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PROPELLANES—XXVII[a]

REACTIONS OF 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE WITH SOME [4.4.3]PROPELLANE ETHERS, IMIDES AND THEIR IRONTRICARBONYL DERIVATIVES

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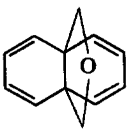
Abstract—The steric course of Diels-Alder reactions of propellane ethers and methylimides, at different oxidation levels, was investigated. Irontricarbonyl derivatives, particularly of the imides, were subjected to reaction with a potent dienophile and the results are described.

We have described the steric course of the Diels-Alder reaction between certain tetraenic propellanes and 4 - phenyl - 1,2,4 - triazoline - 3,5 - dione and have suggested an explanation for the different behavior in the case of the tetraenic ether **1** and the tetraenic methylimide **2**.[1] This explanation comprised both steric and electronic components. In this paper we bring additional evidence in its support.



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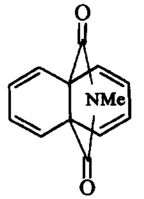

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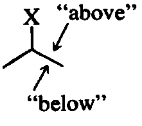

1a

Scheme 1 summarizes the results already published with respect to **1** and two related substrates. Since the Diels-Alder adducts in all three cases were reduced to the same perhydro-derivative and the structure of **7** has been established unequivocally,[1] it is equally proven that the attack of the dienophile upon **3** and **5** is also from below (formula **1a**). This means that when one of the propellane rings is completely reduced or partially reduced and adopts a chair or half-chair conformation, respectively (*cf* Ref 2), the H atoms alpha to the ether oxygen are still the factor controlling the direction of attack by the dienophile (*cf* Ref 1).

In the case of **2** we had available three additional methylimides through which we could test our expectation that the electronic factor would overcome the steric preference for attack from below, and thus favours attack from above. Scheme 2 lists the results of the reaction of our methylimides with the dienophile. Again by interrelation of the 1:1 adducts by reduction to the common perhydro compound **16** and since the structure of **15** was unequivocally established,[1] it is clear that in all of these cases the dienophile attacks from above, again presumably because of second order orbital effects which overcome the steric question of whether one of the rings is a chair, half-chair or practically planar.

In our previous paper we stated that **2** affords with 2 equivalents of the dienophile the symmetrical **17**.[1] However, since we required larger quantities of **17** for another synthetic project this reaction was carried out on a larger scale and it was found that the unsymmetrical **18** accompanies **17** as a reaction product.[3]

In our previous work we have shown that it was possible to displace an irontricarbonyl ligand complexed to a propelladiene ring by means of the above dienophile, with retention of configuration. Since to our knowledge this was the first such case reported we wished to study the scope of such ligand displacement. We had previously reported the five possible irontricarbonyl complexes of **1** three *bis*- and two mono-derivatives.[4,5] We also reported the preparation of a *bis*-irontricarbonyl derivative **19** in 75% yield by treating **2** with iron pentacarbonyl.[4] Repetition of this work confirmed more or less this overall yield (67%) but a series of fractional crystallizations from solvents other than those previously used afforded in addition to the known[4] symmetrical *bis*-complex also the unsym-

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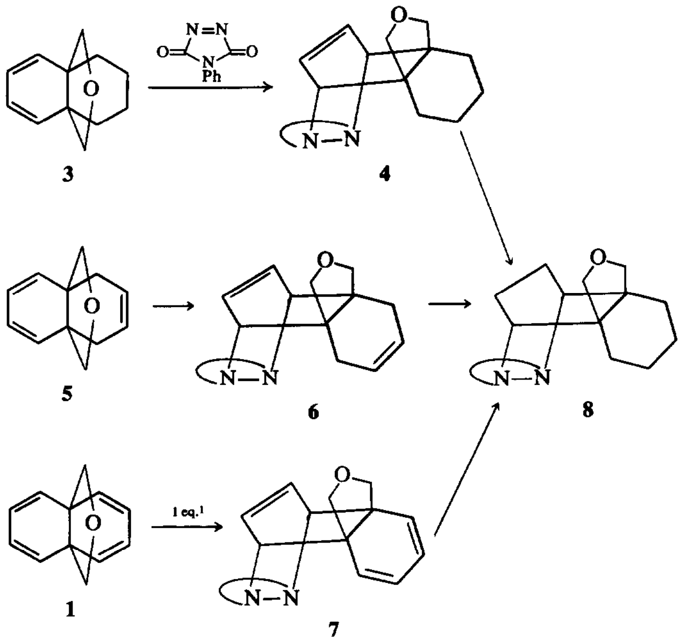
[a] Part XXVI. D. Ginsburg, *Accounts Chem. Res.*, 7, (1974), in press, September issue.



SCHEME 1

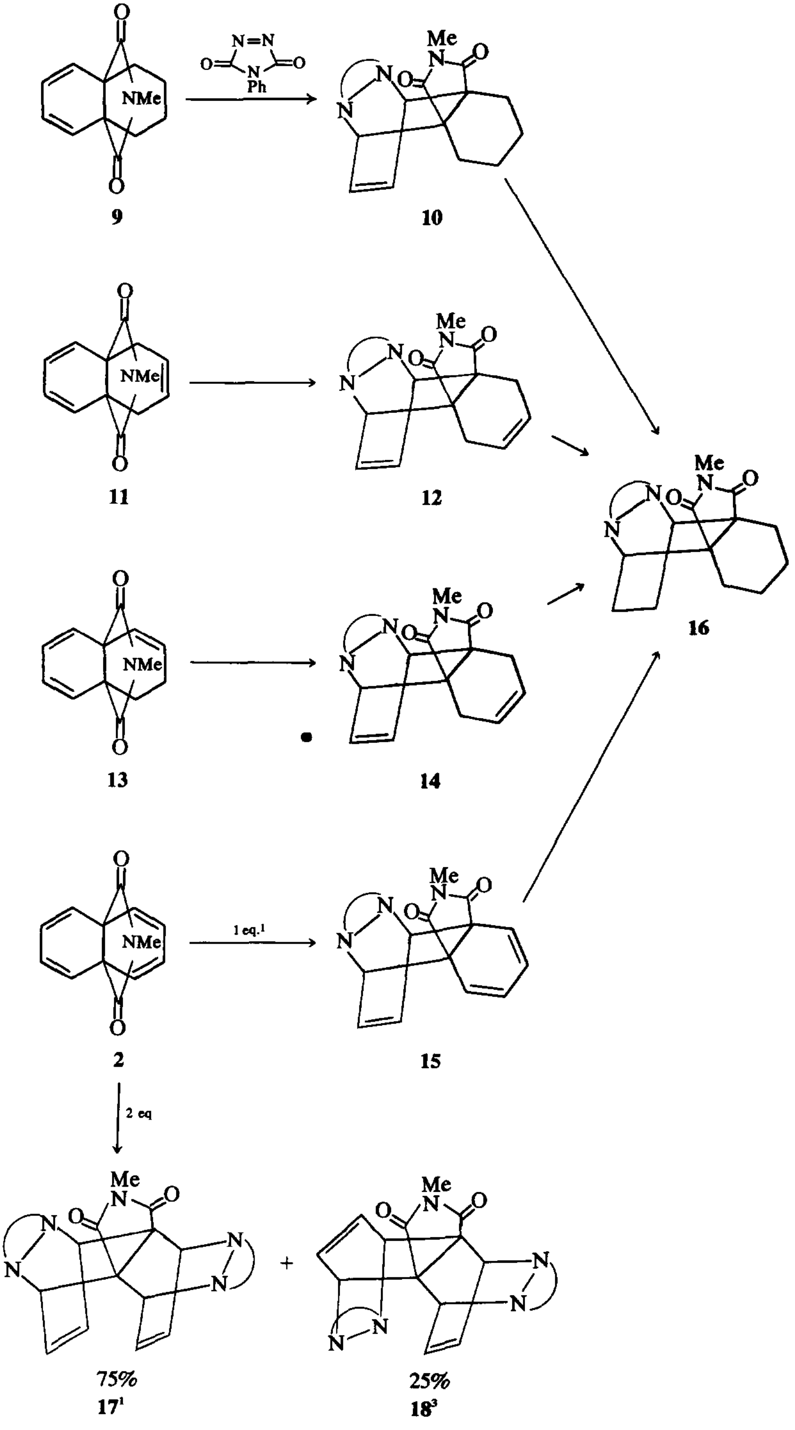
metrical isomer **20** in the ratio of 3 : 1, respectively. The use of $Fe_2(CO)_9$ gave the same product **19** and **20**, but this time in a ratio of 1 : 2, respectively (Scheme 3).

Removal of *one* of the irontricarbonyl groups in **19** by employing one equivalent of ceric ion, afforded **21** whilst in the similar treatment of **20** the "upper" irontricarbonyl group was removed, stereoselectively, affording **22**, the isomer of **21**. This reaction course is exactly analogous to that earlier observed for the corresponding *bis*-irontricarbonyl derivatives of **1**.[5a] For the latter this may be explained by invoking the structure determined by X-ray diffraction for the unsymmetrical *bis*-derivative of **1**, namely **27**.[5c] It is likely that this comformation is maintained in solution and, if so, it is much easier for ceric ion to remove the ligand from the top face of the propellane as the boat form of the cyclohexadiene ring attached to this ligand exerts hindrance to the approach of this ion to the irontricarbonyl group attached to the other cyclohexadiene ring, on the bottom face of the propellane. The structure of **19** was not determined by X-ray crystallography but whether it is similar to that of the ether analog **28** as determined by X-ray diffraction,[5b] or not, the metal group must be removed from the top face, simply because it is there. It is not credible that both irontricarbonyl groups in the symmetrical isomer be on the bottom face, for steric reasons (*cf.* the formation of just such an analog in 1% yield from **1** as compared to 25–30% yields for **27** and **28**[4]). In the case under discussion this *bis*-analog was not isolated even in trace amounts.

We reported in Scheme 3 (and in the Experimental) the products obtained from **11**, **9** and **3**, respectively, when these are treated with iron pentacarbonyl. We have used lanthanide shift reagents in the study of structure and conformation of certain propellanes.[6] We have not been able to form firm conclusions with respect to the structures of **23**–**26** and therefore postpone reporting until a later date (when we have been able to use a computer program tailored for this purpose[7]) our results in this respect as well as on reactions of these compounds with the triazolinedione.

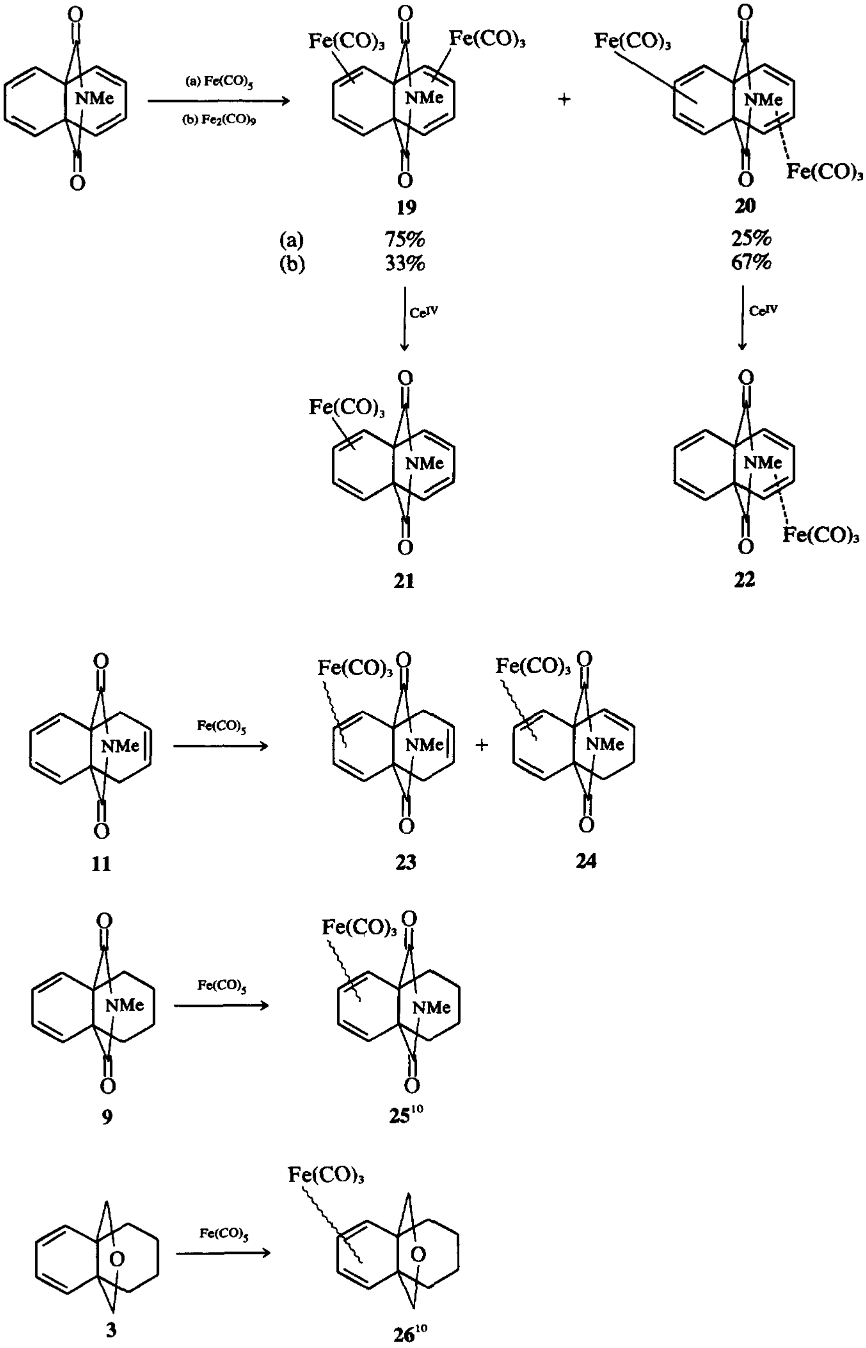
But we report herein those results of displacing irontricarbonyl groups by means of the dienophile as the structures of the substrates are as shown (Scheme 4) and we can draw conclusions with respect to the steric course of these displacements. The transformations **19**→**29**, **29**→**17** and in part **20**→**30**, occur with retention of configuration as in the cases previously studied.[1] More interesting, since there is apparent inversion occurring, at least in part, is the formation of **29** along with **30**.

In point of fact, when **20** was treated with ceric ion selectivity was not total as in the case of **27**. The monoirontricarbonyl derivative **22** was obtained in 90% yield, accompanied, however, by **21** in 10% yield. The lone pair on nitrogen in a methylimide, e.g. **20**, would certainly not be as available to contribute charge to the diene ring complexed to $Fe(CO)_3$ on its bottom face, even if the conforma-

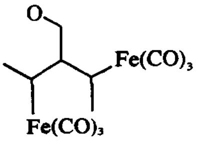


SCHEME 2

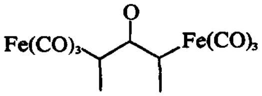
tion of **20** were exactly analogous to that of **27**. Thus, whilst ceric ion would find it easier to remove with total selectivity the irontricarbonyl group on the upper face of **27** for both steric and electronic reasons, it is apparently easier, by comparison, t remove at least in part the Fe(CO)$_3$ group on th bottom face of **20**, either with ceric ion or by mean of the dienophile. When this is removed **21** shoul



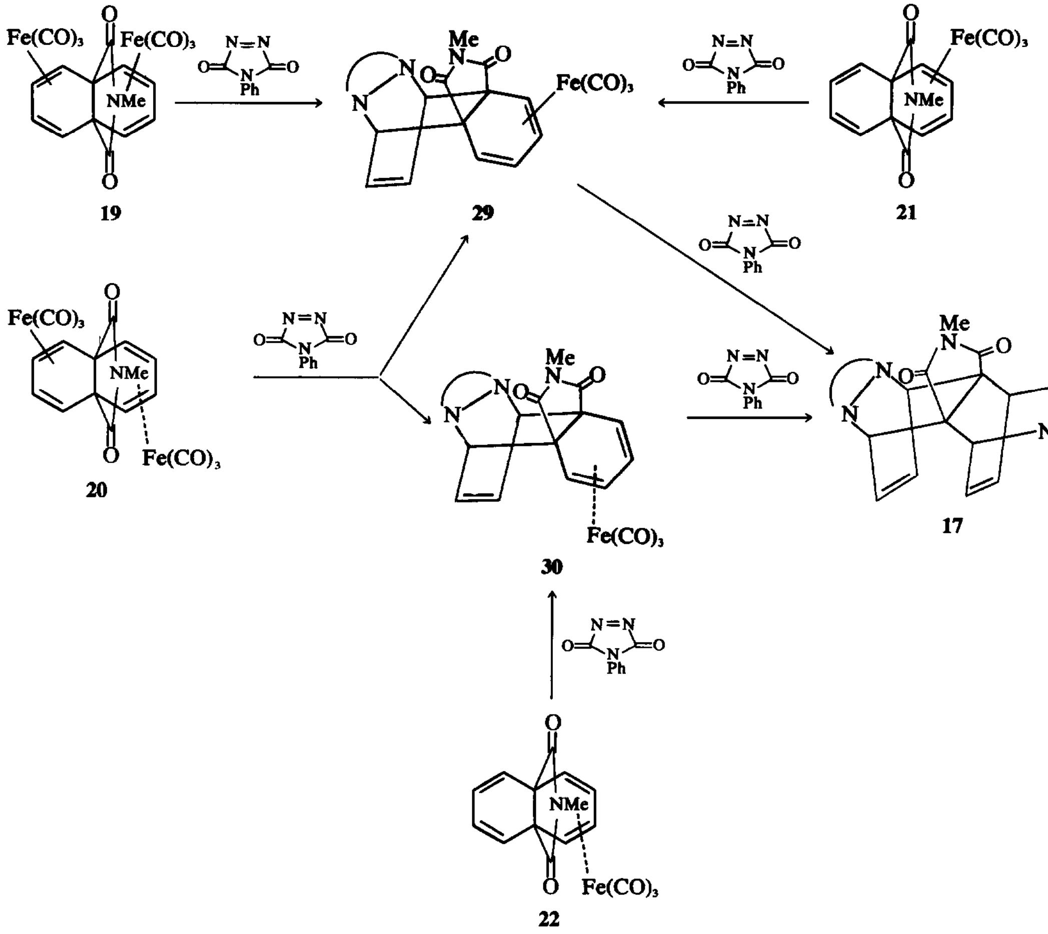
SCHEME 3



27



28



SCHEME 4

be obtained (although it was not isolated). We know from an independent experiment that **21** afforded **29** when treated with the dienophile. It then appeared as though **29** were formed from **20** by inversion of configuration.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were measured on a Perkin Elmer model 237 spectrometer; UV spectra on a Cary 14 or Spectronic 505 instrument; NMR on a Varian A-60 or T-60 instrument and mass spectra on an Atlas CH4 spectrometer maintaining the ionization current at 20 μA and the electron energy at 70 eV.

Preparative TLC was conducted on plates of basic alumina (20 × 20 cm, 40 g, type E) of alumina oxide Pf 254 + 366 made by E. Merck.

Organic sols were dried over $MgSO_4$ unless otherwise specified. Solvents were removed in a rotatory evaporator at 25–30 torr.

Preparation of **2**. The literature preparation affords very low yields.[8] We therefore give details for preparing **2** by two alternate routes both starting with 11,13 - dioxo - 12 - aza[4.4.3]propella - 3,8 - diene.[9]

(a) A mixture of the diene (0·5 g), dry freshly recrystallized NBS (0·9 g), a catalytic amount of dibenzoyl peroxide and dry CCl_4 (40 ml) was heated gently by placing the 150 ml flask over an IR lamp, until succinimide fully formed on surface of the solvent (*ca* 30 min). After cooling and filtration the solvent was removed. Dry DMF (50 ml) was added and the whole was heated with magnetic stirring at 100° for 12 hr. The clear brownish soln was cooled to room temp and poured into water (300 ml) with stirring. Even if solid appeared the whole was extracted with ether (3 × 100 ml) and the extract dried. Removal of solvent afforded the *tetraenic imide* in 50–60% yield, m.p. 164–165°. Lit.[8] m.p. 164–165°.

A soln of the imide (3 g) in MeOH (50 ml) was treated with ethereal diazomethane until the yellow color survived. Removal of solvent gave **2** (3 g), m.p. 156° (acetone). Lit. m.p. 151–152°.

(b) A methanolic (50 ml) soln of the dienic imide (3 g) gave after treatment with ethereal diazomethane and workup as above the dienic methylimide (3·1 g), m.p. 150–152° (EtOH). Lit.[8] m.p. 161–162°.

The methylimide (2 g), NBS (3·3 g), dibenzoyl peroxide (8 mg) and CCl_4 (200 ml) were heated as above for *ca* 30 min. After the same workup DMF (200 ml) was added and the whole heated at 100° for 12 hr. After workup as above a greyish solid was obtained. Trituration with MeOH gives colorless **2** in high purity. The analytical sample was obtained by recrystallization, m.p. 156°

(acetone) or by chromatography on basic alumina with benzene as eluent. The overall yield of pure product was 50–70%. (Found: C, 73·08; H, 5·26; N, 6·17; M.W. 213. $C_{13}H_{11}NO_2$ requires C, 73·22; H, 5·20; N, 6·57%; M.W. 213·23). UV(MeOH): λ_{max} 244, 275(sh)nm. ϵ_{max} 9200, 4700; IR($CHCl_3$): 1778, 1695 (imide CO), 1658 (C=C), 1375 cm^{-1} (NCH_3); NMR($CDCl_3$): τ 3·91–4·50 (AA'BB', 8 vinylic H); 6·93 (s, $NC\underline{H}_3$); M.S. *m/e* 213 (M^+), 185, 128.

Diels-Alder adduct **4**. To a soln of 3^{10} (200 mg) in acetone (5 ml) was added dropwise with stirring an acetone soln (5 ml) of the 4 - phenyl - 1,2,4 - triazoline-3,5 - dione (200 mg). The colorless precipitate of **4** was removed by filtration and washed several times with MeOH (245 mg; 70%), m.p. 229–230°. (Found: C, 67·76; H, 6·02; N, 12·34; M.W. 351. $C_{20}H_{21}O_3N_3$ requires C, 68·36; H, 6·02; N, 11·96%; M.W. 351·39); IR(KBr): 1790, 1720 (ureide CO); 1620 cm^{-1} (arom C=C); NMR ($CDCl_3$): τ 2·53 (br s, 5 arom H); 3·40 (t, 2 vinylic H); 5·38 (t, 2 allylic H); 6·17, 6·37 (ABq, J_{AB} = 10 Hz, 4 $C\underline{H}_2O$); 7·76–8·75 (m, 8 $C\underline{H}_2$); M.S. *m/e* 351 (M^+), 227 ($C_{12}H_9N_3O_2^+$)*, 178, 176 (M^+-dienophile), 157.

Reduction of **4**. The adduct **4** (40 mg) was reduced during 2·5 hr with PtO_2 (3 mg) in EtOAc (10 ml) at atm pressure of hydrogen. Removal of catalyst and solvent afforded **8** (38 mg), m.p. 189–190° (MeOH) (Found: C, 67·47; H, 6·34; N, 11·90. $C_{20}H_{23}N_3O_3$ requires: C, 67·97; H, 6·56; N, 11·89%).

Similar reduction of **6**[1] and **7**[1] also afforded **8**, identical to the product obtained by reduction of **4**.

Diels-Alder adduct **10**. A soln of 9^{10} (55 mg) in methylene chloride (1 ml) was added with magnetic stirring to a soln of triazoline dione (50 mg) in the same solvent (3 ml) at 0°. After removal of solvent the product **10** was obtained in quant yield, m.p. 263–263·5° (EtOH and MeOH). (Found: C, 64·03; H, 5·19; N, 14·18; M.W. 392. $C_{21}H_{20}N_4O_4$ requires: C, 64·27; H, 5·14; N, 14·28%; M.W. 392·41); IR(KBr): 1770, 1710, 1690 cm^{-1} (ureide and imide CO); NMR ($CDCl_3$): τ 2·57 (s, 5 arom H); 3·40 (t, 2 vinylic H); 3·92 (t, 2 allylic H); 6·88 (s, $NC\underline{H}_3$); 7·67–8·67 (br m, 8 $C\underline{H}_2$); M.S. *m/e* 392 (M^+), 227.

Reduction of **10**. A soln of **10** (40 mg) in EtOAc (10 ml) was reduced during 2 hr using PtO_2 (3 mg) at atm pressure of hydrogen. The perhydrocompound **16** was obtained, m.p. 240–243°, identical in all respects, including mixed m.p. determination, to the product already reported.[11]

Diels-Alder adduct **12**. Prepared as above from the triene **11** (121 mg, see below) in CH_2Cl_2 (2 ml) and the dienophile (99 mg) in same solvent (6 ml). The product **12** was obtained as colorless crystals (130 mg; 55%), m.p. 261–263° (MeOH). (Found: C, 64·39; H, 4·78; N, 14·64; M.W. 390. $C_{21}H_{18}N_4O_4$ requires: C, 64·60; H, 4·65; N, 14·35%, M.W. 390·39); IR(KBr): 1780, 1725, 1700 cm^{-1} (CO); NMR($CDCl_3$): τ 2·57 (s, 5 arom H); 3·33 (t, 2 vinylic H in diaza ring system); 4·20 (t, 2 vinylic H), 4·85 (t, 2 allylic $C\underline{H}N$); 6·97 (s, $NC\underline{H}_3$); 7·17, 8·09 (ABq, J_{AB} = 14 Hz, 4 allylic H); M.S. *m/e* 390 (M^+), 227, 129, 119.

Reduction of **12** afforded as above during 24 hr, **16**, m.p. 240–244° identical to the above product.

Diels-Alder adduct **14**. This was prepared as above from a soln of the triene **13** (16 mg; see below) in CH_2Cl_2 (1 ml) and the dienophile (12 mg) in CH_2Cl_2 (1 ml). The solvent was replaced by a few drops of MeOH. The colorless leaf-like crystals (18 mg; 65%) had m.p. 280–281° (MeOH). From the mother liquid another crop (3 mg; 10%) was obtained. (Found: C, 63·98; H, 4·68; N, 13·98; M. W. 390. $C_{21}H_{18}N_4O_4$ requires: C, 64·60; H, 4·65; N, 14·35%; M.W. 390·39); UV(MeOH): 254 nm (1850); IR(KBr): 1800, 1785, 1715, 1705 cm^{-1} (CO); NMR($CDCl_3$): τ 2·58 (s, 5 arom H); 3·45 (t, 2 vinylic H in diaza system); 3·87–4·37 (m, 2 vinylic H); 4·58–5·09 (m, 2 allylic $C\underline{H}N$); 6·93 (s, $NC\underline{H}_3$); 7·67–8·50 (m, 2 allylic H + 2$C\underline{H}_2$); M.S. *m/e* 390 (M^+), 227, 129, 119.

Reduction as above during 2 hr gave **16**, m.p. 241–242·5° identical to the above.

Preparation of bis-*irontricarbonyl complexes* **19** *and* **20**. (a) To a soln of **2** (1·8 g) in dry n-dibutyl ether (200 ml) was added iron pentacarbonyl (10 g) and the whole was heated under N_2 and reflux with stirring during 15 hr. The mixture was cooled and filtered, all under N_2. The solid was washed with boiling EtOAc. The combined filtrates were evaporated to dryness affording a crude yellow solid (2·94 g; 67%). According to NMR this consisted of 75% of **19**[4] and 25% of **20**. After fractional crystallization from hexane methylene chloride, pure crystals of **19** were first obtained. Concentration of mother liquirs gave cubes of nearly analytically pure **20**. Recrystallization afforded yellow **20**, m.p. 179–180° (hexane (19) –CH_2Cl_2(1)). Turbid solns (containing decomposition products) are best filtered through cotton wool as clarification is a prerequisite to crystal formation.

(b) A mixture of **2** (1·01 g) and $Fe_2(CO)_9$ (10·5 g) and dry thiophene-free benzene (400 ml) was heated under N_2 and reflux with stirring for 17 hr. After cooling, the green (formation of $Fe_3(CO)_{12}$) soln was filtered under N_2. Removal of solvent gave a green viscous oil containing products and $Fe_3(CO)_{12}$. Separation was effected on basic alumina (Merck grade I; 62 g) with hexane-benzene as eluent, polarity increasing by 10% for each 250 ml of solvent mixture. First **19** was obtained (432 mg after crystallization), then **20** (870 mg after crystallization). Total yield 54% in a ratio of 1 : 2, respectively. **20**: (Found: C, 46·52; H, 2·48; N, 2·93; M.W. 493. $C_{19}H_{11}NO_8Fe$ requires: C, 46·29; H, 2·25; N, 2·84%; M.W. 492·99); UV(MeOH): 302 nm (9200); IR(KBr): 2060, 2050, 1985 (CO of iron tricarbonyl); 1775, 1705 cm^{-1} (imide CO). NMR ($CDCl_3$): τ 4·38 (q, 2 central dienic H complexed to metal); 4·73 (q, 2 central dienic H complexed to metal); 6·80 (q, 4 term dienic H complexed to metal) 7·10 (s, $NC\underline{H}_3$); M.S. *m/e* 493 (M^+), 465 (M^+–CO), 437 (M^+–2CO); 409 (M^+–3CO); 381 (M^+–4CO), 353 (M^+–5CO), 325 (M^+–6CO), 269 (M^+–6CO–Fe), 212 (M^+–2Fe$(CO)_3$–H).

Irontricarbonyl complex **21**. To a solution of **19** (303 mg) in EtOAc–MeOH (1 : 1, 40 ml) was added dropwise with magnetic stirring at room temp during 10 min a soln of ceric ammonium nitrate (1·00 g) in MeOH (20 ml). Stirring was continued for 30 min more, the solvent was removed and the residue was washed with water (100 ml) and extracted with EtOAc thrice. Drying and removal of the solvent gave a highly pure light yellow solid (209 mg; 96%). It gave crystals, m.p. 173–173·5° (hexane). (Found: C, 54·06; H, 3·28; N, 4·37; M.W. 353. $C_{16}H_{11}NO_5Fe$ requires: C, 54·42; H, 3·14; N, 3·97%; M.W. 353·11); IR(KBr): 2060, 2050, 2000 (CO of $Fe(CO)_3$, 1770,

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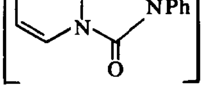
*The ion at 227 is usually of high abundance in mass spectra of the Diels-Alder adducts of the triazolinedione. It corresponds to



1705 (imide CO), 1650 cm^{-1} (conj C=C); NMR ($CDCl_3$): τ 4·13 (s, A_4, 4H in free diene); 4·77 (q, 2 cent H in complexed diene); 6·27 (q, 2 term H in complexed diene); 7·01 (s, $NC\underline{H}_3$); M.S. *m/e* 353 (M^+), 325 (M^+–CO), 297 (M^+-2CO), 269 (M^+-3CO), 252, 241, 226.

Irontricarbonyl complex **22**. A soln of **20** (202 mg) in EtOAc–MeOH (1 : 1; 26 ml) was treated dropwise with a methanolic (12 ml) soln of ceric ammonium nitrate (665 mg) and worked up as described for **21**. The crude product contained (NMR) 90% of **22** and 10% of **21**. Fractional crystallization afforded **22** as the first fractions, m.p. 199–200° (Hexane-methylene chloride). (Found: C, 54·42; H, 3·23; N, 4·47; M.W. 353. $C_{16}H_{11}NO_5Fe$ requires: C, 54·42; H, 3·14; N, 3·97%; M.W. 353·11); IR(KBr): 2060, 2005, 1990 (CO of $Fe(CO)_3$), 1780, 1705 (imide CO), 1655 cm^{-1} (conj C=C); NMR($CDCl_3$): τ 3·90–4·47 (AA'BB', 4 dienic H); 4·67 (q, 2 cent complexed dienic H); 6·95 (q, 2 term complexed dienic H); 7·17 (s, $NC\underline{H}_3$); M.S. *m/e* 353 (M^+), 325 (M^+–CO); 297 (M^+–2CO), 269 (M^+–3CO), 213 (M^+–$Fe(CO)_3$).

Attempts at reducing **21** and **22** in EtOAc, MeOH, AcOH in the presence of PtO_2 or Pd/C at atm pressure and 40 psi during hours or days failed and starting materials were recovered.

Irontricarbonyl complex **23**. The dienic methylimide,[8] m.p. 150–152° (see preparation of **2** above) (1·9 g) was brominated as above with NBS (1·57 g) in CCl_4 (150 ml). After the usual workup with DMF (150 ml), extraction with ether and EtOAc and removal of solvent, an oil was obtained containing the triene **11** with the tetraene **2** and some starting diene. However, the above ether extract contains a roughly 1 : 1 mixture of the triene and diene. This extract afforded starting material (500 mg) for the preparation of **23**.

(a) When this was treated with $Fe_2(CO)_9$ (1·5 g) in dry benzene (80 ml) and the whole heated under N_2 and reflux for 16 hr with stirring and worked up as above, a crude yellow product was obtained (790 mg). This contained a 1 : 1 mixture (NMR) of the starting diene and **23**. Crystallization afforded pure **23** (325 mg; 40%), m.p. 155–156° (Hexane-methylene chloride).

(b) An alternative route started from a mixture of the triene (3)-tetraene **2** (1) (2·9 g) treated as above with $Fe(CO)_5$ (2·5 g). After the usual workup as above fractional crystallization from hexane–CH_2Cl_2 first afforded pure **19** as yellow needles (580 mg). At a later stage **23** crystallized as yellow conglomerates (1·01 g), m.p. 155–156°. Additional amounts of each were obtained. At one stage the mother liquor deposited an orange-brown oil. The supernatant was decanted. Slow and difficult crystallization of the oil gave the yellow **24** m.p. 123–124°, which according to its spectral properties is the complex of the rearranged triene.[12] Total yields: **23** (1·45 g; 30%), **24** (0·62 g; 13%), **19** (870 mg). **23**: (Found: C, 54·15; H, 3·77; N, 4·01; M.W. 355. $C_{16}H_{13}NO_5Fe$ requires: C, 54·11; H, 3·69; N, 3·95%; M.W. 355·12); IR(KBr): 2045, 1990, 1970 (CO of $Fe(CO)_3$), 1775, 1710 cm^{-1} (imide CO); NMR($CDCl_3$): τ 4·20 (t, 2 vinylic H); 4·57 (q, 2 cent complexed dienic H); 6·63 (q, 2 term complexed dienic H); 7·03 (s, $NC\underline{H}_3$); **24**: (Found: C, 54·06; H, 3·62; N, 3·88%; M.W. 355).

Treatment of **23** with NBS caused no reaction. Heating **23** with $Fe(CO)_5$ in dibutyl ether did not give **24**.

11,13 - *Dioxo* - 12 - *methyl* - 12 - *aza*[4.4.3]*propella* - 2,4,8 - *triene*, **11**. The complex **23** (556 mg) was stirred overnight at room temp with ceric ammonium nitrate (2·7 g) in MeOH–EtOAc (1 : 1; 80 ml). After the usual workup the colorless **11** was obtained (308 mg; 90%), m.p. 72–79°. The analytical sample had m.p. 79–84° (light petroleum 40–60°). (Found: C, 72·75; H, 5·84; N, 14·93; M.W. 215. $C_{13}H_{13}NO_2$ requires: C, 72·54; H, 6·09; N, 14·87%; M.W. 215·25). UV(MeOH): 264 (2280), 274 (2180), 285 nm (sh, 1290). IR($CHCl_3$): 1765, 1700 (imide CO), 1650 cm^{-1} (conj C=C). NMR ($CDCl_3$): τ 3·90–4·75 (m, 6 vinylic H); 7·00 (s, $NC\underline{H}_3$); 7·20, 7·98 (ABq, 4 allylic H).

11,13 - *Dioxo* - 12 - *methyl* - 12 - *aza*[4.4.3]*propella* - 2,4,7 - *triene*, **13**. The complex **24** (90 mg) in acetone (3 ml) was treated dropwise with the ceric salt (0·55 g) in acetone (7 ml) and the whole was stirred overnight. After removal of solvent, water was added to the residue and the whole was extracted with ether. The extract was dried ($CaCl_2$) and the solvent removed. An oil was obtained which began to solidify on standing (52 mg; 98%). It was distilled (130° 0·1 torr) affording **13**, m.p. 65–66°. (Found: C, 72·71; H, 5·62; N, 15·01; M.W. 215); IR($CHCl_3$): 1770, 1705 (imide CO), 1650 cm^{-1} (C=C); NMR($CDCl_3$): τ 3·80–4·53 (m, 6 vinylic H); 7·00 (s, $NC\underline{H}_3$); 7·03 (m, 2 allylic H); 7·63–8·33 (m, 2 $C\underline{H}_2$).

Irontricarbonyl complex **25**. A soln of the diene **9** (215 mg) and $Fe_2(CO)_9$ (1·32 g) in dry benzene (100 ml) was heated under reflux for 16 hr. After the usual workup the crude product was dissolved in EtOAc and the soln filtered rapidly through basic alumina. Removal of the solvent afforded the yellow complex **25** (299 mg; 84%). It was identical to that obtained from **9** and $Fe(CO)_5$.[10]

Reduction of **23** (58 mg) with PtO_2 (5 mg) in EtOAc (15 ml) at atm pressure of hydrogen during 3 days afforded **25**.

Reaction of **25** *with triazolinedione*. To a soln of **25** (106 mg) in CH_2Cl_2 -light petroleum 60–70° (1 : 1, 8 ml) was added dropwise a soln of the dienophile (213 mg) in CH_2Cl_2 (10 ml) at room temp with magnetic stirring. After 20 min a slight colorless suspension appeared. This was removed by filtration (1 mg) and the whole was stirred for 48 hr. The solvent was removed and the resulting mixture was separated on a column of basic alumina (10 g) using CH_2Cl_2. At first **25** was obtained (67 mg). Then a mixture of **25** with the Diels-Alder adduct (2 : 3 by NMR) was obtained. The latter was separated by preparative TLC on alumina plates using CH_2Cl_2. More of **25** was obtained ($R_f = 0·8$) and adduct **10** ($R_f = 0·5$; 5% yield but quant. on basis of recovered **25**) identical to product **10** described above.

Reaction of **23** *with triazolinedione*. To a soln of **23** (294 mg) in CH_2Cl_2 (10 ml) was added dropwise a soln of the dienophile (300 mg) in CH_2Cl_2 (8 ml) during 20 min. The red color persisted throughout the day but after 24 hr the color was darker. The solvent was removed and the residue was separated using preparative alumina plates and CH_2Cl_2. The upper fraction was **23** (30 mg; $R_f = 0·8$). The second fraction was **29** (!) (30 mg; 7%). The brown material remaining at the bottom of the plate was extracted with CH_2Cl_2 containing 2% MeOH. The brown material dissolved in MeOH afforded several spots in TLC. Evaporation of its soln in CH_2Cl_2 very slowly gave reddish-brown crystals of which only the IR spectrum could be determined (KBr): 2060, 1990 (CO of Fe $(CO)_3$), 1780, 1700 (imide CO), 1600 cm^{-1} (arom C=C). Perhaps the product **31**, dec 225°, is a mixed complex of **23** with CO and the dienophile (see discussion above).

Reaction of **24** *with triazolinedione*. To a soln of **24** (100 mg) in CH_2Cl_2 (6 ml) was added as for **23** a soln of the dienophile (230 mg) in CH_2Cl_2 (12 ml). After exactly the same workup the first fraction was **24** (12 mg; $R_f = 0{\cdot}7$), then the adduct **14** (15 mg; 10%; $R_f = 0{\cdot}5$), identical to **14** obtained without intervention of the complex. A brown material did not move from its original position on the plate.

Reaction of **26** *with triazolinedione.* To a solution of **26**[10] (156 mg) in CH_2Cl_2 (3 ml) was added dropwise a soln of the dienophile (203 mg) in CH_2Cl_2 (7 ml). No gas was evolved until 20 min had elapsed. The 12 ml was collected during 2 hr. After 48 hr stirring no change in volume was observed. Removal of solvent and preparative TLC on alumina as above gave **26** (45 mg; $R_f = 0{\cdot}8$) and then adduct **4** (107 mg; quant based on recovered **26**; $R_f = 0{\cdot}5$) identical to **4** obtained directly from **3**.

Reaction of **20** *with triazolinedione.* (a) To a soln of **20** (39 mg) in CH_2Cl_2 (1 ml) was added dropwise a soln of the dienophile (36 mg) in CH_2Cl_2 (3 ml). After stirring for 36 hr the solvent was removed. Separation as above by TLC gave **20** (29 mg) and a mixture (7 mg) which by NMR is composed of equal amounts of **29** and **30**.

(b) To a soln of **20** (33 mg) in CH_2Cl_2 (1 ml) was added dropwise a soln of the dienophile (85 mg) in CH_2Cl_2. After stirring for 48 hr more dienophile (100 mg) was added and this was added (100 mg) also after 96 hr. After a total of 120 h the solvent was removed. By TLC a mixture (39 mg) of **20**, **29** and **30** was obtained and then the *bis*-adduct **17** (7 mg) identical to product obtained directly from **2**.

Reaction of **22** *with triazolinedione.* A soln of **22** (35 mg) in CH_2Cl_2 (0·5 ml) was treated as above with one of the dienophile (20 mg) in CH_2Cl_2 (0·5 ml). The color disappeared at once (3 min). After stirring 20 min more the solvent was removed and the residue triturated with MeOH. Very light yellow crystals of **30** precipitated (42 mg; 80%), m.p. 225–240° (dec). (Found: M.W. 528. $C_{24}H_{16}N_4O_7Fe$ requires M.W. 528·24); IR(KBr): 2050, 1995, 1985, (CO of $Fe(CO)_3$), 1780, 1760, 1690 cm^{-1} (imide and ureide CO); NMR($CDCl_3$): τ 2·63 (s, 5 atom H); 3·30 (t, 2 vinylic H); 4·62 (q, 2 cent complexed dienic H); 4·78 (m, allylic H); 6·90 (q, 2 term complexed dienic H); 7·00 (s, $NC\underline{H}_3$).

Reaction of **30** (23 mg) dissolved in MeOH–EtOAc (1:1; 12 ml) with ceric ammonium nitrate (175 mg) in MeOH (10 ml) and the usual workup afforded **15**, identical to that formed directly from **2**.

11,13 - *Dioxo* - 12 - *methyl* - 12 - *aza*[4.4.3]*propellane.* Reduction of **2** (50 mg) dissolved in EtOAc (15 ml) was accomplished at atm pressure of hydrogen using PtO_2 (3 mg) during 1·5 hr. Removal of catalyst and solvent gave a quant yield (50 mg) of the octahydro derivative. The crude solid was distilled (100°/0·2 torr) affording a colorless solid, m.p. 70–72°. (Found: C, 70·65; H, 8·74; N, 6·45; M.W. 221. $C_{13}H_{19}NO_2$ requires: C, 70·55; H, 8·65; N, 6·33%; M.W. 221·29); IR($CHCl_3$): 1775, 1695 (imide CO), 1380 cm^{-1} ($NC\underline{H}_3$); NMR($CDCl_3$): τ 7·03 (s, $NC\underline{H}_3$); 8·17–8·75 (m, $16C\underline{H}_2$).

12 - *Methyl* - 12 - *aza*[4.4.3]*propellane.* A soln of the dienic methylimide (1·07 g; see preparation of **2** above) in dry dimethoxyethane (50 ml) was added under N_2 with stirring to a soln of LAH (0·8 g) in dry dimethoxyethane (50 ml). The whole was heated under reflux for 7 days. Decomposition was effected by adding water (2·4 ml), 15% of NaOH (0·8 ml), water (0·8 ml). The solid formed was removed by filtration and extracted with boiling dimethoxyethane. After removal of solvent the oily residue was dissolved in CH_2Cl_2 and dried (Na_2SO_4). Removal of solvent afforded the amine as a colorless oil, b.p. 65–66°/0·6 torr (571 mg; 67%).

The picrate formed in MeOH had m.p. 215–216° (acetone). (Found: C, 54·06; H, 5·30; N, 13·02; M.W. 418. $C_{19}H_{22}N_4O_7$ requires: C, 54·54; H, 5·30; N, 13·39%; M.W. 418·40); NMR of free amine ($CDCl_3$): τ 4·48 (t, 4 vinylic H); 7·18 (s, $4\ C\underline{H}_2N$); 7·50 (s, $NC\underline{H}_3$); 7·98 (q, 8 allylic H); M.S. of picrate *m/e* 229 (M^+-amine), 189 (M^+-picric acid), 174, 160.

The amine could be obtained in similar yield and after 48 hr reduction of the same starting material when $NaA1H_2(OCH_2CH_2OCH_3)_2$ was used.

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