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PROPELLANES–XXI[a,b]

PREPARATION AND DECOMPOSITION OF AZOPROPELLANES

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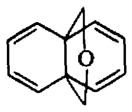
Abstract—Several mono- and *bis*-azopropellanes have been prepared from adducts of **1** and **2**. An intramolecular oxidation-reduction during hydrolysis of such adducts leads to novel results. Thermal and photolytic cleavage of the azopropellanes has been studied.

We have reported the preparation of the two possible monoadducts **3** and **4** of the tetraenic propellane ether **1** with the potent dienophile **2**, as well as two of the three possible *bis*- adducts, **5** and **6**.[1]



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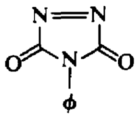

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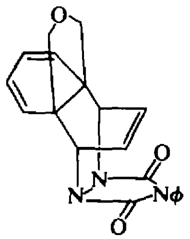

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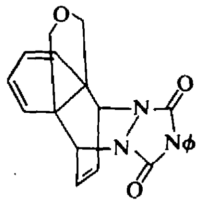

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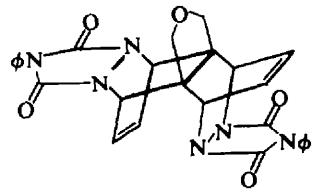

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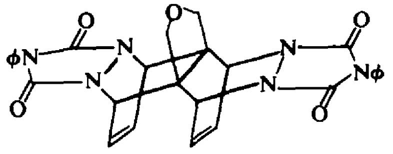

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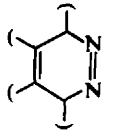
Clearly these adducts can serve as precursors for azopropellanes. These in turn can be decomposed. Their products would be of great interest in view of the different configurations of the substrates themselves and of the intermediates during decomposition. The first problem, however, was a more prosaic one, that of hydrolysis of the N-phenyltriazolinedione ring. Such hydrolyses have been accomplished by potassium hydroxide to yield the substituted, cyclic, hydrazine.[2] The latter is then oxidized to the azo compound by means of air, mercuric oxide or manganese dioxide,[2] or by means of cupric chloride.[3] In the last case the azo compound formed complexes with cuprous chloride and addition of ammonium hydroxide releases it from the complex. Azo compounds of type **7** cannot normally be isolated as they are known to undergo, spontaneously, retro-Diels-Alder reaction to afford the corresponding diene and nitrogen. Thus we decided *a priori* that we would investigate mainly the behavior of the dihydro derivatives of **3** and **4** (isolated double bond is reduced) and the tetrahydro derivatives of **5** and **6**. Catalytic reduction of the two isolated double bonds in the latter presented no difficulty



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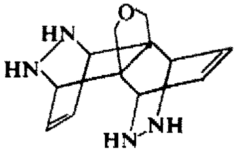
[a] Dedicated to the 60th birthday of our esteemed colleague F. Sorm, Prague.

[b] Part XX. C. Amith and D. Ginsburg, *Tetrahedron*.

and gave **13** and **17**, respectively. The selective reduction of an isolated double bond in **3** or **4** in the presence of a diene system (also capable of undergoing catalytic reduction) was accomplished by reducing the irontricarbonyl complexes of the respective dienes,[5] followed by removal of the $Fe(CO)_3$ group with ceric ion.

Although we appreciated the fact that compounds of type **7** would be unstable thermally we hydrolyzed **5**, at first, with potassium hydroxide in ethylene glycol at 150° as one expects the hydrazo compound **8** to form. The result was nevertheless unexpected. The product of hydrolysis had the structure **9** or **10**. We were unable to distinguish at this stage between the two possible configurations. In any event, nitrogen was lost, a diene system appeared and an intramolecular oxidation-reduction had evidently taken place.



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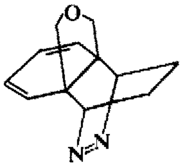

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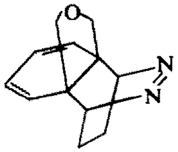

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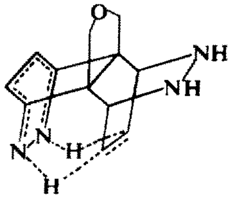
Scheme 1 presents an explanation of the course of hydrolysis.

If scheme 1 be correct then the product of hydrolysis of **5** would appear to be the hydrazo compound **11** which is readily oxidized by air during workup to afford **10**, thus settling the configuration of **10**.

Scheme 1 is reminiscent in its oxidation-reduction step, of the transition state usually written for diimide reduction of a double bond.[6,7] Here the transition state **12** is aided and abetted by the rigid configurations in the *bis*-adduct **5** and its primary hydrolysis product. The driving force in both cases is the formation of a molecule of nitrogen: from diimide after transfer of two H atoms to the double bond undergoing reduction and in the present case via a retro-Diels-Alder



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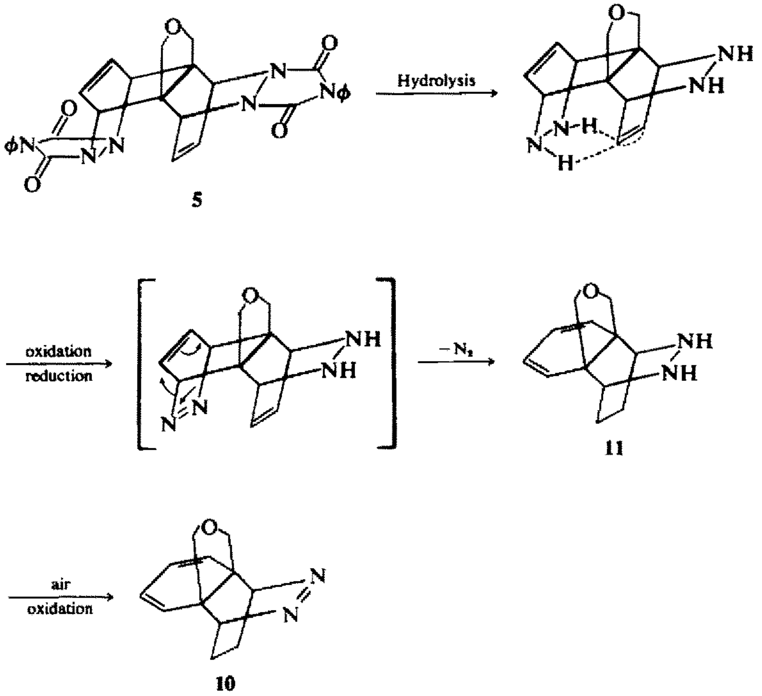


Scheme 1

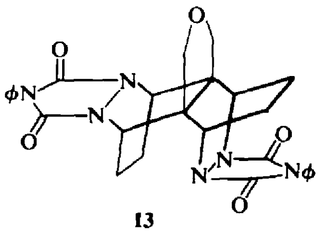
reaction in the dienic (C=C, N=N) system formed after transfer of two H atoms to a proximate double bond.

Hydrolysis of dihydro-**3** afforded **9**, the only possible isomer of **10**.

Catalytic reduction of **5** afforded the tetrahydro derivative **13**. Alkaline hydrolysis of **13** did not afford the *bis*-hydrazo compound as this evidently was readily oxidized by the air present throughout workup. The *bis*-azo compound **14** was thus isolated, albeit in 25% yield. Attempts to lower the temperature of hydrolysis (KOH in boiling aqueous methanol rather than in ethylene glycol at 150°) afforded a mixture of phenylureides **15** and **16**.

Catalytic reduction of **6** was possible only with concurrent reduction of the N-phenyl group. Thus hydrolysis of **17** (KOH in boiling aqueous ethanol) afforded an analogous mixture of cyclohexylureides **18** and **19**. The bottleneck in the hydrolytic process is in the second step in which ureide groups must be cleaved. This problem has been solved[8] by the use of cupric chloride to oxidize the system-NH-NCONHR to give the azo compound complexed to CuCl. The latter upon treatment with ammonium hydroxide releases to azo compound. By employing this procedure for **17** which is more difficult to hydrolyze than the N-phenyl derivative **13**, as well as for **13** itself, **20** and **14** were obtained in 55 and 60 percent yield, respectively, and our synthetic bottleneck was overcome.

Heating of **14** at 200° afforded **9** in 35% yield, 11% of the starting material was recovered and the balance was insoluble material which was not characterized. The result is reminiscent of that obtained during hydrolysis of **5** (scheme 1), and may be explained as shown in scheme 2. The transfer of hydrogen as shown in the oxidation-reduction step in scheme 2 is an allowed reaction.[9,10] It was possible to prove the intermediacy of **21** through trapping by succinic anhydride. When **14** was pyrolyzed at 200° in the presence of excess



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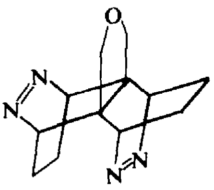

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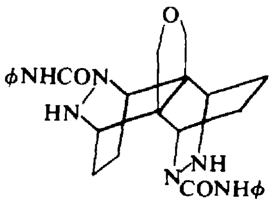

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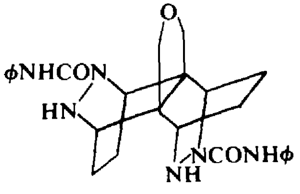

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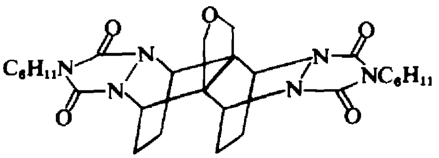

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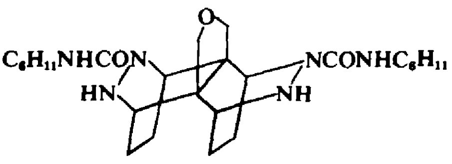

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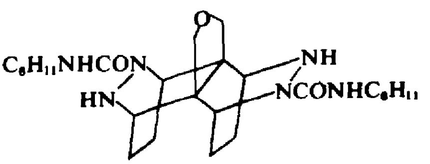

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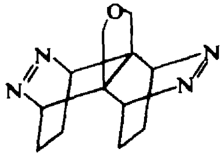

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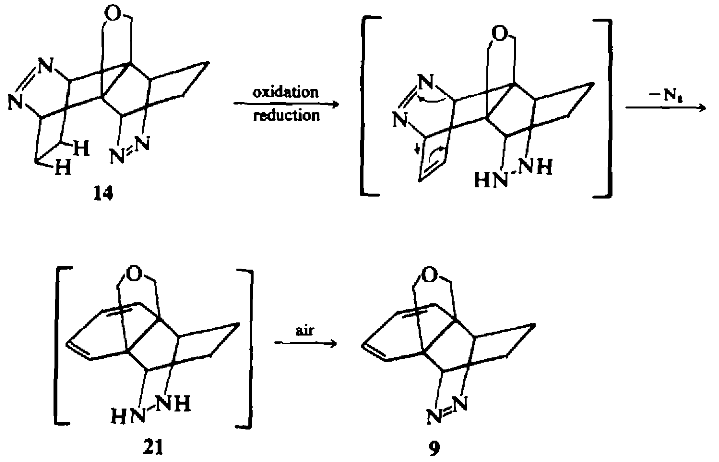
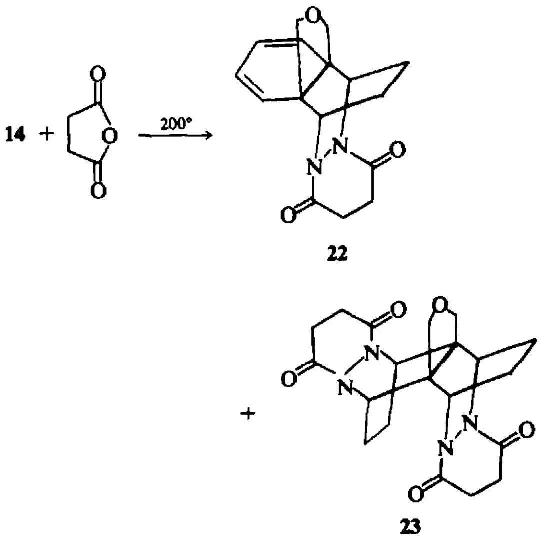
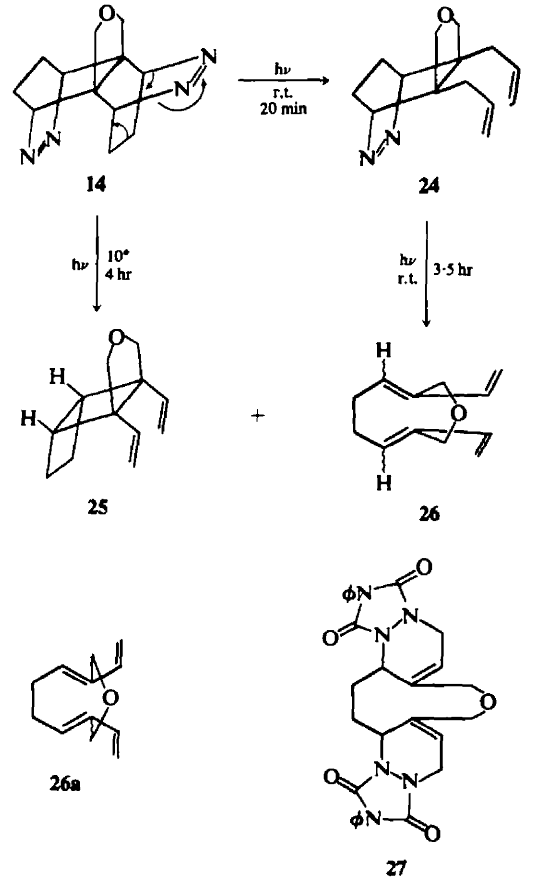


SCHEME 2

succinic anhydride, **22** was isolated (in 40% yield) as well as **23** (in 6·3% yield). The formation of the *bis*-adduct **23** points to the possibility that an intermolecular hydrogen-transfer mechanism exists in addition to the intramolecular step described in scheme 2.

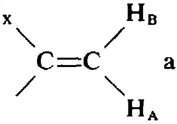


Scheme 3 summarizes the results of irradiation of **14** through pyrex. Room temperature irradiation for 20 min gave **24** (57% yield) with concurrent formation of one equivalent of nitrogen. Irradiation of the product for an additional 3·5 hr yielded a mixture of nitrogen-free products, **25** and **26** (33 and 22%, respectively) as well as recovered **24** (5%) and insoluble material. Alternatively, irradiation of **24** for 4 hr at 10° afforded the mixture of oils, **25** and **26**. At these irradiation temperatures **25** does not isomerize thermally to give **26**. The latter is either stable in, or readily attains, the conformation **26a** as it readily reacts with two equivalents of 4-phenyl-1,2,4-triazoline-3,5-dione to afford the *bis*-adduct **27**. Compounds **24** and **25** do not react with this dienophile.



SCHEME 3

It is possible to interpret the NMR spectrum of compounds **24**–**26** in order to deduce the structure of **24**. Whilst **25** and **26** exhibit ideal ABX systems



as shown in Fig 1, in contrast, the vinyl groups in **24** do not appear as an ABX system.

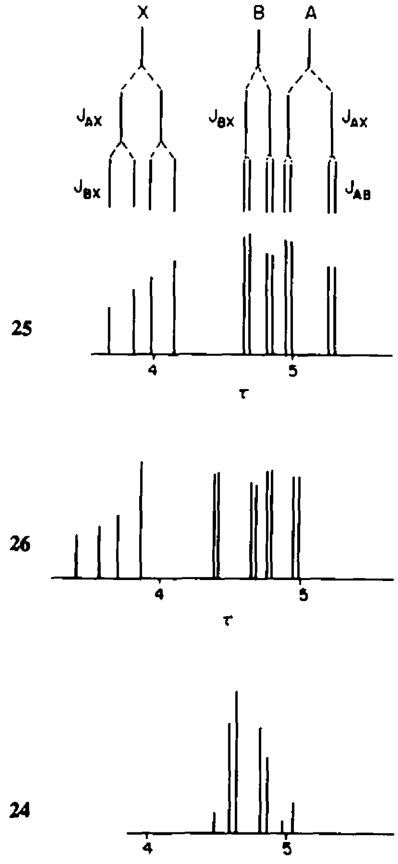
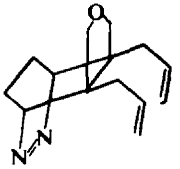


Fig 1.

Such a drastic difference may be ascribed to the influence of the magnetic field of the azo group in **24** upon its vinyl groups. This is significant only if the configuration of **24** is as shown in its structural formula.

In the first photolytic step in scheme 3 only one mono-azo isomer is obtained, **24**, not **28**. This requires **14** to decompose selectively in order to afford nitrogen only from its "upper" (*syn* with respect to ether ring) azo group (as written in scheme 3). Evidently a contributing factor to this selectivity is the orthogonal overlap during rehybridization between the two incipient sp^2 orbitals of the azo group and the π orbitals of the double bond (**29**). A similar explanation has been used to explain stereoselectivity during a thermal isomerization.[11]



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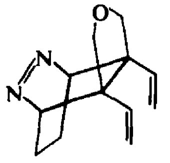

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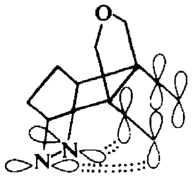

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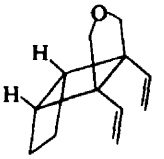
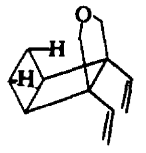
The configuration of **25** was determined with the aid of $Eu(DPM)_3$. Clearly the bridgehead protons in the bicyclohexane moiety in **25** would be shifted further downfield in the presence of the shift reagent that the other four cyclobutane protons, if the cyclobutane ring is *anti* with respect to the ether ring (**25a**). In the *syn*-configuration, of course the hydrogens shown in **25b** would suffer the largest downfield shift. The results show (Experimental section) that the configuration corresponds to **25a** as already recorded in scheme 3.



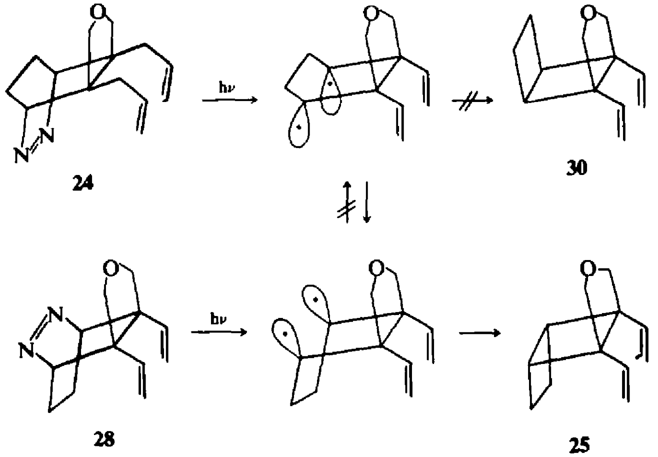
25a



25b

Irradiation for 20 min of the symmetrical *bis*-azo compound **20**, necessarily leads to loss of a nitrogen molecule from the "upper" side. The monoazo compound **28** resulting in quantitative yield is an isomer of **24**. This fact proves its configuration unequivocally and is supported by the appearance of an ABX system for the vinyl groups (albeit the bridgehead methine proton hides part of the ABX system). This also supports the assignment of configuration to **24** (no ABX for vinyl group) on the grounds of the proximity of its vinyl groups to its azo group. When irradiation was carried out for 10 hr the same products, **25** and **26**, already mentioned above (from **24**), were obtained. Clearly then, there must be inversion of configuration somewhere along the line if the same products **25** and **26** were obtained from isomers of varying configuration, **24** and **28**.

This problem of whether intermediate biradicals in such reactions invert or retain their configuration is a more general one and we shall discuss the results obtained from our propellane substrates. A concerted photochemical [$\sigma 2s + \sigma 2s$] process is allowed.[12] We believe, however, that since **24** and **28** both afford the same **25** and **26**, the 1,4-biradical mechanism obtains (scheme 4).

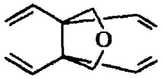


Scheme 4

The mechanistic dichotomy and related problems appear in a number of published examples in both thermal and photochemical examples.[13] In our case there is clearly inversion of configuration during the process **24** → **25**. Perhaps retention is achieved in irradiation of **28** due to too great steric interaction between the hydrogens α- to the ether oxygen and the hydrogens shown in **30** (scheme 5).

It was found that the half-life of **20** was much lower during irradiation than that of **14** (relative $t_{1/2} = 10$ min and 12 hr, respectively). It may very well be that the larger non-bonded interactions between hydrogens of the two sets of parallel methylene groups in **20** cause its more rapid decomposition. When one mole of nitrogen has been formed, the mono-azo compound **28** in which this interaction no longer exists has a relative half-life of *ca* 16 days. We have explained the stereoselective photo-decomposition of **14** in terms of the intermediate **29**. This may also explain the relative stability of **28** during irradiation as compared to **24** (relative $t_{1/2} \sim 9$ days).

One might ask why irradiation of a *bis*-azo compound such as **14** or **20** does not lead to 3,3,4,4-tetravinyltetrahydrofuran **31** but rather leads ultimately to a mixture of **25** and **26**.



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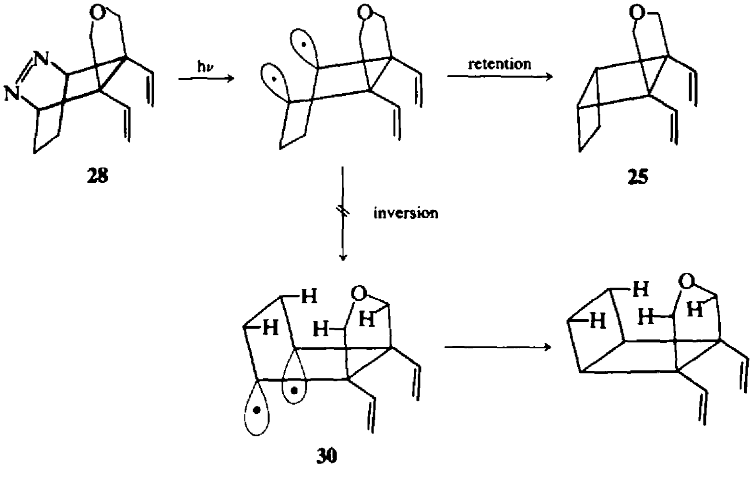
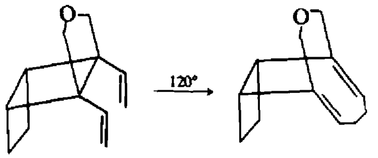


Scheme 5

It was found that heating **25** at 120° in tetrachloroethylene for 1 hr yielded the cyclic diene **32** in a classic (thermal) Cope rearrangement. Had **31** been formed it could also, in principle, undergo a Cope rearrangement leading to **26**!



25 **32**

If such actually occurs at low temperature it is understandable that **31** is not isolated. Comparison of NMR spectra of crude irradiation mixtures at different times and temperatures enables one to observe a singlet belonging perhaps to the protons α- to the ether oxygen of **31** which disappears with time, whilst the corresponding singlet attributed to **26** increases. Concurrently two doublets and three singlets which could be attributed to the ABX vinylic system in **31** disappear. Although this picture does not constitute proof for the formation and existence of **31** in the reaction mixture, the thermal behavior of **25** and the NMR behavior provides some support for such a view. Low temperature photochemical work with this system would presumably provide the proof.

EXPERIMENTAL

UV spectra were measured on a Cary 15 instrument. IR spectra were measured on a Perkin-Elmer model 237 grating spectrophotometer. 60 MHz NMR spectra were measured on the corresponding Varian instrument. Mass spectra were measured on an Atlas CH 4 instrument using the heated inlet system at 200°. The electron energy was maintained at 70 eV and the ionization current at 20 μA. All m.ps are uncorrected.

Preparation of irontricarbonyl derivative of **3**. To a soln of **3**[1] (0·5 g) in toluene (100 ml) was added iron pentacarbonyl (3·9 g) and the whole was heated under reflux for 17 hr with stirring, under N_2. After cooling the solid formed was removed. After removal of solvent at reduced pressure the residue was triturated with light petroleum (60–70°), affording the *organometallic derivative* (0·57 g; 81%), m.p. >350° (dec begins at 250°; benzene-hexane). On the basis of previous work it is tentatively assumed that the $Fe(CO)_3$ group enters from "above".[1] (Found: C, 56·73; H, 3·93; N, 8·20; M.W. 459. $C_{23}H_{17}N_3O_6Fe$ requires: C, 56·69; H, 3·48; N, 8·62%; M.W. —CO, 459·23); IR($CHCl_3$): 2050, 1980 (Fe-CO), 1760, 1710 (imide CO), 1600 cm^{-1} (arom C=C); UV-(CH_3CN): nm(ε) 214 end (38500); 218 sh (37600); 245 sh (18800). NMR($CDCl_3$): τ 2·50 (s, 5 ArH); 3·48 (t, J = 3·5 Hz, 2 vinyl H); 4·25–4·44 (m, 2 dienic central H); 5·43 (t, J = 3·5 Hz, 2 allylic methine H); 5·96, 6·25 (ABq, J = 9·5 Hz, $4C\underline{H}_2O$); 7·15–7·34 (m, 2 terminal dienic H).

Catalytic reduction of irontricarbonyl derivative of **3**. Reduction was carried out with substrate (0·33 g) in EtOAc (60 ml) in the presence of Pd-C (5%; 90 mg) at room temp and atmospheric pressure during 25 hr. After removal of catalyst and solvent the residue of *dihydro compound* (0·31 g; 93%) had m.p. >350° (dec beg at 235°; light petroleum 60–80°). In cases when reduction was incomplete catalyst was added and the reduction conducted until the theoretical volume of H_2 was absorbed. (Found: C, 56·69; H, 4·08; N, 8·44; M.W. —CO, 461. $C_{23}H_{19}N_3O_6Fe$ requires: C, 56·44; H, 3·90; N, 8·57%; M.W. —CO, 461·16); IR($CHCl_3$): 2050, 1980, 1750, 1690 cm^{-1}; UV(CH_3CN): 214 end (37600); 218 sh (36500); 275 sh (3100); NMR($CDCl_3$): τ 2·21–2·52 (m, 5 ArH); 4·47–4·65 (m, 2 cent dienic H); 5·68–5·80 (br s, 2 methine H); 6·02 (s, 4 CH_2O); 7·00–7·20 (m, 2 term dienic H); 7·92–8·14 (m, 4 CH_2).

Removal of irontricarbonyl group. The complex of dihydro **3** (78 mg) dissolved in EtOAc (15 ml) was treated dropwise while stirring with a soln of ceric ammonium nitrate (288 mg; 10% excess) in MeOH (15 ml). Gas (CO) is evolved during 30 min. Measurement of the volume permits control of the reaction. After a total of 1 hr stirring, the solvent was removed in a vacuum and the residue was treated with water and extracted with CH_2Cl_2. After drying (Na_2SO_4), removal of solvent and trituration of the residue with MeOH, *dihydro*-**3** was obtained (40 mg; 72%), m.p. 281–283° (dec 270°; aq MeOH). (Found: C, 68·25; H, 5·34; N, 12·10; M.W. 349. $C_{23}H_{19}N_3O_3$ requires: C, 68·75; H, 5·48; N, 12·03%; M.W. 349·38); IR($CHCl_3$): 1760, 1700 (imide CO), 1600, 1500 cm^{-1}; UV(CH_3CN): 220 (15650); 260 sh (2980); 270 sh (2100); NMR ($CDCl_3$): τ 2·54 (s, 5 ArH); 3·72–4·39 (A_2B_2 m, 4 dienic H); 5·67, 6·53 (ABq, J = 10 Hz, $4C\underline{H}_2O$); 5·65–5·84 (br s, 2 methine H); 7·90–8·04 (m, 4 $\underline{C}H_2$).

Direct reduction of **3**. (a) A soln of **3**[1] (0·2 g) in EtOAc (40 ml) was reduced in the presence of PdC (5%; 35 mg) at room temp and atm pressure during 8·5 hr. After the usual workup *hexahydro*-**3** was obtained (185 mg; 91%), m.p. 189–190° (aq MeOH). (b) Dihydro-**3** (20 mg) in EtOAc (4 ml) was similarly reduced to give the identical compound using the same conditions as in (a) with 10 mg of the catalyst. (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%); UV(CH_3CN); 217 (17300); NMR($CDCl_3$): τ 2·24–2·72 (m, 5 ArH); 5·98 (br s, 2 methine H); 5·96, 6·31 (ABq, J = 10 Hz, $4C\underline{H}_2O$); 7·61–8·90 (m, 12 $C\underline{H}_2$).

Reduction of irontricarbonyl derivative of **4**. Reduction was carried out as described above, using the substrate[1] (0·33 g), EtOAc (80 ml), PdC (90 mg) during 22 hr. After the usual workup the *dihydro-compound* was obtained (0·32 g; 97%), m.p. 238° (dec 210°, benzene-hexane). (Found: C, 56·87; H, 4·03; N, 8·53; M.W. 461. $C_{23}H_{19}N_3O_6Fe$ requires: C, 56·44; H, 3·90; N, 8·57%; M.W. —CO, 489·16); UV(CH_3CN): 214 end (39800); 218 sh (39600); 275 sh (59500); NMR($CDCl_3$); τ 2·52 (s, 5ArH); 4·34–4·52 (m, 2 cent dienic H); 5·63–5·77 (m, 2 methine H); 5·28, 6·11 (ABq, J = 10 Hz, $4C\underline{H}_2O$); 7·03–7·28 (m, 2 term dienic H); 7·83–8·10 (m, 4 $C\underline{H}_2$).

Removal of irontricarbonyl group was carried out as described above, using the complex of dihydro-**4** (0·18 g), EtOAc (45 ml) and methanolic (30 ml) ceric ammonium nitrate (0·66 g). After a total of 70 min stirring and the above workup followed by filtering the soln of the residue in CH_2Cl_2 through neutral alumina (5 g), *dihydro*-**4** was obtained (105 mg; 80%), m.p. 230–231° (aq MeOH). (Found: C, 69·18; H, 5·48; N, 11·88; M.W. 349. $C_{20}H_{19}N_3O_3$ requires: C, 68·75; H, 5·48; N, 12·03%; M.W. 349·38); UV(CH_3CN): 217 (16400); 267 (2050); NMR

($CDCl_3$): τ 2·58 (s, 5 ArH); 3·84–4·74 (A_2B_2m, 4 dienic H); 5·55, 6·65 (ABq, $J = 10$ Hz, 4 $C\underline{H}_2O$); 5·74–5·90 (m, 2 methine H); 7·95–8·40 (m, 4 $C\underline{H}_2$).

Preparation of **13**. Reduction of **5**[1] was carried out as above using **5** (1·0 g) EtOAc (200 ml), catalyst (200 mg) during 4 hr. After 1 hr the product began to precipitate. Methylene chloride was therefore added to the mixture and the catalyst was removed. After removal of the solvent mixture at reduced pressure **13** was obtained (0·96 g; 95%), m.p. > 350° (acetone). (Found: C, 63·68; H, 5·00; N, 15·96. $C_{28}H_{26}N_6O_5$ requires: C, 63·87; H, 4·98; N, 15·96%); IR($CHCl_3$): 1760, 1720, 1600, 1500 cm^{-1}; UV(CH_3CN): 222 (37000); NMR($CDCl_3$): τ 2·43 (s, 10 ArH); 5·42–5·57 (br s, 4 methine H); 5·74, 5·92 (ABq, $J = 10$ Hz, 4$C\underline{H}_2O$); 7·17–8·24 (m, 8$C\underline{H}_2$).

Preparation of **17**. Reduction of **6**[1] was carried out using **6** (250 mg) in glacial AcOH (250 ml) with PtO_2 (50 mg) at room temp and atm pressure during 20 hr. After the usual workup **17** was obtained (quant), m.p. > 360° (CH_3CN). (Found: C, 62·62; H, 7·14; N, 15·72; M.W. 539. $C_{28}H_{38}N_6O_5$ requires: C, 62·43; H, 7·11; N, 15·60%; M.W. 538·63); IR($CHCl_3$): 1760, 1700 cm^{-1}; UV(CH_3CN): 230 (5780); 233 (5850); NMR($CDCl_3$): τ 5·53–5·72 (br s, 4 methine H); 5·86 (s, 4 $C\underline{H}_2O$); 6·05–6·33 (m, 2 $C\underline{H}N$); 7·62–8·64 (complex m, 28 $C\underline{H}_2$).

Syn, anti-2,5-7,10-bis-*Azo*-12-*oxa*[4.4.3]*propellane*, **14**

(a) A mixture of **13** (0·23 g), KOH (1·3 g) and ethylene glycol was heated while bubbling in N_2 at 130° for 90 min. After cooling, water (10 ml) was added and the whole was extracted with CH_2Cl_2 (4 × 15 ml). After drying (Na_2SO_4) and removal of solvent in a vacuum the residue was chromatographed on a preparative plate of alumina (E. Merck, PF 254, type E) using CH_2Cl_2 as eluent. The *product* **14** was obtained (26 mg; 25%) identical to the product described below.

(b) A mixture of **13** (0·25 g), KOH (0·7 g), aq (5 ml) MeOH (20 ml) was heated under reflux for 5 hr under N_2. The solvent was removed in a vacuum and the residue extracted with CH_2Cl_2. After workup as above a mixture of two products **15** and **16** was obtained; IR ($CHCl_3$): 3350(NH), 1670(CO), 1600 cm^{-1} (arom C=C). To this mixture was added a soln of cupric chloride (1·48 g) in water (10 ml). Scratching the colorless solid began to form a dark brown solid. The whole was stirred magnetically for 3 hr and the solid was removed and washed consecutively with water, EtOH and ether. The cuprous chloride complex (0·61 g) was decomposed by adding it to cold ammonium hydroxide (conc; 6 ml). The blue soln was extracted with CH_2Cl_2 (3 × 20 ml). After drying (Na_2SO_4) and removal of solvent **14** was obtained (90 mg). Sublimation (90° at 0·1 mm) afforded pure **14** (67 mg; 60%), m.p. 219–220° (dec 206°). (Found: C, 62·07; H, 7·08; N, 23·94; M.W. 232. $C_{12}H_{16}N_4O$ requires: C, 62·05; H, 6·94; N, 24·12%; M.W. 232·28); IR($CHCl_3$): 3000, 2960, 2900 cm^{-1} (CH); UV(CH_3CN): 243 (1455); 247 (1450); 250 (1430); 361 sh (185); 371 (190); 382 (90); NMR ($CDCl_3$): τ 4·75–5·04 (m, 4 methine H); 6·23, 6·54 (ABq, $J = 10$ Hz, 4$C\underline{H}_2O$); 7·80–9·20 (m, 8 $C\underline{H}_2$).

Syn-7,10-*Azo*-12-*oxa*[4.4.3]*propella*-2,4-*diene*, **10**

Hydrolysis of **5**[1] (0·25 g) was similarly effected with KOH (1·5 g) in glycol (10 ml) at 150° during 2 hr stirring with N_2. After workup as for preparing **14** by route (a) above, the azo-compound **10** was obtained (23 mg; 26%), m.p. 200° (dec 175°). (Found: M.W. 202. $C_{12}H_{14}N_2O$ required: M.W. 202·25); IR($CHCl_3$): 2990, 2950, 2860 cm^{-1} (CH); UV(CH_3CN): 242 (3750); 250 (3800); 260 sh (2980); 270 sh (1820); 370 sh (105); 380 (140); NMR($CDCl_3$): τ 3·80–4·67 (A_2B_2m, 4 dienic H); 4·30–5·00 (br s, 2 methine H); 5·94, 6·51 (ABq, 4 $C\underline{H}_2O$); 8·12–8·44, 8·79–9·10 (m, 4 $C\underline{H}_2$).

Syn, syn-2,5-7,10-bis-*Azo*-12-*oxa*[4.4.3]*propellane*, **20**

Hydrolysis of **17** (0·17 g) was effected by heating at 160° with KOH (2·0 g) in aq (8 ml)-EtOH (23 ml) while stirring under N_2 during 45 hr. After workup similar to route (b) for preparing **14** (above) a mixture of **18** and **19** was obtained (0·12 g); IR($CHCl_3$): 3400(NH), 2940, 2870(CH), 1640 cm^{-1} (CO). Workup was continued as above using an aq (7 ml) soln of cupric chloride (0·95 g), affording the complex (0·17 g). Its analogous decomposition and workup afforded **20** (50 mg; 65%), m.p. 204–205° (dec). (Found: M.W. 232. $C_{12}H_{16}N_4O$ requires: M.W. 232·28); IR ($CHCl_3$): 3000, 2960, 2940, 2890 cm^{-1} (CH); UV(CH_3CN): 230 end (520); 258 (410); 360 sh (60); 369 (105); 409 (85).

Anti-7,10-*Azo*-12-*oxa*[4.4.3]*propella*-2,4-*diene*, **9**

(a) Hydrolysis of dihydro-**3** (84 mg) was effected at reflux with KOH (0·39 g) in aq EtOH (1 : 1; 9 ml) while stirring under N_2 during 25 hr. After the usual workup **9** was obtained as an oil which immediately crystallized (34 mg; 70%), m.p. 169–170° (hexane). (Found: C, 71·09; H, 6·98; N, 13·96; M.W. 202. $C_{12}H_{14}N_2O$ requires: C, 71·26; H, 6·98; N, 13·85%; M.W. 202·25); IR(KBr): 3050 (=CH), 2960, 2930, 2850 (CH), 1600 cm^{-1} (C=C); UV(CH_3CN): 240 (2390); 245 sh (2370); 265 sh (2190); 270 (2100); 368 (85); 381 (140); NMR($CDCl_3$): τ 4·05–4·55 (m, 4 dienic H); 4·75–4·94 (br s, 2 methine H); 5·74, 6·62 (ABq, $J = 10$ Hz, 4 $C\underline{H}_2O$); 7·91–8·24, 8·75–9·08 (m, 4 $C\underline{H}_2$).

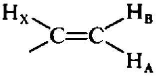
(b) *By pyrolysis of* **14**. The *bis*-azo compound **14** (60 mg) was heated in an open tube at 200° for 6 hr. The mixture was separated on a preparative plate of alumina (E. Merck) using benzene-CH_2Cl_2 for elution. Some **14** was recovered (6·5 mg; 11%), **9** was obtained (18 mg; 35%) identical to that obtained above and a mixture (3·5 mg) of products remained unresolved.

Pyrolysis of **14** *in the presence of succinic anhydride*. A mixture of **14** (60 mg) and succinic anhydride (0·36 g) was heated in a sealed tube under N_2 for 14 hr at 200°. The residue was triturated with CH_2Cl_2 and the insoluble material was removed. After removal of solvent from the filtrate, the use of a preparative plate of alumina (E. Merck) with CH_2Cl_2-$CHCl_3$ as eluent, afforded **22** (29 mg; 40%), m.p. 209–210° (light petroleum 60–70°-acetone) and **23** (6·5 mg; 6%), m.p. 305–308° (dec 285°). **22**. (Found: C, 67·10; H, 6·30; N, 9·63; M.W. 286. $C_{16}H_{18}N_2O_3$ requires: C, 67·11; H, 6·34, N, 9·78%; M.W. 286·32); IR($CHCl_3$): 2940, 2850(CH), 1650 cm^{-1} (CO); NMR($CDCl_3$): τ 3·90–4·60 (A_2B_2m, 4 dienic H); 5·32–5·47 (br s, 2 methine H); 5·64, 6·52 (ABq, $J = 10$ Hz, 4 $C\underline{H}_2O$); 7·47 (s, 4 $C\underline{H}_2CO$); 7·64–8·34 (m, 4 $C\underline{H}_2$). **23**. (Found: M.W. 400. $C_{20}H_{24}N_4O_5$ requires: M.W. 400·44); IR($CHCl_3$): 2300(CH), 1660 cm^{-1} (CO); UV(CH_3CN): 224 (10300); 254 (1860); NMR ($CDCl_3$): τ 5·04–5·34 (m, 4 methine H); 5·94, 6·28 (ABq, $J = 10$ Hz, 4 $C\underline{H}_2O$); 7·35 (s, 8 $C\underline{H}_2CO$); 7·74–8·10 (m, 8 $C\underline{H}_2$).

Photolysis of **14**. A soln of **14** (110 mg) in dry benzene (110 ml) was irradiated under N_2 at room temp with a Hanovia 450 watt lamp during 20 min. The solvent was removed at reduced pressure at room temp and the residue was placed on a preparative silica plate (E. Merck, 20 × 20 cm, 35 g silica gel PF_{254}) with benzene as eluent, followed by benzene-CH_2Cl_2 (1:1). The mono-azo derivative **24** was obtained (55 mg; 57%) and sublimed (55° at 0·3 mm), m.p. 71–72°. In addition **25** (9 mg; 11%) and **26** (5 mg; 6%) were isolated, b.p. 28° (0·1 mm) (see below).

Photolysis of **24**. A solution of **14** (80 mg) in dry benzene (90 ml) was irradiated as above at 10°. Progress of the reaction was monitored by TLC. After 20 min compound **14** is observed but this disappears upon continued irradiation. After 4 hr irradiation was stopped, the solvent removed in a vacuum and the residue was chromatographed on neutral alumina (2 g) using light petroleum 60–70° as eluent. A mixture of **25** and **26** was obtained (3:4, by NMR). Finally, benzene eluted **24** (6 mg; 10%). The mixture of **25** and **26** was separated as above on a prep plate of silica, affording **25** (20 mg; 33%) and **26** (13 mg; 22%). It is possible to isolate **25** rapidly by forming a Diels-Alder adduct of **26** (see below) followed by rapid filtration through a column of neutral alumina.

Compound **24**. (Found: C, 70·45; H, 7·93; N, 13·87; M.W. 204. $C_{12}H_{16}N_2O$ requires: C, 70·56; H, 7·90; N, 13·72%; M.W. 204·25); IR($CHCl_3$): 2990, 2950, 2860 (CH), 1640 cm^{-1} (C=C); UV(CH_3CN): 246 sh (1255); 249 sh (1270); 251 sh (1280); 254 (1390); 367 (85); 370 (100); NMR($CDCl_3$): τ 4·42–5·05 (m, 6 $=C\underline{H}$ and 2 methine protons); 6·00, 6·41 (ABq, J = 10 Hz, 4 $C\underline{H}_2O$); 7·84–8·30, 8·64–9·10 (m, 4 $C\underline{H}_2$).

Compound **25**. (Found: M.W. 176. $C_{12}H_{16}O$ requires: 176·25); IR($CHCl_3$): 2940, 2870 (CH), 1640, 1610 (C=C), 1140 cm^{-1} (CH_2—O); UV(CH_3CN): 225 (4100); NMR($CDCl_3$): τ  $H_X(-)C{=}CH_BH_A$: τ_A 5·10; τ_B 4·84; τ_X 3·87; J_{AX} = 18 Hz, J_{BX} = 11 Hz; J_{AB} = 2 Hz; 6·16, 6·29 (ABq, J = 9 Hz, 4 $C\underline{H}_2O$); 7·24–7·45 (m, 2 methine H); 7·61–7·90 (m, 4 $C\underline{H}_2$).

Compound **26**. (Found: M.W. 176. $C_{12}H_{16}O$ requires: 176·25); IR($CHCl_3$): 3010 (=CH), 2960, 2890 (CH), 1650, 1620 (C=C), 1140 cm^{-1} (CH_2—O); UV(CH_3CN): 225 (9600). NMR ($CDCl_3$): τ ABX: τ_B 4·90; τ_A 4·57; τ_X 3·63; J_{AX} = 17 Hz, J_{BX} = 11 Hz, J_{AB} = 1·5 Hz; 3·72–4·12 (m, 2 $CH_2CH_2C\underline{H}=$); 5·88 (s, 4 $C\underline{H}_2O$); 7·62–8·03 (m, 4 $C\underline{H}_2$).

Diels-Alder adduct of **26**. To a soln of **26** (6 mg) in acetone (0·5 ml) was added an acetone (1 ml) soln of 4-phenyl-1,2,4-triazoline-3,5-dione at room temp. The color was immediately discharged. After removal of solvent the residue was dissolved in benzene and purified by filtering through a column of neutral alumina (0·7 g); **27** had m.p. 194–196°. (Found: M.W. 526. $C_{28}H_{26}N_6O_5$ requires: 526·51); IR($CHCl_3$): 1780, 1720 (CO), 1610, 1510 cm^{-1} (Ar C=C); UV(CH_3CN); 227 (25600); 257 sh (1350); NMR($CDCl_3$): τ 2·28–2·71 (m, 10 ArH); 3·86–4·18 (m, 2 =CH); 5·08–5·44 (4 allylic $C\underline{H}_2$); 5·52–5·68 (m, 2 allylic $C\underline{H}$); 5·77 (br s, 4 $C\underline{H}_2O$); 7·51–7·81 (m, 4 $C\underline{H}_2$).

Thermal isomerization of **25**. A soln of **25** (12 mg) in tetrachloroethylene (0·3 ml) was heated in an NMR tube at 120° and its disappearance was observed concurrently with the appearance of **32**. After 1 hr 90% of the starting material isomerized to give **32**; NMR($CDCl_3$): τ 4·46–4·69 (m, 2 $=C\underline{H}$); 5·17, 5·97 (ABq, J = 11 Hz, 4 $C\underline{H}_2O$); 6·35–6·67 (m, 2 methine H); 7·32–8·09 (m, 4 allylic and 4 cyclobutyl H).

Photolysis of **20**. A soln of **20** (15 mg) in benzene (3 ml) was placed in a UV-cell and irradiated with an Osram HBO 200 watt lamp in a Wild MTr 14 instrument during 20 min. After removal of solvent in a vacuum the mono-azo compound **28** was obtained (100% yield), m.p. 61–62°. (Found: M.W. 204. $C_{12}H_{16}N_2O$ requires: M.W. 204·25); IR($CHCl_3$): 2980, 2950, 2860 (CH), 1630 cm^{-1} (C=C); UV(CH_3CN): 228 (7680); 233 (7550); 268 sh (115); 368 sh (75); 376 (90); NMR($CDCl_3$): τ|ABX: τ_A 4·93; τ_B 4·71; τ_X 4·09; J_{AX} = 17 Hz, J_{BX} = 11 Hz, J_{AB} = 1 Hz; 4·64–4·85 (br s, 2 methine H); 5·98, 6·42 (ABq, J = 10 Hz, 4 $C\underline{H}_2O$) 7·20–8·42, 8·65–9·87 (m, 4 $C\underline{H}_2$).

Photolysis of **28**. A solution of **28** (30 mg) in benzene (60 ml) was irradiated under N_2 at room temp with a Hanovia 450 watt lamp. The progress of the slow reaction was monitored by TLC. Irradiation was stopped after 10 hr. The solvent was removed in a vacuum and the residue was chromatographed on a column of neutral alumina (0·9 g) using light petroleum 60–70° as eluent. A mixture of **25** and **26** was obtained (11 mg; 3:8 by NMR).

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