Tetrahedron. Vol. 28, pp 2315 to 2332. Pergamon Press 1972 Printed in Great Britain

PROPELLANES—XIX

DIELS–ALDER REACTIONS OF TETRAENIC PROPELLANES[1]

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(*Received in the UK 9 December* 1971; *Accepted for publication 29 December* 1971)

Abstract—The behaviour of several tetraenic propellanes **1b–d** in their reactions with a variety of dienophiles has been studied. It appears that for the imides **1b–c** the dienophile adds to the face of the cyclohexadiene ring adjacent to the imide ring (from "above") whilst for the ether **1d** it adds to the face adjacent to the other cyclohexadiene ring (from "below").

DIMERIC CAGE COMPOUNDS are obtained by heating tetraenic propellanes, e.g. the anhydride **1a** and the methylimide **1b**.[2] The ether **1d**, however, behaves differently upon heating and does not undergo dimerization *via* a Diels–Alder mechanism.[3]

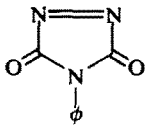
1a R,R: =O; X = O
b R,R: =O; X = NMe
c R,R: =O; X = NH
d R = H; X = O

Since chemical attempts to prove the structures of the dimers failed, it was believed that subjecting tetraenic propellanes to the action of various dienophiles might cast light on the mechanism of dimerization and **1b** and **1c** were used as the dienic components in a series of Diels–Alder reactions. Although meanwhile the cage structure of the dimer of **1b** has been elucidated by INDOR spectroscopy,[2] the results of the reactions with the simpler dienophiles merit discussion.

Clearly, tetraenic propellanes such as **1b–d** comprise two distinct dienic systems. It will be shown below that they are also disparate. In principle it should be possible to add two moles of dienophile to each of the tetraenic propellanes but in fact this could only be realized in special circumstances. The first mole of dienophile may approach the tetraenic propellane from "above", *i.e.* from the side of the ring containing the hetero-atom (bold arrow) or from the "under" side of the two cyclohexadiene rings (dotted arrow).

It is perhaps better to begin with the one dienophile which has proved itself efficacious in adding to both diene systems, namely 4-phenyl-1,2,4-triazolinedione, **2**.

When **1d** was treated with 1 equivalent of **2**, a 1:1 adduct was obtained. When **1d** was treated with 2 equivalents of **2**, a 2:1 adduct was obtained. The $C\underline{H}_2O$ protons



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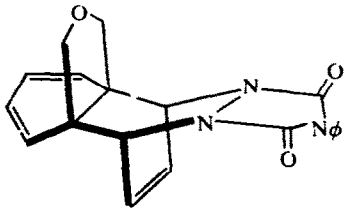

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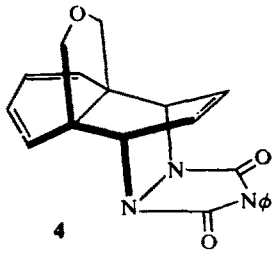

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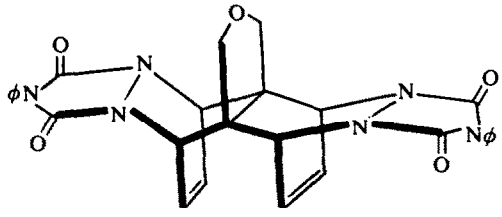
in the ether ring of **1d** serve as a very useful diagnostic tool regarding symmetry of the adducts. Thus, since an AB quartet was observed for these protons in the 2:1 adduct, the latter is clearly unsymmetrical. This does not yet determine the structure of the 1:1 adduct which may be either **3** or **4**. However, the structure of the 2:1 adduct cannot be **5** or **6** but must be the unsymmetrical **7**.



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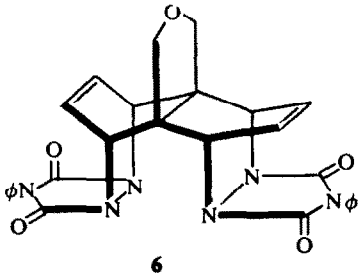

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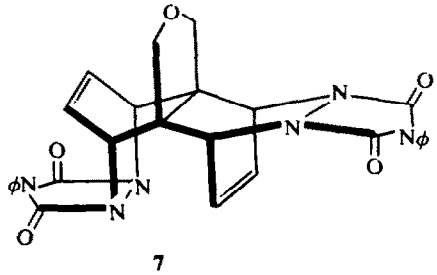

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Does the equivalent of dienophile attack **1d** from "above" or from "below"? We believed that we would be able to answer this question unequivocally by employing one of the *bis*-irontricarbonyl derivatives of the tetraenic ether, **8**, whose structure was known unequivocally to be one in which each "top" face of the diene systems was blocked by an $Fe(CO)_3$ group.[4] Thus, if **8** could be induced to react with excess dienophile, the latter would apparently have to attack **8** from its underside, apparently displacing an irontricarbonyl group.

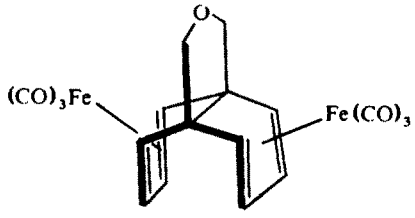
This could be an S_N2-like reaction in which the dienophile would attack the back-side ("underside") of the diene ring, displacing the metal-carbonyl grouping known to be attached to the upper side. Attractive though this hypothesis is, we must also consider the possibility that the dienophile might complex with the metal on the upper side, replace one or more carbonyl groups from the irontricarbonyl group on the upper side and once this had decomposed, an additional mole of dienophile would react with the diene system from above rather than from below.

Eventually there was an unequivocal way to determine the positions of the double bonds surviving after the completion of the Diels–Alder cycloadditions. When the *bis*-irontricarbonyl derivative **8** of **1d** was treated with **2**, one of the irontricarbonyl groups was replaced and a monoirontricarbonyl derivative **9** of a 1:1 adduct between **1d** and **2** was obtained. Oxidative removal of the second irontricarbonyl group with ceric ion afforded the 1:1 adduct itself of **1d** and **2** whose structure must be either **3** (if the dienophile attacked from "above", the *same* side as the $Fe(CO)_3$ group) or **4** (if the dienophile attacked from "below" in a quasi-S_N2 type displacement). This 1:1 adduct was an isomer of that obtained by treating **1d** directly with one mole of **2**. Thus, if the indirectly formed 1:1 adduct is **3** then the one formed directly is **4** and *vice versa*.

The indirectly formed 1:1 adduct, when treated with another mole of **2**, afforded a *symmetrical* bis-adduct **5** which upon irradiation underwent [2 + 2] photochemical cycloaddition to yield **11**. This unequivocally proves that the 1:1 adduct formed indirectly is **3** (attack of dienophile from "above") and the isomer formed directly from **1d** is **4** (attack of dienophile from below) (Scheme 1).

It may also be seen from scheme 1 that the monoirontricarbonyl derivative **10** of **1d**[4] also gives **9** when treated with one mole of **2**. Furthermore, the unsymmetrical *bis*-irontricarbonyl derivative **12** when treated with **2** give the symmetrical *bis*-Diels–Alder adduct **5**.

The reason for this behaviour appears trivial at first sight. We know from the X-ray structure of **8** in the solid phase that the two cyclohexadiene rings are quasi-boats as shown in the drawing of its more likely conformation presumed to exist also in solution:



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Thus attack from the "under" side is sterically quite hindered and **9** is formed. That **9** is formed also from **10** means that attack from below is sufficiently hindered in the latter also. There appears to be little doubt that the diazabicyclo[2.2.2] octane ring system in **3** exerts the same boat-like conformational hindrance on attack from below on the free diene ring and the second mole of **2** also attacks **3** from above.

In the direct attack on **1d** by **2**, however, the two cyclohexadiene rings are certainly freer to breathe between their quasi-chair and quasi-boat conformations than their organometallic derivatives. It appears that here attack can not only occur from below but does so exclusively. Here the hydrogen atoms adjacent to the ether oxygen are evidently exerting their desire for "lebensraum" and insofar as the steric factor alone is concerned, attack occurs preferentially from below (however, see ref. 8). Once **4** has been formed, however, the boat-like conformation of the diazabicyclo-[2.2.2]octane portion of the molecule hinders attack from below much more so

SCHEME 1

Fe(CO)3
Fe(CO)3
2 from "above"
8
Fe(CO)3
9
Ce^IV
2 from "above"
10
2 from "above"
3
2 from "above"
5
1d
2 from "below"

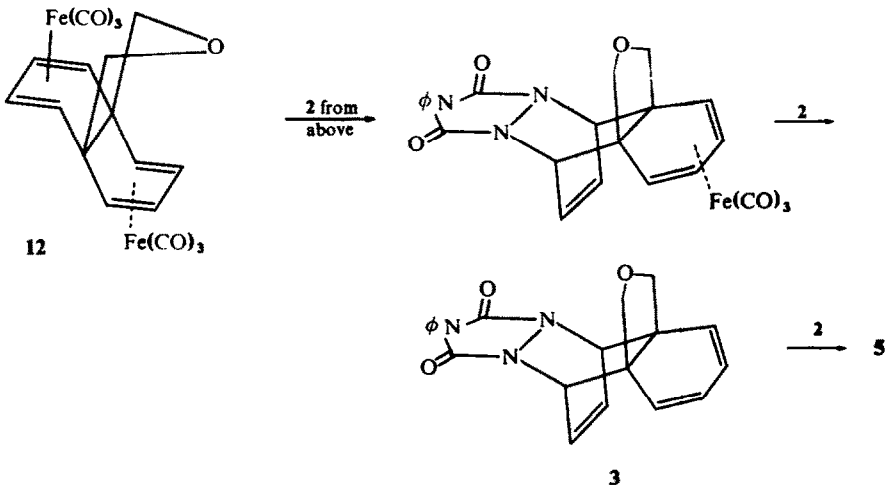
hν
11
12
Fe(CO)3
Fe(CO)3
4
2 from "above"
7

than the two hydrogens adjacent to the ether oxygen hinder such attack from above (models show that the relevant hydrogens exert much more hindrance to topside attack by **2** than in the more rigid **4**).[7] Thus **7** is formed from **4**.

From the viewpoint of the steric factor, this argument would imply that **1b** which has no alpha hydrogens adjacent to the nitrogen atom, should be readily attacked by **2** from above (see below).

Finally, in Scheme 1, **12** when treated with **2** affords **5**. This would imply the sequence summarized in Scheme 2. We do not have evidence of the correctness of this sequence because the rate of formation of **5** from **3**, if indeed **3** be an intermediate, is so rapid that it is not surprising that **3** was not isolated with **5**. The crystal structure of **12** shows[5] that the envelope of the ether ring is folded towards the cyclohexadiene ring which is complexed to an irontricarbonyl group from its under side as shown. Thus the irontricarbonyl group on the top side is removed first. After the second group is removed we have **3** which has already been shown in Scheme 1 to give **5** when attacked by **2**.

SCHEME 2

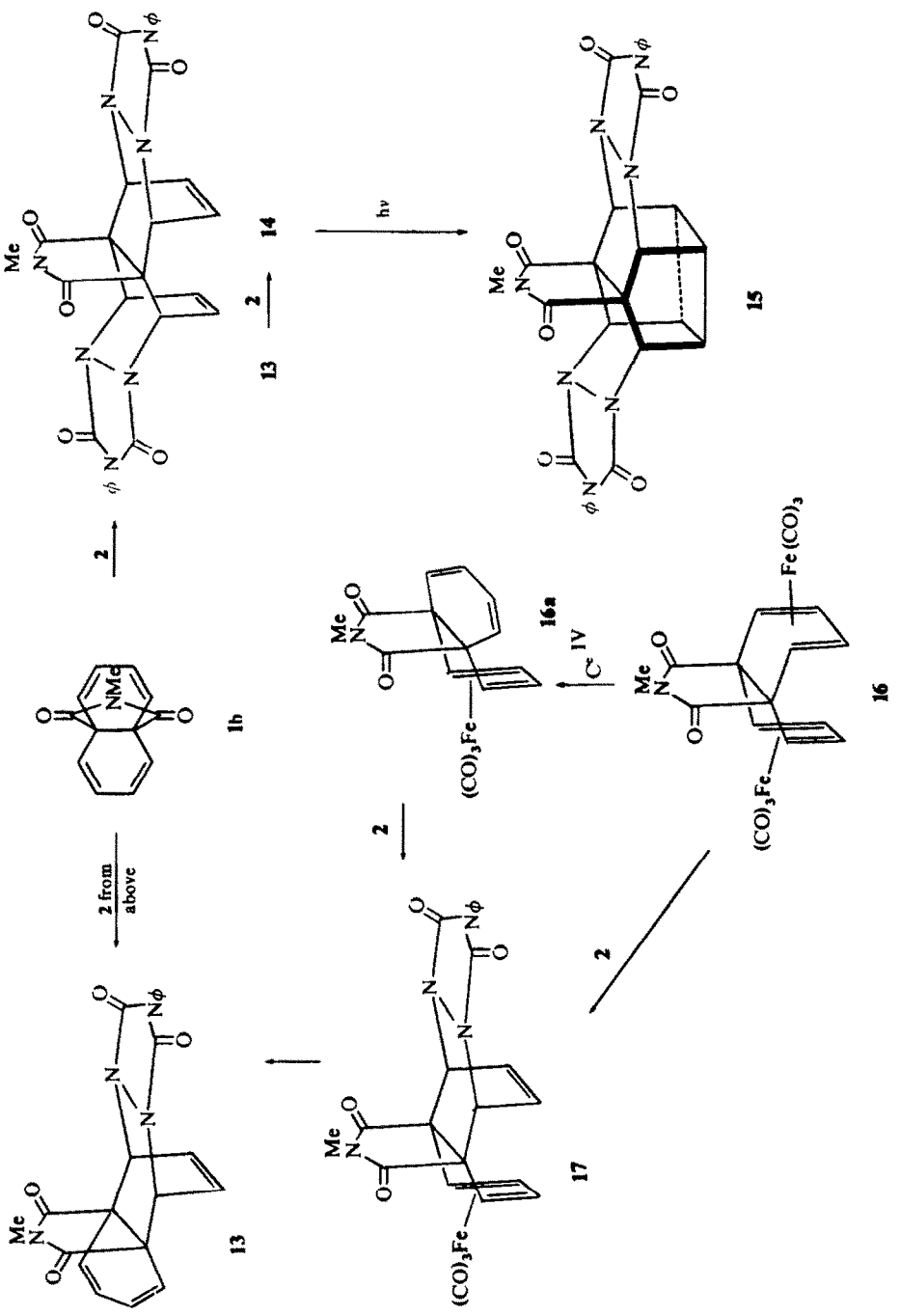


The behaviour of **1b**, when attacked by **2**, indeed appeared to support the idea that when hydrogen atoms do not exist in the heterocyclic ring and hence cannot interfere with the approach of the dienophile, attack may come from "above" Scheme 3 summarizes the results of the various reactions conducted.

The first mole of **2** attacks **1b** from above as does the second. This is clear first from the fact that the vinylic protons in **14** from one triplet (compare with one triplet for same protons in **5** and two triplets for 2 sets of vinylic protons in **7**). But unequivocal proof that the symmetrical *bis* adduct is indeed **14** stems from its irradiation. Again a [2 + 2]photochemical cycloaddition occurs and **15** is obtained. The approach of the dienophile from the "top" side of **1b** is reminiscent of the behaviour of **1b** on thermal dimerization. In that case, the molecule of **1b** which acts as the dienophile approaches its neighbouring diene molecule of **1b** from the top.[2]

The structure of **16** is not known unequivocally.[6] It is clear from its NMR spectrum

SCHEME 3

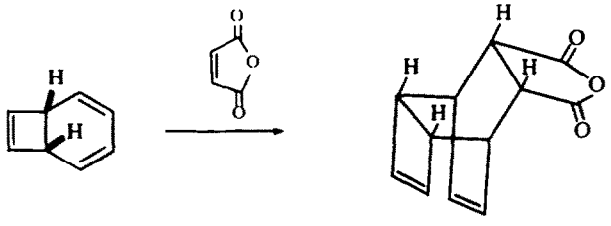


that it is a symmetrical *bis*-irontricarbonyl derivative. It was assigned this structure in analogy with **8** whose structure has been determined by X-ray crystallography.[4] Yet, the sequence **16** → **17** → **13** (Scheme 3) taken together with the results summarized in Scheme 1 (**8** → **9**), supports the structure formulated for **16**.

The fact that **2** may and does attack **1b** from above still does not explain why this mode of attack occurs exclusively. The ether **1d** is attacked from below and it is not immediately apparent why such attack is ruled out in the case of **1b**.

One tends to invoke the obvious electronic difference between the top sides of **1b** and **1d**, respectively. In the former there are two carbonyl groups of the imide ring (as well as the lone pair on nitrogen) whilst the only repository of extra electronic wealth in **1d** is the ether oxygen atom.

To be sure there are numerous examples of the Diels–Alder reaction in which the dienophile orients itself on the less hindered side of the diene.[7] We should like to cite in addition the reaction of cyclooctatetraene (which reacts in the bicyclic form) with maleic anhydride, affording the *endo*-adduct.[8] The attack by the dienophile from above is contrary to the analogous attack of the tetraenic ether **1d**. In the case

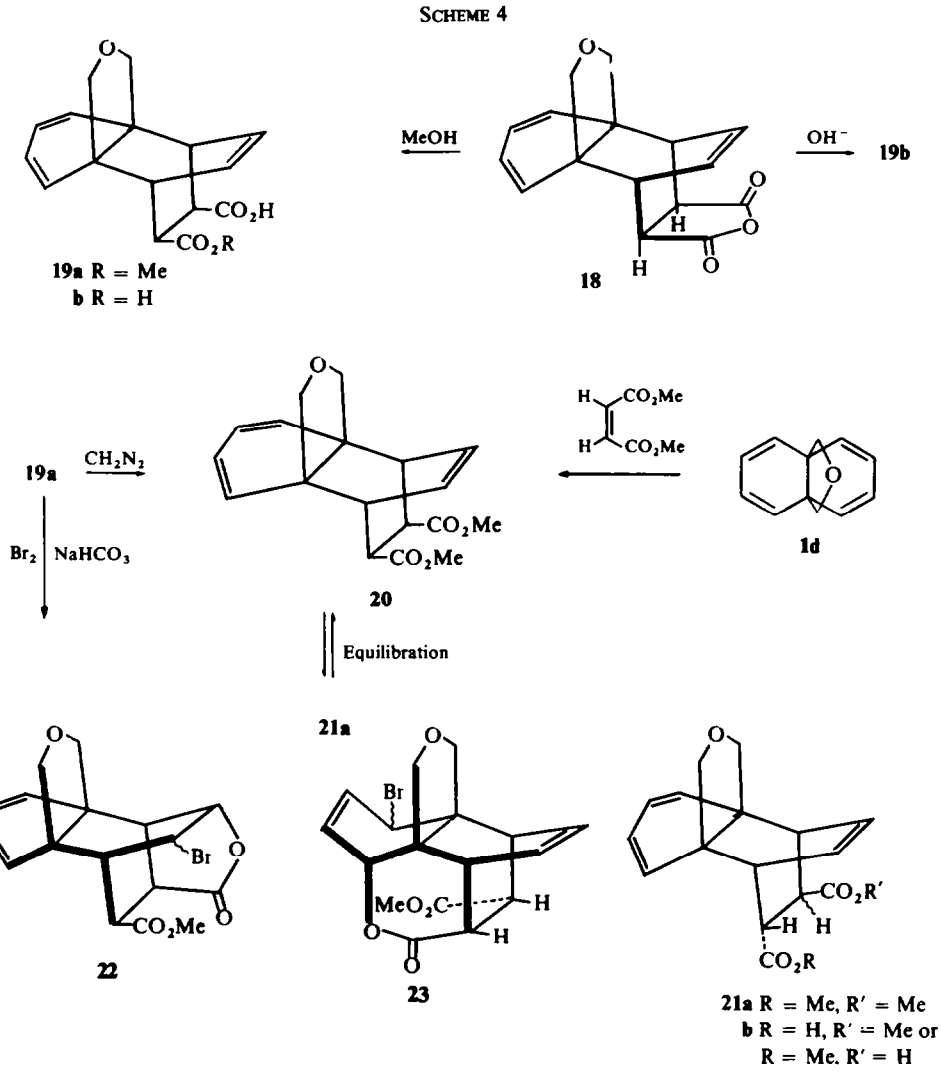


of cyclooctatetraene perhaps it may also be claimed that second order orbital interactions with the cyclobutene double bond also support attack of COT from above. It is this kind of second order orbital interaction with the carbonyl groups in the imide ring which may be the explanation for the attack of the dienophile on **1b** from the top rather than from below.

We assume by analogy with the above behaviour of **1d** with **2** that other dienophiles also attack **1d** from below. We do not, however, have unequivocal proof for this, as we have in the above case. Thus since we could only get **1d** to form 1:1 adducts with a good many additional dienophiles, we were unable to get a second mole of such a dienophile to form a *bis*-1:2 adduct. The only dienophile sufficiently reactive to add to a 1:1 adduct was the triazolone derivative **2**, in which case a di-1:2 adduct rather than a *bis*-1:2 adduct was formed. In this context, therefore, the formulations in Scheme 4 must be regarded as tentative, the basis for discussion and interrelation, insofar as this has been carried out, being that attack of each dienophile leading to the 1:1 adduct occurs from below.

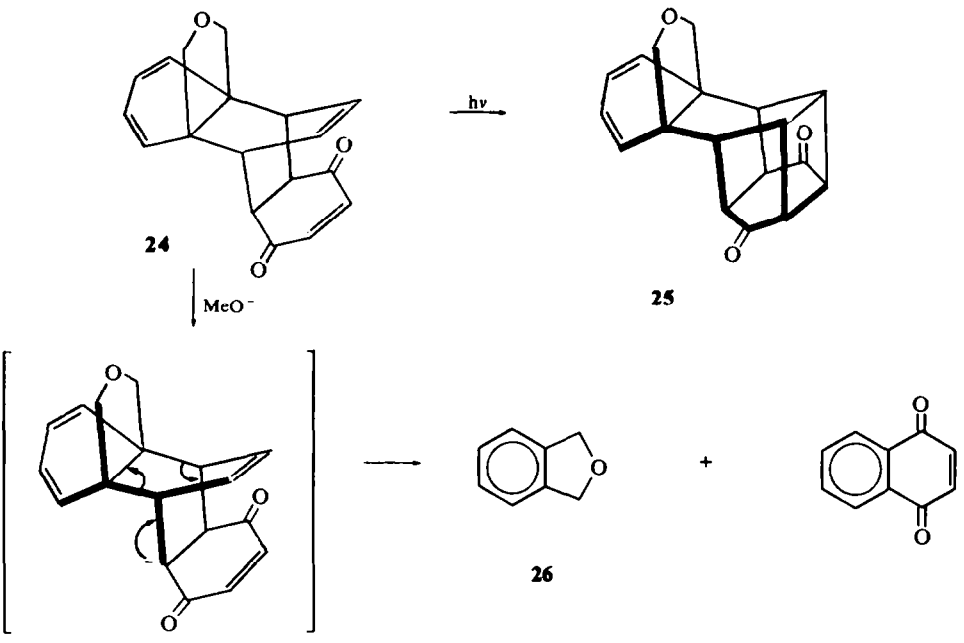
It is, in principle, possible here as in other cases to obtain an *endo*- or an *exo*-adduct. We have assigned the *endo*- configuration (emphasized by heavy lines in formula **18**) to the Diels–Alder adduct of **1d** with maleic anhydride. (It should be noted that this configuration is also *anti*- with respect to the remaining unreacted cyclohexadiene ring, whilst the hydrogen atoms at the pertinent ring junctions are *syn*- to the latter and, of course *exo*- with respect to the cyclohexadiene ring which had undergone reaction). All of the compounds listed in Scheme 4 are of the same family, as **18** was methanolyzed to give **19a** which was further methylated with diazomethane to give

SCHEME 4



20, identical to the adduct of **1d** with dimethyl maleate. Hydrolysis of **18** afforded **19b**. The adduct **21a** was obtained from the tetraenic ether **1d** and dimethyl fumarate. Alkaline hydrolysis of this adduct gave the half ester **21b**. The *cis*-diester (**20**) and the *trans*-diester (**21a**) were equilibrated by means of base. Hence, if maleic anhydride attacks **1d** from below, then clearly dimethyl maleate and dimethyl fumarate react from the same direction and all give *endo*-adducts. That the adducts are indeed of the *endo* type, as formulated, was shown by formation a *five*-membered bromolactone (**22**) by bromination of the half ester **19a** in weakly basic solution. If all of these compounds had the *exo*-configuration it would be possible to consider another structure, **23**, for the bromolactone but this would involve a much less strained six-membered lactone ring. The bromolactone exhibited carbonyl absorption at 1790

SCHEME 5



24 25 26

cm^{-1} in its IR spectrum in keeping with that expected for the rather rigidly fixed five-membered ring in **22**.

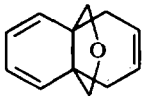
p-Benzoquinone gave a monoadduct **24** with **1d**. On standing in light this was converted into the saturated diketone **25** *via* a [2 + 2]photochemical cycloaddition. Attempted aromatization of **24** failed. When sodium methoxide was employed, a retro-Diels–Alder reaction occurred (Scheme 5) and phthalan **26** was isolated. When **24** was heated with acetic anhydride in pyridine, 1,4-diacetoxynaphthalene was isolated. In Scheme 5 the adduct **24** is again assigned the analogous structure resulting from attack by benzoquinone from below. The *endo*-configuration is fully justified on the basis of the sequence **24** → **25**.

A similar retro-Diels–Alder reaction of a well-known type[9] took place when dimethyl acetylenedicarboxylate was reacted with **1d**. Dimethyl phthalate was isolated.

The tetraenic-ether **1d** also gave adducts **27**, **28**, and **29** with tetracyanoethylene, N-methylmaleimide and N-phenylmaleimide, respectively.

The 1:1 adducts of **1d** with maleic anhydride (**18**) and both **28** and **29** were converted upon treatment with 4-phenyl-1,2,4-triazolinedione (**2**) into the diadducts **30**, **31** and **32**, respectively. The only dienophile tried which added to a 1:1 adduct of the ether **1d** was **2** despite attempts to add a second mole of other dienophiles.[10]

It should be noted that the first time we isolated the triene (**33**) it was through



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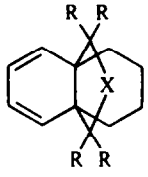
its presence as an impurity in **1d** and when **1d** reacted with **2**, the impurity gave the adduct **34** which was separated from **4** and **7** by crystallization. Later on when we had pure triene (**33**), the same adduct **34** was isolated directly.

Various miscellaneous adducts were prepared from **1b** (**35–39**) as well as from **1c** (**40–43**) (see experimental).

Further work remains to be done to provide additional evidence regarding the structures of the compounds discussed. For example, irradiation of **30**, **31** and **32** would presumably fail whilst we believe, also by analogy, that such irradiation of **38** and **39** would lead to [2 + 2]photochemical cycloaddition.

We are also preparing dienes of type **44**. We believe on the basis of work carried



44a R,R: = O; X = O
b R,R: = O; X = NMe
c R,R: = O; X = NH
d R = H; X = O

out by Dunitz and Ermer[11] that the reduced cyclohexane ring would be present in the chair conformation and thus be quite different in its steric demands than a cyclohexadiene ring in tetraenes of type **1**. Thus one may hope to study the course of the Diels–Alder reaction with compounds of type **44** and interrelate them with monoadducts obtained from **1**. This may perhaps shed further light upon the reason for one direction of attack of dienophiles upon **1d** and another direction upon **1b**.

If one tabulates the positions of the lines corresponding to the AB quartet generally exhibited by the —C$\underline{H}_2$O—C$\underline{H}_2$ protons in adducts of **1d** one finds in general that when attack occurs from below, *i.e.* a double bond is in the field of these protons, the τ values range from 6·00 to 6·64. When, however, a triazolone ring is a component of the adduct the same holds true in **4** where attack occurred from below. But in **3** or **7** where at least one mole of **2** has attacked from above and the nitrogen atoms are nearer to the pertinent protons α to the ether oxygen, the values are 5·51; 6·47 and 5·70; 6·25 respectively. For **5** where both moles of **2** have entered from above to give a symmetrical *bis*-adduct, the quartet no longer exists but the singlet is at 5·53

In the adduct **30** τ values in DMSO are 6·07; 6·28, for **31** in DMSO 6·00; 6·36 but for **32** in pyridine-d_5 they are 5·54; 6·12. It has not been determined unequivocally whether solvent effects play a role here or whether the direction of attack by the dienophile is different in these cases.

So far, in the cases in which the structures have been determined with certainty, e.g. **3**, **4**, **5**, **7**, it appears that one may generalize and say that when part of the AB quartet lines fall below τ 6·00, the attack by the dienophile has occurred from above. Alternatively, however, we are not as certain in saying that if this quartet falls above τ 6·00 we are certain that attack has occurred from below.

EXPERIMENTAL

UV spectra were measured on Perkin–Elmer model 137 or a Bausch and Lomb spectronic 505 spectrophotometer. IR spectra were measured on a Perkin–Elmer model 237 grating spectrophotometer. 60 MHz spectra were measured on a Varian T-60 spectrometer. Mass spectra were measured on an Atlas CH4 mass spectrometer 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.

Adducts **4** *and* **7** *of* **1d** *with* 4-*phenyl*-1,2,4-*triazoline*-3,5-*dione* (a) To a solution of **1d** (216 mg) in dry acetone (5 ml) was added slowly at room temp with magnetic stirring a solution of the sublimed dienophile **2** (220 mg) in dry acetone (4 ml). The deep red colour of the added reagent was discharged instantaneously. When addition was complete the product began to precipitate. After 30 min standing, the solvent was removed in vacuum and the residue triturated with MeOH. The *mono adduct* **4** (380 mg; 88%) had m.p. (sint. 220°) 227–228° (acetone–pet ether 60–70°). (Found: C, 69·04; H, 5·04; N, 12·04; MW 347. $C_{20}H_{17}N_3O_3$ requires: C, 69·15; H, 4·93; N, 12·10%; MW 347·36). IR($CHCl_3$): 1770, 1715 cm^{-1} (CO). UV(MeCN): $\lambda\lambda_{max}$ 216, 248, 256 (sh) nm, $\varepsilon\varepsilon_{max}$ 11,570, 6765, 6240. NMR ($CDCl_3$): τ 2·58 (s, 5 arom H); 3·38 (t, J = 3·5 Hz, 2 vinylic H); 4·05 (m, 4 dienic H); 5·20 (t, J = 3·5 Hz, 2 bridgehead H); 6·05, 6·45 (AB quartet, J = 9·5 Hz, 4 $C\underline{H}_2O$).

(b) To a solution of **1d** (1·08 g) in dry acetone (30 ml) was added as above a solution of the sublimed dione (2·32 g) in dry acetone (25 ml). The reaction slows down with addition of second equivalent of dienophile and the product precipitates. After 2 hr the solvent was removed and the *bis*-adduct **7** (2·7 g; 83%) had m.p. (sint. 281°) 301° (EtOAc–acetone). (Found: C, 64·38; H, 4·40; N, 16·31; MW 522. $C_{28}H_{22}N_6O_5$ requires: C, 64·36; H, 4·24; N, 16·09% MW 522·50). IR ($CHCl_3$): 1780, 1730 cm^{-1} (CO). UV (MeCN): $\lambda\lambda_{max}$ 218, 252, $\varepsilon\varepsilon_{max}$ 20,600, 14,470 NMR ($CDCl_3$): τ 2·54 (s, 10 arom H); 3·43 (t, J = 3·5 Hz, 2 vinylic H); 3·57 (t, J = 3·5 Hz, 2 vinylic H); 5·03 (m, 4 bridgehead H); 5·70, 6·25 (AB quartet, J = 9·5 Hz, 4 $C\underline{H}_2O$).

Preparation of monoadduct **3**. To a solution of **8**[4] (110 mg) in CH_2Cl_2 (1·5 ml) was added at room temp with magnetic stirring a solution of sublimed **2** (368 mg) in CH_2Cl_2 (8 ml) After *ca.* 15 min the red mixture appears black. After 50 hr stirring the mixture was rapidly filtered through a column of neutral alumina (12 g) using CH_2Cl_2 as eluent. Purification of the light yellow product was accomplished by using a preparative plate of alumina (Merck, Darmstadt) with benzene–CH_2Cl_2. The *monoiron tricarbonyl derivative* **9** *of the adduct* **3** (50 mg; 43%) had m.p. above 360° (benzene–pet ether 60–70°).

A preferred alternative method was to add slowly at room temp with magnetic stirring a solution of sublimed **2** (62 mg) in acetone (1 ml) to a solution of the *bis*-irontricarbonyl derivative of **1d** (110 mg) in acetone (2 ml). After 2 hr stirring the acetone was removed in a vacuum below 40°. The use of a preparative alumina plate afforded **9** (120 mg; 70%). (Found: C, 56·50; H, 3·62; N, 8·50;MW 487. $C_{23}H_{17}N_3O_6Fe$ requires: C, 56·69; H, 3·48; N, 8·62%; MW 487·74). IR ($CHCl_3$): 2020, 1990 (Fe–CO); 1770, 1725, 1710 cm^{-1} (imide CO). UV (MeCN): λ_{max} 219 nm, ε_{max} 26,000. NMR ($CDCl_3$): τ 2·57 (s, 5 arom H); 3·64 (t, J = 3·0 Hz, 2 vinylic H); 4·75 (m, 2 cent dienic H); 5·35 (t, J = 3·0 Hz; 2 bridgehead H); 5·67, 6·00 (AB, quartet, J = 10·5 Hz; 4 $C\underline{H}_2O$); 7·15 (m, 2 term dienic H).

Removal of the $Fe(CO)_3$ group is effected as follows: A solution of ceric ammonium nitrate (0·57 g) in MeOH (12 ml) was added dropwise rapidly at room temp to a solution of **9** (160 mg) in MeOH (20 ml)–EtOAc (20 ml) with magnetic stirring. Evolution of CO began immediately upon addition and was complete after 20 min. Stirring was continued for 30 min and the solvent removed in a vacuum. CH_2Cl_2 (15 ml) was added and the solution washed with water and dried (Na_2SO_4). Removal of solvent afforded the *monoadduct* **3**. (an isomer of **4**) (105 mg; 90%), (sint. 225°). m.p. 243–244° (MeOH). (Found: C, 69·59; H, 5·09; N, 11·98; MW 347. $C_{20}H_{17}N_3O_3$ requires: C, 69·15; H, 4·93; N, 12·10%; MW 347·36). IR ($CHCl_3$): 1775, 1718 cm^{-1} (imide CO). UV (MeCN): $\lambda\lambda_{max}$ 217, 243 nm (sh), $\varepsilon\varepsilon_{max}$ 7470, 3185. NMR ($CDCl_3$): τ 2·57 (s, 5 arom H); 3·44 (t, J = 3·5 Hz, 2 vinylic H); 4·27 (m, 4 dienic H); 5·27 (t, J = 3·5 Hz, 2 bridgehead H); 5·51, 6·47 (AB quartet, J = 11 Hz, 4 $C\underline{H}_2O$)

Preparation of symmetrical bis-*adduct* **5**. (a) To a solution of **3** (27 mg) in acetone (2·5 ml) was added slowly with stirring at room temp a solution of sublimed **2** (13·7 mg) in acetone (0·5 ml). After 30 min slow precipitation began. After standing for 3 hr the *solid* bis-*adduct* **5** was collected (25 mg; 61%). m.p. above 360° (AcOH). (Found: C, 63·80; H, 4·26; N, 15·99; MW 522. $C_{28}H_{22}N_6O_5$ requires: C, 64·36; H, 4·24; N, 16·09%; MW 522·50). IR ($CHCl_3$): 1780, 1730, 1720 cm^{-1} (imide CO). UV (MeCN): $\lambda\lambda_{max}$ 219, 265 nm, $\varepsilon\varepsilon_{max}$ 20,170, 6990. NMR (DMSO-d_6): τ, 2·37 (s, 10 arom H); 3·55 (t, J = 3·5 Hz, 4 vinylic H); 4·79 (t, J = 3·5 Hz, 4 bridgehead H); 5·53 (s, 4 $C\underline{H}_2O$).

(b) To a solution of the unsymmetrical *bis*-irontricarbonyl derivative **12** (45 mg) in dry CH_2Cl_2 (3 ml) was added as above a solution of sublimed **2** (82 mg) in dry CH_2Cl_2 (1 ml). After *ca.* 30 min the mixture

turned black. After 46 hr stirring the whole was filtered quickly through a column containing neutral alumina (10 g) to remove black impurity. $CHCl_3$ was used as eluent. After removal of solvents and trituration with ether the *bis*-adduct **5** was again obtained (12 mg). Removal of ether from the mother liquor and preparative TLC on alumina afforded starting material (25 mg).

Preparation of the cage compound **11**. A magnetically stirred solution of **5** (30 mg) in acetone (180 mg) was irradiated in a pyrex vessel with a Hanovia 450 watt lamp at 25° in an inert atmosphere during 3 hr. After removal of solvent and trituration of the residue with ether, the cage compound **11** (26 mg; 85%) was obtained, m.p. above 350°. (Found: C, 64·50; H, 4·40; N, 16·15; MW 522. $C_{28}H_{22}N_6O_5$ requires: C, 64·36; H, 4·24; N, 16·09%; MW 522·50). UV (MeCN): λ_{max} 221 nm, ε_{max} 22,000.

IR (KBr): 1765, 1715, 1695 cm^{-1}. NMR (DMSO-d_6): τ 3·48 (s, 10 arom H); 5·15–5·35 (m, 4 C<u>H</u>NCO); 6·11 (s, 4 C$\underline{H}_2$O), 6·74–6·92 (m, 4 C<u>H</u>).

Monoadduct **13** *of* **1b** *with* **2**. To a solution of **1b**[12] (426 mg) in acetone (5 ml) was added dropwise with stirring at room temp a solution of sublimed **2** (350 mg) in acetone (4 ml) at the rate of disappearance of the colour of **2** (rapid addition). After about half of the reagent had been added, precipitation began. The solvent was removed in a vacuum. Trituration with MeOH and filtration afforded the adduct **13** (0·73 g; 93%), m.p. 256–257° (dec 230°, MeOH). (Found: C, 65·02; H, 4·40; N, 14·37; MW 389. $C_{21}H_{16}N_4O_4$ requires: C, 64·94; H, 4·15; N, 14·43%; MW 388·37). IR ($CHCl_3$): 1775, 1720 cm^{-1} (CO). UV (MeCN): $\lambda\lambda_{max}$ 218, 260 (sh) nm. $\varepsilon\varepsilon_{max}$ 5255, 1625. NMR ($CDCl_3$): τ 2·57 (s, 5 Ar <u>H</u>); 3·36 (t, 2 = C<u>H</u>, J = 3·5 Hz); 3·99–4·17 (m, 4 conjug = C<u>H</u>), 4·73 (t, 2 bridgehead H, J = 3·5 Hz); 6·90 (s, 3 NC$\underline{H}_3$).

Bis-*adduct* **14** *of* **1b** *with* **2**. To a solution of **1b** (426 mg) in CH_2Cl_2 (20 ml) was added dropwise with stirring at room temp, at the rate of discharge of the colour, a solution of sublimed **2** (0·77 g) in CH_2Cl_2 (8 ml). The colour was discharged less rapidly for the second equivalent of **2**. Towards the end of addition, precipitation began. The solvent was removed in a vacuum. Trituration with MeOH and filtration afforded **14** (1·01 g; 90%), m.p. 284° (dec. 265°, $CHCl_3$). (Found: C, 61·71; H, 4·13; N, 17·17; MW 563. $C_{29}H_{21}N_7O_6$ requires: C, 61·80; H, 3·75; N, 17·39%; MW 563·51). IR (KBr): 1785, 1725 cm^{-1} (CO). UV (MeCN): $\lambda\lambda_{max}$ 218, 259 nm, $\varepsilon\varepsilon_{max}$ 6850, 2400. NMR (Py-d_5): τ 3·62 (t, 4 = C<u>H</u>, J = 3 Hz); 4·27 (t, 4 bridgehead H, J = 3 Hz); 6·95 (s, 3 NC$\underline{H}_3$). Reaction of **13** with **2** gave **14** (83% yield).

Irradiation of **14**. A Hanovia 450 w lamp was used to irradiate in pyrex equipment a solution of **14** (100 mg) in acetone (180 ml) while stirring for 3 hr at room temp under N_2. After removal of solvent at reduced pressure and trituration with CH_2Cl_2 the cage compound **15** (70 mg; 70%) was obtained, m.p. >350° (MeCN). (Found: 61·76; H, 3·97; N, 17·49; MW 563. $C_{19}H_{21}N_7O_6$ requires: C, 61·80; H, 3·75; N, 17·39%; MW 563·51). IR (KBr): 1770, 1725 cm^{-1} (CO). UV (MeCN): λ_{max} 221 nm, ε_{max} 21,850. NMR (DMSO-d_6): τ 2·40 (s, 10 Ar <u>H</u>); 4·58–4·76 (m, 4 C<u>H</u>NCO); 6·50–6·70 (m, 4C<u>H</u>); 6·79 (s, 3 NC$\underline{H}_3$).

Preparation of **17** (a) A solution of **16** (50 mg) and sublimed **1** (212 mg) in dry CH_2Cl_2 was heated at 90° in a sealed tube for 45 hr. The black mixture was filtered rapidly through a column of neutral alumina (10 g) using CH_2Cl_2 as eluent. The yellowish product was placed on a TLC plate (Merck alumina) and eluted with C_6H_6–CH_2Cl_2. The starting material (**15**, 24 mg) was recovered and **17** (11 mg) m.p. >350° isolated. (Found: C, 54·93; H, 3·18; N, 10·45; MW 528. $C_{24}H_{16}N_4O_7Fe$ requires: C, 54·56; H, 3·05; N, 10·60%; MW 528·24). IR ($CHCl_3$): 2060, 1890 (Fe —<u>C</u>O), 1770, 1720, 1710 cm^{-1} (imide CO). NMR ($CDCl_3$): τ 2·60 (s, 5 Ar <u>H</u>); 3·60 (t, 2 = C<u>H</u>, J = 3·5 Hz); 4·56–4·74 (m, 2 cent conjug =C<u>H</u>); 4·89 (t, 2 bridgehead H, J = 3·5 Hz); 6·75–6·90 (m, 2 term conjug =C<u>H</u>); 6·90 (s, 3 NC$\underline{H}_3$). UV (MeCN); λ_{max} 219, 264 (sh) nm, ε_{max} 33,000, 7000.

(b) To a solution of **16a** (0·37 g) in CH_2Cl_2 (6 ml) was added dropwise with stirring at room temp a solution of sublimed **2** (0·20 g) in CH_2Cl_2 (7 ml). The colour of the reagent was discharged rapidly. The solvent was removed at reduced pressure. After trituration of the residue with MeOH and filtration, the product **17** (0·42 g, 76%) was obtained, m.p. >350° (dec. 280°, benzene–hexane) identical with the product obtained by route (a) above.

Conversion of **17** *into* **13**. A solution of ceric ammonium nitrate (312 mg) in MeOH (10 ml) was added rapidly with stirring at room temp to a solution of **17** (50 mg) in MeOH–EtOAc (1:1, 24 ml). After 18 hr the solvent was removed, CH_2Cl_2 (10 ml) added, the whole washed (2x) with water and dried (Na_4SO_4). After removal of solvent and purification by TLC on a preparative plate (Merck alumina) using C_6H_6–CH_2Cl_2 as eluent, the monoadduct **13** (20 mg, 60%), identical with that described above, was obtained.

Diels–Alder adduct of **1d** *with maleic anhydride*. A mixture of **1d** (172 mg), the anhydride (108 mg) and C_6H_6 (5 ml) was heated under reflux for 14 hr. After removal of solvent at the water pump the *monoadduct* **18**, (170 mg: 63%) was obtained, m.p. 232–233° (acetone–pet ether 60–70°). (Found: C, 70·84; H, 5·48; MW 270. $C_{16}H_{14}O_4$ requires: C, 71·10; H, 5·22%; MW 270·27). IR ($CHCl_3$): 1865, 1790 cm^{-1}

(anhydride CO). UV (MeCN): $\lambda\lambda_{max}$ 247 (sh), 255, 264, 274 nm (sh). $\varepsilon\varepsilon_{max}$ 2640, 3500, 2620, 2100. NMR ($CDCl_3$): τ 3·60 (q, 2 vinylic H); 3·83–4·53 (m, 4 dienic H); 6·19, 6·36 (AB quartet, J = 9·0 Hz, 4 C$\underline{H}_2$O); 6·70–6·97 (m, 4 C$\underline{H}$).

Methanolysis of **18**. The anhydride (200 mg) and MeOH (7 ml) were heated under reflux for 2 hr. After removal of solvent, the *half ester* **19a** (180 mg; 95%) was obtained, m.p. 149–150° (EtOAc). (Found: C, 68·32; H, 6·36; MW 302. $C_{17}H_{18}O_5$ requires: C, 67·54; H, 6·00%; MW 302·31). IR (KBr): 3460–3430 (OH); 3200–3000 (H bonded OH); 1750 cm^{-1} (CO). NMR ($CDCl_3$): τ 0·35 (s, $CO_2\underline{H}$); 3·60 (t, 2 vinylic H); 3·89–4·56 (m, 4 dienic H); 6·19, 6·41 (AB quartet, J = 9·0 Hz. 4 C$\underline{H}_2$O); 6·42 (s, $CO_2C\underline{H}_3$); 6·80 (br s, C$\underline{H}CO_2H$ + C$\underline{H}CO_2CH_3$); 7·05–7·30 (m, 2 bridgehead C$\underline{H}$).

Preparation of the diester **20**. Treatment of the half ester dissolved in MeOH with excess ethereal CH_2N_2 at 0°, standing overnight and removal of solvent afforded the *diester* **20** identical in spectroscopic properties with the product obtained from the reaction of dimethyl maleate with **1d** (see below).

Preparation of the bromolactone **22**. Bromine (55 mg) was added dropwise to a solution of the half ester **19a** (100 mg) in $NaHCO_3$ aq (5%; 8 ml) with ice cooling. The mixture was set aside overnight. The yellow crystalline precipitate of *bromolactone* **22** had m.p. 110° (dec.; MeOH). IR($CHCl_3$): 1790 cm^{-1} (5 membered lactone CO). The product decomposed on standing.

Hydrolysis of **18**. A mixture of **18** (100 mg), water (2 ml) and NaOH aq. (5%; 1 ml) was heated at 90° for 4 hr. After cooling and acidifying with 2 N HCl to pH 4, the diacid **19b** precipitated as colourless crystals (80 mg; 75%), m.p. 236° (AcOH). It may be that during drying of the analytical sample the anhydride is formed and the m.p. is actually that of the anhydride. (Found: MW 288. $C_{16}H_{16}O_5$ requires: 288·29). However (Found: C, 70·92; H, 5·32. $C_{16}H_{16}O_5$–H_2O) requires: C, 71·10; H, 5·22%). IR (KBr): 3140–3020 (OH), 1730 cm^{-1} CO of carboxyl). NMR (DMSO-d_6): τ – 1·80 (br s, 2 $CO_2\underline{H}$); 3·78 (q, 2 vinylic H); 3·91–4·51 (m, 4 dienic H); 6·32, 6·53 (AB quartet, J = 8·0 Hz, 4 C$\underline{H}_2$O); 7·07–7·32 (m, 4 C$\underline{H}$).

Adduct **20** of **1d** *with dimethyl maleate*. A mixture of **1d** (500 mg), dimethyl maleate (450 mg) and toluene (10 ml) was heated under reflux for 48 hr. After removal of solvent the residual oil was dissolved in C_6H_6 and the solution chromatographed on a florisil (15 g) column. C_6H_6–$CHCl_3$ (1:1) eluted the desired diester **20** (400 mg; 54%). It was an oil, b.p. 145° (0·02 mm) and formed a single peak in GLC. (Found: MW 316. $C_{18}H_{20}O_5$ requires: 316·34). IR ($CHCl_3$): 2950, 2860 (CH), 1750 cm^{-1} (ester CO). UV (MeCN): $\lambda\lambda_{max}$ 247 (sh), 255, 264, 273 nm (sh), $\varepsilon\varepsilon_{max}$ 2550, 3000, 3050, 3100. NMR ($CDCl_3$): τ 3·58 (t, 2 vinylic H); 3·88–4·57 (m, 4 dienic H); 6·25, 6·34 (AB quartet, J = 9 Hz, 4 C$\underline{H}_2$O); 6·42 (s, 6 $CO_2C\underline{H}_3$); 6·83 (s, 2 C$\underline{H}CO_2CH_3$); 7·18 (t, 2 bridgehead C$\underline{H}$).

Adduct **21a** *of* **1d** *with dimethyl fumarate*. A mixture of **1d** (342 mg), dimethyl fumarate (295 mg) and toluene (5 ml) was heated under reflux for 72 hr. After workup similar to that for **20**, C_6H_6 eluted unreacted **1d** (120 mg) from the florisil column, followed by unreacted fumarate. The *trans*-diester **21a** was eluted by CH_2Cl_2 and obtained as an oil (150 mg; 38%) after removal of the solvent, b.p. 135° (0·02 mm). It formed a single peak in GLC (10%) silicone rubber SE30, 2 m × $\frac{1}{8}$". (Found: MW 316. $C_{18}H_{20}O_5$ requires: 316·34). IR ($CHCl_3$): 2980 (CH), 1740–1730 cm^{-1} (ester CO). UV (MeCN): $\lambda\lambda_{max}$ 256, 265, 277 nm (sh), $\varepsilon\varepsilon_{max}$ 2750, 2800, 1600: NMR ($CDCl_3$): τ 3·50–4·52 (m, 2 vinylic + 4 dienic H); 6·20, 6·47 (AB quartet, J = 9·0 Hz, additional A coupling J = 1·5 Hz, 4 C$\underline{H}_2$O); 6·35 (s, 3 $CO_2C\underline{H}_3$); 6·39 (s, $CO_2C\underline{H}_3$); 6·69 (m, 1 C$\underline{H}CO_2CH_3$); 6·93 (m, 2 bridgehead C$\underline{H}$); 7·30 (m, 1 C$\underline{H}CO_2CH_3$).

Preparation of trans *half ester* **21b**. A mixture of the diester **21a** (100 mg), MeOH (2 ml) and NaOH aq. (5%; 2 ml) was allowed to stand at room temp for 90 min. The solution was concentrated in a vacuum without heating. The resulting solution was acidified with dilute HCl and extracted with ether-C_6H_6. After drying ($MgSO_4$) and removal of solvent the *half ester* **21b** (80 mg; 85%) was obtained, m.p. 185° (EtOAc). (Found: C, 67·01; H, 5·82; MW 302. $C_{17}H_{18}O_5$ requires: C, 67·54; H, 6·00%; MW 302·31). IR ($CHCl_3$): 3400 (OH): 1745–1730 cm^{-1} (carboxylic and ester CO). NMR ($CDCl_3$): τ 1·28 (br s, 1 $CO_2\underline{H}$); 3·52 (q, 2 vinylic H); 3·70–4·62 (m, 4 dienic H); 6·20, 6·47 (AB quartet, J = 9·0 Hz additional A coupling, J = 1·5 Hz; 4 C$\underline{H}_2$O); 6·39 (s, $CO_2C\underline{H}_3$); 6·68 (m, 1 C$\underline{H}CO_2CH_3$); 6·92 (m, 2 bridgehead C$\underline{H}$): 7·38 (m, 1 C$\underline{H}CO_2H$). When saponification is attempted at higher temp, the adduct decomposes.

Equilibration **20** → **21a**. A mixture of *cis*-diester **20** (100 mg), dry MeOH (1 ml) and t-BuOK (2 mg) was allowed to stand under N_2 for 72 hr at room temp. 2 N NaH_2PO_4 aq. was added to pH 5 and the whole extracted with 2 portions of ether-C_6H_6 (25 ml). After washing with water, drying ($MgSO_4$) and removal of solvent a mixture of epimeric **20** and **21a** (80 mg) was obtained The ratio **20**:**21a** was found by GLC on a 10% silicone rubber SE-30 column, 2 m by $\frac{1}{8}$" to be 5:1.

Adduct **24** *of* **1d** *with* p-*benzoquinone*. A mixture of **1d** (110 mg), freshly sublimed benzoquinone (69 mg) and toluene (5 ml) was heated under reflux under N_2 for 2 hr. After cooling and concentrating the solution

at the water pump, ether was added. The greenish *mono-adduct* **24** precipitated (100 mg; 61%), m.p. 137–139°. The analytical sample had m.p. 147–149° (acetone–hexane). (Found: C, 76·94; H, 5·72; MW 280. $C_{18}H_{16}O_3$ requires: C, 77·12; H, 5·75%; MW 280·31). IR ($CHCl_3$): 2990–2930 (CH), 1680 (conjug CO), 1620 cm^{-1} (C=C). UV (MeCN): $\lambda\lambda_{max}$ 258 (sh) 265, 276 (sh), 320 nm (tail), $\varepsilon\varepsilon_{max}$ 2460, 2650, 1760, 70. NMR ($CDCl_3$): τ 3·40 (s, 2 COC<u>H</u>=); 3·71 (t, 2 vinylic H); 3·48–4·50 (m, 4 dienic H); 6·21, 6·38 (AB quartet, J = 8·0 Hz, 4 C<u>H</u>$_2$O); 6·75–6·93 (m, 4 C<u>H</u>).

Photochemical cyclization of **24**. When **24** was allowed to stand in a pyrex flask in daylight, it became colourless. The saturated diketone **25** thus obtained had m.p. 246–247° (acetone). (Found: C, 77·69; H, 5·87; MW 280. $C_{18}H_{16}O_3$ requires: C, 77·12; H, 5·75%; MW 280·31). IR ($CHCl_3$): 2860 (CH), 1765 cm^{-1} (5 membered cyclic CO). UV (MeCN): $\lambda\lambda_{max}$ 248 (sh), 255, 264, 275 nm (sh), $\varepsilon\varepsilon_{max}$ 2700, 2770, 3900, 2200. NMR (pyridine-d_5): 4·16–4·72 (m, 4 dienic H); 5·80, 6·58 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 7·10 (s, 2 COC<u>H</u>—), 7·00–7·25 (m, 2 bridgehead C<u>H</u>); 7·40 (m, 2 COC<u>H</u> in cyclobutane ring); 7·80 (m, 2 cyclobutane C<u>H</u>).

Attempted aromatization of **24**. (a) To a solution of NaOMe (2 mg) in C_6H_6 (5 ml) was added dropwise under N_2 at room temp a solution of **24** (150 mg) in C_6H_6 (5 ml). After standing for 18 hr water was added and the C_6H_6 solution dried ($MgSO_4$). After removal of C_6H_6, **24**[13] (90 mg) was recovered. The aqueous phase was cautiously acidified with 3 N HCl to pH 6 and extracted with ether-C_6H_6. After removal of solvent an oil (25 mg) was obtained, whose NMR spectrum ($CDCl_3$) indicated that it was phthalan **26** τ 2·73 (s, 4 arom H); 4·87 (s, 4 benzylic H).

(b) To a solution of **24** (100 mg) in dry pyridine (2 ml) was added a solution of Ac_2O (120 mg) in dry pyridine (1 ml). The mixture was warmed in an oil bath at 85° for 36 hr. After cooling, addition of ice, ether extraction, washing ether extracts with 10% HCl, water, and drying ($MgSO_4$), the ether was removed, affording 1,4-diacetoxynaphthalene, m.p. 119–121° (benzene–ether). Lit.[14] m.p. 124–125°. The diacetate obtained above was identical (spectroscopically and m.m.p.) with the diacetylated authentic 1,4-naphthalenediol. (Found: MW 244. Calc. for $C_{14}H_{12}O_4$ MW 244·24). NMR ($CDCl_3$): τ 2·00–2·55 (m, 4 arom H); 2·75 (s, 2 AcOC=C<u>H</u>); 7·57 (s, 6 COC<u>H</u>$_3$).

Attempted reaction of **1d** *with dimethyl acetylenedicarboxylate*. A mixture of **1d** (250 mg), the acetylenic ester (180 mg) and C_6H_6 (5 ml) was heated under reflux for 6 hr. After removal of solvent in a vacuum an oily residue was obtained. The products were separated on an Al_2O_3 (type E, E. Merck) 20 × 20 cm plate of 1 mm thickness, C_6H_6 being used as eluent. The fractions consisted of recovered **1d** (20 mg); dimethyl phthalate (120 mg) identified by its NMR spectrum ($CDCl_3$): τ 2·38 (m, 4 arom H); 6·10 (s, 6 CO_2C<u>H</u>$_3$) and polymeric material (75 mg).

Adduct **27** *of* **1d** *with tetracyanoethylene*. A mixture of **1d** (100 mg), tetracyanoethylene (80 mg) and *sym*-tetrachloroethane (5 ml) was heated in an oil bath at 100° for 24 hr. The solvent was removed in a high vacuum. The black residue (150 mg) was triturated with boiling MeOH which removed part of the dark colour. The colourless analytical *tetranitrile* **27** (120 mg: 68%) had m.p. 290° (dec, MeCN). (Found: C, 71·69; H, 4·08; N, 18·46; MW 300. $C_{18}H_{12}N_4O$ requires: C, 71·99; H, 4·03; N, 18·66%; MW 300·31). IR (KBr): 2970, 2920, 2860 (CH), 2250 (CN), 1640 cm^{-1} (C=C). UV (MeCN): λ_{max} 275 nm (br), ε_{max} 3280. NMR (DMSO-d_6): τ 3·32 (t, 2 vinylic H); 3·80–4·25 (m, 4 dienic H); 5·83 (m, 2 bridgehead C<u>H</u>); 6·05, 6·64 (AB quartet, J = 10·0 Hz 4 C<u>H</u>$_2$O).

Adduct **28** *of* **1d** *with N-methylmaleimide*. A mixture of **1d** (200 mg), N-methylmaleimide (140 mg) and C_6H_6 (5 ml) was heated under reflux for 5 hr. After removal of solvent in a vacuum the *adduct* **28** (215 mg; 68%) was obtained, m.p. 201° (acetone–ether). (Found: C, 72·29; H, 5·96; N, 4·66; MW 283. $C_{17}H_{17}NO_3$ requires: C, 72·08; H, 6·01; N, 4·95%; MW 283·31). IR ($CHCl_3$): 2945, 2865 (CH), 1780, 1710 (imide CO), 1435, 1388 cm^{-1} (NMe). UV (MeCN): $\lambda\lambda_{max}$ 254, 263, 274 nm (sh), $\varepsilon\varepsilon_{max}$ 2750, 2750, 1600. NMR ($CDCl_3$): τ 3·75 (q, 2 vinylic H); 3·86–4·50 (m, 4 dienic H); 6·20, 6·38 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 6·85–7·10 (m, 4 C<u>H</u>); 7·18 (s, 3 NC<u>H</u>$_3$).

Adduct **29** *of* **1d** *with N-phenylmaleimide*. A mixture of **1d** (350 mg), N-phenylmaleimide (375 mg) and C_6H_6 (6 ml) was heated under reflux for 6 hr. After removal of solvent the *adduct* 29 (500 mg; 71%) was obtained, m.p. 241–242° (acetone). (Found: C, 76·70; H, 5·39; N, 4·04; MW 345. $C_{22}H_{19}NO_3$ requires: C, 76·50; H, 5·55; N, 4·06%; MW 345·38). IR ($CHCl_3$): 2860 (CH), 1780, 1715 (imide CO), 1600 cm^{-1} (arom C=C). UV (MeCN): $\lambda\lambda_{max}$ 225, 265, 274 nm (sh), $\varepsilon\varepsilon_{max}$ 3670, 3600, 1900. NMR ($CDCl_3$): τ 2·51–2·96 (m, 5 arom H); 3·64 (q, 2 vinylic H); 3·85–4·49 (m, 4 dienic H); 6·16, 6·36 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 6·78–6·92 (m, 4 C<u>H</u>).

Diadduct **30** *from* **18** *and* **2**. To a solution of **18** (50 mg) in acetone (2 ml) was added dropwise during 90 min a solution of **2** (34 mg) in acetone at room temp. The colourless *di-adduct* **30** (40 mg; 50%) pre-

cipitated, m.p. 275–278° (dec, MeCN). (Found: C, 64·13; H, 4·65, MW 445. $C_{24}H_{19}N_3O_6$ requires: C, 64·71; H, 4·30%; MW 445·42). IR (KBr): 3075, 2950, 2880 (CH); 1850, 1790, 1720 (anhydride and imide CO); 1600 cm^{-1} (arom C=C). UV (MeCN): λ_{max} 253 nm, ε_{max} 5250. NMR (DMSO-d_6): τ 2·55 (s, 5 arom H); 3·38 (t, 2 vinylic H adj. thiazoline ring); 3·62 (quartet, 2 vinylic H adj. anhydride ring); 4·87 (t, 2 N-C<u>H</u>); 6·07, 6·28 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 6·71 (s, 2 CO-C<u>H</u>); 6·82 (m, 2 bridgehead C<u>H</u>).

Diadduct **31** *from* **28** *and* **2**. To a solution of **28** (283 mg) in acetone (3 ml) was added as above a solution of **2** (192 mg) in acetone (3 ml). After similar workup the *diadduct* **31** (330 mg; 71%) was obtained, m.p. 301° (dec, aq MeOH). (Found: C, 62·66; H, 4·73; N, 11·34; M^+-H_2O, 458. $C_{25}H_{22}N_4O_5 \cdot H_2O$ requires: C, 63·01; H, 5·05; N, 11·74%; MW 458·46 + 18). IR (KBr): 3060–2890 (CH), 1770, 1720 (CO); 1600 cm^{-1} (arom C=C). UV (MeCN): λ_{max} 252 nm, ε_{max} 4400. NMR (DMSO-d_6): τ 2·55 (s, 5 arom H), 3·35 (t, 2 vinylic H adj. triazoline ring); 3·80 (quartet, 2 vinylic H adj. imide ring); 4·85 (t, 2 N-C<u>H</u>); 6·02, 6·33 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 6·70 (s, 3H, NC<u>H</u>$_3$); 7·28 (s, 2 COC<u>H</u>); 7·15–7·35 (m, 2 bridgehead C<u>H</u>).

Diadduct **32** *from* **29** *and* **2**. To a solution of **29** (100 mg) in acetone (3 ml) was added as above a solution of **2** (55 mg) in acetone (3 ml). The precipitated *diadduct* **32** (100 mg; 66%) had m.p. 299° (dec, AcOH). (Found: C, 68·80; H, 4·67; N, 10·54; MW 520. $C_{30}H_{24}N_4O_5$ requires: C, 69·23; H, 4·61; N, 10·77%; MW 520·52). UV (MeCN): λ_{max} 253 nm, ε_{max} 5250. NMR (pyridine-d_5): 2·55 (s, 5 H <u>N</u>-arom); 2·34–2·70 (m, 5 arom H of maleimide ring); 3·37 (t, 2 vinylic H adj. triazoline ring); 3·58 (t, 2 vinylic H adj. maleimide ring); 4·65 (t, 2 N-C<u>H</u>); 5·54, 6·12 (AB quartet, J = 9·0 Hz, 4 C<u>H</u>$_2$O); 6·50 (m, 2 bridgehead C<u>H</u>); 6·84–6·98 (m, 2 COC<u>H</u>).

Adduct **34** *of* **33** *with* **2**. To a solution of 12-oxa[4.4.3]propella-2,4,8-triene **33** (52 mg) in acetone (3 ml) was added dropwise at room temp a solution of **2** (53 mg) in acetone (1·5 ml). The colour of the reagent was discharged instantaneously. After 1·5 hr the solvent was removed and the residue triturated with ether. The solid **34** was removed by filtration (84 mg; 81%), m.p. 209–211° (dec. 207°, petroleum ether 60–70°-acetone). (Found: MW 349. $C_{20}H_{19}N_3O_3$ requires: MW 349·38). IR ($CHCl_3$): 1773, 1718 cm^{-1} (CO). NMR ($CDCl_3$); τ 2·55 (s, Ar <u>H</u>); 3·39 (t, 2=C<u>H</u>, J = 3·5 Hz); 3·97 (m, 2=C<u>H</u>); 5·35 (t, 2 bridgehead H, J = 3·5 Hz); 6·33, 6·48 (AB quartet, 4 C<u>H</u>$_2$O, J = 9·5 Hz); 7·31–7·82 (m, 4 allylic H).

Diels–Alder adduct **35** *of* **1b** *with* N-*methylmaleimide*.—A solution of **1b**[12] (160 mg) and N-methylmaleimide (90 mg) in C_6H_6 (5 ml) was heated under reflux for 4 hr. After removal of C_6H_6 and crystallization the adduct **35** (190 mg; 80%) had m.p. 192° (CH_2Cl_2-ether). (Found: C, 66·72; H, 4·80; N, 8·55; MW 324. $C_{18}H_{16}N_2O_4$ requires: C, 66·66; H, 4·94; N, 8·65%; MW 324·32). IR ($CHCl_3$): 1775, 1715 (imide CO), 1435, 1380 cm^{-1} (N-methyl). UV (MeCN): $\lambda\lambda_{max}$ 265, 276, 288 (sh) nm. $\varepsilon\varepsilon_{max}$ 1670, 1600, 920. NMR ($CDCl_3$): τ 3·72 (t, 2 isolated =C<u>H</u>); 3·75–4·33 (m, 4 conjug =C<u>H</u>); 6·43 (m, 2 bridgehead C<u>H</u>); 6·93 (br s, 2 C<u>H</u>); 7·10 (s, 3 NC<u>H</u>$_3$); 7·13 (s, 3 NC<u>H</u>$_3$).

Adduct **36** *of* **1b** *with* N-*phenylmaleimide*. A solution of **1b** (100 mg) and N-phenylmaleimide (85 mg) in C_6H_6 (5 ml) was heated under reflux for 6 hr. After removal of the solvent and crystallization the adduct **36** (135 mg; 71%) had m.p. 204° (CH_2Cl_2-hexane). (Found: C, 70·93; H, 4·66; N, 7·23; MW 386. $C_{23}H_{18}N_2O_4$ requires: C, 71·50; H, 4·70; N, 7·25%; MW 386·39). IR ($CHCl_3$): 1775, 1710 (imide CO), 1600 cm^{-1} (phenyl). UV (MeCN): $\lambda\lambda_{max}$ 265, 276, 287 (sh) nm. $\varepsilon\varepsilon_{max}$ 2100, 1850, 1100. NMR ($CDCl_3$): τ 2·52–2·96 (m, 5 Ar <u>H</u>); 3·74 (q, 2=C<u>H</u>); 3·85–4·30 (m, 4 conj =C<u>H</u>); 6·35 (m, 2 bridgehead C<u>H</u>); 6·77 (br s, 2 C<u>H</u> adj to imide ring); 7·10 (s, 3 N C<u>H</u>$_3$).

Adduct **37** of **1b** *with dimethyl maleate*. A solution of **1b** (100 mg) and dimethyl maleate (75 mg) in toluene (5 ml) was heated under reflux for 24 hr. After removal of solvent an oily solid remained. This was chromatographed on florisil (15 g) using petroleum ether (60–70°)-CH_2Cl_2. After the starting materials the diester **37** was eluted (60 mg; 32%), m.p. 158° (ether). (Found: C, 64·21; H, 5·37; N, 4·08; MW 357. $C_{19}H_{19}NO_6$ requires: C, 63·87; H, 5·36; N, 3·92%; MW 357·35). IR ($CHCl_3$): 1750 (ester CO), 1780, 1710 (imide CO), 1435, 1380 cm^{-1} (N-Me). UV (MeCN): $\lambda\lambda_{max}$ 266, 276, 288 (sh) nm. $\varepsilon\varepsilon_{max}$ 3450, 3430, 2040. NMR ($CDCl_3$): τ 3·70 (q, 2 isolated=C<u>H</u>); 3·80–4·49 (m, 4 conjug=C<u>H</u>); 6·40 (s, 6 $CO_2C\underline{H}_3$); 6·75 (m, 4 C<u>H</u>); 7·10 (s, 3 NC<u>H</u>$_3$).

Bis-adduct **38** *of* **1b** *and* N-*methylmaleimide*. A solution of the monoadduct **35** (150 mg) and N-methylmaleimide (60 mg) in toluene (6 ml) was heated under reflux for 12 hr in N_2 atmosphere. Crystallization after removal of solvent afforded the *bis-adduct* **38** (120 mg; 60%), m.p. 334° (dec, CH_2Cl_2). (Found: N, 9·60; MW 435. $C_{23}H_{21}N_3O_6$ requires: N, 9·65%; MW 435·42). IR ($CHCl_3$): 1780, 1720 (imide CO), 1620 (C=C), 1390 cm^{-1} (N-Me). UV (MeCN): λ_{max} 255 nm, ε_{max} 1030. NMR ($CDCl_3$): τ 3·80 (m, 4=C<u>H</u>); 6·41 (m, 4 bridgehead C<u>H</u>); 7·12 (s, 6 H, NC<u>H</u>$_3$); 7·14 (s, 3 H, NC<u>H</u>$_3$); 6·92–7·25 (m, 4 C<u>H</u> adj to imide rings.

Bis-adduct **39** *of* **1b** *and* N-*phenylmaleimide*. A solution of the monoadduct **36** (150 mg) and N-phenylmaleimide (70 mg) in toluene (5 ml) was heated under reflux for 16 hr. The solvent was removed and the

bis-adduct **39** crystallized (110 mg; 57%), m.p. 328° (dec, MeCN). (Found: N, 7·04; MW 559. $C_{33}H_{25}N_3O_6$ requires: N, 7·51%; MW 559·55). IR (KBr): 1775, 1720 (imide CO), 1605 cm^{-1} (phenyl). UV (MeCN): λ_{max}255 nm, ε_{max} 1030. NMR (DMSO-d_6): τ 2·40–2·95 (m, 10 Ar H); 3·70 (m, 4=CH); 6·48 (m, 4 bridgehead CH); 6·70 (s, 3 NCH_3); 6·78–7·06 (m, 4 CH adj to imide rings).

Adduct **40** *of* **1c** *with maleimide.* A solution of **1c** (70 mg) and maleimide (35 mg) in benzene (5 ml) was heated under reflux for 8 min. The product precipitated. After an additional hour of heating the solvent was removed. The adduct **40** (70 mg; 70%) had m.p. 188–190° (MeCN). (Found: C, 63·41; H, 4·35; N, 9·68; MW 296. $C_{16}H_{12}N_2O_4$ requires: C, 64·86; H, 4·08; N, 9·46%; MW 296·27). IR (KBr): 3180, 3080 (NH), 1770, 1710 cm^{-1} (imide CO). UV (MeCN): $\lambda\lambda_{max}$ 266, 275, 287 (sh) nm. $\varepsilon\varepsilon_{max}$ 1820, 1780, 1100. NMR (DMSO-d_6): τ 3·60 (t, 2 isol=CH); 3·62–4·34 (m, 4 conjug=CH); 6·70 (m, 2 bridgehead CH); 7·00 (d, 2 CH).

Adduct **41** *of* **1c** *with* N-*methylmaleimide.* A solution of **1c** (140 mg) and N-methylmaleimide (80 mg) in benzene was heated under reflux for 15 min whereupon colourless crystals precipitated. The mixture was allowed to stand for 2 hr, the solvent removed and the adduct **41** (180 mg; 84%) had m.p. 184° (MeOH). (Found: C, 64·94; H, 4·58; N, 9·12; MW 310. $C_{17}H_{14}N_2O_4$ requires: C, 65·80; H, 4·55; N, 9·03%; MW 310·30). IR($CHCl_3$): 3390 (NH), 1780, 1720 (imide CO), 1440, 1380 cm^{-1} (N-Me). UV (MeCN): $\lambda\lambda_{max}$ 266, 275, 287 (sh) nm, $\varepsilon\varepsilon_{max}$ 1700, 1650, 1000. NMR (DMSO-d_6): τ − 1·17 (br s, imide NH); 3·73 (t, 2 isolated =CH); 3·75–4·35 (m, 4 conjug=CH); 6·70 (m, 2 bridgehead CH); 7·02 (d, 2 CH); 7·27 (s, 3 NCH_3).

Adduct **42** *of* **1c** *with* N-*phenylmaleimide.* A solution of **1c** (100 mg) and N-phenylmaleimide (90 mg) in C_6H_6 (5 ml) was heated under reflux for 15 min. The product precipitated. After an additional hr the solvent was removed. The adduct **42** (150 mg; 80%) had m.p. 196–197° (MeCN). (Found: C, 70·90; H, 4·26; N, 7·67; MW 327. $C_{22}H_{16}N_2O_4$ requires: C, 70·96; H, 4·33; N, 7·52%; MW 327·36). IR ($CHCl_3$): 3390 (NH), 1780, 1720 (imide CO), 1600 cm^{-1} (phenyl). UV (MeCN): $\lambda\lambda_{max}$ 265, 275, 287 (sh) nm. $\varepsilon\varepsilon_{max}$ 1550, 1430, 820. NMR (DMSO-d_6): τ 2·40–2·97 (m, 5 ArH); 3·60 (q, 2 isol=CH); 3·65–4·30 (m, 4 conjug=CH); 6·65 (m, 2 bridgehead CH); 6·85 (d, 2 CH).

Adduct **43** *of* **1c** *with* **2**. To a solution of **1c** (100 mg) in acetone (2 ml) was added dropwise at 0° a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (90 mg) in acetone (2 ml). The red colour of **2** disappeared instantaneously. The adduct **43** precipitated (70 mg; 40%) and had m.p. 255–258° (dec, acetone). (Found: C, 63·70; H, 4·17; N, 14·77; MW 374. $C_{20}H_{14}N_4O_4$ requires: C, 64·17; H, 3·77; N, 14·97%; MW 374·34). IR (KBr): 3180 (NH), 1780, 1710 (imide CO), 1600 (phenyl), 1500 cm^{-1} (C—N). UV (MeCN): λ_{max}252 nm, ε_{max} 4700. NMR (DMSO-d_6): τ − 2·00 (br s, imide NH); 2·58 (m, 5 Ar H); 3·30 (t, 2 isol=CH); 3·85–4·30 (m, 4 conjug=CH); 4·69 (m, 2 bridgehead CH adj to N).

Acknowledgement—We thank Dr. J. Altman for help and discussion at the early stages of this work.

REFERENCES

[1] Propellanes, XVIII. R. Bar-Adon, S. Schlick, B. L. Silver and D. Ginsburg, *Tetrahedron Letters* 325 (1972)

[2] O. Sciacovelli, W. von Philipsborn, C. Amith and D. Ginsburg, *Tetrahedron* **26**, 4589 (1970)

[3] J. Altman and D. Ginsburg, *Ibid.* **27**, 93 (1971)

[4] K. B. Birnbaum, J. Altman, T. Maymon and D. Ginsburg, *Tetrahedron Letters* 2051 (1970); *cf.* K. B. Birnbaum, *Acta Crystallog.* (in press)

[5] G. I. Birnbaum (in press)

[6] J. Altman, E. Cohen, T. Maymon, J. B. Petersen, N. Reshef and D. Ginsburg, *Tetrahedron* **25**, 5115 (1969)

[7] A. S. Onischchenko, *Diene Synthesis*, pp. 56–60, Israel Program for Scientific Translations, Jerusalem (1964)

[8] [a] M. Avram, G. Mateescu and C. D. Nenitzescu, *Liebigs Ann. Chem.* **636**, 174 (1960);
[b] M. Avram, E. Sliam and C. D. Nenitzescu, *Ibid.* **636**, 184 (1960);
[c] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ibid.* **560**, 1 (1948)

[9] H. L. Holmes, *Organic Reactions*, Vol. IV, pp. 82–83, 153–160. Wiley, New York (1948)

[10] D. Tatarsky, M. Sc. Thesis, Technion, November 1970

[11] Private communication from Professor J. D. Dunitz

[12] C. Amith, unpublished results from this laboratory; *cf.* E. R. Wagner and A. D. Rudzik, *J. Med. Chem.* **10**, 607 (1967)
[13] J. Entel, C. H. Ruof and H. C. Howard, *J. Am. Chem. Soc.* **74**, 441 (1952)
[14] V. O. Lukashevich and E. N. Dokunikhina, *Dokl. Akad. Nauk SSSR* **167** (2), 357 (1966); *Chem. Abstr.* **64**, 19511e (1966)