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PROPELLANES—III[1]

SYNTHESIS OF CARBOCYCLIC AND HETEROCYCLIC COMPOUNDS

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Abstract—Syntheses of carbocyclic, oxa-, aza-, and thiapropellanes, their physical properties and behaviour on electron impact are described.

THE growing number of papers on propellanes demonstrates the interest evinced in these compounds, both chemically[2a–o] and pharmacologically.[2p] Indeed, during the preparation of this paper, the synthesis of a thiapropellane has been announced,[2l] as well as that of a dioxapropellane identical with compound **33** in this paper, albeit prepared by a somewhat different procedure.[2m]

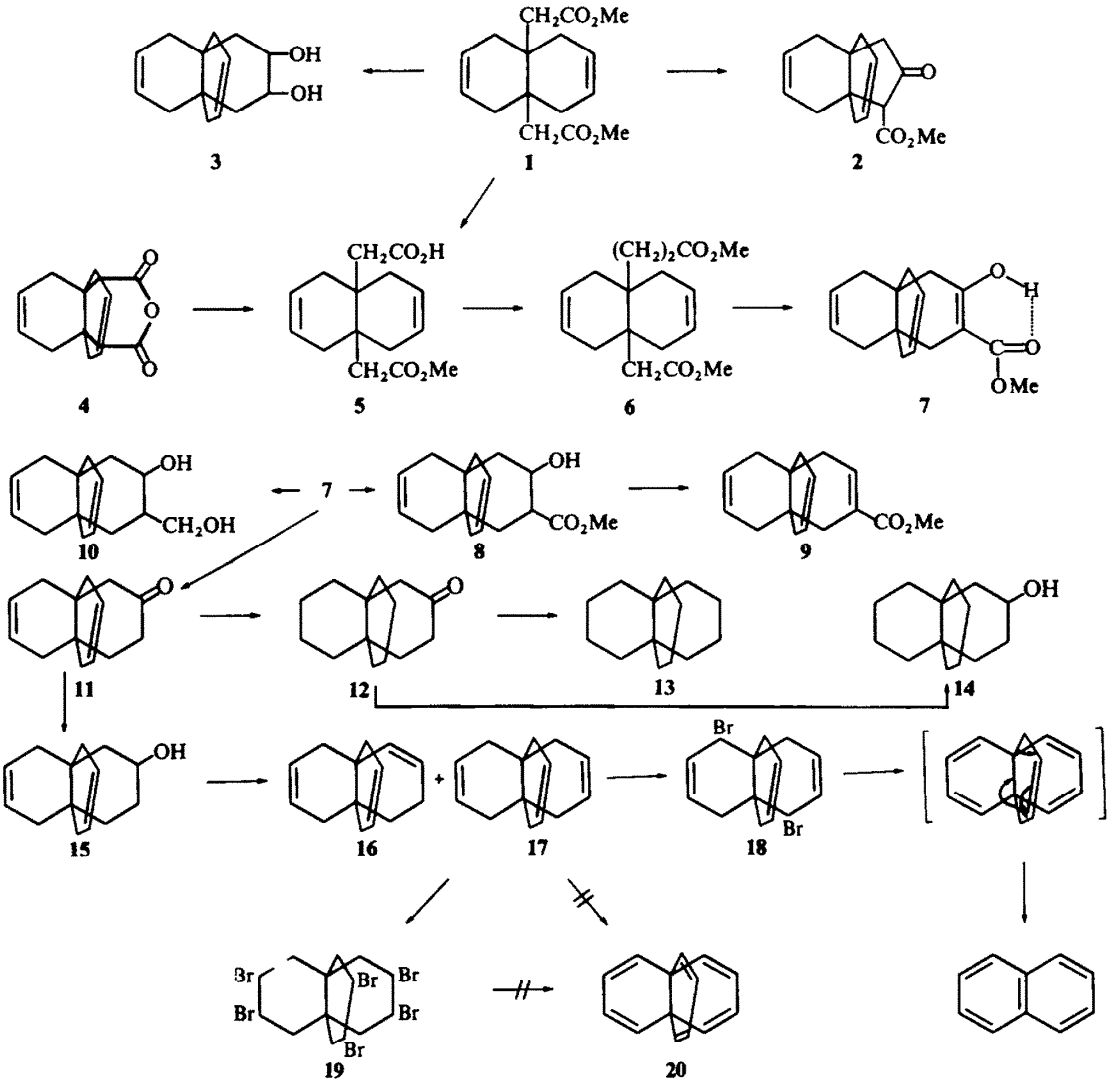
Synthesis of [4.4.4]*propellanes* (*Scheme* 1). Since the overall yield of the tetrahydro derivative of **3**[1a] was not promising and particularly because of our interest in the conformations and photochemical behaviour of [4.4.4]propellanes containing more or less double bonds (e.g. **17**, **20**), the acyloin condensation of the diester **1**[1a] was studied. Although **3** was obtained in very low yield when sodium in liquid ammonia was used, other conditions employing sodium–potassium alloy in diglyme or sodium in toluene afforded the Dieckmann condensation product **2**, rather than an acyloin of the [4.4.4]propellane series.

The half-ester **5** was therefore prepared by alkaline saponification of **1** with 1 equivalent of base or by heating the corresponding 7-membered anhydride **4** with methanol. The monoester monoacid chloride was then subjected to Arndt–Eistert homologation conditions and the diester **6** was obtained. Dieckmann condensation then afforded the β-keto-ester **7** which exists completely in the enolic form stabilized by hydrogen bonding, in contradistinction to the behaviour of **2** which exists for all practical purposes in the ketonic form.

When **7** was reduced by sodium borohydride in methanol, however, it was reduced normally to give the hydroxy ester **8**. Dehydration with phosphorus oxychloride in pyridine afforded exclusively the α,β-unsaturated ester **9**. Alkaline saponification of **7** with subsequent acidification and concomitant decarboxylation led to the dienic ketone **11**.[1b] Reduction using Adams' catalyst in glacial acetic acid gave the saturated ketone **12**, Wolff–Kishner reduction of which gave the parent saturated hydrocarbon [4.4.4]propellane, **13**.

We are indebted to Professor F. H. Herbstein of this Department for determining the following parameters for the unit cell (monoclinic): $a = 13{\cdot}03$ Å, $b = 7{\cdot}9$ Å, $c = 11{\cdot}97$ Å, $\beta = 105°$. On the assumption that there are 4 molecules in the unit cell, the calculated density is 1·15 g/cm^3, falling within the density range of crystalline

SCHEME 1.



saturated aliphatic compounds. A complete X-ray crystallographic investigation of the conformation of **13** has been undertaken.* The NMR spectrum of **13** over a large temperature range is much more complex than those of 9,10-disubstituted *cis*-decalins which we have examined.[3] The activation energy for ring inversion in [4.4.4]propellane has therefore not yet been determined but on the basis of the disubstituted *cis*-decalins[3,4] one might guess, perhaps too optimistically that one may be approaching the borderline of practical possibility for a low-temperature resolution of a suitable derivative of [4.4.4]propellane. The hydrocarbon **13** is, of course, itself chiral. A theoretically suitable substrate for potential resolution would be [4.4.4]propellan-3-ol, **14**, and work in this direction is in progress.

* By Professor J. D. Dunitz of the E.T.H., Zürich and the results will be reported elsewhere.

Sodium borohydride reduction of **11** gave the dienic alcohol **15**. Dehydration of the latter with phosphorus oxychloride in pyridine led to the symmetrical triene **17** contaminated by a few per cent (GLC) of the unsymmetrical isomer **16**. We are very interested in studying the photochemistry of the hexaene **20**. A good many potentially interesting photochemical reaction courses may be envisaged for this substrate. Thus far we have not succeeded in isolating **20** although it may have been in our hands fleetingly. Addition of bromine to **17** afforded the hexabromide **19** in good yield. Dehydrobromination using various reaction conditions led to intractable mixtures which after partial separation by column chromatography still consisted mainly of bromine-containing fractions. Gas chromatographic separation was also unsuccessful although a small yield of **20** may have been demonstrated by the observation of a naphthalene peak in one of the chromatographic fractions. When the diallylic dibromide **18** was prepared by treatment of **17** with 2 moles of NBS, followed by treatment with lithium chloride in DMF, naphthalene was isolated, not unexpectedly, by the reverse Diels–Alder mechanism shown in Scheme 1.

In order to circumvent the driving force of such retrogressive cleavage of the tricyclic system, the dienic ketone **11** is being used as starting material for bromination–dehydrobromination experiments, followed by reduction to an alcohol and dehydration in the ultimate step. It is hoped that this type of synthetic approach will lead successfully to the hexaene **20**.

Oxapropellanes (*Scheme* 2). The synthesis of the tetraenic oxapropellane **25** has already been reported, although in only 7–10% yield.[5] It is, nevertheless, useful to discuss the synthesis and behaviour of this compound as our procedure affords it in better yield and because an aberration in its UV spectrum appears to have gone unnoticed.[6]

The dienic diol **21** was converted into the dienic ether **22**[1a, 5, 6]* by treatment with *p*-toluenesulphonic acid in toluene. Addition of bromine to **22**, using glacial acetic acid as solvent, led to a mixture of the two possible tetrabromides **23** (major product) and **24** whose stereochemistry was determined by employing NMR spectroscopy (Experimental).[7] Alternatively, treatment of **22** with 2 moles of NBS gave the diallylic dibromide. Dehydrobromination of the latter or of the tetrabromide **23** afforded the tetraenic oxapropellane **25** in 70% and 25–40% yield, respectively.

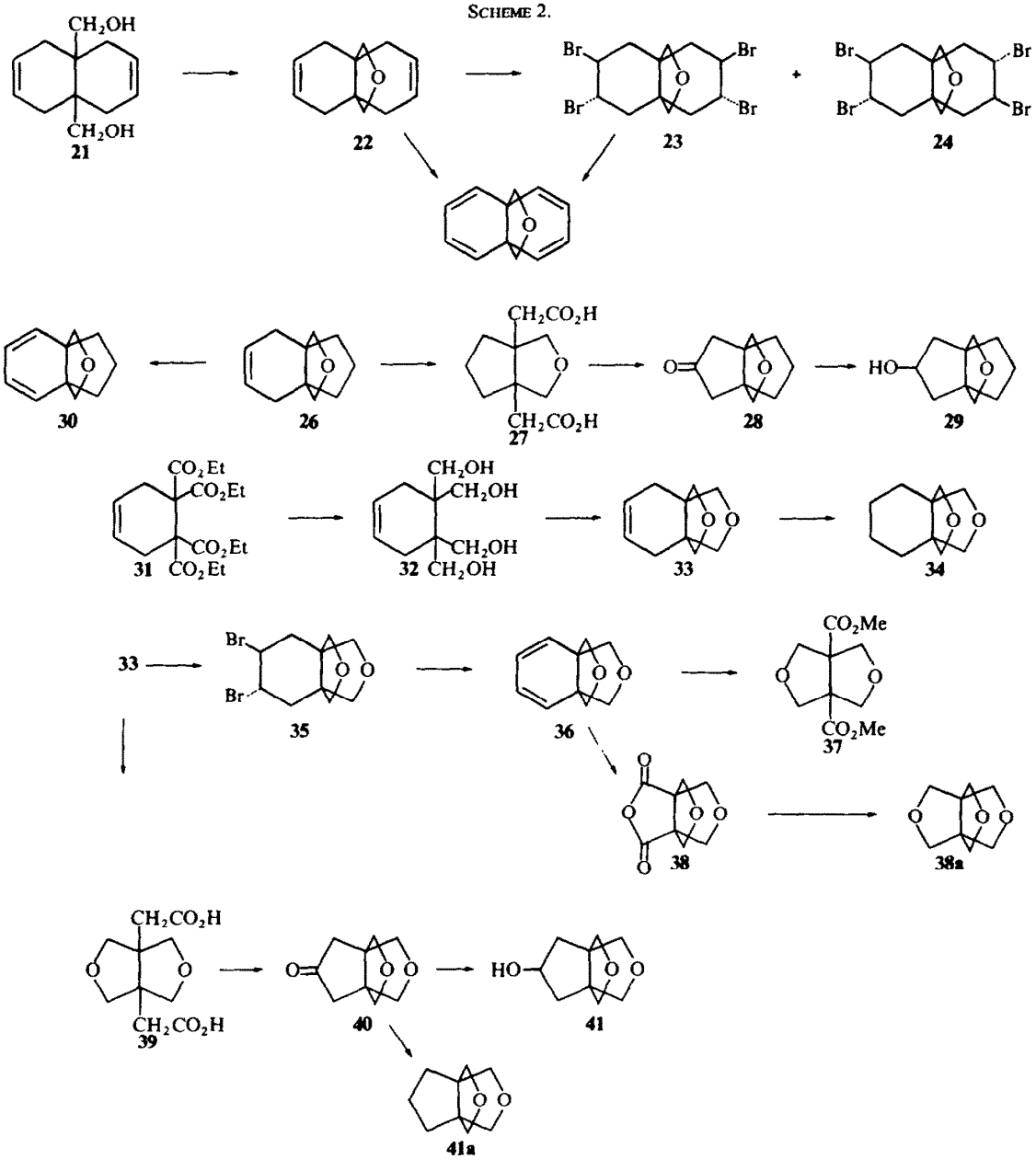
The UV absorption max of **25** in cyclohexane appears at 244 nm, a hyprochromic shift of some 20 nm if one uses Woodward's rules to calculate the absorption for the corresponding tetrasubstituted cyclohexadiene chromophore (calc. ca. 265 nm). The corresponding tetraenic thiapropellane **45** exhibits the same hypsochromic shift in its UV spectrum, the max is again at 245 nm whilst the trienic thiapropellane **44** (Scheme 3) has its absorption max at the expected 266 nm. The reason for this behaviour of **25** and **45** will be discussed elsewhere.†

The alcohol **29** was prepared by a sequence starting by ozonolysis of **26**. The ether diacid **27** in refluxing acetyl chloride gave a 7-membered anhydride which was pyrolysed at 300–350°, without purification, to yield the ketone **28**. Sodium borohydride reduction of the ketone gave the alcohol **29**, isolated in low yield, whose

* Its photochemical behaviour has also been studied some 8–10 years ago by V. Prelog, W. H. Laarhoven and M. F. Lynch but no final structural assignment was made for the product isolated after irradiation (private communication from Professor V. Prelog). This work is now being repeated.

† By Professor E. Heilbronner of the E.T.H., Zürich.

SCHEME 2.



stereochemistry is clear because it is the intramolecularly hydrogen-bonded isomer.

The starting material for the preparation of 8,11-dioxa[4.3.3]propellane, **34**, was the Diels–Alder adduct **31** obtained from butadiene and tetracarbethoxyethylene.[8,9] Reduction of the adduct with LAH gave the tetrol **32** which upon treatment with *p*-toluenesulphonic acid in toluene gave the diether **33** in 55% yield. Reduction of **33** with Adams' catalyst in methanol gave **34**. Addition of bromine to **33** gave the

dibromide **35** which upon dehydrobromination with lithium chloride in DMF afforded the dienic diether **36**. Ozonolysis of the latter, followed by oxidative decomposition of the ozonide and diazomethane methylation gave the diester diether **37**. Alternatively, treatment with boiling acetic anhydride instead of diazomethane gave the diether anhydride **38**. The latter upon reduction with LAH to the corresponding diether diol followed by treatment of the latter with *p*-toluenesulphonic acid gave the fully symmetrical 3,7,10-trioxa[3.3.3]propellane **38a**.

Ozonolysis of **33** afforded the diether diacid **39** which in refluxing acetic anhydride, and pyrolysis, in analogy to the behaviour of **27**, gave the ketonic diether **40**, which does not undergo hydrogenolysis in the presence of Adams' catalyst in glacial acetic acid (cf. Ref. 1*a*). Reduction with sodium borohydride gave the corresponding alcohol **41**. The thioketal of **40** gave on treatment with Raney nickel the diether **41a**.

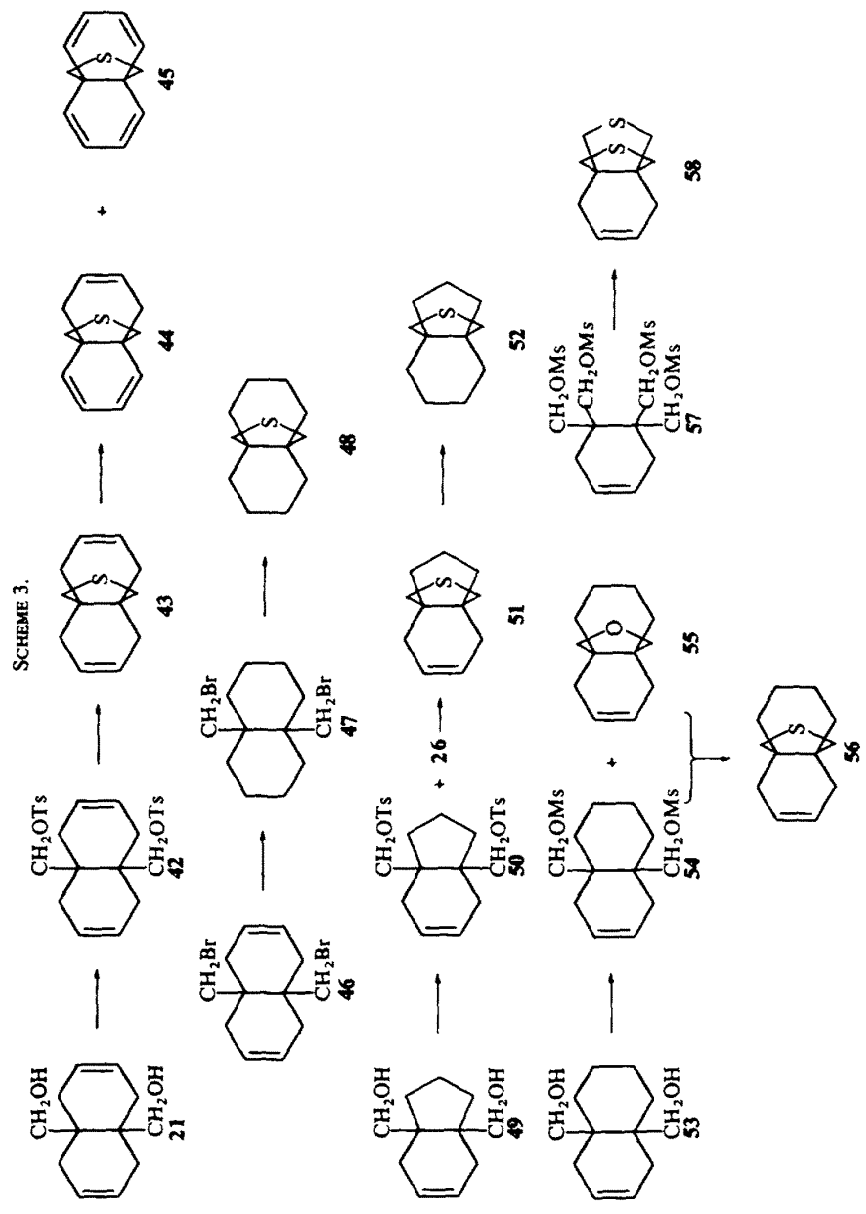
The dienic ether **30** was obtained by two different brominations of **26**, addition of bromine to the double bond of **26** or by allylic bromination with 1 mole of NBS, and dehydrobromination of the respective dibromide and allylic monobromide with lithium chloride in DMF. The UV spectrum of **30** in cyclohexane shows a maximum at 257 nm.

Thiapropellanes (*Scheme* 3). The dienic thiapropellane **43** was readily prepared by treating the ditosylate **42** of the diol **21**[1a] with sodium sulphide in DMSO. Bromination of **43** with 2 moles of NBS, followed by dehydrobromination with lithium chloride in DMF affords a complex mixture of products from which it was possible to isolate the trienic thiapropellane **44** in pure form and the relatively unstable tetraenic analogue **45**, 93% pure (by NMR) contaminated by 7% of the triene **44**. Thiapropellanes may be oxidized in methanolic solution to the corresponding sulphoxides by means of sodium periodate. Work is in progress to isolate pure stereoisomeric sulphoxides where the possibility for such isomerism exists. Sulphones may be obtained from thiapropellanes by oxidation with hydrogen peroxide in acetic acid and even in the presence of double bonds. Because of the relative instability of the tetraene **45**, this was subjected to UV irradiation as soon as batches of it were obtained as investigation of its photochemistry was the motive for its synthesis.

Reduction of the dienic dibromide **46**[1a] with platinum in acetic acid gave the saturated dibromide **47** which has also been reported,[1a] but was earlier prepared by another route. Treatment of **47** with sodium sulphide in DMSO led to the saturated 12-thia[4.4.3]propellane **48**. The lower homologue, 8-thia[4.3.3]propellane **52** was prepared from the diol **49**[1a] as starting material. In this case (cf. **21** → **42**) the ditosylate **50** is not formed exclusively when **49** is treated with tosylchloride in pyridine. It is accompanied by the oxapropellane **26**. Since **50** and **26** are not readily separable, the mixture was treated with sodium sulphide in DMSO, yielding **51** which is still contaminated by **26**. The thioether was separated from the ether through formation of the complex of the former with mercuric chloride (Experimental). Treatment of the complex with aqueous sodium sulphide then regenerates **51** in pure form. Reduction of **51** using diimide gave the fully saturated thiapropellane **52**.

A similar reaction sequence beginning with the diol **53** led to **56**, the higher homologue of **51**. Here it turned out that treatment of **53** with methanesulphonyl chloride gave a higher yield of mesylate than could be obtained of tosylate by employing tosyl chloride, but here also the dimesylate **54** was accompanied by the corresponding ether **55**. The mixture was therefore again treated with sodium

SCHEME 3.

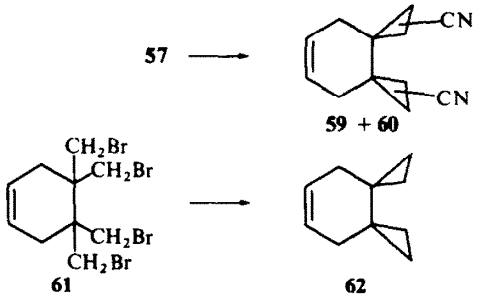


sulphide in DMSO, the complex of **56** with mercuric chloride again being used to separate **56** from **55**.

Finally, the tetramesylate **57** of the tetrol **32** proved to be an excellent starting material for the preparation of dithiapropellanes and of propellanes with more than one hetero-atom.* Treatment of **57** with sodium sulphide in DMSO afforded the dithiapropellane **58**, whose structure is clear (two thiophan rings rather than thietan rings) from its UV spectrum, $\lambda\lambda_{max}$ 215, 220 (sh); log $\varepsilon\varepsilon$ 3·70, 2·81. Thietans exhibit λ_{max} at 250–290 nm.[10]

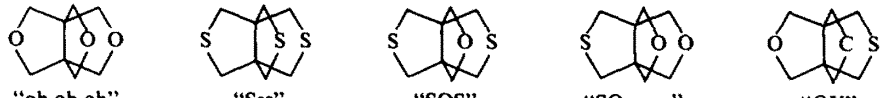
Reaction scheme 4 shows that the tetramesylate **57** upon treatment with sodium cyanide in DMSO did not lead to formation of dinitriles having the [4.2.2]propellane skeleton. Indeed, analogy to the more rigid geometry of a di-angularly substituted *cis* decalin,[1a] could not be expected. Instead, 2 isomeric dispirodinitriles **59** and **60**, were isolated. Also when **57** was converted into the tetrabromide **61**, and this was subjected to treatment with zinc in aqueous methanol, the very interesting dispiran **62** was isolated. The preparative details and reactions of these spirans, not being germane to the chemistry of propellanes, will be reported elsewhere.

SCHEME 4.



Azapropellanes (*Scheme* 5). As we reported earlier,[1a] we were unsuccessful in reaching the triazapropellane **73** via a number of routes. This compound was synthesized by a rather lengthy procedure from the ketone diimide **63**. The ketonic function was protected by ketalization with ethylene glycol and the ketal **64** was reduced with LAH to the ketal diamine **65**. Removal of the protecting group permitted attack of the two positions adjacent to the carbonyl group with *i*-amyl nitrite in the presence of HCl and the dioximino-ketone **67** (R = H) was submitted to the conditions of a second order Beckmann rearrangement employing acetic anhydride at room temperature. The diacetyl derivative **67** (R = Ac) thus isolated was converted into the dinitrile **68** by treatment with aqueous sodium carbonate. Either the diacetyl derivative or the dinitrile upon refluxing with aqueous-methanolic potassium

* There is, of course, strong motivation for preparing some of these compounds as their structures can be disclosed to a lecture audience at a certain point (or lull) in the proceedings. Consider, for example, the utility of the following structures:



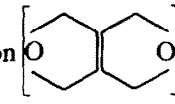
hydroxide gave the imide diamine **71** which upon diazomethane methylation gave the methylimide diamine **72**. Reduction of **72** with LAH in THF gave the desired 3,7,10-trimethyl-3,7,10-triaza[3.3.3]propellane, **73**. The diamine alcohol **80** was obtained by direct reduction of **63** with LAH, without protection of the carbonyl function of the starting material.

The oxime **69**, isolated as both the monohydrochloride and the dihydrochloride, was prepared from **66** and required stringent conditions (30% oleum) in order to carry out the Beckmann rearrangement to the ring enlarged triazapropellane **70** of the [4.3.3] series.

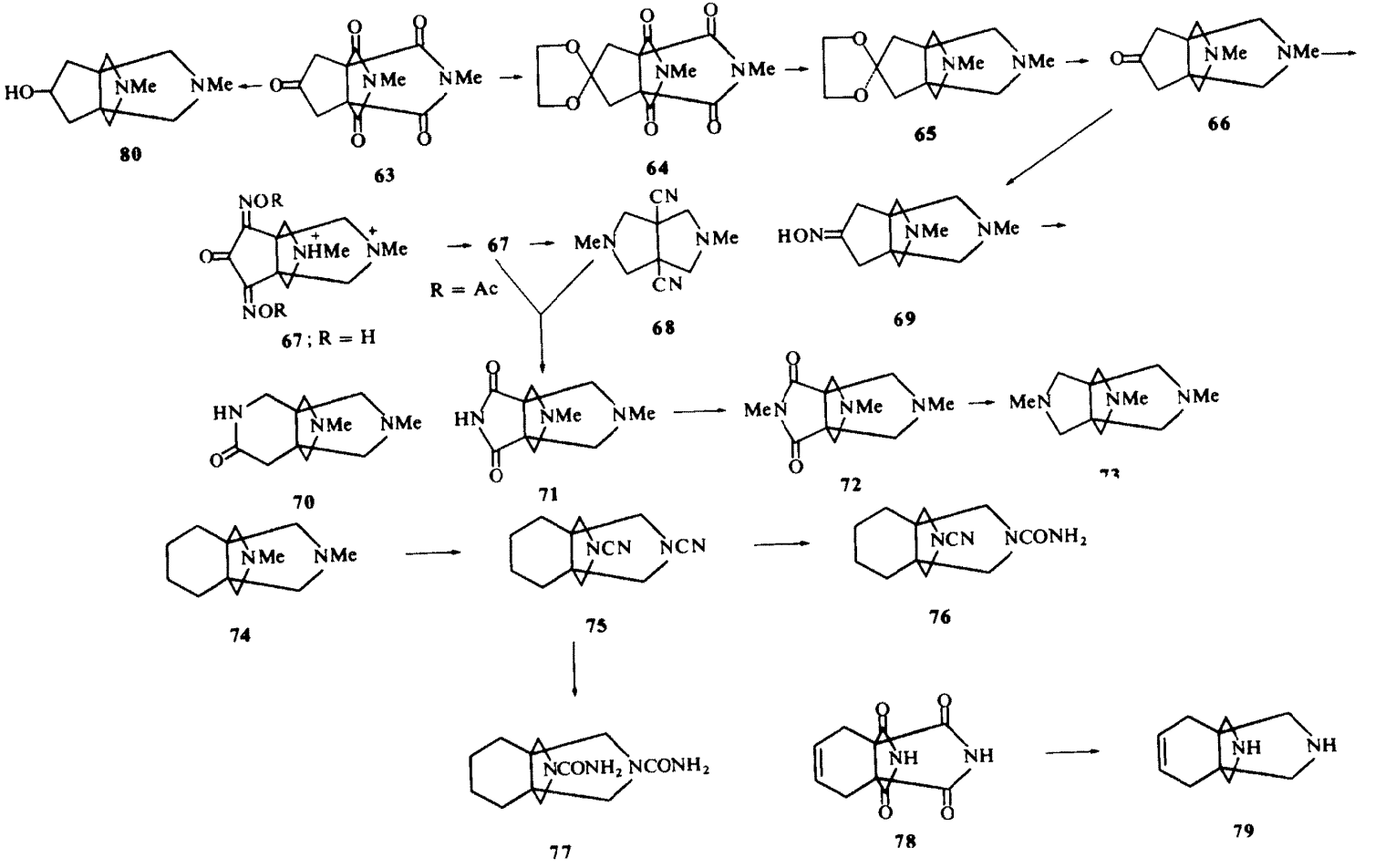
Since preliminary experiments with the tertiary amine propellanes indicated that coordination with various metal ions was possible, we wished also to have the secondary amines for similar studies. An example of the latter type, **79**, could, in principle, be easily obtained by LAH reduction of **78**, but the yield obtained by reducing the very insoluble **78** left much to be desired. In this connection we also studied the von Braun reaction of **74**. Although it is known that cyanogen bromide cleaves the ring bond adjacent to the nitrogen atom in N-methylpyrrolidine rather than the N-Me bond,[11] cyanogen bromide in THF smoothly cleaved both N-Me bonds in **74** and gave the dicyanamide **75**. Percolation of a solution of **75** on basic alumina gave the monocyanamide monourea **76** whilst alkaline saponifaction of **75** afforded the diurea **77** which was extremely stable to both further alkaline or acidic saponification to the dicarbamic acid. Thus, this sequence did not appear a reasonable one for obtention of the corresponding disecondary amine.

Behaviour of propellanes on electron impact

(a) *Alicyclic propellanes.* [4.4.4]propellane **13** exhibits the molecular ion *m/e* 192. Fragmentation of the first ring gives an ion corresponding to *m/e* $[M-(CH_2)n]^+$, $n = 1$–4. Also observed are strong peaks corresponding to *m/e* $[M-(CH_2)_3-H]^+$ and $[M-(CH_2)_4-H]^+$. The trienic propellane **17** exhibits the molecular ion *m/e* 186. Retro-Diels–Alder (RDA) fragmentation leads to a strong peak of the ion *m/e* 132 $(M-54)^+$. The occurrence of a metastable peak indicates that concurrently 55 m.u. are lost through a rearrangement of a hydrogen atom. The alcohol **15** exhibits the molecular ion and the ion $(M-18)^+$. Subsequently the mass spectrum is superimposable on that of **17**.

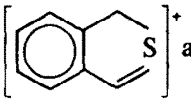
(*b*) *Oxa- and thiapropellanes.* Several generalizations may be made from a comparison of these classes of compounds. The oxapropellanes, e.g. **25**, **26**, **30**, **55** exhibit fragmentations in which formaldehyde (30 mass units), CH_2OCH_2 (44 m.u.) and CH_3OCH_2 (McLafferty-type hydrogen migration is involved) (45 m.u.) are lost. In the ketonic ether, the molecular ion *m/e* 166 loses CH_2O (→ *m/e* 136), loses the CH_3OCH_2 fragment (→ *m/e* 121) and the latter loses CO (→*m/e* 93). Retro-Diels–Alder type fragmentation is also observed to a lesser extent in most of the ethers (e.g. **25**, **26**, **55**) but besides the loss of butadiene (54 m.u.) there is also a concurrent loss of 55 m.u. from the molecular ion. This type of fragmentation is particularly marked in the dioxapropellane, **33** leading to the ion  *m/e* 112. RDA fragmentation is practically unobserved in the saturated oxa-propellanes.

SCHEME 5.


HO
NMe
NMe
80
63
64
65
66
NOR
NHMe
NOR
67 ; R = H
R = Ac
67
MeN
CN
68
HON
69
HN
70
71
72
73
NCN
NCONH2
74
75
76
77
78
NH
79

Whilst in the oxapropellanes the loss of CH_2OH is observed, albeit leading to weak peaks, the analogous loss of CH_2SH is much more marked in the thiapropellanes. In the latter, however, the loss of CH_2S is much less marked. Hydrogen transfers are much more obvious in the sulphur compounds, in the thioethers as well as in the sulphoxides and the sulphones. Thus, also the ion which often corresponds to the base peak in the mass spectra of the thioethers corresponds to $[M—CH_3SCH_2]^+$; this is in contradistinction to the peaks resulting from the $[M—CH_3OCH_2]^+$ ions in the mass spectra of the ethers. In the case of **52** the base peak corresponds to $[M—CH_2SH]^+$, *m/e* 135. This undergoes a RDA-type fragmentation (-ethylene → *m/e* 107). The ion *m/e* 121 $[M—CH_3SCH_2]^+$ is, however, also a very strong peak. Similarly for **48**, the molecular ion *m/e* 196 loses CH_2SH ($\xrightarrow{m^*}$ *m/e* 149 $\xrightarrow{-CH_2=CH_2}$ *m/e* 121). Alternatively, $M^+ \xrightarrow{-CH_3SCH_2}$ *m/e* 135 $\xrightarrow{-CH_2=CH_2}$ *m/e* 107. For **51** M^+, *m/e* 180 $\xrightarrow{RDA}$ *m/e* 126 (weak); *m/e* 180 $\xrightarrow{-CH_2SH}$ *m/e* 133; *m/e* 180 $\xrightarrow{-CH_3SCH_2}$ *m/e* 119; $\xrightarrow{-CH_2=CH_2}$ *m/e* 91 (tropylium ion). It may be mentioned parenthetically that in all of the propellanes, towards the lower end of the mass spectrum the well-known cleavages leading to tropylium ion (*m/e* 91), phenyl ion (*m/e* 77) and intermediate ions resulting from successive loss of hydrogens, are observed.

It is not surprising that the RDA fragmentation of **43**, M^+, *m/e* 192 leads to a strong peak (−54 m.u. → *m/e* 138). The cleavages leading to ions, *m/e* 131 (—CH_3SCH_2) and *m/e* 145 (—CH_2SH) are well evident and the latter affords an ion, *m/e* 117 through the loss of ethylene. Analogous fragmentations are observed for the dienic oxa-analogue, **22**. M^+, *m/e* 176 gives ions *m/e* 145 (—CH_2OH) and *m/e* 131 (—CH_3OCH_2). The RDA fragmentation leads to *m/e* 122 but the peak at *m/e* 121 is stronger than *m/e* 122 (i.e. loss of 55 m.u.). The ion *m/e* 158 is also observed in this case, $[M—H_2O]^+$.

The trienic thioether **44** exhibits as its base peak that of the ion *m/e* 129 (M^+, *m/e* 190 —CH_3SCH_2). The ion *m/e* 128, corresponding to the naphthalene ion, is weaker. Also observed are the ions *m/e* 143 $[M—CH_2SH]^+$ ($\xrightarrow{-CH_2=CH_2}$ *m/e* 115) and *m/e* 136 $[M—butadiene]^+$. Not surprisingly, the ion *m/e* 135 is particularly strong  as well as the corresponding cation radical *m/e* 134.

The base peak in the tetraenic thioether **45** spectrum is the ion *m/e* 128 (naphthalene). Other strong peaks correspond to *m/e* 127 $[M—CH_3SCH_2]^+$ or [naphthalene—H]$^+$ and *m/e* 153 $[M—CH_2SH]^+$. The tetraenic oxa-analogue **25**, M^+, *m/e* 172, undergoes the fragmentations $M^+ \xrightarrow{-CH_2O}$ *m/e* 142 $\xrightarrow[m^*]{-H}$ *m/e* 141; $M^+ \xrightarrow{-CH_2OCH_2}$ *m/e* 128. The further portions of the spectra of **45** and **25** are practically superimposable.

The sulphoxide fragmentations are similar to those of their thioether parents except that here the loss of the following fragments are generally observed (—O, —SOH, —CH_2SOH, —CH_3SOCH_2). Again, not unexpectedly the base peak in the mass spectrum of the sulphoxide of **45** is the ion *m/e* 128 (naphthalene) although again the peak *m/e* 127 $[M—CH_3COCH_2]^+$ is nearly as strong. Whilst the mass spectrum of the sulphoxide of **52**, following the cleavage $M^+ \xrightarrow{-O}$ *m/e* 182 is superimposable on that of the parent thioether **52**, in the higher saturated homologue the sulphoxide of **48** the first fragmentation is $M^+ \xrightarrow[m^*]{-OH}$ *m/e* 195, followed by losses of CH_2S (or CH_2SOH from M^+) → *m/e* 149; the loss of CH_2SCH_2 from the latter or

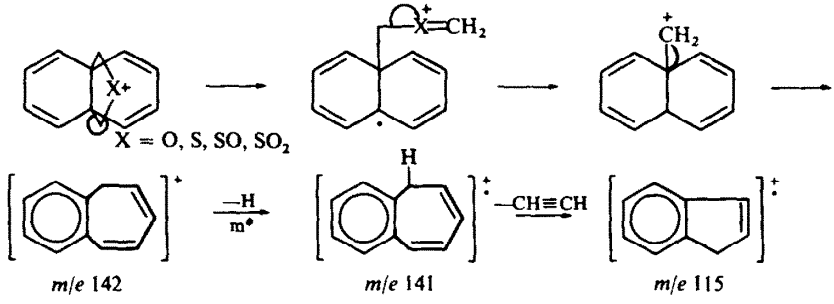
CH_2SOCH_2 from $M^+ \rightarrow$ *m/e* 135. The ion *m/e* 149 also loses ethylene and $(CH_2)_3$ to afford the ions *m/e* 121 and *m/e* 107, respectively. In the sulphoxide of **43**, RDA fragmentation of *m/e* 192, from M^+ —O leads through RDA fragmentation to an ion *m/e* 138. The ion *m/e* 137 is also found. Here also M^+, *m/e* 208 $\xrightarrow[-OH]{m^*}$ *m/e* 191. Also observed are the fragmentations *m/e* 192 $\xrightarrow{-CH_2SH}$ *m/e* 145 and the ion *m/e* 131 resulting from M^+ —CH_3SOCH_2 or *m/e* 191–CH_2SCH_2.

The sulphones behave similarly. The sulphone of **52**, M^+, *m/e* 214 $\xrightarrow[m^*]{-OH}$ *m/e* 197. Loss by M^+ of SO_2H gives *m/e* 149 $\xrightarrow{-(CH_2)_3}$ *m/e* 107; M^+ —$CH_2SO_2H \rightarrow$ *m/e* 135; M^+ —$CH_2SO_2CH_2 \rightarrow$ *m/e* 122; M^+ —$(CH_2)_3 \rightarrow$ *m/e* 162. The sulphone of **48**: $M^+ \xrightarrow[m^*]{-OH}$ *m/e* 211 $\xrightarrow{-CH_2SOCH_2}$ *m/e* 133. The ion *m/e* 149 arises from M^+ —CH_2SO_2H or from *m/e* 211 —$SOCH_2$. Also observed, $M^+ \xrightarrow[m^*]{-SO_2H}$ *m/e* 163 $\xrightarrow[m^*]{-(CH_2)_2}$ *m/e* 121. In the dienic sulphone of **43** the base peak *m/e* 131 arises from loss of $CH_3SO_2CH_2$ from M^+. M^+ also loses OH to give *m/e* 207, CH_2SO_2H to give *m/e* 145, SO_2H to give *m/e* 159, butadiene to give a strong peak for RDA fragmentation, *m/e* 170. *m/e* 145 also undergoes an RDA type fragmentation to give *m/e* 117.

The spectrum of the dithiapropellane **58** exhibits the molecular ion M^+, *m/e* 198 and the following fragmentations: $M^+ \xrightarrow{-H_2S}$ *m/e* 164 $\xrightarrow{-CH_2SH}$ *m/e* 117; $M^+ \xrightarrow{-SH}$ *m/e* 165; $M^+ \xrightarrow{-CH_2SH}$ *m/e* 151 $\xrightarrow{-H_2S}$ *m/e* 117; *m/e* 151 $\xrightarrow{RDA}$ *m/e* 97; $M^+ \xrightarrow{-CH_2SCH_2}$ *m/e* 137; $M^+ \xrightarrow{-CH_2SCH_2}$ *m/e* 136.

All of the above fragmentations have been observed in ethers[12] and in thioethers, sulphoxides and sulphones.[13]

An ion *m/e* 115 exhibits a strong peak in the mass spectra of the tetraenic ether **25**, the tetraenic thio-ether **45** and in the corresponding sulphoxide and sulphone. A reasonable mechanism for its formation is:



The trioxapropellane **38a** exhibited the molecular ion M^+, *m/e* 156, and loss by M^+ of CH_2OH gave to base peak in the mass spectrum, *m/e* 125. The latter ion lost CH_2O to give the very strong peak *m/e* 95, lost OH to give *m/e* 108, and lost CH_2OCH_2 to give the stable ion, *m/e* 81.

The triazapropellane **73** exhibited the molecular ion M^+, *m/e* 195 and the following fragmentations: $M^+ \xrightarrow{-CH_3}$ *m/e* 180; $M^+ \xrightarrow[m^*]{-CH_2NHCH_3}$ *m/e* 151 $\xrightarrow[m^*]{-CH_3NCH_3}$ *m/e* 108 (base peak); $M^+ \xrightarrow[m^*]{-NH_2CH_3}$ *m/e* 164 $\xrightarrow[m^*]{-H}$ *m/e* 163.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were measured on a Perkin–Elmer infracord in $CHCl_3$ unless otherwise stated. NMR spectra were measured on a Varian -A-60 in $CDCl_3$, unless otherwise stated. Mass spectra were measured on an Atlas CH-4 mass spectrometer using the heated inlet system at 200°. The electron energy was maintained at 70 eV and the ionization current at 20 μA. UV spectra were measured in cyclohexane on a Bausch and Lomb Spectronic 505, unless otherwise stated.

11-*Carbomethoxy* [4.4.3] *propella*-3,8-*diene*-12-*one* (**2**)

A soln of **1** (556 mg) in diglyme (30 ml) was added during 1 hr to a strongly stirred suspension of K–Na alloy (1:1; 272 mg) in abs diglyme (70 ml) under N_2. (A blue color appeared when the reaction mixture was cooled in a dry-ice–CCl_4 bath.) Stirring was maintained for 24 hr at room temp. After addition of solid NH_4Cl (1 g) and stirring for 1 hr the mixture was filtered, the solvent was removed at room temp in a high vacuum. The residue was taken up in ether and the soln was washed with water and dried (Na_2SO_4). Evaporation of the ether and sublimation of the residue at 75° (0·01 mm) afforded the *keto-ester* **2** (420 mg, 85%), m.p. 88°. (Found: C, 73·36; H, 7·32; O, 19·45. M.W. 246. $C_{15}H_{18}O_3$ requires: C, 73·14; H, 7·37; O, 19·49%. M.W. 246·29.) IR: 1730, 1760 (CO), 1665 cm^{-1} (C=C). NMR: τ 4·33 (m) (4H, olefinic), 6·25 (s) (3H, OCH_3), 6·56 (s) (1H, $CHCO_2$), 7·5–8·9 (m) (CH_2CO and allylic). The same product was obtained in lower yield (20–30%) when the alloy was used in refluxing benzene or when sodium in refluxing toluene is employed.

3,4-*Dihydroxy*[4.4.4]*propella*-8,12-*diene* (**3**)

Treatment of **1** with Na in liquid ammonia under the conditions used for its saturated analog[1a] gave a complex mixture of products which could be separated on florisil, on silica or on neutral alumina, and from which starting material could be recovered (5%). **2** was obtained in 10% yield and the *diol* **3** was isolated in 7% yield, m.p. 158° (benzene–hexane). (Found: C, 76·81; H, 9·11; O, 13·99. M.W. 220. $C_{14}H_{20}O_2$ requires: C, 76·32; H, 9·15; O, 14·53%. M.W. 220·30.) IR: 3580, 3400 (OH), 1660 cm^{-1} (C=C). NMR: τ 4·47 (m) (olefinic), 5·00 (s) (OH), 5·9–6·2 (m) (CHOH), 7·2–8·7 (m) (CH_2 and allylic). The IR spectrum of a large fraction of the product indicated that ammonolysis of the ester groups in **1** had taken place.

cis-4a-*Carboxymethyl*-8a-*carbomethoxymethyldecalin*-2,6-*diene* (**5**)

(a) A soln of **1** (9·3 g) in dioxan (15 ml) was mixed with an equiv of MeONa (from 0·77 g Na) in MeOH (20 ml)–water (35 ml) and the whole was refluxed for 12 hr at which time the pH was 7·4. The mixture was cooled to 0° and 10% NaOHaq was added to pH 10. Rapid extraction with ether afforded unreacted **1** (1·6 g; 17%). Acidification of the aqueous phase, extraction with AcOEt, drying ($MgSO_4$), evaporation of solvent and trituration of the residue with CH_2Cl_2 gave the diacid (2·55 g; 30·5%), m.p. 229–230°. Chromatography of the concentrated CH_2Cl_2 soln over silica (200 g) and elution with $CHCl_3$–AcOEt (4:1) gave pure *ester-acid* **5** (4·8 g; 53%) which after sublimation at 65° (0·01 mm) had m.p. 72–73°. (Found: C, 68·21; H, 7·69; O, 24·13. $C_{15}H_{20}O_4$ requires: C, 68·16; H, 7·63; O, 24·21%.) IR: 3500, 3100 (OH), 1730, 1710 cm^{-1} (CO). NMR: τ −1·26 (s) (1H, CO_2H), 4·36 (broad s) (4H, olefinic), 6·30 (s) (3H, OCH_3), 7·55 (s) (4H, CH_2CO), 7·82 (broad s) (CH_2 and allylic).

(b) Refluxing **4** in abs MeOH gave **5** in quantitative yield.

cis-4a-*Carbomethoxyethyl*-8a-*carbomethoxymethyldecalin*-2,6-*diene* (**6**)

A mixture of **5** (3·7 g; 0·014 mole), oxalyl chloride (3·6 g; 0·024 mole) and dry benzene (25 ml) was permitted to stand overnight at room temp. After removal of the solvent the crude acid chloride showed the characteristic IR absorption (in $CHCl_3$: 1800 (COCl), 1730 cm^{-1} (CO_2Me). It was dissolved in abs THF (30 ml) and this was added dropwise to an ethereal soln of diazomethane. After 2 hr the solvents were removed at the water pump at room temp. The crude diazoketone showed IR absorption (in $CHCl_3$) at 2110, 1730, 1640 cm^{-1}. It was dissolved in abs MeOH (100 ml) and freshly prepared Ag_2O (0·5 g) was added portionwise, whereupon strong evolution of N_2 began. After addition was complete the mixture was heated at 60° for 1 hr. After filtration and evaporation of solvent the *diester* **6** was distilled, b.p. 154° (0·05 mm) (3·4 g; 83%). (Found: C, 69·32; H, 8·13; O, 22·67. M.W. 292. $C_{17}H_{24}O_4$ requires: C, 69·83; H, 8·27; O, 21·89%. M.W. 292·36.) IR: 1735, 1725 cm^{-1}. NMR: τ 4·42 (4H, olefinic), 6·33, 6·35 (6H, OCH_3), 7·5–8·1 (m) (CH_2 and allylic).

3-*Hydroxy*-4-*carbomethoxy*[4.4.4]*propella*-3,8,12-*triene* (**7**)

A soln of **6** (3·75 g) in toluene (100 ml) was added dropwise with stirring during 4 hr, under N_2, to a soln of MeONa (from 0·95 g Na) in toluene (750 ml), MeOH being removed azeotropically. After 48 hr (60 ml distillate was removed), the mixture was cooled and neutralized with AcOH. After washing with water and drying (Na_2SO_4) and removal of solvent the *keto-ester* **7** was distilled, b.p. 105–110° (0·01 mm) (3·1 g; 92%). An analytical sample was prepared by chromatography on silica and elution with benzene, m.p. 82–84°. (Found: C, 74·00; H, 7·80; O, 18·38. $C_{16}H_{20}O_3$ requires: C, 73·82; H, 7·74; O, 18·44%). IR: 3100 (very broad H...OH), 1660 (H....O=C—OMe), 1620 cm^{-1} (C=C). The β-keto ester is entirely

in the enolic form. NMR: τ – 2·2 (s) (1H, O$\underline{H}$), 4·46 (m) (4H, olefinic), 6·27 (s) (3H, OC$\underline{H}_3$), 7·3–8·5 (b.m.) (C$\underline{H}_2$).

3-*Hydroxy-4-carbomethoxy*[4.4.4]*propella*-8,12-*diene* (**8**)

A mixture of **7** (641 mg), $NaBH_4$ (250 mg) ether (20 ml), MeOH (15 ml) and water (5 ml) was allowed to stand at 0° for 5 hr. It was acidified with AcOH, the solvents were removed and the residue was taken up in CH_2Cl_2, washed with water, $NaHCO_3$aq and dried (Na_2SO_4). Chromatography on silica (100 g) and elution with CH_2Cl_2 gave the *hydroxy-ester* **8**, b.p. 120° (0·01 mm) (518 mg; 80%), m.p. 78°. Continued elution gives a mixture of two epimers; the second epimer was not characterized. (Found: C, 73·60; H, 8·44; O, 17·94. $C_{16}H_{22}O_3$ requires: C, 73·25; H, 8·45; O, 18·30%.) IR: 3500 (broad OH), 1718 (CO), 1668 cm^{-1} (C=C). NMR: τ 4·50 (m) (4H, olefinic), 5·63 (broad s) (1H, C$\underline{H}$OH), 6·28 (s) (3H, OC$\underline{H}_3$), 6·58 (broad s) (1H, C$\underline{H}CO_2$), 6·80–8·80 (m) (12H, C$\underline{H}_2$).

Reduction of **7** with $NaBH_4$ in abs MeOH gave as the major product the *diol* **10**, m.p. 125° (benzene–hexane). (Found: C, 77·44; H, 9·62. M.W. 234. $C_{15}H_{22}O_2$ requires: C, 76·88; H, 9·46%. M.W. 234·33.) IR: 3610, 3500 (OH), 1660 cm^{-1} (C=C).

3-*Carbomethoxy*[4.4.4]*propella*-3,8,12-*triene* (**9**)

A mixture of **8** (160 mg), $POCl_3$ (186 mg) and dry pyridine (2 ml) was allowed to stand at – 5° for 2 hr and was refrigerated overnight. After the usual workup the *ester* **9** was distilled, b.p. 107° (0·01 mm) (140 mg; 94%). (Found: C, 78·91; H, 8·30, M.W. 244. $C_{16}H_{20}O_2$ requires: C, 78·65; H, 8·25%. M.W. 244·32.) IR: 1720–1700 (CO), 1660 cm^{-1} (C=C). NMR: τ 4·47 (broad s) (5H, olefinic), 6·25 (s) (3H, OC$\underline{H}_3$), 7·20–8·80 (m) (12H, allylic).

[4.4.4]*Propella*-8,12-*diene*-3-*one* (**11**)

The ester **7** (2 g) was saponified by boiling with 5% NaOHaq (20 ml) and EtOH (20 ml) for 12 hr. After cooling a crystalline ppt of salt was obtained. Upon acidification with 10% H_2SO_4, evolution of CO_2 commenced. The *ketone* **11** was removed by filtration and the aqueous phase was extracted with CH_2Cl_2 to yield additional **11**, m.p. 78–80° (1·54 g; 99%). Two crystallizations from MeOH or sublimation at 65° (0·1 mm) gave m.p. 84°. (Found: C, 83·12; H, 9·16; O, 7·87, M.W. 202. $C_{14}H_{18}O$ requires: C, 83·12; H, 8·97; O, 7·91%. M.W. 202·28.) IR: 1720–1700 (CO), 1660 cm^{-1} (C=C). UV (Cyclohexane): $\lambda\lambda_{max}$ 288, 296 (sh), 307 (sh) nm; $\varepsilon\varepsilon$ 50, 48, 35 (Cary 14). NMR: τ 4·4 (b.s., olefins), 7·4–8·2 (unresolved multiplet, C$\underline{H}_2$).

[4.4.4]*Propellan*-3-*one* (**12**)

A soln of **11** (870 mg) in AcOH (25 ml) in the presence of Adams' catalyst absorbed 2 equiv H_2 during 1 hr. Removal of catalyst and solvent and sublimation at 95° (0·5 mm) gave the *ketone* **12** in quantitative yield, m.p. 120–121° (MeOH). (Found: C, 81·86; H, 10·92; O, 7·30, M.W. 206. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75; O, 7·76%. M.W. 206·32.) IR: 1710 cm^{-1}. UV (cyclohexane): $\lambda\lambda_{max}$ 288, 305 (sh) nm; $\varepsilon\varepsilon$ 16·1, 11·6 (Cary 14). NMR: τ 7·4–7·7 (m) (C$\underline{H}_2$CO), 8·38 (b.s.) (C$\underline{H}_2$).

[4.4.4]*Propellane* (**13**)

A mixture of **12** (700 mg), KOH (1 g), hydrazine (90%; 1 ml) and ethylene glycol (20 ml) was heated under reflux for 3 hr. After the usual workup, chromatography of the product in light petroleum over basic alumina (20 g) and elution with the same solvent gave the *propellane* **13** (520 mg; 80%), m.p. 116–119°. Recrystallization from MeOH or sublimation at 100° (24 mm) gave m.p. 119–120°. (Found: C, 87·82; H, 12·24. M.W. 192. $C_{14}H_{24}$ requires: C, 87·42; H, 12·58%. M.W. 192·33.) IR: 2940 (s), 2910 (sh, s), 2865 (s), 1468 (m), 1455 (m), 1438 (m). NMR: τ at 30°, 8–9·5 (b. multiplets), at 80°, 8·5 (b.s.).

[4.4.4]*Propellan*-3-*ol* (**14**)

The ketone **12** (397 mg) was reduced at 0° with $NaBH_4$ (250 mg) in ether (5 ml)–MeOH (12 ml). After standing overnight at room temp and the usual workup, the *alcohol* **14** (376 mg; 93·5%) was obtained, m.p. 119–120° (pet. ether). (Found: $[M-18]^+$, 190. $C_{14}H_{24}O—H_2O$ requires: 190·34). IR: 3600, 3450 (OH), 2950 (s), 2910 (sh), 2870 (s) (CH stretch), 1475 (m), 1455 (m), 1440 (m) (CH bend), 1040 cm^{-1} (C—O). NMR: τ 6·0 (m) (1H, C$\underline{H}$OH), 7·60–9·30 (m) (22H, C$\underline{H}_2$).

3-*Hydroxy*[4.4.4]*propella*-8,12-*diene* (**15**)

A mixture of **11** (315 mg), $NaBH_4$ (160 mg), ether (3 ml) and MeOH (10 ml) stood overnight at room

temp. After evporation to half the volume, ether extraction, washing with water and drying (Na_2SO_4) the solvent was removed and the *alcohol* **15** (306 mg) had m.p. 126° (hexane). (Found: C, 81·86; H, 9·95; O, 8·00. $[M-18]^+$, 186. $C_{14}H_{20}O$ requires: C, 82·30; H, 9·87; O, 7·83%. M.W. −18, 186·30.) IR: 3600 (OH), 1665 cm^{-1} (C=C). NMR: τ 4·48 (m), (4H, olefinic), 6·00 (m) (1H, CHOH), 7·20–9·00 (m) (14H, CH_2).

[4.4.4]*Propella*-3,8,12-*triene* (**17**)

Dehydration of **15** (306 mg) in dry pyridine (4 ml) was effected by adding $POCl_3$ (382 mg) at −5° and setting aside overnight at room temp. After the usual workup and extraction with hexane, the *triene* **17** was distilled, b.p. 110° (24 mm) (245 mg; 88%). (Found: C, 90·01; H, 9·81, M.W. 186. $C_{14}H_{18}$ requires: C, 90·26; H, 9·74%. M.W. 186·28.) Purification by GLC on a column (5 m) of carbowax 20 on celite 40/60 at 150° (introduced at 170°) gave 2 peaks, retention time 35 min of the symmetrical triene **17** and the 2,8,12-triene **16**, retention time 48 min in a ratio of 10:1. The unsymmetrical triene **16** is an oil which polymerizes on standing for several weeks at room temp. The triene **17** had m.p. 49–51°. IR: 2960 (w), 2895 (s), 2835 (s), 1650 cm^{-1} (w). NMR (CCl_4): τ at 30°: 4·50 (t) (6H, olefinic), 7·52, 8·56 (AB quartet, J_{AB} 16 c/s) (12H, allylic) at 80°: 4·50 (t) (6H, olefinic), 8·02 (broad s) (12H, allylic).

Brominations of **17** *and attempted dehydrobrominations*

(a) A soln of Br_2 (0·45 ml) in AcOH (3 ml) was added to an AcOH soln (10 ml) of **17** (516 mg). The Br_2 reacted immediately and the *hexabromide* **19** precipitated. Filtration and drying in a high vacuum gave pure **19** (1·34 g, 73%), m.p. 310° (dec., $CHCl_3$). (Found: C, 25·50; H, 2·53; Br, 72·30; M.W. 666. $C_{14}H_{18}Br_6$ requires: C, 25·25; H, 2·72; Br, 72·01%. M.W. 665·78.) Attempted bromination with Br_2 in CCl_4 is accompanied by spontaneous partial dehydrobromination and no pure product could be isolated.

Attempted dehydrobromination of **19** with LiCl in DMF at varying temp and time or potassium t-butoxide followed by attempted chromatographic purification on alumina or silica–$AgNO_3$ were unsuccessful. No pure product could be isolated with the exception of naphthalene (ca. 10% yield).

(b) Allylic bromination of **17** with 3 equiv NBS gave a tribromide. The last equiv of NBS reacts more slowly than the first two. Attempts at dehydrobromination to obtain **20** failed. All chromatographic fractions still contained bromine.

(c) Allylic bromination of **17** with 2 equiv NBS and dehydrobromination of **18** with LiCl in DMF led to fractions containing Br and to naphthalene (35% yield) obviously produced by a retro-Diels–Alder reaction of the intermediate [4.4.4]propella-2.4.7,9,12-pentaene present in the reaction mixture.

Brominations of 12-*oxa*[4.4.3]*propella*-3,8-*diene* (**22**)

(a) To a soln of **22** (352 mg) prepared by dehydration of **21**,[1a] in glacial AcOH (30 ml) was added dropwise with stirring and cooling a soln of Br_2 (0·25 ml) in glacial AcOH (30 ml). When all of the Br colour had been discharged a 10% excess of Br_2 in AcOH was added. After stirring for 10 hr at room temp, the colourless crystals of the *tetrabromide* **24** which began to ppt during addition of Br_2 were removed by filtration (33 mg; 3·3%), m.p. 270–272°. (Found: M.W. 496. $C_{12}H_{16}OBr_4$ requires: M.W. 495·79.) NMR ($CHBr_3$): τ 5·68–6·50 (unresolved m) (8H, CHBr and CH_2O), 7·50–7·90 (m) (8H, CH_2). The solvent was removed from the mother liquor. Trituration of the residual yellow oil with AcOEt gave the isomeric *tetrabromide* **23** (530 mg; 50%), m.p. 170–172° ($CHCl_3$–hexane). (Found: C, 29·56; H, 3·50; O, 2·93; Br, 63·90. M.W. 496. $C_{12}H_{16}OBr_4$ requires: C, 29·04; H, 3·23; O, 3·23; Br, 64·40%. M.W. 495·79). NMR ($CHBr_3$): τ 5·25–5·55 (m) (4H, CHBr), 5·85 (s) (2H, CH_2O), 6·18 (s) (2H, CH_2O), 7·00–7·90 (m) (8H, CH_2). From these values the structure and stereochemistry of **23** is clear and **24** must have the structure and stereochemistry shown in Scheme 2 because of the symmetry of the molecule. The NMR spectrum of **24** was taken in $CHBr_3$ as it is highly insoluble in water, acetone, $CHCl_3$, CCl_4, benzene, hexane, trifluoroacetic acid

(b) A mixture of **22** (1·76 g; 0·01 mole), NBS (3·56 g; 0·02 mole), benzoyl peroxide (5 mg) and CCl_4 (40 ml) was heated under reflux. All of the NBS had reacted during 1 hr. After the usual workup the crude dibromide was dehydrobrominated (see below).

12-*Oxa*[4.4.3]*propella*-2,4,7,9-*tetraene* (**25**)

Dehydrobromination of **23**: A mixture of the tetrabromide (6·7 g), LiCl (15 g) and DMF (200 ml) was heated at 130° under N_2 for 24 hr and at 140° under N_2 for an additional 24 hr. After the usual workup (cf. Ref. 1a) the residue was chromatographed on silica (65 g) containing 15% $AgNO_3$. Elution with light petroleum gave a bromide (513 mg) whose NMR spectrum indicates that it is 3-bromo-12-oxa[4.4.3]-

propellan-3,7,9-triene but this was not further characterized. Elution with benzene gave the *tetraene* **25** (930 mg, 40%), m.p. 70–72°. Lit. m.p. 74–75°,[5] 71·5–72°.[6] In different experiments the yield varied within the range 25–40%.

(b) Dehydrobromination of the diallylic dibromide: The dibromide (from 1·76 g of **22**) was heated with LiCl (5 g) and DMF (100 ml) at 100° for 24 hr. After the usual workup and chromatography on basic alumina (under N_2) and elution with pet. ether (60–80°)–benzene (4:1) a mixture of triene and tetraene was obtained in the first fractions. Finally, the *tetraene* **25** was obtained (1·19 g; 69%). After sublimation at 65° (24 mm) it had m.p. 70–72°. NMR (CCl_4): τ 4·1–4·6 centered at 4·37, (A_2B_2 multiplet, olefinic), 6·02 (s) ($C\underline{H}_2O$) in ratio 2:1 (cf. Ref. 5). UV (cyclohexane or MeOH); λ_{max} 244, ε_{max} 6500 (degassed).

Ozonization of 8-*oxa*[4.3.3]*propell*-3-*ene* (**26**)

O_3 was passed through a soln of **26** (0·76 g) in abs MeOH (30 ml) at −78° until the appearance of a blue colour (ca. 10 min). The solvent was removed at the water pump at room temp and formic acid (12 ml) and H_2O_2 (30%; 6 ml) was added to the residue and set aside overnight at room temp. After removal of the solvents in a high vacuum the crystalline *diacid* **27** (0·64 g; 60%) remained, m.p. 245° (dec; aq EtOH). (Found: C, 58·23; H, 7·06; O, 34·85. $C_{11}H_{16}O_5$ requires: C, 57·88; H, 7·07; O, 35·05%.) IR (KBr): 3200–3000 (OH), 1720–1700 (CO), 1098, 1065 cm^{-1} (—O—). NMR (pyridine): τ 5·74, 5·87 (AB quartet, J_{AB} 9·5 c/s) (4H, $C\underline{H}_2O$), 7·26 (s) (4H, $C\underline{H}_2CO_2$), 7·75–8·42 (m) (6H, $C\underline{H}_2$).

7-*Oxa*[3.3.3]*propellan*-3-*one* (**28**)

The diacid **27** (1 g) was heated under reflux with AcCl (10 ml) during 20 hr. After removal of the solvent at the water pump the residual 7-membered anhydride (IR in $CHCl_3$: 1790, 1750 cm^{-1}) was heated at 300–350° at water-pump vacuum; the ketone distilled out. Chromatography on neutral alumina (10 g) with light petroleum–benzene (9:1) gave the pure *ketone* **28** (0·18 g; 25%), m.p. 143° (hexane). (Found: M.W. 166. $C_{10}H_{14}O_2$ requires: M.W. 166·21.) IR: 1745 (CO), 1055, 1035 cm^{-1} (—O—). NMR: τ 6·27 (s) (4H, $C\underline{H}_2O$), 7·57 (s) (4H, $C\underline{H}_2CO$), 7·82–8·48 (m) (6H, $C\underline{H}_2$). The orange 2,4-*dinitrophenylhydrazone* has m.p. 170° (EtOH). (Found: C, 55·83; H, 5·07; N, 15·84. $C_{16}H_{18}O_5N_4$ requires: C, 55·84; H, 5·24; N, 16·18%.)

7-*Oxa*[3.3.3]*propellan*-3-*ol* (**29**)

A mixture of **28** (185 mg), $NaBH_4$ (173 mg), ether (5 ml) and MeOH (17 ml) was stirred for 12 hr at room temp. After acidification with dil HCl and the usual workup, the crude alcohol was obtained (180 mg; 96%). Chromatography on neutral alumina (8 g) and elution with benzene-$CHCl_3$ (19:1) gave the intramolecularly hydrogen-bonded epimeric *alcohol* **29** (0·1 g; 54%), m.p. 152–154° (from pet ether, 60–80°), as shown by IR dilution experiments. (Found: C, 70·76; H, 9·32. $[M.W. - 18]^+$, 150. $C_{10}H_{16}O_2$ requires: C, 71·39; H, 9·59%. $C_{10}H_{16}O_2 - H_2O$ requires: 150·22.) IR: 3610, 3440–3400 (OH), 1055 cm^{-1} (—O—). NMR: τ 5·50–5·90 (m) (1H, C$\underline{H}$OH), 6·36, 6·51 (AB quartet, J_{AB} 9·3 c/s) (4H, $C\underline{H}_2O$), 7·52 (s) (1H, O$\underline{H}$), 7·80–8·74 (m) (10H, $C\underline{H}_2$).

8-*Oxa*[4.3.3]*propella*-2,4-*diene* (**30**)

(a) A soln of Br_2 (1·2 ml) in CCl_4 (50 ml) was added dropwise to an ice-cold stirred soln of **26** (3·5 g) in CCl_4 (100 ml), during 50 min. Stirring of the clear soln was continued at room temp for 17 hr. The solvent was removed at the water pump and the residual dibromide (6·5 g; m.p. 68–75°) was recrystallized (benzene–pet. ether) to give 3,4-*dibromo*-8-*oxa*[4.3.3] *propellane* (4·4 g; 70%), m.p. 86–88°. (Found: C, 41·02; H, 5·38; Br, 48·53. M.W. 324. $C_{11}H_{16}OBr_2$ requires: C, 40·77; H, 4·98; Br, 49·32%. M.W. 324·07.) IR: 3000–2890 (CH), 1450, 1045, 915 cm^{-1}. NMR (CCl_4): τ 5·60–6·00 (m) (2H, C$\underline{H}$Br), 6·20 (d) (2H, $C\underline{H}_2O$), 6·37 (s) (2H, $C\underline{H}_2O$), 7·30–8·00 (complex multiplet) (4H, $C\underline{H}_2$ CBr), 8·17 (broad s) (6H, $C\underline{H}_2$).

The crude dibromide (3·74 g) was added to a soln of LiCl (3·7 g) in DMF (100 ml) and stirred under N_2 at 100–105° for 21 hr. After the usual workup the residual oil (1·19 g) was distilled and gave the pure *dienic ether*, **30**, b.p. 106–107° (22 mm). Ether extraction of the diluted mother liquor gave more of **30** (0·33 g; overall yield 62%). (Found: C, 80·66; H, 8·47, M.W. 162. $C_{11}H_{14}O$ requires: C, 81·44; H, 8·70%. M.W. 162·22.) IR: 2995–2850 (CH), 1600 (C=C). NMR: τ 4·10–4·50 (A_2B_2 multiplet) (4 olefinic H), 6·12, 6·48 (AB quartet, J_{AB} 9 c/s) (4H, $C\underline{H}_2O$), 7·90–8·80 (m) (6H, $C\underline{H}_2$). UV (cyclohexane): λ_{max} 257, log ε 3·85 (Cary 14).

(b) A mixture of **26** (1·64 g), NBS (2·09 g), a trace of dibenzoyl peroxide and CCl_4 (75 ml) was heated under reflux for 1 hr. After the usual workup a yellow oil of the allylic bromide was treated without further

purification with LiCl (4·0 g) in DMF (100 ml) as described below for **43** → **44** + **45**. The product obtained from the pet. ether extract (0·51 g; b.p. 106–108° (22 mm)) and from the ether extract (0·34 g; b.p. 106–108° (22 mm); 52% overall yield) was identical in physical properties to **30** prepared by procedure (a).

8,11-*Dioxa*[4.3.3]*propell*-3-*ene* (**33**)

(a) The tetraester **31**[8] (37 g) was dissolved in THF (400 ml) and reduced during 4 days with LAH (18 g). After the usual workup the tetrol **32**[2m] (17·2 g; 85%) was obtained m.p. 256–270° (MeOH–benzene). Recrystallization lowered the m.p. to 230–233°. Lit.[2m] m.p. 281–284° (with change of crystalline form at 220°).

(b) The tetrol (22 g) and *p*-toluenesulphonic acid (0·3 g) where heated under reflux in toluene (2 l.) during 24 hr the water formed being removed azeotropically. After the usual workup, distillation gave the desired *diether* **33** (10 g; 56%), b.p. 120° (15 mm), sublimed at 65° (24 mm) in the presence of CaH_2,* m.p. 103–108°. Lit.[2m] m.p. 105–108°. NMR: τ 4·13 (t) (2H, olefinic), 6·45 (s) (8H, CH_2O), 7·87, 7·92 (d) (4H, CH_2) (cf. Ref. 2*m*).

8,11-*Dioxa*[4.3.3]*propellane* (**34**)

A soln of **33** (756 mg) in abs EtOH (10 ml) in the presence of Adams' catalyst absorbed one molar equiv H_2 during 2 hr. After the usual workup the *propellane* **34** (727 mg; 95%) was obtained. Chromatography on basic alumina (30 g) using benzene–$CHCl_3$ (9:1) and sublimation in the presence of CaH_2 at 80° (24 mm) gave the hygroscopic analytical sample, m.p. 119–122°. (Found: C, 70·95; H, 8·99. $C_{10}H_{16}O_2$ requires: C, 71·39; H, 9·06%). IR: 1070, 1055 cm^{-1} (—O—). NMR: τ 6·3 (s) (8H, CH_2O), 8·43 (s) (8H, CH_2); rel. intens. 1:1

3,4-*Dibromo*-8,11-*dioxa*[4.3.3]*propellane* (**35**)

Br_2 (1 ml) in CCl_4 (40 ml) was added dropwise with stirring to a soln of **33** (3·07 g) in CCl_4 (40 ml.) at room temp during 30 min. After removal of solvent at the water pump the colorless crystalline residue of *dibromide* **35**, (5·1 g; 85%) was recrystallized, m.p. 130–131° (light pet.). (Found: C, 37·23; H, 4·60; Br, 49·23. $C_{10}H_{14}O_2Br_2$ requires: C, 36·82; H, 4·33, Br, 49·04%.) IR: 1090, 1060 cm^{-1} (—O—). NMR: τ 5·47–6·06 (m) (2H, CHBr), 6·18, 6·21 (d) (8H, CH_2O), 7·23–8·07 (m) (4H, CH_2).

8,11-*Dioxa*[4.3.3]*propella*-2,4-*diene* (**36**)

A mixture of **35** (2·55 g), LiCl (8 g) and DMF (60 ml) was heated under N_2 with stirring at 130° for 24 hr. After the usual workup the crystalline *diene* **36** was obtained (1 g; 78%). Sublimation in the presence of CaH_2 at 70° (24 mm), m.p. 63–66° (hygroscopic). (Found: C, 73·78; H, 7·46, M.W. 164. $C_{10}H_{12}O_2$ requires: C, 73·14; H, 6·87%. M.W. 164·20.) IR: 1600 (diene), 1100, 1050 cm^{-1} (—O—). NMR (CCl_4): τ 3·93–4·45 (A_2B_2) (4H, olefinic), 6·13, 6·43 (AB quartet, J_{AB} 9 c/s) (8H, CH_2O). UV (cyclohexane): $\lambda\lambda_{max}$ 251, 260, 269 (sh) nm; log $\varepsilon\varepsilon$ 3·69, 3·69, 3·49 (Cary 14).

Ozonization of **36**

Compound **36** (0·5 g) in abs MeOH (50 ml) was ozonized (5 min) at −78°. The workup was analogous to that of the ozonization product of **26**. The diacid thus obtained was very soluble in water. It was therefore methylated with diazomethane in ether. Chromatography on neutral alumina (20 g) and elution with CH_2Cl_2–light petroleum (1:3) gave the *dimethyl ester* **37** as an oil, b.p. 91° (0·05 mm) (190 mg; 27%). (Found: M.W. 230. $C_{10}H_{14}O_6$ requires: M.W. 230·21). IR: 1755–1735 (CO), 1140, 1100 cm^{-1} (—O—). NMR: τ 5·84, 6·28 (AB quartet, J_{AB} 9·5 c/s) (CH_2O), 6·40 (s) (CH_3).

Alternatively, if the residual crude diacid (IR in KBr: 3430–3000 (OH), 1750–1735 (CO)) was heated under reflux with Ac_2O for 20 hr, the solvent removed and the residue sublimed at 120° (0·05 mm), the *anhydride* **38** was obtained (276 mg; 49%), m.p. 165–168°. (Found: C, 51·83; H, 4·44; O, 43·50. $C_8H_8O_5$ requires: C, 52·18; H, 4·38, O, 43·44%.) IR: 1865, 1795 (anhydride CO), 1095 cm^{-1} (—O—). NMR: τ 5·59, 6·05 (AB quartet, J_{AB} 10 c/s) (CH_2O).

3,7,10-*Trioxa*[3.3.3]*propellane* (**38a**)

(a) A mixture of **38** (0·56 g), LAH (0·53 g) and THF (100 ml) was heated under reflux for 48 hr. The mixture was decomposed with $MgSO_4$ aq (1·9 ml). The ppt was removed by filtration and the soln was dried

* The ethers are often quite hygroscopic. Hence sublimation is best carried out in the presence of either CaH_2 or LAH

($MgSO_4$). Removal of solvent at the water pump gave the crude diol (0·45 g; 85%). IR: 3600, 3440–3320 (OH), 1095, 1055 cm^{-1} (—O—).

(b) A mixture of the crude diol (0·45 g), *p*-toluenesulphonic acid (0·3 g) and toluene (100 ml) was heated under reflux for 15 hr. After the usual workup the solid triether was sublimed in the presence of LAH at 80° (24 mm) and gave the pure *trioxapropellane* m.p. 182–187° (195 mg; 41%). (Found: M.W. 156. $C_8H_{12}O_3$ requires: M.W. 156·17.) IR: 2980, 2940 (sh), 2875 (CH), 1100, 1035 cm^{-1} (—O—) NMR: τ 6·27 (s) ($C\underline{H}_2O$).

Ozonization of **33**

Compound **33** (2·8 g) in abs MeOH (100 ml) was ozonized (15 min) at −78°. After the usual workup (cf. ozonization of **26**) the colorless crystalline residue of the *diacid* **39** was obtained (3 g; 70%), m.p. 190–194° (water). The analytical sample contains 1·5 moles of water of hydration which cannot be removed at 110° (0·01 mm). (Found: C, 46·20; H, 6·57. $C_{10}H_{14}O_6 \cdot 1\frac{1}{2}\ H_2O$ requires: C, 46·69; H, 6·66%.) IR (KBr): 3470, 3390 (OH), 1710 (CO), 1100, 1090 (—O—). NMR (pyridine): τ 6·03, 6·24 (AB quartet, J_{AB} 9·5 c/s) (8H, $C\underline{H}_2O$), 7·68 (s) (4H, $C\underline{H}_2$).

7,10-*Dioxa*[3.3.3]*propellan*-3-*one* (**40**)

The diacid **39** (1 g) was heated under reflux with Ac_2O for 20 hr. After removal of solvent a 7-membered anhydride was obtained (IR in chloroform: 1790, 1740 (anhydride CO), 1090, 1080 cm^{-1} (—O—)). The crude anhydride was heated to 320° at the water pump and the *ketone* **40** distilled at 155–170° (0·33 g; 45%). The analytical sample was obtained by 3 sublimations in the presence of molecular sieve (BDH type 4A) at 110° (24 mm), m.p. 166–169°. (Found: M.W. 168. $C_9H_{12}O_3$ requires: M.W. 168·19.) IR: 1745 (CO), 1085 cm^{-1} (—O—). NMR: τ 6·24, 6·42 (AB quartet, J_{AB} 9·1 c/s) (8H, $C\underline{H}_2O$), 7·57 (s) (4H, $C\underline{H}_2CO$).

7,10-*Dioxa*[3.3.3]*propellan*-3-*ol* (**41**)

A mixture of **40** (153 mg), $NaBH_4$ (86 mg) and MeOH (15 ml) was stirred at room temp for 12 hr. After the usual workup the *alcohol* **41** (140 mg; 90%) was obtained. Chromatography on neutral alumina (7 g) and elution with benzene–$CHCl_3$ (7:3) gave the analytical sample, m.p. 174–177° (sintering at 160°; pet. ether). (Found: $[M-18]^+$: 152. $C_9H_{14}O_3$–H_2O requires: 152·18). IR: 3590, 3420 (OH) 1115, 1065 cm^{-1} (—O—). NMR: τ 5·30–6·00 (m) (C$\underline{H}$OH and $C\underline{H}_2O$), 7·65–8·50 (m) ($C\underline{H}_2$).

3,7-*Dioxa*[3.3.3]*propellane* (**41a**)

(a) The thioketal was prepared from the ketone **40** (0·67 g), ethanedithiol (1 ml) and BF_3-etherate (1 ml) at 0°, followed by standing overnight. After the addition of cold NaOH aq (10 ml) and removal of the ppt by filtration, the *thioketal* was washed with water and dried (0·65 g; 67%), m.p. 105°. (Found: M.W. 244. $C_{11}H_{16}O_2S_2$ requires: M.W. 244·23). IR: 1130, 1110, 1058 cm^{-1} (—O—). NMR: τ 6·03, 6·37 (AB quartet, J_{AB} 9·5 c/s) (8H, $C\underline{H}_2O$), 6·69 (s) (4H, $C\underline{H}_2S$), 7·60 (s) (4H, $C\underline{H}_2$).

(b) A mixture of the thioketal (0·53 g), Raney Ni (3 g) and dry EtOH (50 ml) was heated under reflux for 12 hr. After the usual workup the oily product (0·22 g; 65%) was chromatographed on neutral alumina (11 g) and eluted with a mixture of light petroleum–CH_2Cl_2 (17:3). Sublimation at 120° in the presence of LAH (760 mm) gave the diether, m.p. 129–132°. (Found: $[M-CH_2OH]^+$, 123. $C_9H_{14}O_2$—CH_3O requires: 123·20). IR: 2960, 2940, 2860 (CH), 1092, 1070, 1055 cm^{-1} (—O—). NMR: τ 6·37 (s) (8H, $C\underline{H}_2O$), 8·22–8·32 (m) (6H, $C\underline{H}_2$).

Tosylation of the diol **21**

A soln of *p*-toluenesulphonyl chloride (9·5 g) in dry pyridine (150 ml) was added at 0° to a stirred solution of **21**[1a] (4 g) in dry pyridine (150 ml) during 2 hr. After stirring for an additional 6 hr at 0–5° and refrigeration overnight the mixture was poured on ice (300 g), acidified with 50% H_2SO_4 and the crude precipitated tosylate was removed by filtration, washed with water and dried (8·8g; 86%), m.p. 123–126°. The pure sample (7·6 g; 71%) formed colorless needles of the *ditosylate* **42**, m.p. 125–126°. (THF–pet. ether). Lit.[2a] m.p. 126°. IR: 1650 (C=C), 1600 (ArC=C), 1360, 1175 cm^{-1} (OSO_2). The aqueous filtrate was extracted with ether several times and the combined extracts were washed with $NaHCO_3$ aq, water and dried (Na_2SO_4). Removal of solvent and distillation of the residue gave 12-oxa-[4.4.3]propella-3,8-diene[1a] (1·3 g; 3·3%), b.p. 125–126° (24 mm).

12-*Thia*[4.4.3]*propella*-3,8-*diene* (**43**)

(a) A mixture of **42** (7·6 g), $Na_2S \cdot 9H_2O$ (4·2 g) and DMSO (400 ml) was stirred under N_2 for 20 hr at

125–135°. The dark reaction mixture was poured into water (1 l.) and extracted with ether (5 × 200 ml). The combined extracts were washed with water and dried (Na_2SO_4). After treatment with active carbon the solvent was removed at the water pump and the *thio-ether* **43** was obtained (26·5 g; 92%), m.p. 37–39°. Filtration of a pet. ether (50 ml) soln of **43** through basic alumina (Merck, 760 g) and elution with pet. ether (60–80°; 2 l). followed by removal of solvent gave a colorless oil (22·2 g; 80%), which solidified on standing, m.p. 52–53° (with sintering at 38–39°), b.p. 79–80° (0·05 mm). Sublimation at 80° (30 mm) afforded the analytical sample, m.p. 52–53°. (Found: C, 74·84; H, 8·42; S, 16·72. M.W. 192. $C_{12}H_{16}S$ requires: C, 74·96; H, 8·39; S, 16·65%. M.W. 192·35.) IR: 3000–2820 (CH), 1660 (C═C), 655 cm^{-1} (C—S). NMR: τ 4·45 (t) (4 olefinic H), 7·15 (s) (4H, $C\underline{H}_2S$), 7·85 (m) (8 allylic H).

(b) A soln of the dibromide **46**[14] (0·89 g) and $Na_2S.9H_2O$ (0·8 g) in DMSO (10 ml) was stirred under N_2 for 37 hr, at 74–75°, followed by 10 hr at 130°. The mixture was poured into saturated salt soln and then extracted with ether (50 ml). After the usual workup, crude **43** was obtained (0·34 g; 60%), m.p. 48–52°. The m.p. was raised to 54–55° after 3 crystallizations (EtOH; sintering at 39–40°). This was identical in all respects with **43** prepared by method (a).

The *sulphoxide* was obtained by adding a methanolic soln (30 ml) of **43** (1·0 g; 5·2 mmole) to a soln of sodium periodate (0·5M; 11·0 ml; 5·5 mmole) in aqueous MeOH (1:1) at 0°. After stirring for 7 hr at 0–5° the precipitated $NaIO_3$ was removed by filtration, the filtrate was diluted with water and extracted with $CHCl_3$. After drying (Na_2SO_4), the solvent was removed at the water pump. The residual oil (0·92 g; 85%) solidified on standing, m.p 65–67°. The analytical sample of the sulphoxide was obtained by 3 recrystallizations (pet. ether), m.p., 66–67°. (Found: C, 69·25; H, 7·73; S, 14·96, M.W. 208. $C_{12}H_{16}OS$ requires: C, 69·18; H, 7·76; S, 15·39%. M.W. 208·35.) IR: 3000–2825 (CH), 1660 (C═C), 1020 cm^{-1} (SO). NMR: τ 4·35 (t) (2 olefinic H), 4·45 (t) (2 olefinic H), 6·51, 7·16 (AB quartet, J_{AB} 13 c/s) (4H, $C\underline{H}_2SO$), 7·65 (t) (4 allylic H), 8·00 (m) (4 allylic H).

The *sulphone* was prepared by slowly adding H_2O_2 (30%, 1·50 g; 13·2 mmole) to a stirred water-cooled solution of **43** (1·0 g; 5·2 mmole) in glacial AcOH (20 ml). Stirring was continued for 46 hr, the solvents were removed at the water pump and the residue was dried in a vacuum. The product obtained (1·2 g, m.p. 86–91°) consisted of a mixture of the sulphone and sulphoxide (IR: 1305, 1128 (SO_2), 1015 cm^{-1} (SO)). After 2 recrystallizations (pet. ether, aq. EtOH) the pure sulphone (0·27 g; 23%) was obtained, m.p. 114–115°. (Found: C, 64·52; H, 7·24; S, 14·01, M.W. 224. $C_{12}H_{16}O_2S$ requires: C, 64·25, H, 7·19; S, 14·30%. M.W. 224·35.) IR: 3000–2840 (CH), 1675 (C═C), 1310, 1130 cm^{-1} (SO_2). NMR: τ 4·35 (t, J = 1·6 c/s) (4 olefinic H), 6·80 (s) (4H, $C\underline{H}_2SO_2$), 7·70 (octet, AB part of ABX) (8 allylic H).

Repetition of this procedure with an excess of H_2O_2 (125%) and a reaction period of 4 days gave crude sulphone, m.p. 97–100°, free from sulphoxide but contaminated by epoxidation and cleavage products (IR: 3620–3280 cm^{-1} (OH)) and decrease in the intensity of the C═C band at 1675 cm^{-1}).

Bromination of **43** *and dehydrobromination*

A mixture of **43** (2 g), NBS (3·56 g), a trace of dibenzoylperoxide and CCl_4 was heated under reflux for 4·5 hr. After the usual workup, the pale yellow residual oil (3·33 g) was dissolved in DMF (100 ml) and LiCl (4 g) was added. The mixture was stirred under N_2 at 105° for 24 hr. After cooling, the dark soln was extracted with pet. ether (3 × 30 ml). The usual workup gave a pale yellow oil (fraction A; 520 mg) whose NMR spectrum indicated that it was a mixture of **43** (20%), the triene **44** (60%) and the tetraene **45** (20%). The DMF soln was poured into ice water (200 ml) and extracted several times with ether. After the usual workup a brown oil was obtained (fraction B; 1·17 g) containing the triene **44** (50%) and the tetraene **45** (50%) (by NMR analysis).

Fraction A (502 mg) was dissolved in the minimal portion of pet. ether and chromatographed on basic alumina (Merck, column ht 36 cm, diam 1·5 cm). Elution with pet. ether (400 ml) gave solid fractions (total wt. 361 mg), m.p. range 28–34°. The middle fractions (118 mg; 6·3%) consisted of colorless needles of the *triene* **44**, m.p. 33–34°. Sublimation at room temp (0·05 mm) gave the analytical sample. (Found: M.W. 190. $C_{12}H_{14}S$ requires: M.W. 190·33). IR: 2995–2840 (CH), 1670 (C═C), 655 cm^{-1} (C—S). NMR (CCl_4): τ 3·90–4·50 (m) (6 olefinic H) 7·07, 7·18 (AB quartet, J_{AB} 9 c/s) (4H, $C\underline{H}_2S$), 7·85 (m) (4 allylic H). UV (cyclohexane): λ_{max} 265, ε_{max} 2100 (degassed).

Subsequent elution with pet. ether (260 ml) gave an oil (76 mg) consisting of (NMR) 93% of **45** and 7% of **44**.

Fraction B (1·17 g) was worked up as described for fraction A. Elution with pet. ether (300 ml) gave fractions containing varying amounts of a colourless solid, m.p. 26–30°. The middle fractions (97 mg)

consisted of 85% of **44** and 15% of **45**. Subsequent elution (700 ml) afforded oily fractions (total recovery 187 mg). The pure *tetraene* **45** was found in the middle fractions (42 mg; 2·2%). NMR (CCl_4): τ 3·96–4·60 (A_2B_2 multiplet) (8 olefinic H), 6·92 (s) (4H, $C\underline{H}_2S$). UV (cyclohexane): λ_{max} 245, ε_{max} 4800 (degassed). After storage in the refrigerator the material appears to polymerize; it was no longer soluble in pet. ether and was therefore subjected to photochemical study as soon as it was isolated.

Catalytic reduction of **46**

A soln of **46**[1a] (5·0 g) in glacial AcOH (150 ml) in the presence of Adams' catalyst absorbed 2 molar equivs of H_2 during 8 hr. After the usual workup **47** was obtained (4·93 g; 97%), m.p. (unrecrystallized) 108–109°. Lit.[1a] m.p. 112°.

12-*Thia*[4.4.3]*propellane* (**48**)

A mixture of crude **47** (2·5 g), $Na_2S.9H_2O$ (2·3 g) and DMF (30 ml) was stirred under N_2 at 125–130° for 20 hr. After the usual workup (see above) the *thio-ether* **48** was obtained (1·45 g; 89%), m.p. 116–117°. Recrystallization (EtOH) or sublimation at 100° (28 mm) did not alter the m.p. (Found: C, 73·25; H, 9·98; S, 16·60. M.W. 196. $C_{12}H_{20}S$ requires: C, 73·43; H, 10·27; S, 16·30%. M.W. 196·39). IR: 2990–2850 (CH), 1470, 1460, 1010, 898 cm^{-1}. NMR (CCl_4): τ 7·28 (s) (4H, $C\underline{H}_2S$) (16H, $C\underline{H}_2$).

The sulphoxide was prepared in the usual way (see above) from **48** and methanolic periodate. It was obtained as a crude colourless solid (73% yield), m.p. 150–157°. Many recrystallizations (pet. ether) gave colourless needles, m.p. 167–168°. The same m.p. was obtained by subliming the crude sulphoxide at 100° (0·05 mm). (Found: M.W. 212. $C_{12}H_{20}OS$ requires: M.W. 212·39). IR: 1055 cm^{-1} (SO). NMR: τ 6·46, 7·11 (AB quartet, J_{AB} 14 c/s) (4H, $C\underline{H}_2SO$), 8·30 (s) (8H, $C\underline{H}_2$), 8·35–8·70 (m) (8H, $C\underline{H}_2$).

The sulphone was prepared in the usual way with 30% H_2O_2 and AcOH as a crude solid (quant. yield). Recrystallization (benzene–pet. ether) gave colourless needles. (75%), m.p. 178–179°. (Found: C, 62·61; H, 8·86; S, 13·96. M.W. 228. $C_{12}H_{20}O_2S$ requires: 63·13; H, 8·83; S, 14·02%. M.W. 228·39). IR: 2950–2870 (CH), 1305, 1135, 1115 cm^{-1} (SO_2). NMR: τ 6·80 (s) (4H, $C\underline{H}_2SO_2$), 8·35 (s) (16H, $C\underline{H}_2$).

8-*Thia*[4.3.3]*propell*-3-*ene* (**51**)

The ditosylate **50** of the diol **49**[1a] (18 g) was prepared as described above for the preparation of **42**. However, in this case **56** was accompanied by the ether **26** in roughly equal proportions. NMR of mixture (CCl_4): τ 2·22, 2·62 (AB quartet, J_{AB} 8 c/s) (arom. H of **50**), 4·13 (t) (olefinic H of **26**), 4·52 (s) (olefinic H of **50**), 6·18 (s) ($C\underline{H}_2OSO_2$), 6·54 (s) ($C\underline{H}_2O$ of **26**), relative intensity 1:1, 7·55 (s) (arom. CH_3), 7·90–8·15 (m) (allylic H of **26**), 8·42 (s) ($C\underline{H}_2$ of **26**). IR: 1600 (ArC=C), 1365, 1175 cm^{-1} (OSO_2).

The crude mixture was dissolved in DMSO (50 ml) and added to a soln of $Na_2S.9H_2O$ (18·5 g) in DMSO (150 ml) and stirring was maintained under N_2 at 120–125° for 21 hr. After the usual workup (see above) a dark oil was obtained (11 g) which contained equal parts of **51** and **26**. NMR (CCl_4): τ 6·50 (s) ($C\underline{H}_2O$), 7·25 (quartet) ($C\underline{H}_2S$), rel. intens. 1:1. The crude oil was dissolved in MeOH (200 ml) and added with stirring to a soln of $HgCl_2$ (17·8 g) in aqueous MeOH (1:2; 180 ml). The $HgCl_2$ adduct of **51** (12·42 g), m.p. 125–130°, was obtained after filtration and drying in a vacuum. Recrystallization (EtOH) gave glistening plates of the pure *adduct*, m.p. 138–139°. The filtrate from the adduct was treated with sat Na_2Saq until precipitation of HgS was complete. After filtration, the filtrate was diluted with water, saturated with salt, extracted with ether and CH_2Cl_2, the solvents dried ($MgSO_4$) and then removed, yielding crude ether **26** (3·95 g). Its soln in pet. ether was filtered through basic alumina (Merck; 30 g). Elution with the same solvent gave **26** (3·77 g; 22% based on **49**), m.p. (unrecrystallized) 78–82°. Lit.[1a] m.p. 83°.

The thioether **51** was regenerated by treating the $HgCl_2$ adduct (12·4 g) in MeOH (200 ml) with Na_2Saq. After the usual workup, crude **51** (4·5 g; 86% based on adduct) was obtained. Filtration of its pet. ether soln through basic alumina (Merck; 30 g) gave the pure *thioether* **51** (4·37 g; 24% based on **49**), m.p. 83–86°. IR: 3000–2840 (CH), 1660 (C=C), 665 cm^{-1} (broad, CS). NMR (CCl_4): τ 4·32–4·42 (t, $J \approx 1{\cdot}4$ c/s) (2 olefinic H), 7·20, 7·33 (AB quartet, J_{AB} 10 c/s) (4H, $C\underline{H}_2S$), 7·82–7·96 (d, J 1·4 c/s) (4 allylic H), 8·15–8·35 (m) (6H, $C\underline{H}_2$). Sublimation at 90° (30 mm) gave the analytical sample, m.p. 88–89°. (Found: C, 73·19; H, 8·81; S, 17·50. M.W. 180. $C_{11}H_{16}S$ requires: C, 73·30; H, 8·89; S, 17·75%. M.W. 180·34.)

The *sulphoxide* was formed in the usual way. The crude sulphoxide (95% yield) had m.p. 132–135° (IR: 1040–1010 cm^{-1} (SO)). Chromatography of its soln in pet. ether on basic alumina (Merck; 20 g) and successive elution with benzene–pet. ether mixtures (750 ml), benzene (500 ml) and benzene–$CHCl_3$ mixtures (500 ml) gave solids with m.p. ranges 114–126° (28 mg), 135–139° (178 mg) and 90–105° (173 mg), respectively. This indicates the possibility that the two isomeric sulphoxides may be isolated and efforts

will be made with this in view. The NMR spectra (CCl_4) of all the fractions, were, however, identical: τ 4·03–4·32 (m) (2 olefinic H), 7·12 (s) (4H, $C\underline{H}_2SO$), 7·5–8·5 (complex multiplet, 10H). Sublimation at 115° (0·05 mm) gave the analytical sample, m.p. 137–139°. (Found: C, 66·82; H, 8·15; S, 15·91, M.W. 196. $C_{11}H_{16}OS$ requires: C, 67·32; H, 8·22; S, 16·31%. M.W. 196·34.)

The *sulphone* was prepared in the usual way in 10% yield, accompanied by the sulphoxide. Recrystallization (pet. ether, aq. EtOH) gave the pure sulphone as colourless plates, m.p. 138–140°. (Found: C, 63·00; H, 7·60; S, 14·82; M.W. 212. $C_{11}H_{16}O_2S$ requires: C, 62·23; H, 7·57; S, 15·10%. M.W. 212·30.) IR: 2980–2820 (CH), 1685 (C=C), 1315, 1140, 1115 cm^{-1} (SO_2). NMR (CCl_4): τ 4·10–4·25 (t) (2 olefinic H), 7·00, 7·09 (AB quartet, J_{AB} 14 c/s) (4H, $C\underline{H}_2SO_2$), 7·65–7·85 (m) (4 allylic H), 7·92–8·45 (m) (6H, $C\underline{H}_2$). Reoxidation gave a mixture of sulphone as well as epoxidation and cleavage products.

8-*Thia*[4.3.3]*propellane* (**52**)

Freshly prepared potassium azodicarboxylate[14] (6·0 g) was added to a soln of **51** (1·68 g) in pyridine (60 ml). A soln of glacial AcOH (3 g) in pyridine (20 ml) was added with stirring during 30 min. After stirring for 17 hr under N_2, an additional similar AcOH–pyridine soln was added and stirring was continued for an additional 48 hr. The mixture was poured into ice water (200 ml), was acidified with 50% H_2SO_4 and extracted several times with ether. After washing and drying, GLC analysis showed the presence of about 30% of **51** in the crude product (1·68 g). The whole diimide reduction procedure was therefore repeated again leading to crude saturated thio-ether **52** (1·55 g; 91%), m.p. 115–122° containing about 10% **51** (GLC). Chromatography over basic alumina (Merck; 30 g) and elution with pet. ether afforded in the initial fractions (100 ml) the *thio-ether* **52** (1·06 g; 62%), m.p. 126–127°. Sublimation at 60° (24 mm) gave the analytical sample, m.p. 128–130°. (Found: C, 72·52; H, 9·60; S, 17·47, M.W. 182. $C_{11}H_{18}S$ requires: C, 72·49; H, 9·96; S, 17·56%. M.W. 182·36.) IR: 2940, 2865 (CH), 1465 cm^{-1}. NMR: τ 7·25 (s) (4H, $C\underline{H}_2S$), 8·25 (s) (6H, $C\underline{H}_2$), 8·55 (s) (8H, $C\underline{H}_2$).

The *sulphoxide* was prepared in the usual way in 93% yield, m.p. 174–177°.The analytical sample was obtained by two sublimations at 115° (0·05 mm), m.p. 178–180°. (Found: C, 66·58; H, 8·94; S, 15·37, M.W. 198. $C_{11}H_{18}OS$ requires: C, 66·64; H, 9·15; S, 16·14%. M.W. 198·36). IR: 3000–2865 (CH), 1065, 1040, 1030, 1015 cm^{-1} (SO). NMR (CCl_4): τ 6·60, 7·23; 6·63; 7·13 (two overlapping AB quartets: J_{AB} 13 c/s; $J_{A'B'}$ 14 c/s) (4H, $C\underline{H}_2SO$), 7·65–8·70 (complex multiplet) (14H, $C\underline{H}_2$).

The *sulphone* was prepared in the usual way in 89% yield, m.p. 169–172°. Sublimation at 130° (0·05 mm) gave the pure sulphone, m.p. 187–190°. (Found: S, 14·84. M.W. 214. $C_{11}H_{18}O_2S$ requires: S, 14·93%. M.W. 214·36.) IR: 2940, 2865 (CH), 1315, 1140, 1130, 1115 cm^{-1} (SO_2). NMR (CCl_4): τ 7·00 (s) (4H, $C\underline{H}_2SO_2$), 8·12 (s) (6H, $C\underline{H}_2$), 8·45 (s) (8H, $C\underline{H}_2$).

Preparation of the diol **53**

A soln of the bicyclic anhydride adduct of the Diels–Alder reaction between 3,4,5,6-tetrahydrophthalic anhydride and butadiene[15] (15 g) in dry THF (150 ml) was added dropwise to a suspension of LAH (8 g) in dry THF (200 ml) and strong stirring was continued overnight. After the usual workup (decomposition with dil H_2SO_4), AcOEt extraction and removal of solvent gave the *diol* **53** (12·4 g; 87·5%, m.p. 155–156° (acetonitrile or acetone). (Found: C, 73·63; H, 10·20; O, 16·52. $C_{12}H_{20}O_2$ requires: C, 73·43; H, 10·27; O, 16·30%.) IR: 3610, 3450 (OH), 1660 cm^{-1} (C=C). NMR: τ 4·4 (t) (2H, olefinic), 6·35 (broad s) (4H, $C\underline{H}_2O$), 7·18 (broad s) (2H, $O\underline{H}$), 7·92 (d) (4H, allylic), 8·47 (broad s) (8H, $C\underline{H}_2$)

12-*Thia*[4.4.3]*propell*-3-*one* (**56**)

The dimesylate **54** was prepared in analogy to **42** by adding a solution of methanesulphonyl chloride (4·8 g) in pyridine (30 ml) to an ice cold solution of the diol **53** (3·7 g) in pyridine (30 ml) during 1 hr. After similar workup the crude product (3·64 g; m.p. 105–108°) containing the dimesylate **54** (IR: 1370–1335, 1170 cm^{-1} (OSO_2) was added without additional purification to a solution of $Na_2S.9H_2O$ (3·12 g) in DMSO (50 ml) and the mixture was stirred under N_2 at 125–130° for 24 hr. After the usual workup a brown oil was obtained (2·04 g) containing ca. 58% of **56** and 42% of **55**. NMR of mixture in CCl_4: τ 6·32, 6·51 (AB quartet, J_{AB} 8 c/s) ($C\underline{H}_2O$), 7·22, 7·35 (AB quartet, J_{AB} 10 c/s) ($C\underline{H}_2S$), rel intens. 1:1·3.

A methanolic soln (50 ml) of the mixture was added to an aqueous methanolic soln (65 ml) of $HgCl_2$ (3·52 g), affording the adduct (1·99 g) of **56**, m.p. 137–139°. After the usual workup (see preparation of **51**) the crude ether **55** (0·71 g; 21%) was chromatographed on basic alumina (Merck; 20 g) using pet. ether as eluant. The pure *ether* **55** (0·53 g) had b.p. 136° (22 mm), m.p. 20°. (Found: M.W. 178. $C_{12}H_{18}O$ requires:

M.W. 178·16). IR: 3000–2860 (CH), 1680 (C═C), 1070 cm^{-1} (—O—). NMR (CCl_4): τ 4·45 (t) (2 olefinic H), 6·30, 6·52 (AB quartet, J_{AB} 7·6 c/s) (4H, CH_2O), 8·30 (s) (4 allylic H), 8·52 (broad s) (8H, CH_2).

The thioether **56** was regenerated from its $HgCl_2$ adduct as described above (see prep of **51**). The crude product (0·32 g; 9% based on diol **53**) had m.p. 52–55°. Purification by filtration through a column of basic alumina (Merck; 20 g) using light petroleum as eluant, followed by the usual workup gave pure *thioether* **56** (0·25 g), m.p. 73–76°. (Found: M.W. 194. $C_{12}H_{18}S$ requires: M.W. 194·37). IR: 2940, 2890, 2880 (CH), 1675 (C═C), 1460, 1430 cm^{-1}. NMR (CCl_4): τ 4·52 (m) (2 olefinic H), 7·22, 7·35 (AB quartet, J_{AB} 10 c/s) (4H, CH_2S), 7·95 (broad s) (4 allylic H), 8·45 (broad s) (8H, CH_2).

The ether **55** may be obtained directly from the diol **53** (4 g) by boiling with *p*-toluenesulphonic acid (100 mg) in toluene (50 ml) for 15 hr, the water formed being removed azeotropically. After the usual workup and chromatography on neutral alumina (100 g) using hexane as eluant, the ether **55** was obtained (2·6 g; 72%), b.p. 134° (20 mm), m.p. 20°. It was identical with the product reported above.

8,11-*Dithia*[4.3.3]*propell*-3-*ene* (**58**)

A soln of **57** m.p. 152–153° (283 mg) prepared from the tetrol **32** and mesyl chloride in pyridine in quantitative yield (cf. Ref. 2*m*) and $Na_2S.9H_2O$ (316 mg) in DMSO (10 ml) was stirred under N_2 at 125–130° for 22 hr. After the usual workup the crude product was obtained (103 mg). A conc soln of this in benzene was filtered through a column of basic alumina (Merck; 5 g). Elution with light petroleum afforded the *dithioether* **58** (86 mg; 80%), m.p. 101–108°. IR: 3000–2940 (CH), 1670 (C═C), 1465, 1455, 1430 cm^{-1}. NMR (CCl_4): τ 4·48 (t) (2 olefinic H), 6·95, 7·22 (AB quartet, J_{AB} 10 c/s) (8H, CH_2S), 7·73 (d) (4 allylic H). Sublimation at 100° (24 mm) gave the analytical sample, m.p. 108–112°. (Found: C, 60·37; H, 6·74; S, 31·92. M.W. 192. $C_{10}H_{14}S_2$ requires: C, 60·59; H, 7·12; S, 32·29%. M.W. 198·38.)

3-*Ethanedioxy*-7,10-*dimethyl*-6,8,9,11-*tetraoxo*-7,10-*diaza*[3.3.3]*propellane* (**64**)

A mixture of **65** (0·8 g), EtOH (72 ml) and dil H_2SO_4 (8%; 14·4 ml) was heated under reflux in a N_2 atmosphere for 6 days. The EtOH was removed, 15% NaOH aq was added to strongly alkaline pH and the product was taken up in $CHCl_3$ and its soln dried (Na_2SO_4). Chromatography over florisil with $CHCl_3$ as eluant, followed by sublimation at 90° (30 mm) gave the pure *ketone* **66** (0·5 g; 76%), m.p. 61–62°. (Found: C, 67·84; H, 9·07; O, 8·77; N, 14·47, M.W. 194. $C_{11}H_{18}ON_2$ requires: C, 68·00; H, 9·34; O, 8·24; N, 14·42%. M.W. 194·27). IR: 2940, 2900, 2840, 2780 (CH), 1745–1730 cm^{-1} (CO). NMR: τ 7·31, 7·55 (AB quartet, J_{AB} 9·2 c/s) (8H, CH_2N), 7·57 (s) (4H, CH_2), 7·68 (s) (6H, NCH_3).

3-*Ethanedioxy*-7,10-*dimethyl*-7,10-*diaza*[3.3.3]*propellane* (**65**)

A mixture of **64** (3·5 g), LAH (5 g) and THF (300 ml) was heated under reflux in an atmosphere of N_2 for 90 hr. After the usual workup the *amine ketal* **65** was distilled (1·8–2·0 g; 63–70%), b.p. 118–120° (2·2 mm). (Found: M.W. 238. $C_{13}H_{22}O_2N_2$ requires: M.W. 238·34). IR: 2940, 2880, 2830, 2780 cm^{-1} (CH). NMR: τ 6·12 (s) (4H, CH_2O), 7·42, 7·51 (AB quartet, J_{AB} 8·9 c/s) (8H, CH_2N), 7·68 (s) (6H, NCH_3), 8·11 (s) (4H, CH_2).

The yellow *dipicrate* had m.p. 204–206° (dec., EtOH–acetone). (Found: C, 43·52; H, 4·03; O, 36·35; N, 16·17. $C_{25}H_{28}O_{16}N_8$ requires: C, 43·09; H, 4·05; O, 36·77; N, 16·09%.)

7,10-*Dimethyl*-7,10-*diaza*[3.3.3]*propellan*-3-*one* (**66**)

A mixture of **65** (0·8 g), EtOH (72 ml) and dil H_2SO_4 (8%; 14·4 ml) was heated under reflux in a N_2 atmosphere for 6 days. The EtOH was removed, 15% NaOH aq was added to strongly alkaline pH and the product was taken up in $CHCl_3$ and its soln dried (Na_2SO_4). Chromatography over florisil with $CHCl_3$ as eluant, followed by sublimation at 90° (30 mm) gave the pure *ketone* **66** (0·5 g; 76%), m.p. 61–62°. (Found: C, 67·84; H, 9·07; O, 8·77; N, 14·47, M.W. 194. $C_{11}H_{18}ON_2$ requires: C, 68·00; H, 9·34; O, 8·24; N, 14·42%. M.W. 194·27). IR: 2940, 2900, 2840, 2780 (CH), 1745–1730 cm^{-1} (CO). NMR: τ 7·31, 7·55 (AB quartet, J_{AB} 9·2 c/s) (8H, CH_2N), 7·57 (s) (4H, CH_2), 7·68 (s) (6H, NCH_3).

2,4-*Dioximino*-7,10-*dimethyl*-7,10-*diazo*[3.3.3]*propellan*-3-*one dihydrochloride* (**67**; R = H)

To a stirred soln of **66** (326 mg) in freshly distilled isoamylnitrite (1 ml) was added with ice cooling dropwise, under N_2, a sat soln of HCl gas in glacial AcOH (5 ml). After 1 hr cooling was discontinued and stirring was maintained for an additional 24 hr. The microcrystalline ppt was removed by centrifugation, washed with dry EtOH and dried in a vacuum. The *dioximinoketone*, **67** (R = H) was sufficiently pure for

further synthesis (485 mg; 88%). The yellow analytical sample was obtained by crystallization (aq. acetone), m.p. 266° (dec). (Found: C, 40·84; H, 5·66; N, 17·60; Cl, 21·24. $C_{11}H_{16}O_3N_4 \cdot 2HCl$ requires: C, 40·63; H, 5·58; N, 17·23; Cl, 21·80%.) IR (KBr): 3100–2400 (CH; ammonium), 1740 (CO), 1630, 1620 cm^{-1} (C=N). NMR (D_2O with acetone as internal standard): τ 5·96 (broad s) (8H, $C\underline{H}_2\overset{+}{N}$), 7·03 (s) (6H, $\overset{+}{N}C\underline{H}_3$).

2,4-*Diacetoximino*-7,10-*dimethyl*-7,10-*diaza*[3.3.3]*propellan*-3-*one dihydrochloride* (**67**; R = Ac)

The dioximino ketone **67** (R = H) (150 mg) was suspended in freshly distilled Ac_2O (1 ml) and stirred for 72 hr at room temp. The very insoluble and sensitive *diacetoximinoketone*, **67** (R = Ac) was not purified and served for further synthesis (180 mg; 95%). It must be kept in a dessicator over NaOH. IR (KBr): 3080–2800 (CH), 2700–2200 (ammonium), 1820, 1790 (CO of acetoximino), 1740 (w), 1730 (w) (CO), 1640, 1630 cm^{-1} (C=N).

Ring opening was effected by refluxing under N_2 a mixture of the diacetoximinoketone (170 mg) and sat Na_2CO_3 aq (2 ml), for 2 hr. After cooling, $CHCl_3$ extraction and drying (Na_2SO_4), the solvent was removed and the *dinitrile* **68** was purified by chromatography on basic alumina with benzene as eluant and by sublimation at 80° (0·05 mm) (45 mg; 56%), m.p. 140–142°. (Found: C, 63·33; H, 7·28; N, 29·23, M.W. 190. $C_{10}H_{14}N_4$ requires: C, 63·13; H, 7·42; N, 29·45%, M.W. 190·24). IR: 2950, 2850, 2820, 2800 (CH), 2245 cm^{-1} (CN). NMR: τ 6·94, 7·17 (AB quartet, J_{AB} 9·7 c/s) (8H, $C\underline{H}_2N$), 7·62 (s) (6H, $NC\underline{H}_3$).

2,4-*Dioxo*-7,10-*dimethyl*-3,7,10-*triaza*[3.3.3]*propellane* (**71**).

(a) A mixture of **68** (380 mg), MeOH (5 ml) and KOH aq (25%; 4 ml) was heated under reflux for 2 hr under N_2. The MeOH was removed at the water pump, dil HCl (10%; 5 ml) was added slowly and reflux was continued for 1 hr. After cooling, sat Na_2CO_3 aq was added to pH 7–8 and the soln was extracted with $CHCl_3$. After drying (Na_2SO_4) and removal of $CHCl_3$ the solid residue was sublimed at 95° (0·03 mm). The *imide* **71** (390 mg; 93%) had m.p. 181–183°.

(b) The diacetoximino ketone **67** (R = Ac) (200 mg) was treated with the same reagents as in procedure (a). After the same workup **71** was obtained (65 mg; 61%) identical with the product in procedure (a). (Found: C, 57·55; H, 6·92; O, 15·27; N, 20·01, M.W. 209. $C_{10}H_{15}O_2N_3$ requires: C, 57·40; H, 7·23; O, 15·29; N, 20·08%, M.W. 209·24.) NMR: τ 6·88, 7·42 (AB quartet, J_{AB} 10·0 c/s) (8H, $C\underline{H}_2N$), 7·67 (s) (6H, $NC\underline{H}_3$).

2,4-*Dioxo*-3,7,10-*trimethyl*-3,7,10-*triaza*[3.3.3]*propellane* (**72**)

An ether soln of diazomethane was added to a soln of **71** (300 mg) in dry MeOH (15 ml) until the yellow colour persisted. After 2 hr the solvents were removed at the water pump. The solid residue was dissolved in ether and the undissolved ppt was removed by filtration. Purification was effected by chromatography on basic alumina. The *methylimide*, **72** was eluted with benzene–$CHCl_3$ (4:1) (260 mg; 81%), m.p. 92–93°. (Found: C, 59·56; H, 7·80; O, 14·13; N, 18·56, M.W. 223. $C_{11}H_{17}O_2N_3$ requires: C, 59·17; H, 7·68; O, 14·33; N, 18·82%, M.W. 223·27.) IR: 2960, 2860, 2800 (CH), 1780, 1720–1700 cm^{-1} (imide CO). NMR: τ 6·94, 7·44 (AB quartet, J_{AB} 10·0 c/s) ($C\underline{H}_2N$), 7·00 (s) ($CONC\underline{H}_3$) (together 11H), 7·71 (s) (6H, $NC\underline{H}_3$).

3,7,10-*Trimethyl*-3,7,10-*triaza*[3.3.3]*propellane* (**73**)

A mixture of the methylimide **72** (2·23 g), LAH (1·9 g) and THF (120 ml) was heated under reflux under N_2 for 88 hr. After the usual workup (decomposition with aq. NaOH), the triamine was distilled, b.p. 112° (20 mm) and the product solidified. It was sublimed at 28° (0·01 mm) and though it showed only one spot by TLC, the pure *triamine* **73** (1·47 g; 75%) had m.p. 37–74°. This remained unchanged after chromatography on basic alumina or florisil. (Found: M.W. 195. $C_{11}H_{21}N_3$ requires: M.W. 195·30). IR: 2950, 2900, 2850, 2800 cm^{-1} (CH). NMR: τ 7·46 (s) (12H, $C\underline{H}_2N$), 7·67 (s) (9H, $NC\underline{H}_3$). pK (cf. Ref. 1*a*, p. 286): pK_{a1} 5·8; pK_{a2} 8·2. Under these conditions, pK_{a3} cannot be measured.

The yellow *tripicrate* had m.p. 249–251° (acetone); it contains 1 mole of solvent. (Found: C, 40·60; H, 3·81; O, 37·72; N, 17·75. $C_{29}H_{30}O_{21}N_{12} \cdot C_3H_6O$ requires: C, 40·86; H, 3·86; O, 37·41; N, 17·87%.)

Beckmann rearrangement of 7,10-*dimethyl*-7,10-*diaza*[3.3.3]*propellane*-3-*ketoxime* (**69**)

(a) The oxime was prepared from the ketone **66** (1 g), hydroxylamine hydrochloride (1·2 g) by refluxing under N_2 in ethanolic (15 ml) soln for 4 hr. The ppt (1.1 g) was recrystallized from MeOH and proved to be a mixture of the mono- and dihydrochloride of **69**. It was used as such in the Beckmann rearrangement (see (b) below). The free *oxime* **69** was obtained by treating the salts with $NaHCO_3$ aq, extraction with $CHCl_3$ and evaporation of the solvent. It had m.p. 191–192·5° (AcOEt). (Found: C, 63·18; H, 9·14; N, 20·52,

M.W. 209. $C_{11}H_{19}ON_3$ requires: C, 63·12; H, 9·15; N, 20·08%. M.W. 209·29.) IR: 3580, 3400–3100 (OH), 2940, 2900, 2840, 2790 (CH), 1680 cm^{-1} (C=N). NMR: τ 7·35 (s) ($C\underline{H}_2$), 7·48 (s) ($C\underline{H}_2$), 7·36, 7·57 (AB quartet, J_{AB} 9·3 c/s) ($C\underline{H}_2N$) (altogether 12H), 7·68 (s) (6H, $NC\underline{H}_3$). NMR of hydrochloride mixture (D_2O with acetone as internal standard): τ 6·29 (broad s) (8H, $C\underline{H}_2\overset{+}{N}$), 7·02 (s) (8H, $\overset{+}{N}C\underline{H}_3$ + $C\underline{H}_2$), 7·12 (s) (2H, $C\underline{H}_2$).

(b) The oxime hydrochlorides (527 mg) was added to oleum (30%; 10·5 ml) preheated to 100° and this temp was maintained for 2 hr. After cooling, neutralization with NaOH aq and $CHCl_3$ extraction the lactam, 3-*oxo*-8,11-*dimethyl*-4,8,11-*triaza*[4.3.3]*propellane* **70** was purified by elution ($CHCl_3$) from a column of basic alumina (75 mg; 14%), m.p. 146–147·5°. (Found: M.W. 209. $C_{11}H_{19}ON_3$ requires: M.W. 209·29). IR: 3440 (NH), 2960, 2920, 2860, 2810 (CH), 1680 cm^{-1} (CO). NMR: τ 2·40 (broad s) (1H, N$\underline{H}$), 6·82 (d) (2H, $C\underline{H}_2NHCO$), 7·30–7·72 (m) (10H, $C\underline{H}_2CONH$ and $C\underline{H}_2N$), 7·70 (s) (6H, $NC\underline{H}_3$).

von Braun reaction of **74**

A soln of the diamine **74**[14a] (3·6 g) in dry THF (30 ml) was added dropwise with stirring, under N_2, to a soln of CNBr (4·65 g) in dry THF (36 ml) at room temp. The soln turns green and precipitation occurs. After 48 hr of stirring the ppt (0·9 g) was removed by filtration. It appears to consist of a mixture of hydrobromide and methobromide of the starting material and possibly of the monocyanamide. The solvent was removed from the mother liquor under reduced press. The residual oily solid was triturated with a minimal volume of MeOH. The colourless solid, 8,11-*dicyano*-8,11-*diaza*[4.3.3]*propellane*, **75** was recrystallized (2·0 g; 50%), m.p. 139–140° (light petroleum). The methanolic mother liquor contained more of **75** but this could not be isolated. (Found: C, 66·89; H, 7·45; N, 25·60. M.W. 216. $C_{12}H_{16}N_4$ requires: C, 66·64; H, 7·46; N, 25·91%. M.W. 216·28). IR: 2940, 2890, 2860 (CH), 2220 cm^{-1} (N—CN). NMR: τ 6·51 (s) ($C\underline{H}_2N$), 8·42 (broad s) ($C\underline{H}_2$); rel. intens. 1:1.

The *monocyanamide-monourea* **76** was isolated from a chromatographic column of basic alumina (50 g) onto which a $CHCl_3$ soln of **75** (1 g) was introduced. One of the cyano groups undergoes hydrolysis and elution with $CHCl_3$ gives **76** (0·8 g; 74%) as a colourless glass. IR: 3520, 3420 (NH_2), 2990, 2940, 2890, 2860 (CH), 2220 cm^{-1} (CN), 1670 (urea CO), 1600 cm^{-1} (NH bending). NMR: τ 4·92 (broad s) (2H, $N\underline{H}_2$), 6·51–6·57 (m) (8H, $C\underline{H}_2N$—CN and $C\underline{H}_2NCONH_2$), 8·42 (s) (8H, $C\underline{H}_2$).

Hydrolysis of **75**

A soln of **75** (56 mg) and KOH aq (25%; 0·4 ml) was heated under reflux under N_2 for 2·5 hr. After removal of MeOH, $CHCl_3$ extraction, drying (Na_2SO_4) and evaporation of solvent the *diurea*, **77** was obtained (35 mg; 53%) as a colourless oil. IR: 3520, 3420 (NH_2), 2980, 2930, 2860 (CH), 1660, 1620 (urea CO), 1600 cm^{-1} (NH bending). NMR: τ 5·18 (broad s) (2H, $N\underline{H}_2$), 6·33 (broad s) (2H, $N\underline{H}_2$), 6·58–6·61 (m) (8H, $C\underline{H}_2N$), 8·45 (s) (8H, $C\underline{H}_2$).

The diurea **77** was very stable to further hydrolysis to the dicarbamic acid so that this route is untenable for the obtention of the corresponding diamines, albeit in low yield. Hydrolysis with KOH in ethylene glycol yields quite impure diamines.

8,11-*Diaza*[4.3.3]*propellane* (**79**)

A mixture of **78**[14a] (5 g), LAH (10 g) and THF (600 ml) was heated under reflux, under N_2, for 96 hr. After alkaline decomposition and the usual workup the crude product still showed a strong lactam band at 1700–1680 cm^{-1} in the IR. The crude product was purified via the picrate. Decomposition of the picrate gave the semi-solid diamine which was sublimed at 105° (0·5 mm) to yield the very hygroscopic *diamine*, **79**, m.p. 134–138° (410 mg; 11%). (Found: M.W. 166. $C_{10}H_{18}O_2$ requires: M.W. 166·27). IR: 3370, 3200–3100 (NH), 2930, 2870 cm^{-1} (CH). NMR (CD_3OH): τ 7·08 (s) ($C\underline{H}_2N$), 8·46 (s) ($C\underline{H}_2$); rel. intens. 1:1.

7,10-*Dimethyl*-7,10-*diaza*[3.3.3]*propellan*-3-*ol* (**80**)

A mixture of **63** (5·5 g), LAH (9 g) and THF (400 ml) was heated under reflux under N_2 for 96 hr. After the usual NaOH decomposition and workup the *alcohol*, **80** (1·5 g; 35%) was distilled, b.p. 72° (0·05 mm). It is solid in the refrigerator. (Found: M.W. 196. $C_{11}H_{20}ON_2$ requires: M.W. 196·30). IR: 3640, 3240–3040 (OH), 2940, 2900, 2840, 2780 cm^{-1} (CH). NMR: τ 3·93 (broad) (1H, O$\underline{H}$), 5·76 (quintet, J = 2·9 c/s) (1H, C$\underline{H}$OH), 7·01, 7·84 (AB quartet, J_{AB} 9·7 c/s) (4H, $C\underline{H}_2N$), 7·29, 7·75 (AB quartet, J_{AB} 9·6 c/s) (4H, $C\underline{H}_2N$) 7·67 (s), 7·70 (s) (6H, $NC\underline{H}_3$), 8·11 (d, J = 2·9 c/s) (4H, $C\underline{H}_2$).

The yellow *dipicrate* had m.p. 236–238° (dec., EtOH). (Found: C, 42·24; H, 3·87; O, 36·64; N, 17·00. $C_{23}H_{26}O_{15}N_8$ requires: C, 42·18; H, 4·01; O, 36·68; N, 17·13%.)

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