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Studies of Bridged Benzoheterocycles. Part III.[1] Cycloadditions of 1,4-Epoxy-1,4-dihydronaphthalene to Some Dipolar Compounds and Dienes

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The nature of the 1,4-epoxy-1,4-dihydronaphthalene skeleton was studied by performing MO calculations and by investigating cycloadditions to some dipolar compounds and dienes. Reactions of 1,4-epoxy-1,4-dihydronaphthalene (I) with phenylglyoxylonitrile oxide, 1-methylpyridinium-3-olate, ethyl azidoformate, and phenyl azide gave the corresponding 1 : 1 adducts. Similar treatments of compound (I) with benzenesulphonyl and tosyl azides afforded only imine derivatives. The reaction of compound (I) with 6,6-dimethylfulvene yielded a mixure of isomeric 1 : 1 and 1 : 2 adducts. The stereochemistry of the adducts is discussed in the light of spectroscopic data. Their thermal behaviour is also reported.

ALTHOUGH the dipolarophilicity and dienophilicity of 1,4-epoxy-1,4-dihydronapthalene (I) are expected to be increased by ring strain (relative to 1,4-dihydronaphthalene) and further by orbital participation of the nonbonding electrons of the oxygen atom (relative to 1,4-dihydro-1,4-methanonaphthalene), no systematic study of the cycloaddition reactions of compounds of this type has been reported.

We have already described the cycloaddition reactions of compound (I) with azo- and acetylenic compounds[2] and with tropone and tropolone[1] as the electron-poor components. The abnormally high reactivity in reactions with the troponoid compounds can be explained in terms of a Diels–Alder mechanism with inverse electron demand.

The present paper describes the calculation of the charge distribution in structure (I) and cycloaddition reactions with some dipolar compounds and cyclic dienes.

While this paper was in preparation two similar cycloadditions of compound (I) with dienes such as 3,6-di-(2-pyridyl)-*s*-tetrazine and α-pyrone were reported.[3,4]

INDO Calculation for Structure (I).—Similar studies

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[1] Part II, T. Sasaki, K. Kanematsu, and K. Hayakawa, *J.C.S. Perkin I*, 1972, 1951.

[2] T. Sasaki, K. Kanematsu, and M. Uchide, *Tetrahedron Letters*, 1971, 4855.

[3] R. N. Warrener, *J. Amer. Chem. Soc.*, 1971, **93**, 2346.

[4] D. Wege, *Tetrahedron Letters*, 1971, 2377.

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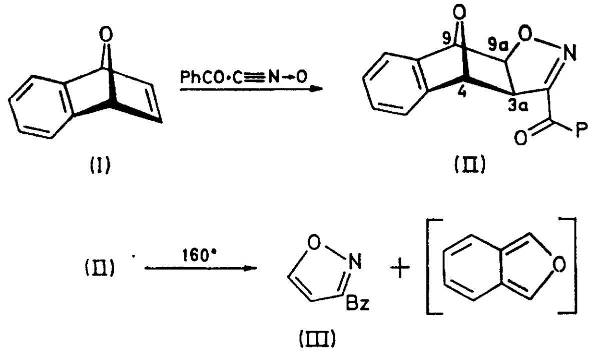
on norbornadiene, norbornene, and related compounds have been reported previously.[5] The charge distribution in structure (I) was calculated by the INDO method (see Experimental section); the results, and those for norbornene and norbornadiene, are shown in the Table. As expected, the value of the $P_{\pi 2 \pi 3}$ for structure (I) is larger than those for norbornene and norbornadiene, presumably owing to orbital participation by the non-bonding electrons of the oxygen atom.

Charge distributions in compound (I) and analogues

	Compound (I)	Norbornene	Norbornadiene *
$P_{\pi 2 \pi 3}$	1·017	0·959	0·958
Charge density at C-2	4·088	4·085	4·075

* See ref. 5.

Reactions with Dipolar Compounds.—The reaction of compound (I) with phenylglyoxylonitrile oxide prepared *in situ*[6] from phenylglyoxylohydroximic acid chloride in ether at ambient temperature gave a 1 : 1 adduct (II) in 60% yield. The i.r. spectrum showed a characteristic benzoyl band at 1648 cm^{-1}, and the n.m.r. spectrum exhibited signals for aromatic protons at τ 1·70—1·87 (2H, m) and 2·39—2·92 (7H, m), for oxygen bridgehead protons (H-4 and H-9) as singlets at τ 4·37 and 4·42, and for ring-junction protons (H-3a and H-9a) as doublets (J 8·0 Hz) at τ 5·01 and 6·06. The absence of vicinal couplings $J_{3a,4}$ and $J_{9,9a}$ indicated the isoxazoline ring to be *exo* to the cyclohexene ring. Thus, the product was identified as the *exo*-1,3-dipolar cycloadduct (II). The mass spectrum had no parent ion peak (m/e 291) but a base peak at m/e 118 (C_8H_6O, isobenzofuran) and prominent fragments at m/e 105 (20%) and 89 (13%). From these results we concluded that the adduct (II) is thermally decomposed to isobenzofuran. In fact, thermolysis of the adduct in *o*-dichlorobenzene gave 3-benzoylisoxazole (III) (40%) together with large amounts of polymeric material. Attempts to isolate isobenzofuran from the mixture were unsuccessful, presumably owing to its rapid polymerization.



Scheme 1

The reaction of compound (I) with 1-methylpyridinium-3-olate[7] under reflux in tetrahydrofuran for 36 h gave a 1 : 1 adduct (IVa) in 80% yield. Structural proof was based on spectroscopic data and chemical conversions. The i.r. spectrum had a characteristic $\alpha\beta$-unsaturated carbonyl band at 1670 cm^{-1}, and the n.m.r. spectrum exhibited signals for aromatic protons at τ 2·83 (4H, m), for vinyl protons as double doublets at 3·13 (1H, J 10·0 and 4·2 Hz) and 4·15 (1H, J 10·0 and 2·0 Hz), for oxygen bridgehead protons as singlets at τ 4·63 (1H) and 4·68 (1H), for nitrogen bridgehead protons at τ 6·34 (1H, s) and 6·15 (1H, d), for ring-junction protons as doublets (J 7·0 Hz) at τ 7·62 (1H) and 7·84 (1H), and for N-methyl protons at τ 7·50 (3H, s). The absence of appreciable couplings $J_{2,3}$ and $J_{7,8}$, and $J_{1,2}$ and $J_{8,9}$ indicated the *exo*-configurations shown. Catalytic hydrogenation of adduct (IVa) in ethanol over palladium–charcoal rapidly yielded a dihydro-compound (no olefinic proton n.m.r. signals. Treatment of adduct (IVa) with polyphosphoric acid (PPA) gave the naphthalene derivative (IVb) in quantitative yield. Compound (IVa) was stable in dichlorobenzene at 130—150°.

For comparison of the cycloaddition reactivity of compound (I), the reaction of dimethyl 7-oxabicyclo[2,2,1]-hepta-2,5-diene-2,3-dicarboxylate (V)[8] with 1-methylpyridinium-3-olate was performed. When the reagents were heated under reflux in tetrahydrofuran for 3 days, the 1 : 1 adducts (VI) (7·4%) and (VII) (8·2%) were obtained. Unequivocal structural assignments were made on the basis of spectroscopic data. The i.r. (1740, 1720, and 1675 cm^{-1}) and n.m.r. [τ ($CDCl_3$) 3·31 (1H, dd, H-5, J 6·0 and 2·0 Hz), 3·35 (1H, q, H-9, J 9·3 and 4·5 Hz), 3·63 (1H, dd, H-4, J 6·0 and 2·0 Hz), 3·73 (1H, dd, H-10, J 9·3 and 1·5 Hz), 5·40 (2H, m, H-3 and H-6), 5·90 (1H, dd, H-8, J 4·5 and 1·5 Hz), 6·15 (1H, m, H-1), 6·82 (3H, s, CO_2Me), 6·84 (3H, s, CO_2Me), and 7·56 (3H, s, NMe)] spectra indicated the product (VI) to be the 1,3-dipolar cycloadduct with two methoxycarbonyl groups on the methine positions (C-2 and C-7). Its exact configuration could not be determined because of the absence of protons on the 2- and 7-positions. However, since C-10 was deshielded by the anisotropic effect of the bridge oxygen atom in comparison with the corresponding positions in structures (IVa) and (VII), the *endo,exo*-configuration as shown is preferred. The i.r. spectrum of adduct (VII) showed characteristic bands at 1735, 1710, 1675, and 1640 cm^{-1}, and the n.m.r. spectrum exhibited signals at τ 2·96 (1H, q, H-9, J 9·0 and 4·5 Hz), 3·95 (1H, dd, H-10, J 9·0 and 2·0 Hz), 4·72 (1H, s, H-3 or H-6), 4·75 (1H, s, H-6 or H-3), 6·13 (1H, d, H-8, J 4·5 Hz), 6·15 (3H, s, CO_2Me), 6·17 (3H, s, CO_2Me), 6·41br (1H, s, H-2), 7·40 (1H, d, H-7, J 8·7 Hz), 7·52 (3H, s, NMe), and 7·66 (1H, d, H-2, J 8·7 Hz).

It was therefore concluded to be the 1,3-dipolar cycloadduct with the two methoxycarbonyl groups on the 4,5-double bond. The coupling pattern in the n.m.r. spectrum, similar to that of adduct (IVa) indicated the *exo,exo*-configuration shown.

When compound (V) and 1-methylpyridinium-3-olate

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[5] H. Konishi, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, 1970, **43**, 1676.

[6] R. Huisgen and W. Mack, *Tetrahedron Letters*, 1961, 583.

[7] A. R. Katritzky and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1970, **92**, 4134.

[8] G. Kaupp and H. Prinzbach, *Chem. Ber.*, 1971, **104**, 182.

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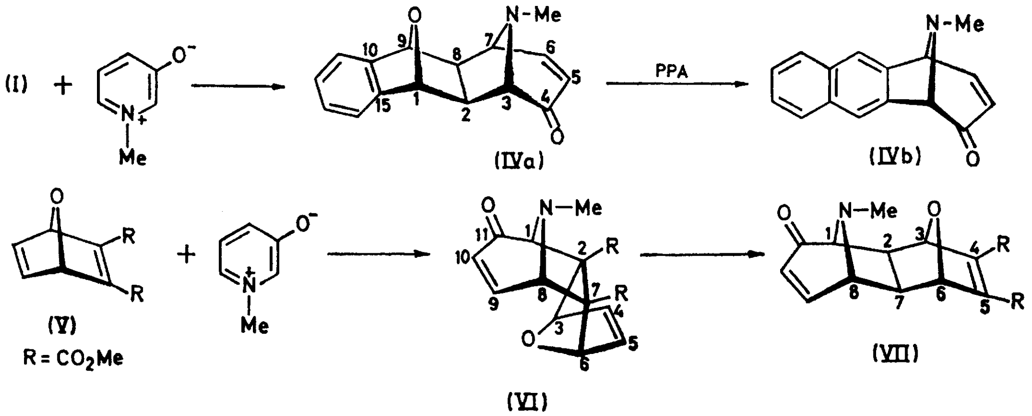
were heated at 130° in chlorobenzene, only the adduct (VII) was obtained (22% yield). Heating the adduct (VI) in chlorobenzene at 130° for 20 h gave the isomer (VII) in appreciable yield. Thus adducts (VI) and (VII) are considered to be the products of kinetic control and thermodynamic control, respectively.



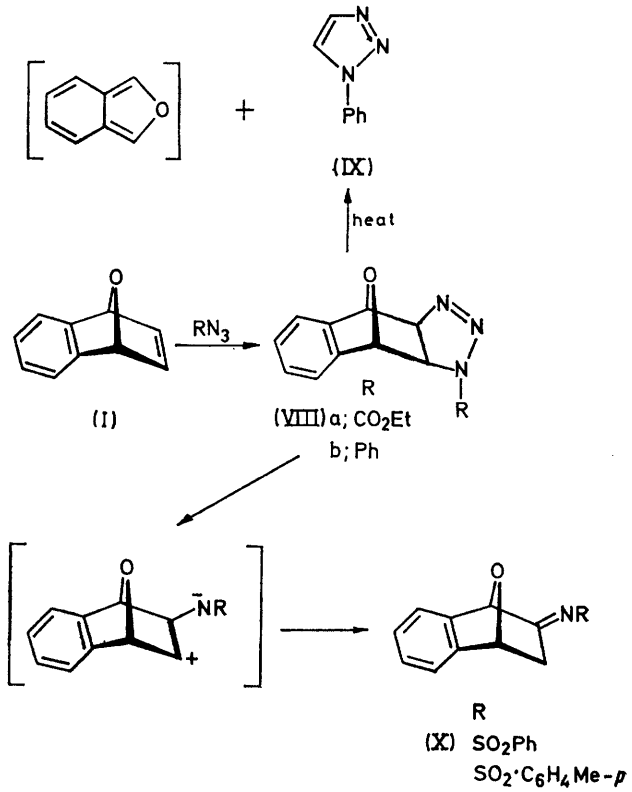
SCHEME 2

Reactions with Azides.—The reactions of compound (I) with ethyl azidoformate and phenyl azide in benzene at room temperature gave adducts (VIIIa) and (VIIIb) in 78 and 98% yield, respectively. Analyses and spectroscopic data (Experimental section) showed the products to be 1,3-dipolar cycloadducts; the *exo*-configurations were confirmed by the n.m.r. spectra. The mass spectra of both adducts had no molecular ion; that of the adduct (VIIIa) had a base peak at *m/e* 130 and prominent fragments at *m/e* 131 (64%), 158 (64), and 118 (61), and that of (VIIIb) exhibited a base peak at 206 and a characteristic peak at *m/e* 118 (40%). These fragmentations indicated the thermal instability of the adducts; the peak at *m/e* 118 was due to isobenzofuran.

Heating adduct (VIIIa) in toluene at 110° gave an intractable tar, whereas heating adduct (VIIIb) in benzene at 170° gave 1-phenyltriazole (IX) in 63% yield.

Similar reactions of compound (I) with benzenesulphonyl azide and tosyl azide in benzene at room temperature gave products (Xa) and (Xb) in 90 and 70% yield, respectively. The loss of nitrogen from the corresponding 1 : 1 adducts was shown by elemental analyses and mass spectra. The i.r. spectra of both products showed a characteristic band at 1627 cm^{-1} (C=N). The n.m.r. spectra had no olefinic proton signals and confirmed the imine structures shown. Hydrolysis gave the corresponding benzensulphonic acids. The imines are probably formed by loss of nitrogen from the initially produced 1,3-dipolar cycloadducts. No direct formation of triazoline, aziridine, or rearranged enamine was observed.

In contrast, the reactions of norbornadiene with benzenesulphonyl azide and cyanogen azide gave the rearranged enamines (C) *via* a Cope rearrangement as illustrated in Scheme 4; the rearrangements would appear to be facilitated by rearside participation of the double bond.[9] Such participation in the 1,4-epoxy-1,4-dihydronaphthalene adduct might be energetically unfavourable because of destruction of the aromaticity in the fused benzene ring.



SCHEME 3

Reactions with Cyclic Dienes.—The reaction of compound (I) with furan at 130° gave a 1 : 1 adduct (XI) in 85% yield, identified as a $[4 + 2]\pi$ cycloadduct by the n.m.r. spectrum (Experimental section). The values of 3·0 Hz for $J_{2,3}$ and $J_{6,7}$ indicated the *exo,endo*-configuration. Heating the adduct (XI) in *o*-chlorobenzene at

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[9] A. C. Oehlschalager and L. H. Zalkow, *J. Org. Chem.*, 1965, **30**, 4205.

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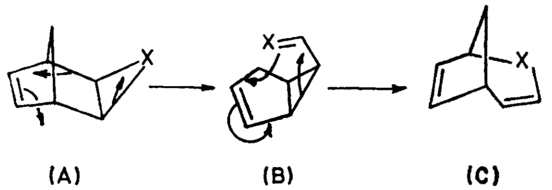
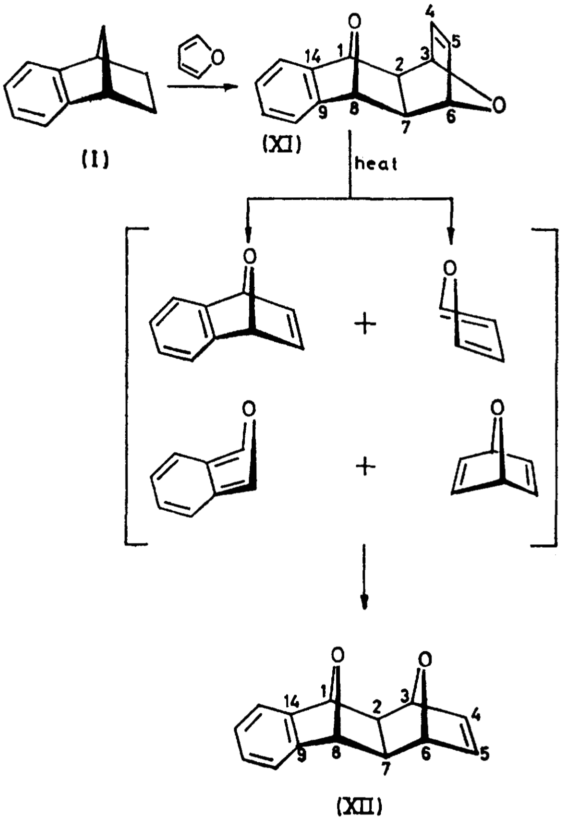
160° for 8 h gave an isomer (XII) in 19% yield. The lack of appreciable couplings $J_{7,8}$ and $J_{1,2}$, and $J_{2,3}$ and $J_{6,7}$ indicated the *exo,exo*-configuration shown. The conversion (XI) ⟶ (XII) could be explained in terms of either of two different pathways. In one case, isomer (XII) could be formed by a Diels–Alder reaction of 1,4-epoxy-1,4-dihydronaphthalene and furan, initially formed by a retro-Diels–Alder reaction of adduct (XI). In the other, a Diels–Alder reaction of isobenzofuran and the epoxide (I), formed by cycloreversion of adduct (XI), could give the isomer (XII). The mass spectrum of adduct (XI) showed a weak parent peak at *m*/*e* 212 and characteristic peaks at *m*/*e* 118 (40%) and 144 (24%); these peaks might be caused by both cycloreversion and retro-Diels–Alder fragmentations.



Scheme 4

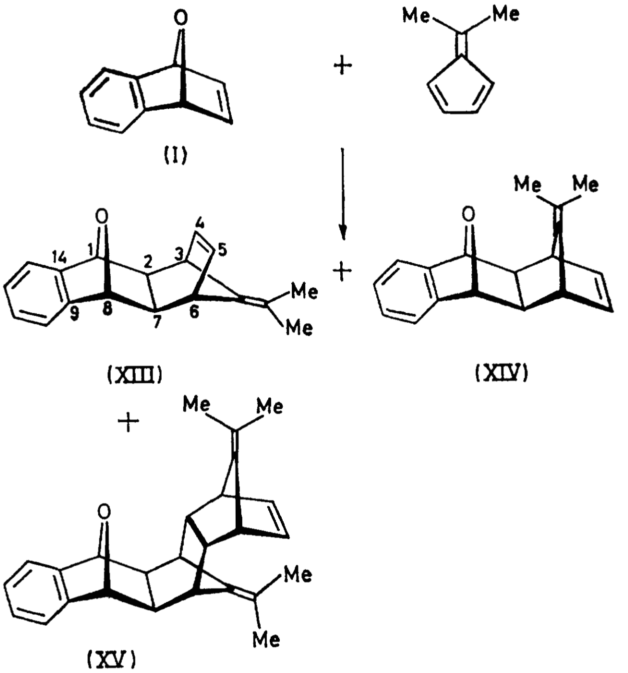


Scheme 5

A similar reaction of compound (I) with 6,6-dimethylfulvene in benzene at 130° for 7 h afforded a mixture of three products (XIII) (60%), (XIV) (8%), and (XV) (7%). Elemental analyses and mass spectra indicated (XIII) and (XIV) to be 1 : 1 adducts and (XV) to be a 1 : 2 adduct. The nature of adducts (XIII) and (XIV) was confirmed by their n.m.r. spectra, which showed the adduct (XIII) to be the *exo,endo*-isomer ($J_{1,2} = J_{7,8} = 0$, $J_{6,7} = J_{2,3} = 2·8$ Hz), and the adduct (XIV) to be the *exo,exo*-isomer ($J_{1,2} = J_{7,8} = J_{6,7} = J_{2,3} = 0$).

The *exo,endo,exo,endo*-configuration of the 1 : 2 adduct (XV) was also confirmed by the n.m.r. spectrum.

The foregoing results show that 1,4-epoxy-1,4-dihydronaphthalene is a more effective dipolarophile and dienophile than the 1,4-methano-analogue.[10] This seems to agree with the result of the MO calculation.



Scheme 6

EXPERIMENTAL

M.p.s were measured with a Yanagimoto apparatus. Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. N.m.r. spectra were taken with a JEOL C-60-XL spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as internal standard. I.r. spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100—150°.

INDO Calculations for Structure (I).—For the geometry of (I), we adapted the data for norbornadiene and norbornene. Thus, we used r(C1–C2) = 1·522 Å, r(C2–C3) = 1·333 Å, r(C1–C8a) = 1·522 Å, r(C4a–C8a) = 1·397 Å, r(C8–C8a) = 1·397 Å, r(C1–H1) = 1·095 Å, r(C2–H2) = 1·085 Å, r(C8–H8) = 1·084 Å, r(C1–O) = 1·430 Å, θ(C3–C2–H) = 125° 27′, θ(C1–C2–C3) = 109° 6′, θ(C7–C8–C8a) = 120°, θ(C2–C1–C8a) = 102° 12′, θ(O–C1–H1) = 105° 59′, θ(C8a–C8–H8) = 120°.

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[10] M. M. Martin and R. A. Koster, *J. Org. Chem.*, 1968, **33**, 3428.

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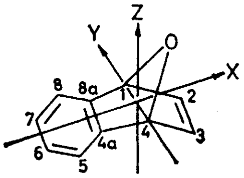
3-*Benzoyl*-3a,4,9,9a-*tetrahydronaphth*[2,3-d]*isoxazole* (II).—Phenylglyoxylonitrile oxide was prepared *in situ* from phenylglyoxylohydroxamic acid chloride (0·336 g) and triethylamine (0·2 g) in anhydrous ether (15 ml) and condensed with compound (I) (0·274 g) in anhydrous ether (15 ml) at room temperature; the mixture was filtered to remove triethylamine hydrochloride. The solution was concentrated *in vacuo* to give the 1 : 1 *adduct* (II) (0·3 g, 60%), m.p. 136—137° (Found: C, 74·0; H, 4·65; N, 4·75. $C_{18}H_{13}NO_3$ requires C, 74·2; H, 4·5; N, 4·8%), τ ($CDCl_3$) 1·70—1·87 (2H, m, ArH), 2·39—2·92 (7H, m, ArH), 4·37 (1H, s, H-4 or H-9), 4·42 (1H, s, H-9 or H-4), 5·01 (1H, d, H-9a, *J* 8·0 Hz), and 6·06 (1H, d, H-3a, *J* 8·0 Hz), *m*/*e* 118 (100%), 105 (20), 89 (13), and 77 (31).



Molecular co-ordinate system and *p*-orbital orientation used for structure (I)

Thermolysis of the Adduct (II).—A solution of adduct (II) (0·153 g) in *o*-dichlorobenzene (3 ml) was heated at 160° for 5 h. Chromatography on silica gel (benzene as eluant), followed by recrystallization from benzene gave 3-benzoylisoxazole (III) (0·035 g, 40%) as an oil, $\nu_{max.}$ (neat) 1660 cm^{-1}, τ ($CDCl_3$) 1·57 (1H, d, *J* 2·0 Hz), 1·7—1·9 (2H, m), 2·4—2·7 (3H, m),and 3·20 (1H, d, *J* 2·0 Hz); 2,4-*dinitrophenylhydrazone*, m.p. 235—239° (Found: C, 54·4; H, 3·45; N, 19·55. $C_{16}H_{11}N_5O_5$ requires C, 54·4; H, 3·15; N, 19·8%).

17-*Methyl*-16-*oxa*-17-*azapentacyclo*[7,6,1,1^{3,7},0^{2,8}0^{10,15}]-*heptadeca*-5,10,12,14-*tetraen*-4-*one* (IVa).—A solution of compound (I) (0·73 g) and 1-methylpyridinium-3-olate (0·55 g) in tetrahydrofuran (20 ml) was refluxed for 36 h. After evaporation to dryness, chromatography on silica gel (benzene as eluant) followed by recrystallization from benzene–hexane gave the *adduct* (IVa) (0·8 g) as yellow prisms, m.p. 158—159° (Found: C, 76·15; H, 6·25; N, 5·7. $C_{16}H_{15}NO_2$ requires C, 75·85; H, 5·95; N, 5·55%), $\nu_{max.}$ (KBr) 1670 cm^{-1}, *m*/*e* 253 (73%) and 118 (49), τ ($CDCl_3$) 2·83 (4H, m, ArH), 3·13 (1H, q, H-6, *J* 10·0 and 4·2 Hz), 4·15 (1H, dd, H-3, *J* 10·0 and 2·0 Hz), 4·63 (1H, s, H-9), 4·68 (1H, s, H-1), 6·15 (1H, d, H-7), 6·34 (1H, s, H-3), 7·50 (3H, s, NMe), 7·62 (1H, d, H-8, *J* 7·0 Hz), and 7·84 (1H, d, H-2, *J* 7·0 Hz).

Hydrogenation of the Adduct (IVa).—Hydrogenation of compound (IVa) (0·68 g) in ethanol over 5% palladium–charcoal (uptake 65 ml at 20° and 1 atm. Calc. for one double bond, 59·5 ml), filtration, evaporation to dryness, and recrystallization gave the 5,6-*dihydro-compound* (0·58 g) as needles, m.p. 153—155° (Found: C, 75·5; H, 6·75; N, 5·5. $C_{16}H_{17}NO_2$ requires C, 75·25; H, 6·7; N, 5·5%), $\nu_{max.}$ (KBr) 2940 and 1700 cm^{-1}, τ ($CDCl_3$) 2·80 (4H, m), 4·62 (1H, s), 4·67 (1H, s), 6·49 (2H, m), 7·49 (3H, s), 7·72 (4H, m), and 8·18 (2H, m).

Dehydrogenation of the Adduct (IVa).—A mixture of adduct (IVa) (0·4 g) and polyphosphoric acid (3 g) was heated on a steam-bath for 3 h with occasional stirring. The mixture was left overnight at room temperature, then added to ice–water (50 ml). Extraction with chloroform followed by evaporation of the extract to dryness and recrystallization from benzene–n-hexane, gave 6,10-*dihydro*-6,10-*methyliminocyclohepta*[b]*naphthalen*-7-*one* (IVb) (0·26 g) as yellow needles, m.p. 131—133° (Found; C, 81·45; H, 5·75; N, 5·75. $C_{16}H_{13}NO$ requires C, 81·7; H, 5·55; N, 5·95%), $\nu_{max.}$ (KBr) 1685 and 1610 cm^{-1}, τ ($CDCl_3$) 2·23 (4H, m), 2·58 (2H, m), 2·65 (1H, q, *J* 9·8 and 6·0 Hz), 4·92 (1H, dd, *J* 9·8 and 1·5 Hz), 5·51 (1H, d, *J* 6·0), 5·54 (1H, s), and 7·55 (3H, s).

Reaction of Dimethyl 7-*Oxabicyclo*[2,2,1]*hepta*-2,5-*diene*-2,3-*dicarboxylate* (V) *and* 1-*Methylpyridinium*-3-*olate*.—(*a*) A solution of the diester (V) (1·16 g) and the zwitterion (0·60 g) in tetrahydrofuran was refluxed for 3 days. Chromatography on silica gel gave *dimethyl* 12-*methyl*-11-*oxo*-13-*oxa*-12-*aza-tetracyclo*[6,3,1,1^{3,6},0^{2,7}]*trideca*-4,9-*diene*-2,7-*dicarboxylate* (VI) (0·13 g) as yellow plates, m.p. 177—179° (decomp.) (Found: C, 60·3; H, 5·45; N, 4·1. $C_{16}H_{17}NO_6$ requires C, 60·2; H, 5·35; N, 4·4%), $\nu_{max.}$ (KBr) 1740, 1720, and 1675 cm^{-1}, *m*/*e* 319 (M^+), and the isomeric 4,5-*diester* (VII) (0·14 g) as yellow prisms, m.p. 161—163° (Found: C, 60·2; H, 5·5; N, 4·7%), $\nu_{max.}$ (KBr) 1735, 1710, 1675, and 1640 cm^{-1}, *m*/*e* 319 (M^+).

(*b*) A solution of the diester (V) (1·55 g) and the zwitterion (0·8 g) in toluene (5 ml) was heated in a sealed tube at 130° for 15 h. The same treatment as in (*a*) gave the adduct (VII) (0·52 g).

Thermolysis of the Adduct (VI).—A solution of compound (VI) (0·05 g) in benzene was heated in a sealed tube at 130° for 1 day. The formation of the isomer (VII) was detected by g.l.c. (retention time 6·4 min at 220°).

Ethyl 4,9-*Epoxy*-3a,4,9,9a-*tetrahydronaphtho*[2,3-d]*triazole*-1-*carboxylate* (VIIIa).—A solution of compound (I) (0·66 g) and ethyl azidoformate (0·7 g) in benzene (4 ml) was stirred at room temperature. Evaporation to dryness and chromatography on silica gel (benzene) gave the *adduct* (VIIIa) (1·07 g, 78%) as prisms, m.p. 163—165° (decomp.) (Found: C, 60·45; H, 5·1; N, 16·5. $C_{13}H_{13}N_3O_3$ requires C, 60·2; H, 5·05; N, 16·2%), τ ($CDCl_3$) 2·72 (4H, m), 4·35 (1H, s), 4·49 (1H, s), 5·05 (1H, d, *J* 8·0 Hz), 5·61 (2H, q, *J* 7·0 Hz), 5·96 (1H, d, *J* 8·0 Hz), and 8·57 (3H, t, *J* 7·0 Hz), *m*/*e* 231 (64%), 158 (64), 131 (48), 130 (100) and 118 (61).

4,9-*Epoxy*-3a,4,9,9a-*tetrahydro*-1-*phenylnaphtho*[2,3-d]*triazole* (VIIIb).—A solution of compound (I) (0·42 g) and phenyl azide (0·4 ml) in ether (20 ml) was stirred at room temperature. Work-up as for compound (VIIIa) gave the *adduct* (VIIIb) (0·66 g), m.p. 169—171° (Found: C, 72·8; H, 4·9; N, 15·9. $C_{16}H_{13}N_3O$ requires C, 73·0; H, 5·0; N, 15·9%), *m*/*e* 206 (100%), 118 (40), and 77 (50).

Thermolysis of the Adduct (VIIIb).—A solution of compound (VIIIb) (0·29 g) in benzene (8 ml) was heated in a sealed tube at 170° for 2 days. Similar work-up gave 1-phenyltriazole (0·1 g, 63%), m.p. 50—54° (lit.,[11] 56°).

1,4-*Epoxy*-1,2,3,4-*tetrahydro*-2-*phenylsulphonyliminonaphthalene* (Xa).—A solution of compound (I) (0·29 g) and benzenesulphonyl azide (0·38 g) in benzene (10 ml) was stirred at room temperature. Similar work-up gave the *product* (Xa) (0·58 g, 90%), m.p. 208—211° (decomp.), $\nu_{max.}$ (KBr) 1627 cm^{-1} (C=N), τ ($CDCl_3$) 2·7 (9H, m), 4·6br (2H), and 6·8br (2H) (Found: C, 64·35; H, 4·55; N, 4·35. $C_{16}H_{13}NO_3S$ requires C, 64·2; H, 4·4; N, 4·7%).*

1,4-*Epoxy*-1,2,3,4-*tetrahydro*-2-p-*tolylsulphonyliminonaphthalene* (Xb).—A solution of compound (I) (0·299 g) and tosyl azide (0·47 g) in benzene (6 ml) was stirred at room temperature. Similar work-up gave the *product* (Xb)

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* Hydrolyses of the enamines (Xa and b) gave the corresponding arylsulphonylamines.

[11] O. Dimroth and G. Fester, *Ber.*, 1910, **43**, 2222.

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(0·438 g), m.p. 145—147° (decomp.), $\nu_{max.}$ (KBr) 1627 cm^{-1} (C=N), τ ($CDCl_3$) 2·8 (8H, m), 4·6br (2H), 6·9br (2H), and 7·60 (3H, s) (Found: C, 64·9; H, 4·85; N, 4·55. $C_{17}H_{15}NO_3S$ requires C, 65·1; H, 4·8; N, 4·45%).*

15,16-*Dioxapentacyclo*[6,6,1,1,^{3,6},$0^{2,7}$,$0^{9,14}$]*hexadeca*-4,9,-11,13-*tetraene* (XI).—A mixture of compound (I) (0·328 g) and furan (2 ml) was heated in a sealed tube at 130° for 8 h. Similar work-up gave the *adduct* (XI) (0·41 g, 85%), m.p. 146—150° (Found: C, 79·15; H, 5·85. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%), τ ($CDCl_3$) 2·91 (4H, m), 3·63 (2H, s), 5·17 (4H, m), and 7·48 (2H, dd, *J* 15 and 3·0 Hz), *m/e* 212 (1%), 144 (24), 128 (15), 118 (40), 116 (100), and 115 (58).

Thermolysis of Adduct (XI).—A solution of compound (I) (0·119 g) in *o*-dichlorobenzene (3 ml) was heated at 160° for 8 h. Work-up as before gave an isomeric *adduct* (XII) (0·023 g, 20%), m.p. 255° (Found: C, 78·2; H, 5·65. $C_{14}H_{12}O_2$ requires C, 78·2; H, 5·7%), τ ($CDCl_3$) 2·9 (4H, m), 3·65 (2H, s), 4·77 (2H, s), 5·01 (2H, s), and 8·03 (2H, s), *m/e* 144 (33%), 118 (100), 116 (95), and 115 (47).

16-*Isopropylidene*-15-*oxapentacyclo*[6,6,1,$1^{3,6}$,$0^{2,7}$,$0^{9,14}$]-*hexadeca*-4,9,11,13-*tetraene* (XIII).—A solution of compound (I) (0·35 g) and 6,6-dimethylfulvene (0·50 g) in benzene (5 ml) was heated in a sealed tube at 130° for 7 h. Work-up as before gave the adducts (XIII) (0·36 g, 60%), (XIV) (0·048 g, 8%), and (XV) (0·06 g, 7%).

Compound (XIII) had m.p. 153—158° (Found: C, 86·6; H, 7·25. $C_{18}H_{18}O$ requires C, 86·35; H, 7·25%), τ ($CDCl_3$) 2·90 (4H, m), 3·77 (2H, dd, *J* 1·8 and 2·1 Hz), 5·01 (2H, s), 6·58 (2H, m), 7·72 (2H, dd, *J* 1·8 and 2·8 Hz), and 8·53 (6H, s), *m/e* 250 (M^+). The *isomer* (XIV) had m.p. 142—146° (Found: C, 86·35; H, 7·4%), τ 2·91 (4H, m), 3·73 (2H, t, *J* 1·9 Hz), 5·04 (2H, s), 6·70 (2H, t, *J* 1·9 Hz), 8·14 (2H, s), and 8·39 (6H, s), *m/e* 250 (M^+). The 1 : 2 *adduct* (XV) had m.p. 161—165° (Found: C, 87·85; H, 8·1. $C_{26}H_{28}O$ requires C, 87·6; H, 7·9%), τ 2·94 (4H, m), 4·12 (2H, t, *J* 1·9 Hz), 4·88 (2H, s), 6·79 (2H, m), 7·40 (2H, s), 7·56 (2H, m), 8·26 (2H, dd, *J* 1·9 and 3·0 Hz), 8·50 (6H, s), and 8·66 (6H, s), *m/e* 356 (M^+).

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* See footnote p. 2754.