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PROPELLANES—IX

CARBOCYCLIC AND HETEROCYCLIC COMPOUNDS AND ORGANOMETALLIC DERIVATIVES OF TETRAENIC PROPELLANES*

J. ALTMAN, E. COHEN, T. MAYMON, J. B. PETERSEN, N. RESHEF and D. GINSBURG
Department of Chemistry, Israel Institute of Technology, Haifa, Israel

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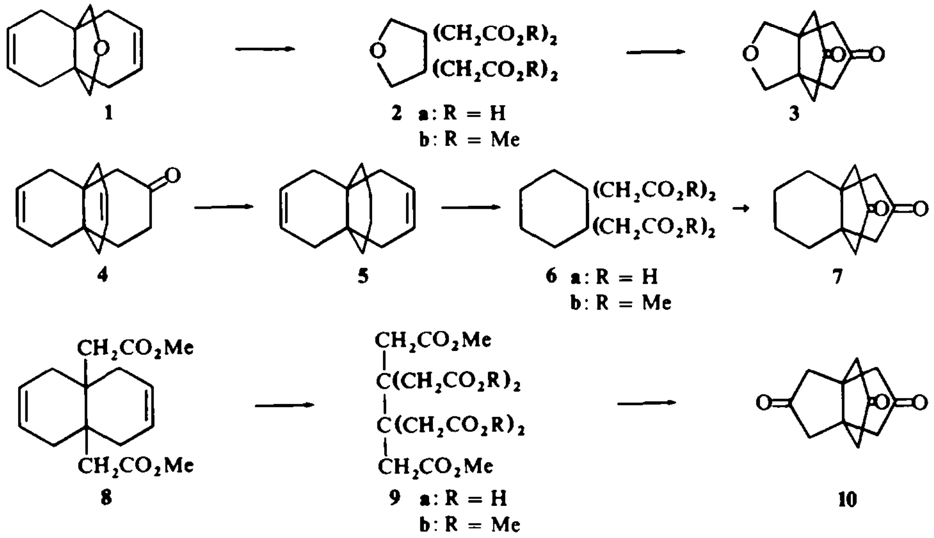
Abstract—Propellane diketones and a propellane triketone have been prepared by multiple (intramolecular) Dieckmann condensations and a propellane tetraone by a Diels–Alder reaction. The synthesis of mixed oxa-thia and polyoxa and polythia[3.3.3]propellanes is described. *Bis*-irontricarbonyl derivatives of tetraenic propallanes have been prepared.

SEVERAL propellane 5-membered ring ketones were required as substrates for potential mercury sensitized decarbonylation in the hope that these would lead to propellanes containing 4-membered rings.[1] We had readily available starting materials **1**, **4** and **8**[2] for the synthesis of the tetraesters **2b** and **6b** and the hexaester **9b**, respectively (Scheme 1).

SCHEME 1



It is of interest that treatment of the thioketal of **4** with Raney Ni did not afford **5**. The symmetrical [4.4.4]propella-3,8,12-triene was formed instead.

Multiple intramolecular Dieckmann cyclizations have been reported for a number of esters but in each of these cases only two rings were formed.[3] Dieckmann condensation indeed afforded double cyclization of **2b** and **6b** and insofar as we know the

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* Part VIII. J. Altman, E. Babad, D. Ginsburg and M. B. Rubin, *Israel J. Chem.* in press.

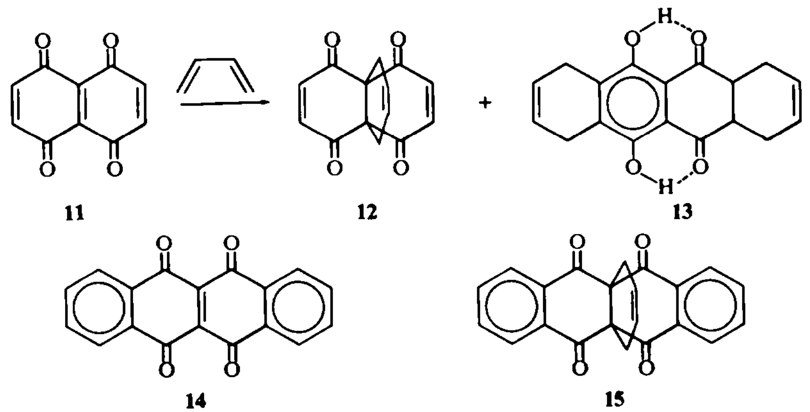
formation of three rings when **9b** was subjected to Dieckmann conditions is the first such case reported. The high yields of ketoesters resulting from these reactions is presumably due to the fact that 5-membered rings are formed in each case. Acidic saponification of the ketoesters obtained from **2b**, **6b** and **9b** gave the diketones **3** and **7** and the triketone **10**, respectively.

The diketone-diester formed from **2b** exists entirely in the strongly H-bonded dienolic form. It may be either the 2,6-diester or the 2,8 diester. One would expect for the latter structure, two singlets, one for each set of $C\underline{H}_2O$ protons in the ether ring and for the former structure, an AB quartet. In actual fact, the NMR spectrum in $CDCl_3$ or DMSO-d_6 show a single singlet corresponding to all four $C\underline{H}_2O$ protons as well as all six $C\underline{H}_3O$ protons! Although in pyridine there are two well resolved singlets for the protons of both these types, all four $C\underline{H}_2O$ protons still form a singlet so that it is impossible to state the structure of the Dieckmann product with certainty.

The diketone-diester formed from **6b** and the triketone-triester formed from **9b** are not fully enolic. Although strong H-bonding exists in the OH region and a strong C=C absorption may be seen in the IR spectrum, there is still weak C=O absorption at 1740 and 1745 cm^{-1}, respectively. We do not know whether the Dieckmann product from **6b** is the 7,10- or the 7,12-diester. Nor do we know whether the corresponding product from **9b** is the 2,6,9- or the 2,8,9-triester although for steric reasons perhaps one would tend to prefer the 2,6-,7,10- and 2,6,9- compounds, respectively.

The UV absorption spectra of these ketones showed the absence of interaction between the CO groups nor would such interaction be expected when the CO groups are at positions β- to the ring junction. Since such interaction might be expected when CO groups are present at positions α- to the ring junction, the Diels-Alder reaction between the diquinone **11**[4] and butadiene was examined as a potential route to such a compound, **12** (Scheme 2). It is not surprising that the corresponding dibenzo-derivative **15** was prepared in good yield from napthacene-9,10,11,12-diquinone[5] as only the central double bond in **14** could reasonably be expected to behave as a dienophilic site. This is not the case in **11** and indeed **12** was obtained in rather low yield, accompanying the strongly intramolecularly hydrogen bonded **13**.

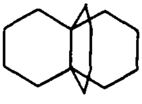
SCHEME 2



It is of interest that no molecular peak was observed in the mass spectrum of the extremely reactive diquinone **11**. This quinone has one of the highest redox potentials ever reported for a quinone (ca. 926 mv).[6b] Quinones are known to exhibit M + 2 ions.[7] The ion of highest *m/e* observed in the mass spectrum of **11** was $[M + 2]^+$ and M^+ was completely absent. The mass spectrum was identical to that of naphthazarin. The following fragmentations were observed in the mass spectrum: $[M + 2]^+ \rightarrow [M + 1]^+$, $[M + 2]^+ \xrightarrow{-28} M^+ - 26$ and $[M + 1]^+ \rightarrow M^+ - 27$, indicating the usual loss of CO by the phenolic $[M + 2]^+$ and $[M + 1]^+$. It has been suggested that there might be a direct correlation between the abundance of such ions and the redox potential of the quinone.[7b] The synthesis of **11** is tedious and unpleasant, particularly that of its precursor, naphthazarin.* It is not surprising that it appears to have been reported in the literature only a very limited number of times.[4,6a]

The structure of **12** follows from its analytical and spectral properties. Its NMR spectrum consists of three lines corresponding to 4 allylic protons, 2 vinylic protons of the unoxygenated ring and 4 vinylic protons α- to CO at lowest field. Its UV absorption spectrum was analogous to those of similar enediones except that in this case there are two identical chromophores of this type. Thus, there appears to be no interaction between the two chromophores. Such interaction is not expected if the two cyclohexenedione rings are more stable in an anti-conformation with respect to the CO groups in adjacent rings.

In view of von Schleyer's work on rearrangement of various hydrocarbons to the stable adamantane ring system[8] we investigated whether carbocyclic propellanes are also likely to undergo similar acid catalyzed rearrangements. [4.4.4]Propellane **16** indeed afforded 1,3,5,7-tetramethyladamantane **17** but this was isolated in only 7% yield after tedious preparative GLC from a complex mixture of products. [4.4.2]Propellane upon treatment with aluminium bromide-t-butyl bromide[8] afforded an even more complex mixture of no less than 9 products (*glc*). It thus appears that carbocyclic propellanes containing more than 10 C atoms are not suitable substrates for this rearrangement. It may perhaps be worthwhile to return to this question when C_{10}-substrates are available e.g. [4.2.2]propellane or [3.3.2]propellane.



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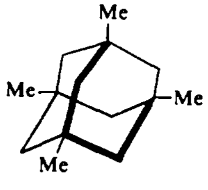

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A series of mixed and unmixed oxa- and thiapropellanes were synthesized from **18**,[9] **23**[10] and **29**,[2] respectively. The same starting material **29** was also used to prepare the oxa-azapropellane **35** (Scheme 3). Thiapropellanes of the [3.3.3] series are of interest as starting materials for the preparation of smaller-ring propellanes e.g. by extrusion of the S atom(s) as sulphur dioxide via the corresponding sulfones.

Finally, we report the synthesis of *bis*-irontricarbonyl derivatives of the tetraenic propellanes **34a–d**. Since each of these contains two cyclohexadiene rings it is possible, in principle, to form two π-dienic bonds to two irontricarbonyl ligands. Treatment of

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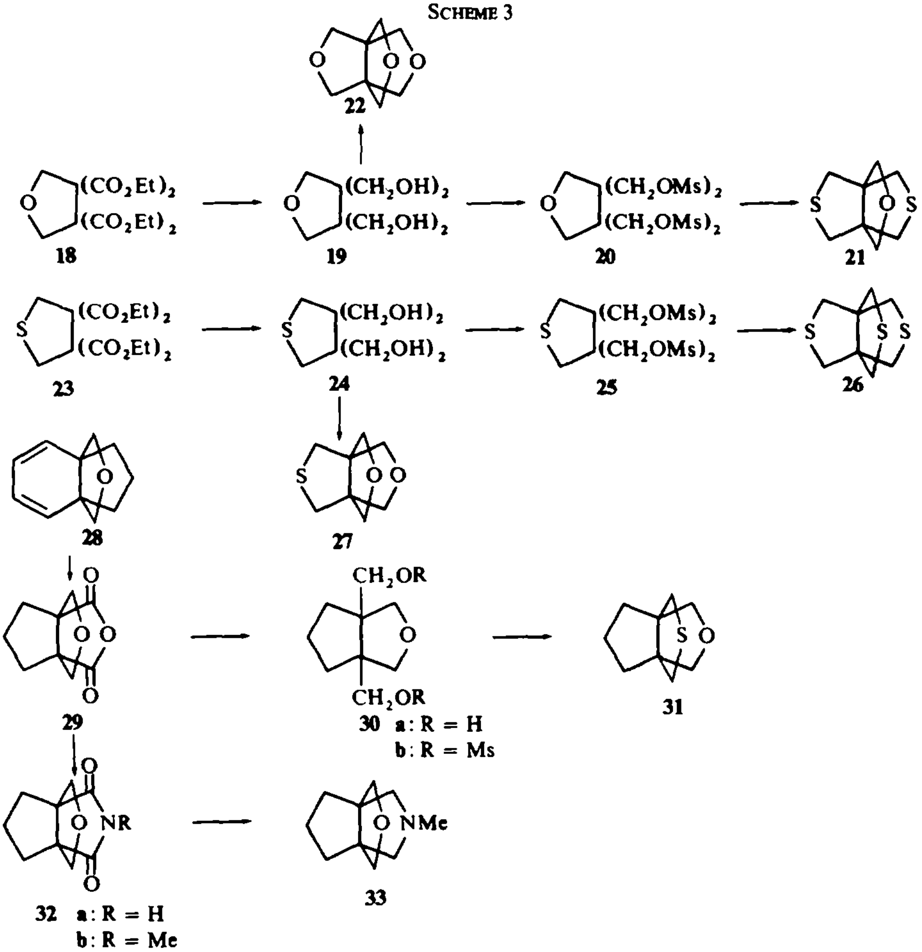
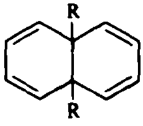
* After preparing naphthazarin we particularly wish to thank Professor V. Prelog for catalyzing the preparation of a large sample and Sandoz, Basel for their generous gift of this compound.

SCHEME 3





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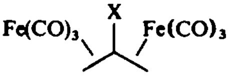
(a) $-CH_2-O-CH_2-$ (b) $-CO-O-CO-$ (c) $-CO-NH-CO-$ (d) $-CO-NMe-CO-$

each of the compounds **34a–d** with ironpentacarbonyl afforded a *bis*-irontricarbonyl derivative. The configurational problem which exists in such derivatives is an intriguing one. Three stereoisomeric *bis*-irontricarbonyl derivatives may, in principle, exist in each case as shown in structures **35–37** in which we view the molecule along the axis of the bond which conjoins the three rings. In these Y-shaped molecules let the line leading to X represent the heterocyclic ring and the two other bonds at the base, the cyclohexadiene rings. Structures **35** and **36** are symmetrical and **37** is unsymmetrical. One need not frown upon **36** as the cyclohexadiene rings very probably exist in a non-planar conformation and may readily turn away from each other as the blades



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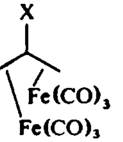

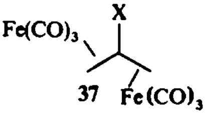

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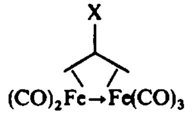

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of a propellor (hence the idea for the simpler naming of this class of compounds).[11] Whilst only one of the stereoisomers was obtained by treatment of **34a–d**, respectively, with iron pentacarbonyl, five organometallic derivatives were obtained when **34a** was treated with diironnonacarbonyl! Two of the *bis*-compounds must correspond to **35** and **36** (X = O) as they both exhibit symmetrical NMR spectra whilst the third compound might have been expected to be **37** (X = O) since it exhibits an unsymmetrical NMR spectrum. Its mass spectrum, however, shows the presence of only 5 CO groups and the analytical results support the structure containing one CO group less than **35** or **36** (X = O). The third diiron product must therefore have structure **38** (X = O). In addition to these three products, two additional monoirontricarbonyl complexes were isolated. The structures of all of these compounds are being investigated further by employing dipole moment measurements, Mössbauer spectroscopy* and X-ray crystallography. In view of our photochemical work with compounds of type **34**[12] we are now investigating the behaviour upon irradiation of the corresponding *bis*-irontricarbonyl derivatives[13] as well as their thermal behaviour.[14]

EXPERIMENTAL

3,3,4,4-Tetracarbomethoxymethyltetrahydrofuran **2b**

(a) Ozone was bubbled into a soln of **1**[2] (1 g) in MeOH (30 ml) at −78° until a blue colour remained. After removal of solvent without warming (water pump), the residue was heated for 2 hr at 70° with formic acid (30 ml) and H_2O_2 (30%; 15 ml). After removal of solvent in a high vacuum the colourless residue was triturated with ether to afford **2a**, m.p. 193–195° (1·42 g; 82·5%). The analytical sample had m.p. 194–196° (MeOH). (Found: C, 47·46; H, 5·25. $C_{12}H_{16}O_9$ requires: C, 47·37; H, 5·30%); IR (KBr): 1730–1700 cm^{-1} (broad, CO). NMR(D_2O): τ 7·30, 7·08 (AB quartet, 8 $C\underline{H}_2CO$, J_{AB} = 16 Hz), 6·00 (s, 4$C\underline{H}_2O$); (pyridine): τ 6·57, 6·27 (AB quartet, 8$C\underline{H}_2CO$, J_{AB} = 16 Hz), 5·37 (s, 4$C\underline{H}_2O$).

(b) To a soln of 3,3,4,4-tetracarboxymethyltetrahydrofuran (9·12 g) in MeOH (250 ml) was added dropwise at 0° an excess of ethereal diazomethane soln. The soln was allowed to stand at room temp for 16 hr. After removal of solvent **2b** was obtained as a solid, m.p. 77–79° (10·51 g; quant). The analytical sample had m.p. 82° (EtOH). (Found: C, 53·48; H, 6·55. $C_{16}H_{24}O_9$ requires: C, 53·33; H, 6·71%); IR($CHCl_3$): 1740–1720 cm^{-1} (broad, CO). NMR($CDCl_3$): τ 7·30, 7·08 (AB quartet, 8$C\underline{H}_2O$, J_{AB} = 16 Hz), 6·33 (s, 12$OC\underline{H}_3$), 6·06 (s, 4$C\underline{H}_2O$).

10-Oxa[3.3.3]propellane-3,7-dione **3**

(a) To a stirred soln of NaOMe prepared from Na (0·35 g) and dry MeOH (7 ml) in dry toluene (300 ml) was added dropwise at 100° under N_2 a soln of **2b** (1·1 g) in dry toluene (200 ml) during 4 hr. The mixture was heated overnight at 100°. After cooling, the whole was extracted with water, the aqueous phase was acidified (HCl) and extracted with ether (3 × 500 ml). Evaporation afforded the diketone-diester (0·81 g; 92·5%), m.p. 206–210° sufficiently pure for further work. The analytical sample was obtained by sublimation at 145°/0·1 mm, m.p. 198–202°. (Found: C, 57·04; H, 5·52. $C_{14}H_{16}O_7$ requires: C, 56·75; H, 5·44%); IR(KBr): 3500–3050 (H bond, enol), 1670 (H-bonded ester), 1630 cm^{-1} (C=C in enol). NMR($CDCl_3$): τ 7·23 (s, 4$C\underline{H}_2$), 6·19 (s, 10$C\underline{H}_2O$, $C\underline{H}_3O$), −0·34 (br, 2C=C—OH) disappears when D_2O is added. (DMSO-d_6): 7·32 (s, 4$C\underline{H}_2$), 6·31 (s, 10$C\underline{H}_2O$, $C\underline{H}_3O$), (pyridine): 7·14 (s, 4$C\underline{H}_2$), 6·33 (s, 6$C\underline{H}_3O$), 6·10 (s, 4$C\underline{H}_2O$).

(b) A mixture of diketone-diester (100 mg), AcOH (10 ml), and HCl (1:1, 4 ml) was heated under reflux for 17 hr. After removal of solvent **3** was obtained as a solid (62 mg; quant), m.p. 181° (dec). The analytical

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* Mössbauer spectra have been measured by Dr. M. Ron of the Physics Department of this Institute; M. Ron, T. Maymon and D. Ginsburg, unpublished results.

sample had m.p. 188° (dec; benzene). (Found: C, 66·31; H, 6·59; M.W. 180. $C_{10}H_{12}O_3$ requires: C, 66·65; H, 6·71%; M.W. 180·20); IR($CHCl_3$): 1745 cm^{-1} (CO); NMR($CDCl_3$): τ 7·48, 7·33 (AB quartet, $8C\underline{H}_2CO$, J_{AB} = 19 Hz), 6·10 (s, $4C\underline{H}_2O$).

The orange di-2,4-dinitrophenylhydrazone had m.p. 243–244° (nitromethane). (Found: N, 20·36. $C_{22}H_{20}N_8O_9$ requires: N, 20·73%).

The colourless *dioxime* had m.p. 214° (EtOH). (Found: C, 56·64; H, 6·56; N, 13·27. $C_{10}H_{14}N_2O_3$ requires: C, 57·13; H, 6·71; N, 13·33%); IR(KBr): 3300–3060 (NH), 1670 cm^{-1} (C=N); NMR (pyridine): τ 7·23 (s, $4C\underline{H}_2$), 7·04 (s, $4C\underline{H}_2$), 6·19 (s, $4C\underline{H}_2O$).

1,1,2,2-*Tetracarbomethoxymethylcyclohexane* **6b**

(a) A mixture of **4**[2] (1·7 g), KOH (3 g), hydrazine (90%; 3 ml) and ethylene glycol (50 ml) was heated slowly up to 130°, maintained at 130° for 1 hr and finally heated under reflux for 3 hr. After the usual workup, the oily diene (1·4 g) was taken up in pet. ether (60–70°) and the soln was filtered through a column of neutral alumina (50 g). The pure [4.4.4]*propella*-3,8-*diene* **5** (1·15 g; 73%) had m.p. 50° (MeOH at −20°). (Found: C, 89·49; H, 10·53; M.W. 188. $C_{14}H_{20}$ requires: C, 89·29; H, 10·71%; M.W. 188·30); IR($CHCl_3$): 2940–2840 (CH), 1660 cm^{-1} (C=C); NMR (CCl_4): τ 9·10–7·50 (broad mult., 16 $C\underline{H}_2$), 6·51 (m, 4 vinylic H).

An alternative preparation of **5** was unsuccessful but products were characterized: A mixture of **4** (206 mg), ethanedithiol (0·2 ml) and BF_3-etherate (0·2 ml) was allowed to stand at 0°. When **4** had dissolved, the mixture warmed up and the whole was allowed to stand for 3 hr at room temp. After the usual workup the *thioketal of* **4** was obtained (255 mg; 89%), m.p. 55° (EtOH). (Found: C, 69·59; H, 7·88; S, 22·99. $C_{16}H_{22}S_2$ requires: C, 69·04; H, 7·97; S, 22·99%); NMR ($CDCl_3$); τ 8·80–7·00 (broad m; 14 $C\underline{H}_2$), 6·70 (s, $4C\underline{H}_2S$), 4·50 (t, 4 vinylic H). A soln of the thioketal (125 mg) in acetone (40 ml) was heated under reflux overnight in the presence of Raney Ni (1 g) which had previously been deactivated by heating under reflux in acetone for 30 min. After filtration and evaporation of solvent the residue (66 mg; 79%) proved to be identical to the known [4.4.4]propella-3,8,12-triene.[2]

(b) Ozone was bubbled into a soln of **5** (0·5 g) in CH_2Cl_2 (20 ml)–MeOH (20 ml) at −78° during 25 min. After removal of solvent (oil pump), formic acid (60 ml) and H_2O_2 (30%; 30 ml) was added to the residue and the whole was heated overnight at 80°. The solvent was removed and the residual oily tetra-acid was triturated with $CHCl_3$ to give solid material (0·83 g), m.p. 180–190° (dec). The analytical sample of **6a** had m.p. 194° (dec, EtOAc-benzene). (Found: C, 52·34; H, 6·29. $C_{14}H_{20}O_8$ requires: C, 53·16; H, 6·37%); IR(KBr): 3550–3100 (H-bonding), 1730–1690 cm^{-1} (CO); NMR (pyridine): τ 8·37 (broad s, $4C\underline{H}_2$), 7·80 (broad s, $4C\underline{H}_2$), 6·70, 6·29 (AB quartet, J_{AB} = 16 Hz, $8C\underline{H}_2CO$).

(c) Ethereal diazomethane was added to a methanolic soln (10 ml) of **6a** (90 mg). After 1 hr at room temp the solvent was removed and the residue was dissolved in CH_2Cl_2 and chromatographed on Florisil (10 g). The pure oily **6b** was eluted with CH_2Cl_2-$CHCl_3$ (4:1; 98 mg; 91·5%). (Found: C, 58·40; H, 7·32; O, 34·99. $C_{18}H_{28}O_8$ requires: C, 58·05; H, 7·58; O, 34·37%); IR($CHCl_3$): 1730 cm^{-1} (CO).; NMR ($CDCl_3$): τ 8·8–8·1 (broad mult., $8C\underline{H}_2$), 7·37, 7·10 (AB quartet, J_{AB} = 16 Hz, $8C\underline{H}_2CO$), 6·34 (s, $12OC\underline{H}_3$).

[4.3.3]*Propella*-8,11-*dione* **7**

(a) *By pyrolysis.* The crude **6a** (from 100 mg **5**) was heated under reflux with Ac_2O for 7 hr. After removal of solvent the crude residue was mixed with powdered glass and pyrolyzed by heating in a metal bath at 250–280°. The oily distillate which collected (40 mg) solidified. It was dissolved in benzene (1 ml) and chromatographed on basic alumina (Merck; 10 g). By elution with benzene-$CHCl_3$ (7:3) the pure **7** was obtained (10 mg; 10%), m.p. 206° (pet. ether 60–70°-benzene). Lit.[15] reports m.p. 174° but recrystallization of their sample as above gave m.p. and mixed m.p. 206°. (Found: C, 75·20; H, 8·30; O, 17·16, M.W. 192. $C_{12}H_{16}O_2$ requires: C, 74·97; H, 8·36; O, 16·65%; M.W. 192·25); IR($CHCl_3$): 1740 cm^{-1} (CO); NMR($CDCl_3$): τ 8·44 (s, $8C\underline{H}_2$), 7·72, 7·55 (AB quartet, J_{AB} = 18·5 Hz, $8C\underline{H}_2CO$).

(b) *Dieckmann cyclization.* To a mixture of NaOMe (from 56 mg Na and 10 ml MeOH) and toluene (150 ml) under N_2 at 100° was added dropwise with stirring a soln of **6b** (100 mg) in toluene (100 ml). A portion of the distillate was removed azeotropically (10 ml) and the bath temp was raised to 110° for 24 hr. After cooling, ice water (50 ml) was added. The toluene phase was washed with cold water (50 ml). The combined aqueous solns were acidified with cold 10% HCl and the whole was extracted with EtOAc (3 × 50 ml). After drying ($MgSO_4$) and removal of solvent the oily Dieckmann product was obtained in quantitative yield; IR($CHCl_3$): 1755 (5 ring C=O), 1725 (ester), 1655 (H-bonded enol–ester), 1615 cm^{-1} (C=C). Saponification of the diketone-diester was effected by heating overnight under reflux its soln in AcOH (10 ml)–HCl (conc, 5 ml). Removal of solvent afforded crude **7**, (48 mg; 93%), m.p. 187–192°. Recrystallization afforded pure **7** (38 mg; 73%), m.p. 206° (pet. ether-benzene) identical in all respects with the product of pyrolysis described above.

Hexacarbomethoxymethylethane **9b**

(a) Ozone was bubbled into a soln of **8**[2] (3·02 g) in MeOH (150 ml) at −78° until the blue colour was retained. After removal of solvent without warming (water pump) the residue was heated at 85° for 15 hr with formic acid (100 ml) and H_2O_2 (30%; 50 ml). After removal of solvent the residual oil was triturated with ether and gave the pure **9a** (4·2 g; 95·5%), m.p. 82° (dec). (Found: C, 46·88; H, 5·55. $C_{16}H_{22}O_{12}$ requires: C, 47·29; H, 5·46%); IR(KBr): 1745–1715 (broad, CO); NMR(pyridine): τ 6·78–5·84 (unresolved multiplets, $C\underline{H}_2O$), 6·40 (s, $C\underline{H}_3O$).

(b) The hexamethyl ester was prepared as described above for **2b**. From **9a** (2·87 g) was obtained oily **9b** (3·12 g; 96%), sufficiently pure for further work. The sample for analysis was prepared by filtering a soln of the hexaester in benzene(3)-$CHCl_3$ (1) through a Florisil column, n_D^{20} 1·4932. (Found: C, 51·50; H, 6·54. $C_{20}H_{30}O_{12}$ requires: C, 51·94; H, 6·54%); IR($CHCl_3$): 1740 cm^{-1} (CO); NMR($CDCl_3$): τ 7·14 (s, $12C\underline{H}_2CO$), 6·36 (s, $18C\underline{H}_3O$).

[3.3.3]*Propellane*-3,7,10-*trione* **10**

(a) Dry benzene (800 ml) was added to a soln of NaOMe prepared from Na (1·35 g) and dry MeOH (180 ml). The whole was stirred under reflux in an atm of N_2 and a soln of **9b** (2·25 g) in dry benzene (200 ml) was added dropwise during 3 hr and reflux was continued with stirring for an additional 15 hr. After cooling, extraction with water, acidification of the aqueous phase, $CHCl_3$ extraction and removal of solvent, the triketone-triester was obtained as a viscous oil (1·46 g; 82%) sufficiently pure for further work. Sublimation at 147°/0·01 mm affords a solid fraction, m.p. 54–56° and an oily fraction. Evidently these differ in enol content but spectral properties are very much the same; IR($CHCl_3$): 3450–3000 (H bonding), 1745(CO), 1665 (H-bonded enolic ester), 1625 cm^{-1} (C═C).

(b) A mixture of crude Dieckmann reaction product (0·67 g), conc HCl (15 ml) and water (70 ml) was heated under reflux overnight. The solvent was removed (oil pump) at room temp and the residue was heated under reflux with $CHCl_3$ and the solid was removed by filtration. This is saponified ester which did not undergo Dieckmann cyclization. Treatment of this fraction (195 mg) with diazomethane afforded **9b** (210 mg). The $CHCl_3$ filtrate was passed through a Florisil column (20 g). The *triketone* **10** was obtained (69 mg; 29% based upon recovered ester), m.p. 290–300° (dec, $CHCl_3$). (Found: C, 67·98; H, 6·27; M.W. 192. $C_{11}H_{12}O_3$ requires: C, 68·73; H, 6·29%; M.W. 192·21); IR($CHCl_3$): 1750 cm^{-1} (CO); NMR($CDCl_3$): τ 7·40 (s).

2,5,7,10-*Tetraoxo*[4.4.4]*propella*-3,8,12-*triene* **12**

The diquinone **11**[4] (3·17 g; 1·62 mmole) was suspended in AcOH (180 ml) and a soln of butadiene (0·90 g; 1·66 mmole) in benzene (20 ml) was added in one portion while stirring. Magnetic stirring in a closed pressure bottle was maintained for 72 hr at room temp affording an almost homogeneous brownish-red soln. The small amount of solid impurity was removed by filtration and the solvent was removed in a vacuum (20 mm). The residual red crystalline solid was crushed, taken up in AcOH and filtered and the solid was washed with AcOH (2 × 5 ml). The combined filtrate and washings were evaporated to dryness and the red residue was washed with ether (10 ml), dissolved in MeOH and a small amount of solid impurity was removed by filtration of the hot soln. After ice-cooling, filtration, washing with MeOH (2 ml) and drying (60°), **12** was obtained (0·36 g) as orange needles, m.p. 174–178°. Concentration of the filtrate afforded another crop (0·18 g; total yield 13%) of similar purity. The analytical sample was obtained by recrystallization as long needles with a faint copper gloss, m.p. 182–184° (MeOH). (Found: C, 69·00; H, 4·47; O, 26·44; M.W. 242. $C_{14}H_{10}O_4$ requires: C, 69·42; H, 4·16; O, 26·42%; M.W. 242·22); IR($CHCl_3$): 1714, 1685 (CO), 1609 cm^{-1} (C═C); UV(MeOH): $\lambda\lambda_{max}$ 208 (end), 215 (sh), 226 (sh), 285, 354 nm. εε, 13400, 11800, 8000, 2100, 290; NMR($CDCl_3$): τ 7·38 (d, $4C\underline{H}_2$, JJ = 1·5 Hz), 4·27 (m, $2C\underline{H}$), 3·20 (s, $4C\underline{H}CO$).

When the red crystalline solid obtained above after removal of AcOH was extracted with toluene (20 ml), the toluene was removed by distillation and the residue was recrystallized from MeOH. **13** was obtained (0·70 g; 28%) as golden leaflets, m.p. 143–148°. The analytical sample afforded golden leaflets m.p. 157–158°, sint. at 147–149° (isopropanol). (Found: C, 72·89; H, 5·47; O, 21·44; M.W. 296. $C_{18}H_{16}O_4$ requires: C, 72·96; H, 5·44; 9, 21·60%; M.W. 296·31); IR($CHCl_3$): 3500–3000 (OH), 1650–1640 (CO), 1584 cm^{-1} (C═C); UV(MeOH): $\lambda\lambda_{max}$ 208 (end), 247, 276, 296 (sh), 392, 398 (sh), 412 (sh) nm, εε, 7100, 11800, 2600, 2050, 5750, 5700, 4650; NMR($CDCl_3$): τ 7·57 (br m, $4C{=}CC\underline{H}_2$), 6·74 (br m, $2C\underline{H}CO$), 6·65 (s, 4 $ArC\underline{H}_2C{=}C$), 6·26, 6·04 ($4{=}C\underline{H}$), −2·34 (s, $2O\underline{H}$).

1,3,5,7-*Tetramethyladamantane* **17**.

To **16**[2] (1·92 g), $AlBr_3$ (1·92 g) and t-BuBr (100 mg) was added at room temp[16] causing the temp to rise to 45–50° and **16** to melt. The $AlBr_3$ appeared to remain largely undissolved and the mixture was stirred magnetically for 24 hr. Samples removed after 15 min and after 24 hr were practically identical (5 peaks, GLC). The reaction mixture was taken up in pentane and washed with dil HCl. Evaporation of the pentane gave a light brown oil (1·85 g). Distillation gave a colourless oil, b.p. 118–140° (25 mm) which was similar in composition (GLC) to the cruder oil. One of the constituents **17** was isolated by preparative GLC on a 20% SE 30 acid washed Chrom W column, 60–80 mesh, 5 feet × ¼ in at 144°. (Retention time 7·5 min; 135 mg; 7%), m.p. 66–67° (MeOH). Lit.[16, 17] m.p. 64°, 67°, respectively. The NMR spectrum is in agreement with structure **17**; NMR(CCl_4): τ 9·22 (s; $12C\underline{H}_3$), 9·00 (s, $12C\underline{H}_2$).

3,3,4,4-*Tetrahydroxymethyltetrahydrofuran* **19**

Compound **18**[9] (45·2 g) was added dropwise with stirring to a suspension of LAH (19·0 g) in THF (500 ml) and the mixture was heated under reflux with stirring for 50 hr. Dil H_2SO_4 (500 ml; 75 ml acid) was added and the organic layer was evaporated (water pump) and the oily residue was added to the aqueous phase. Continuous extraction of the aqueous phase for 24 hr gave after removal of solvent a yellowish oily solid (16·6 g) from which **19** was obtained (4·55 g; 20%) by crystallization from dioxan. This was sufficiently pure for further synthesis. The analytical sample had m.p. 217–219° (dec; dioxan). (Found: C, 49·40; H, 8·29. $C_8H_{16}O_5$ requires: C, 49·99; H, 8·39%). Another crystalline form with identical NMR spectrum, had m.p. 250–260° (dec, dioxan) NMR(DMSO-d_6): τ 6·53 (s, $8C\underline{H}_2OH$), 6·40 (s, $4C\underline{H}_2O$), 6·13 (br s, $O\underline{H}$).

3,3,4,4-*Tetramesyloxymethyltetrahydrofuran* **20**

A soln of **19** (0·96 g) in dry pyridine (10 ml) was added dropwise with stirring to a soln of methanesulfonyl chloride (6·90 g) in dry pyridine (15 ml) at ca. −15°. The soln was refrigerated overnight and then poured on ice. The soft brown solid was treated with boiling isopropanol (50 ml) and gave light brown crystalline **20** which was removed by filtration, washed with isopropanol and ether and dried at room temp (1·90 g; 76%), m.p. 135–155°, sufficiently pure for further synthesis. The analytical sample was obtained as a colourless solid, m.p. 150–155° (MeCN-MeOH). (Found: C, 28·95; H, 4·91. $C_{12}H_{24}O_{13}S_4$ requires: C, 28·57; H, 4·80%); NMR(DMSO-d_6): τ 6·75 (s, $12C\underline{H}_3S$), 6·13 (s, $4C\underline{H}_2O$), 5·63 (s, $8C\underline{H}_2OS$).

3-*Oxa*-7,10-*dithia*[3.3.3]*propellane* **21**

A mixture of **20** (1·68 g) and sodium sulfide nonahydrate (1·60 g) was stirred for 30 hr in DMSO (25 ml) at 120° under N_2. The resulting soln was diluted with water (100 ml) and the whole was extracted with pentane (5 × 25 ml). Evaporation of the pentane afforded colourless crystalline **21** (0·53 g; 85%), m.p. 213–217°. Recrystallization (MeOH) did not change the m.p. (Found: C, 51·21; H, 6·36; S, 33·99; M.W. 188. $C_8H_{12}OS_2$ requires: C, 51·06; H, 6·43; S, 34·02%; M.W. 188·18); NMR($CDCl_3$): τ 7·15 (s, $8C\underline{H}_2S$), 6·24 (s, $4C\underline{H}_2O$).

3,7,10-*Trioxa*[3.3.3] *propellane* **22**

A suspension of **19** (1·13 g) in toluene (140 ml) containing p-toluenesulfonic acid (0·2 g) was heated under reflux for 48 hr; the water formed was removed azeotropically. The resulting clear soln was washed with K_2CO_3 aq (10%; 5 ml), dried ($MgSO_4$) and the solvent was removed at the water pump. The resulting solid residue (0·8 g) gave upon crystallization from methylcyclohexane crude colourless **22** (0·56 g; 61%), m.p. 188–192°. Recrystallization from the same solvent gave m.p. 200–201° (sealed cap.). Lit.[2] m.p. 182–188°.

3,3,4,4-*Tetrahydroxymethylthiophan* **24**.

Compound **23**[10] (30·7 g) was added dropwise to a stirred suspension of LAH (12·2 g) in THF (300 ml) and the whole was heated under reflux for 66 hr followed by decomposition with water (300 ml) and H_2SO_4 (45 ml). After workup similar to that described for **19**, the tetrol **24** separated from the aqueous phase as a colourless solid (5·60 g), m.p. 300–305° (dec). Continuous extraction of the aqueous phase by ether for 72 hr afforded a second crop (2·58 g), m.p. 285–306° (dec), sufficiently pure for further work. The analytical sample had m.p. 281–284° (BuOH), total yield 49%. (Found: C, 46·28; H, 7·81; S, 15·59. $C_8H_{16}O_4S$ requires: C, 46·15; H, 7·75; S, 15·37%). Here also a second crystalline form exists, m.p. 315–320° (dec; BuOH); NMR(Py): τ 6·73 (s, $4C\underline{H}_2S$), 5·80 (s, $8C\underline{H}_2O$).

3,3,4,4-*Tetramesyloxymethylthiophan* **25**

A soln of **24** (0·62 g) in pyridine (10 ml) was added dropwise with stirring to a soln of methanesulfonyl chloride (2·75 g) in pyridine (10 ml) at ca. −15°. The whole was refrigerated overnight and poured on ice. Conc HCl (20 ml) was added at 0° and the ppt formed was removed by filtration, washed with water, MeOH and ether and dried at room temp. The light brown **25** (1·50 g; 96%), m p 130–156° (dec), was sufficiently pure for further work. The analytical sample had m.p. 130–168° (dec; MeCN-i-PrOH). (Found: C, 27·99; H, 4·97. $C_{12}H_{24}O_{12}S_5$ requires: C, 27·70; H, 4·65%); NMR(Py): τ 6·80 (s, $4C\underline{H}_2S$), 6·63 (s, $12C\underline{H}_3S$), 5·19 (s, $8C\underline{H}_2O$).

3,7,10-*Trithia*[3.3.3]*propellane* **26**

A mixture of **25** (2·72 g) and sodium sulfide nonahydrate (2·50 g) was stirred under N_2 in DMSO (25 ml) at 120° for 30 hr. The resulting solution was diluted with water (100 ml) and then extracted with methylcyclohexane (4 × 25 ml). Removal of solvent (water pump) and sublimation (160°/20 mm) of the colourless crystalline residue (0·85 g) gave **26** (0·52 g; 49%), m.p. 235–250°. The analytical sample had m.p. 250–251° (sealed cap, isopropanol). (Found: C, 46·52; H, 5·79; S, 47·60; M.W. 204. $C_8H_{12}S_3$ requires: C, 47·06; H, 5·92; S, 47·03%; M.W. 204·18); NMR($CDCl_3$): τ 7·05 (s, $C\underline{H}_2S$).

3,7-*Dioxa*-10-*thia*[3.3.3]*propellane* **27**

A suspension of **24** (1·04 g) in toluene (100 ml) containing p-toluenesulfonic acid (0·1 g) was heated under reflux for 45 hr, the water formed being removed azeotropically. After workup similar to that described for **22**, the colourless solid obtained was sublimed (120°/20 mm) and gave **27** (0·60 g; 70%), m.p. 188–196°. The analytical sample had m.p. 199–200° (sealed cap.; MeOH). (Found: C, 55·67; H, 7·04; S, 18·55; M.W. 172. $C_8H_{12}O_2S$ requires: C, 55·80; H, 7·03; S, 18·59%; M.W. 172·18); NMR($CDCl_3$): τ 7·19 (s, $4C\underline{H}_2S$), 6·24 (s, $8C\underline{H}_2O$).

6,8-*Dioxo*-7,10-*dioxa*[3.3.3]*propellane* **29**

Ozone was bubbled into a soln of **28**[2] (14·6 g) in dry MeOH (200 ml) at −78° until a blue colour remained (3 hr). The solvent was removed without warming (water pump). Formic acid (80 ml) and H_2O_2 (30%; 40 ml) were added and the soln was allowed to stand for 12 hr at room temp. Removal of solvent in a high vacuum gave a residue of oily diacid. This was dissolved in Ac_2O (100 ml) and the soln was heated under reflux for 12 hr. Distillation at ordinary press removed solvent. The *anhydride* **29** was distilled, b.p. 91°/0·01 mm (7·5 g; 61%). Sublimation (100°/0·01 mm) afforded **29**, m.p. 143–147°. (Found: C, 59·29; H, 5·63. $C_9H_{10}O_4$ requires: C, 59·33; H, 5·53%); IR($CHCl_3$): 1860, 1795 cm^{-1} (CO); NMR($CDCl_3$): τ 6·35, 5·48 (AB quartet, $4C\underline{H}_2O$, $J = 9$ Hz), 8·81–7·52 (m, $6C\underline{H}_2$).

7-*Oxa*-10-*thia*[3.3.3]*propellane* **31**

(a) A mixture of **29** (0·36 g), LAH (0·76 g) and THF (35 ml) was heated under reflux with stirring for 8 hr and then decomposed with dil H_2SO_4 (10%; 60 ml). The aqueous layer was extracted with ether (3 × 20 ml). The combined organic phases were dried (K_2CO_3) and the solvent was removed at the water pump. The waxy *diol* **30a** (0·33 g; 89%) was sufficiently pure for further work; NMR($CDCl_3$): τ 8·35 (br s, $6C\underline{H}_2$), 6·36 (s, $4C\underline{H}_2OH$), 6·45, 6·12 (AB quartet, $4C\underline{H}_2O$, $J = 9$ Hz), 5·52 (br, $2O\underline{H}$).

(b) A soln of **30a** (0·33 g) in pyridine (10 ml) was added dropwise with stirring to a cooled soln (ca. −30°) of methanesulfonyl chloride (2·76 g) in pyridine (10 ml). The resulting soln was kept at 0° for 3 hr and at room temp for a further 20 hr and then poured on ice. Neutralization with 50% H_2SO_4 aq at 0°, ether extraction (7 × 50 ml), drying ($MgSO_4$) and evaporation of solvent at the water pump, afforded soft crystals (0·48 g). Washing with ether and drying gave the *dimesylate* **30b**, m.p. 101–104°; NMR($CDCl_3$): τ 8·22 (s, $6C\underline{H}_2$), 6·93 (s, $6C\underline{H}_3S$), 6·38, 6·10 (AB quartet, $4C\underline{H}_2O$, $4C\underline{H}_2O$, $J = 9$ Hz), 5·72 (br. s, $4C\underline{H}_2OMs$).

(c) The dimesylate **30b** (0·33 g) and sodium sulfide nonahydrate (0·26 g) were stirred under N_2 in DMSO (10 ml) for 8 hr at 100°. The resulting soln was diluted with water (50 ml) and extracted with ether (5 × 25 ml). Removal of solvent followed by two sublimations afforded colourless 7-*oxa*-10-*thia*[3.3.3]*propellane* **31** (32 mg; 19%), m.p. 177–179° (sealed cap). (Found: C, 63·42; H, 8·16; M.W. 170. $C_9H_{14}OS$ requires: C, 63·45; H, 8·28%; M.W. 170·20); NMR($CDCl_3$): τ 8·32 (s, $6C\underline{H}_2$), 7·28 (s, $4C\underline{H}_2S$), 6·40, 6·29 (AB quartet, $4C\underline{H}_2O$, $J = 8$Hz).

9,11,*Dioxo*-7-*oxa*-10-*aza*[3.3.3]*propellane* **32a**

The anhydride **29** (3·1 g) was heated under reflux in conc NH_4OH (150 ml) for 12 hr. The solvent was removed at the water pump and the residue was recrystallized to give the pure *imide* **32a** (2·3 g; 75%), m.p. 217–219° (water). (Found: C, 59·33; H, 6·25; M.W. 181. $C_9H_{11}NO_3$ requires: C, 59·66; H, 6·12%; M.W. 181·19); IR(KBr): 3065, 3175–3115 (NH), 1760, 1715–1680 cm^{-1} (CO); NMR(DMSO-d_6): τ 8·14 (s, 6C$\underline{H}_2$), 6·48, 5·82 (AB quartet, 4C$\underline{H}_2$O, J = 9·9 Hz).

9,11-*Dioxo-10-methyl-7-oxa-10-aza[3.3.3]propellane* **32b**

A soln of **32a** (2·1 g) in MeOH (50 ml) was treated with an excess of an ethereal soln of diazomethane at 0°. After standing for 12 hr, the solvent was removed at the water pump and the oil was triturated with pet. ether (60–70°) and recrystallized. The pure *methylimide* **32b** (2·0 g; 88%) had m.p. 76–77° (pet. ether). (Found: C, 61·66; H, 6·92; M.W. 195. $C_{10}H_{13}NO_3$ requires: C, 61·52; H, 6·71%; M.W. 195·21); IR(CHCl$_3$): 1780, 1710–1695 cm^{-1} (CO); NMR(CDCl$_3$): τ 8·02 (s, 6C$\underline{H}_2$), 7·00 (s, 3NC$\underline{H}_3$), 6·42, 5·62 (AB quartet, 4C$\underline{H}_2$O, J = 9·9 Hz). Methylation of **32a** with diazomethane in THF failed.

10-*Methyl-7-oxa-10-aza[3.3.3]propellane* **33**

A mixture of **32b** (2·6 g) LAH (2·7 g) and THF (300 ml) was heated under reflux in a N_2 atm for 1 week. Decomposition was effected by adding EtOH followed by a sat Na_2SO_4 soln until a ppt appeared and then solid Na_2SO_4. The organic layer was separated by filtration and removal of solvent gave a residue of crude amine. Purification was effected via the *picrate* of **33**, m.p. 206–208° (dec., benzene). (Found: C, 48·32; H, 5·08; N, 13·92. $C_{16}H_{20}N_4O_8$ requires: C, 48·48; H, 5·09; N, 14·14%). The pure picrate was decomposed to afford pure **33**, b.p. 86°/0·1 mm (0·46 g; 20%); NMR(CDCl$_3$): τ 8·46 (s, 6C$\underline{H}_2$), 7·83 (s, 3NC$\underline{H}_3$), 7·67 (s, 4C$\underline{H}_2$N), 6·57, 6·43 (AB quartet, 4C$\underline{H}_2$O, J = 9 Hz). The free amine is unstable to air.

12-*Oxa[4.4.3]propella-2,4,7,9-tetraene* bis-*irontricarbonyl*

(a) A soln of **34a**[2] (1·34 g; 1 eq) and iron pentacarbonyl (6·09 g; 4 eq) in di-n-butyl ether was heated under reflux for 17 hr in an atmosphere of N_2. After cooling and filtration under N_2 the solvent was removed in a high vacuum. The residual solid **36** (X = O) was purified by crystallization (2·58 g; 75%), m.p. 200–204° (sealed cap.; CH_2Cl_2 pet. ether 60–80° or CHCl$_3$). (Found C, 47·49; H, 2·70; Fe, 24·40; M.W. 452. $C_{18}H_{12}O_7Fe_2$ requires: C, 47·83; H, 2·68; Fe, 24·71%; M.W. 451·98); IR(CHCl$_3$): 2060, 2045, 1985 cm^{-1} (CO); UV(CH$_3$OH): $\lambda\lambda$210 (end), 222 (sh), 243 (sh), 307 nm $\varepsilon\varepsilon$ 38200, 38200, 32000, 10800; NMR(CDCl$_3$): τ 7·21–7·00 (sym. mult, 4 term. H), 6·02 (s, 4C$\underline{H}_2$O), 4·84–4·63 (sym. mult; 4 central H). Irradiation at each olefinic band caused the other to collapse to a sharp singlet. The compound may be sublimed without decomposition at 134°/0·01 mm, is stable on a column of basic alumina and may be purified chromatographically.

(b) A soln of **34a** (1·02 g) and diironnonacarbonyl (10·95 g) in dry benzene (350 ml) was heated under reflux for 24 hr in an atm of N_2. After workup similar to that described above the dark green residue (2·34 g; 88%) was taken up in pet. ether 40–60° and chromatographed on activated basic alumina (Merck; 150 g). Elution by benzene-pet. ether 40–60° (1:1) afforded a number of pure and impure fractions. Five pure organometallic derivatives were isolated by a combination of chromatographic separations on activated basic alumina and fractional crystallizations. Enrichment of fractions was monitored by NMR spectroscopy. The products were (in order of elution from the columns; yields calculated on the basis of **34a**):

(1) A *mono-irontricarbonyl derivative of* **34a** (250 mg; 13·5%), m.p. 105–107° (pet. ether 120–160°; sealed capillary). (Found: M.W. 312. $C_{15}H_{12}O_4Fe$ requires: M.W. 312·11); IR(CHCl$_3$): 2055, 1990 cm^{-1} (CO); UV(MeOH): $\lambda\lambda$ 210 (end), 245 (sh) nm $\varepsilon\varepsilon$ 19900, 12200; NMR(CDCl$_3$): τ 6·74–6·53 (m, 2 term H), 6·53, 6·03 (AB quartet, J_{AB} = 9 Hz, 4C$\underline{H}_2$O), 5·16–4·95 (m, 2 cent H), 4·33 (s, 4 H).

(2) A symmetrical compound, **36** (X = O), (720 mg; 27%), m.p. 200–204° identical to the compound described above.

(3) An isomeric *monoirontricarbonyl derivative* of **34a** (470 mg; 22·5%), m.p. 115–130° (dec, sealed cap; pet. ether 60–70°). (Found: M.W. 312. $C_{15}H_{12}O_4Fe$ requires: M.W. 312·11); IR(CHCl$_3$): 2050, 1980 cm^{-1} (CO); UV(MeOH): λ 210 (end) nm ε 35900; NMR(CDCl$_3$): τ 7·23–7·00 (m, 2 term H), 6·78, 6·15 (AB quartet, J_{AB} = 9 Hz, 4C$\underline{H}_2$O), 4·77–4·54 (m, 2 cent H), 4·59–3·97 (m, 4H).

(4) A compound containing two Fe atoms and five CO groups, **38** (500 mg; 20%), m.p. 135–138° (dichloromethane-pet. ether 120–160°; sealed cap). (Found: M.W. 424. $C_{17}H_{12}O_6Fe_2$ requires: 423·97); IR(CHCl$_3$): 2055, 2045, 1980 cm^{-1} (CO); UV(MeOH): $\lambda\lambda$ 211 (end), 220 (sh), 303 nm. $\varepsilon\varepsilon$ 40300, 33100, 7800; NMR(CDCl$_3$) τ 7·17–6·72 (m, 4 term H), 6·37, 6·29 (AB quartet, J_{AB} = 9·5 Hz, 4C$\underline{H}_2$O), 4·92–4·63 (m, 2 cent H), 4·63–4·35 (m, 2 cent H). Double irradiation supported this formulation.

(5) A symmetrical *bis*-irontricarbonyl derivative believed to be **35** (X = O) because of its higher polarity and higher shielding of C$\underline{H}_2$O protons by the Fe atoms (30 mg; 1·1%), m.p. 186–187° (sealed cap; CH_2Cl_2-

pet. ether 120–160°). (Found: C, 47·51; H, 2·64; M.W. 452. $C_{18}H_{12}O_7Fe_2$ requires: C, 47·83; H, 2·68%; M.W. 451·98); IR($CHCl_3$): 2060, 2040, 1995, 1985 cm^{-1}; UV(MeOH): $\lambda\lambda$ 212 (end), 222 (sh), 285 (sh) nm $\varepsilon\varepsilon$ 26000, 20850, 3600; NMR($CDCl_3$): τ 7·30–7·04 (m, 4 term H), 6·50 (s, $4C\underline{H}_2O$), 4·84–4·58 (m, 4 cent H).

11,13-*Dioxo*-12-*oxa*[4.4.3]*propella*-2,4,7,9-*tetraene* bis-*irontricarbonyl*

A soln of **34b**[18, 19] (0·5 g; 1 eq) and iron pentacarbonyl (2·0 g: 4 eq) in di-n-butyl ether (150 ml) was heated under reflux for 17 hr in an atmosphere of N_2. After the usual workup the dark brown solid obtained by filtration was extracted with boiling EtOAc and the hot soln was filtered. The di-n-butyl ether and EtOAc soln were combined and the solvents were removed. The brown-red solid product (0·4 g; 34%) was recrystallized using charcoal, m.p. 188–189° (sealed cap; CH_2Cl_2 pet. ether 60–70° or $CHCl_3$). (Found: C, 44·92; H, 1·87; M.W. 480. $C_{18}H_8O_9Fe_2$ requires: C, 45·04; H, 1·65%; M.W. 479·94); IR($CHCl_3$): 2070, 2060, 2000 (Fe-$\underline{CO}$), 1800, 1785 cm^{-1} (anhydride CO); UV(MeOH): $\lambda\lambda$ 211 (end), 220 (sh), 303 nm $\varepsilon\varepsilon$ 40300, 33100, 7800; NMR($CDCl_3$): τ 7·09–6·68 (mult, 4 term, H), 4·73–4·32 (mult, 4 cent, H).

11,13-*Dioxo*-12-*aza*[4.4.3]*propella*-2,4,7,9-*tetraene* bis-*irontricarbonyl*

A soln of **34c**[20] (0·5 g; 1 eq) and iron pentacarbonyl (2·0 g; 4 eq) in di-n-butyl ether (150 ml) was heated under reflux for 17 hr in an atmosphere of N_2. The dark brown solid was extracted with boiling $CHCl_3$ and the hot soln was filtered in order to get rid of impurities. The di-n-butyl ether and $CHCl_3$ solns were combined and the solvents removed. The residue (1·11 g; 93%) of *bis*-product was purified by crystallization, m.p. 296–297° (dec, sealed cap.; CH_2Cl_2-$CHCl_3$) (0·83 g; 70%). (Found: C, 44·48; H, 2·04; N, 2·98; M.W. 479. $C_{18}H_9NO_8Fe_2$ requires: C, 44·57; H, 1·87; N, 2·89%; M.W. 478·98); IR($CHCl_3$): 2070, 2060, 1998 (Fe-$\underline{CO}$), 1788, 1730 cm^{-1} (imide CO); UV(MeOH): $\lambda\lambda$ 220, 243 (sh), 303 nm $\varepsilon\varepsilon$ 45000, 30000, 10300; NMR(DMSO-d_6) τ 7·02–6·77 (mult, 4 term, H), 4·40–4·17 (mult, 4 cent, H). The product is stable on a column of basic alumina.

11,13-*Dioxo*-12-*methyl*-12-*aza*[4.4.3]*propella*-2,4,7,9-*tetraene* bis-*irontricarbonyl*

A soln of **34d**[20] (2·17 g; 1 eq) and ironpentacarbonyl (8·5 g; 4 eq) in di-n-butyl ether was heated in the usual way for 17 hr. The hot soln was then filtered and the solid was extracted with boiling EtOAc and the hot soln was filtered to remove impurity. Beautiful yellow needles crystallized from the cold di-n-butyl ether soln and were the *bis*-derivative. The di-n-butyl ether and EtOAc mother liquors were combined and the solvents were removed to give more of the product (3·54 g; total yield 75%), m.p. 221–223° (sealed cap.; CH_2Cl_2-$CHCl_3$). (Found: C, 45·78; H, 2·55; N, 2·89; M.W. 493. $C_{19}H_{11}NO_8Fe_2$ requires: C, 46·29; H, 2·25; N, 2·84%; M.W. 492·99); IR($CHCl_3$): 2055, 2050, 1998 (Fe-$\underline{CO}$), 1775, 1705 cm^{-1} (imide CO); UV(MeOH): $\lambda\lambda$ 210 (end), 222 (sh), 303 nm. $\varepsilon\varepsilon$ 32400, 32400, 8800; NMR($CDCl_3$): 6·95–6·76 (mult, 4 term, H), 6·91 (s, $NC\underline{H}_3$), 4·69–4·50 (mult, 4 cent, H).

The identical compound (m.p. and spectral properties) was obtained in quantitative yield by treating the *bis*-irontricarbonyl derivative of **34c** in a minimal volume of methanol with ethereal diazomethane.

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