{13}\text{H}_{17}\text{NO} \) requires: 179.25). IR (CHCl₃): 1740 cm⁻¹ (CO). NMR (CDCl₃): \( \tau \) 7.20-7.65 (m) (8H, \( \text{CH}_2\text{CO} \) and \( \text{CH}_2\text{N} \)), 7.72 (s) (3H, NCH₃), 8.0-8.7 (m) (6H, \( \text{CH}_2 \)).