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PROPELLANES—XXIV[1]

PHOTOCHEMISTRY OF [4.4.3]PROPELLA-2,4-DIENES

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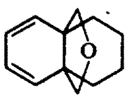
Abstract—Several [4.4.3]propella-2,4-dienes upon irradiation afforded "open" trienes. These revert photochemically and thermally and afford the starting materials. In some cases cyclobutenes are obtained.

The photochemistry of [4.4.3]propellatetraenes follows the same lines as that of the parent compound *cis*-9,10-dihydronaphthalene.[2] It was of interest to investigate their analogs containing only one rather than two cyclohexadiene rings, particularly since compounds of this type (**1**–**4**) were required for additional reasons.[3]



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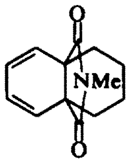

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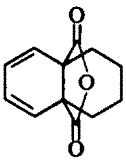

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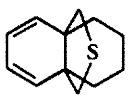

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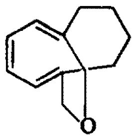
Irradiation of **1**[1] (Vycor, 254 nm) caused symmetry-allowed conrotatory opening of the *cis-cis*-cyclohexadiene to the *cis-cis-trans*-triene **5**. A photochemical equilibrium is eventually established, the mixture containing about 80% of **5**. Two isosbestic points may be observed at 243 and 288 nm. Irradiation of the mixture at 313 nm reduces the absorbance at 313 nm (triene) and increases that at 263 nm (diene).



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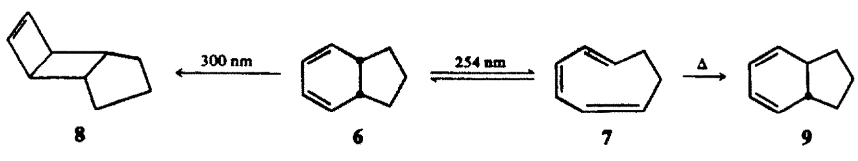
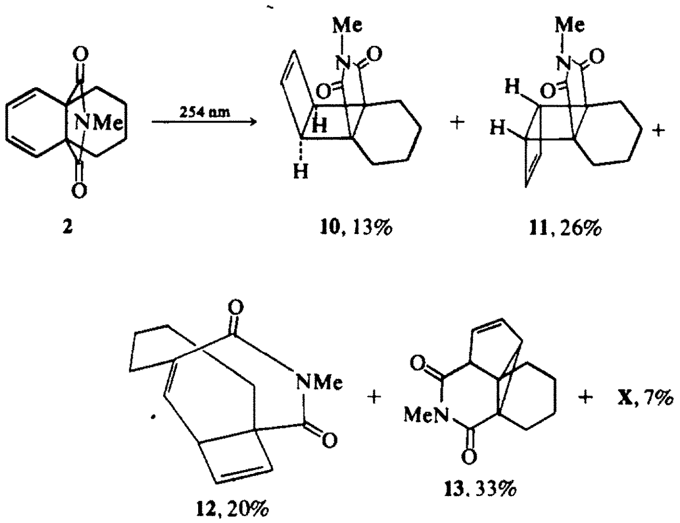
The triene is converted into the starting material **1** in a thermally forbidden process and the rate of this reaction may be followed by observation of the NMR spectrum of **5**. The half-life of the reaction in CCl_4 at room temperature, $t_{1/2} = 18 \pm 2$ h (Fig 1 and NMR data in Experimental). The NMR absorption of **5**, expanded in the region pertaining to the protons adjacent to the O atom, is shown in Fig 2. The four protons involved form two AB systems with $J_{A_1B_1} = 12\cdot4$ Hz and $J_{A_2B_2} = 9\cdot2$ Hz, showing the lack of symmetry in **5**.

Clearly the structure of **1** is far from being analogous to that of bicyclo[4.3.0]nona-2,4-diene **6** albeit the latter contains one cyclohexadiene ring and one 5-membered carbocyclic ring rather than a 5-membered ether ring as in **1**. The bicyclic **6** affords the *cis-cis-trans*-triene **7** upon irradiation at 254 nm. At 300 nm it affords the alternative symmetry-allowed product of disrotatory cyclization, the cyclobutene **8**. In this particular case heating of **7** affords the thermally allowed product, **9**, of disrotatory cyclization.[4a] The role of ground state conformations is being more and more emphasized in the photochemistry of cyclohexadienes. These are all the more important in the tricyclic systems described herein as compared to the bicyclic hexalins reported recently.[4b]

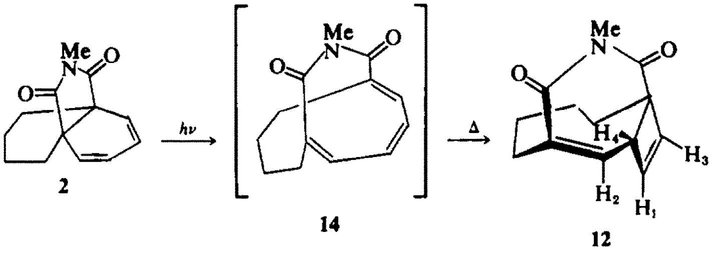
In the case of the methylimide **2**,[1] however, the route towards cyclobutenes was much more important. Here the same products were obtained whether irradiation was carried out at 254 nm or at longer (270–300 nm) wavelength. However, the rel-





$$\mathbf{2} \xrightarrow{270\text{–}300\ \text{nm}} \mathbf{10},\ 15{\cdot}5\% + \mathbf{11},\ 67{\cdot}5\% + \mathbf{12},\ 10{\cdot}5\% + \mathbf{13},\ 6\% + \mathbf{X},\ \text{trace}$$

SCHEME 1



SCHEME 2

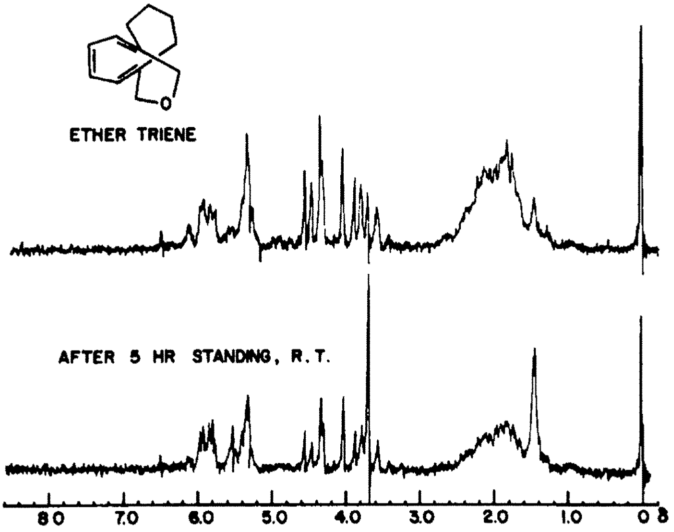


Fig 1. Thermal reversion of 5 into 1.

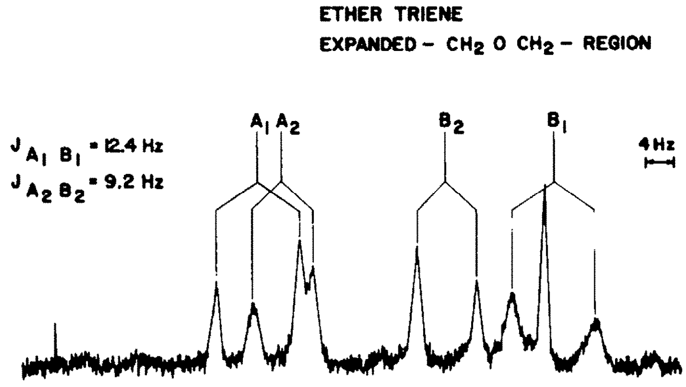


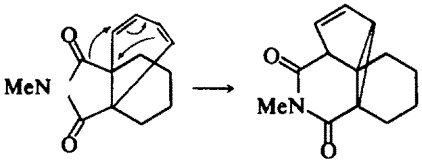
Fig 2. NMR spectrum of **5** in ether region.

ative percentages of products differed dramatically. Scheme 1 lists the reaction products obtained by irradiation of **2** and their relative amounts.

Clearly, the major products at long wavelength are the cyclobutenes **10** and **11** (83% of total). A conrotatory symmetry-allowed cyclization of **14**, the triene analog of **5**, is impossible. Thus the cyclobutene **12**, if indeed formed from **14**, must be obtained in a forbidden disrotatory process (Scheme 2).

We prefer structure **12** rather than alternative ones which may be written because the *trans*-double bond is in an 8-membered ring and is *cis* in the 7-membered imide ring. Addition of a lanthanide shift reagent shows the greatest shift for the doubly allylic proton shown in **12** and this definitely supports the geometry implied by structure **12** (Fig 3).

The formation of **13** may be explained as a photochemical acyl rearrangement resulting from exciting the CO group at 254 nm and migration of allylic double bonds for which there is ample analogy[5] (Scheme 3). It may be that it is formed, at least in part, thermally from the triene **14**.



2 **13**

SCHEME 3

An additional product, termed "X" has also been obtained but its structure has not been elucidated.

The NMR spectra of the various products were very informative in the elucidation of structures **12** (Fig 3) and **13** (Fig 4). The addition of a lanthanide shift reagent enabled sorting out the pertinent signals belonging to the *syn*- and *anti*-cyclobutenes, **10** and **11**, respectively.

Irradiation of the anhydride **3**,[1] in analogy to the behavior of the methylimide **2**, led to the cyclobutenes **15** and **16**. Here too no triene was isolated but in contra-distinction to **2**, in this case decarbonylation and decarboxylation may occur, leading to tetralin **17** (Scheme 4). About one quarter of the product mixture obtained during irradiation at longer wavelength was **17** but the amount increased to one half of the mixture when irradiation was carried out at 254 nm. It is reasonable that at this wavelength the CO chromophore is excited, α-cleavage occurs, leading to more efficient loss of CO and CO_2.

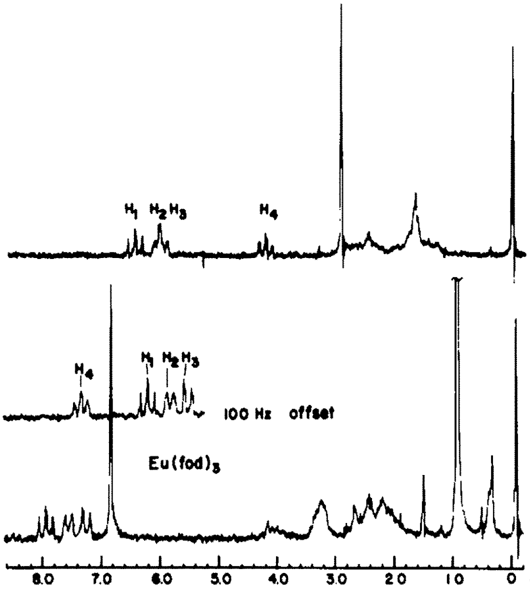


Fig 3. NMR spectrum of **12**.

Irradiation of the thio-ether **4** paralleled that of the ether **1**. The photochemical equilibrium mixture contained about equal amounts of **4** and its corresponding triene **18**.

Irradiation of **19**, the sulfone of **4**, afforded **20**, the sulfone of **18**. This reverted cleanly to the start-

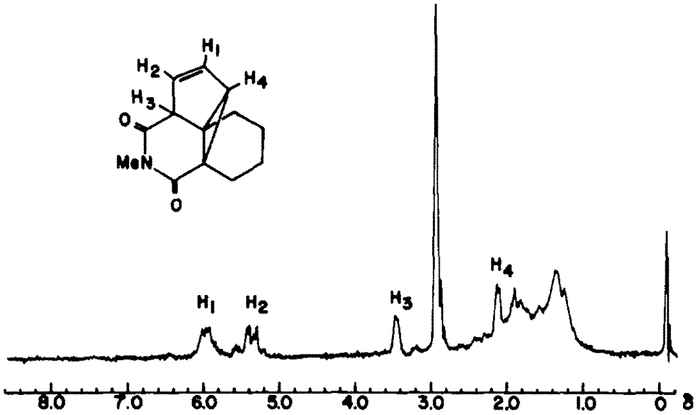
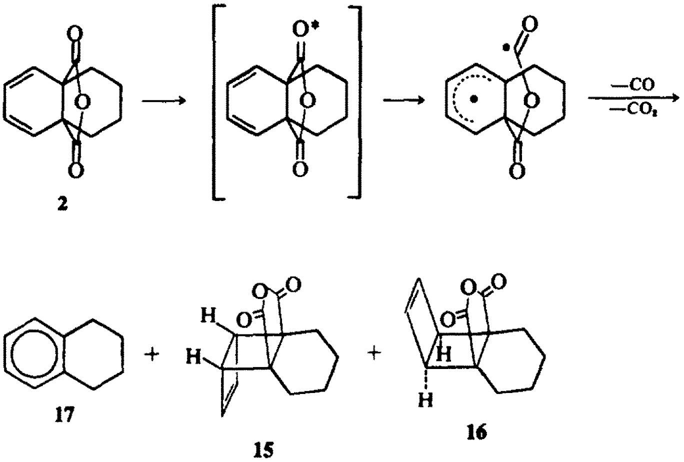
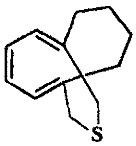


Fig 4. NMR spectrum of **13**.



Scheme 4



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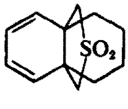

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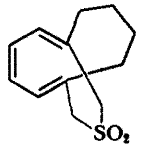

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ing material after standing at room temp for 6 days.

The activation energy and entropy of activation were determined for the thermal reactions **5** → **1**; **18** → **4** and **20** → **19**.

Reaction	$\Delta H^{\ddagger}$ (Kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
5 → **1**	19·4 ± 0·2	−16
18 → **4**	23·8 ± 1·8	−12
20 → **19**	20·4 ± 0·2	−15

The thermal conversion of **5** into **1** as followed by UV spectroscopy is shown in Fig 5.

Although these reactions are forbidden[6] the values obtained for enthalpy and entropy of activation are quite similar to those obtained for thermal allowed concerted reactions, *cis-cis-cis*-1,3,5-cyclononatriene → *cis*-bicyclo [4.3.0]nona-2,4-diene ($\Delta H^{\ddagger} = 23{\cdot}0$; $\Delta S^{\ddagger} = -4{\cdot}7$)[7] and the corresponding *cis-cis-trans* compound to the corresponding *trans*-bicyclo-product ($\Delta H^{\ddagger} = 20{\cdot}1$; $\Delta S^{\ddagger} = -12{\cdot}8$).[8] It will be noted that in all five cases the values for entropy of activation are, more or less, negative.

EXPERIMENTAL

Irradiation of **1**. A soln of dienic ether (150 mg) in MeOH (150 ml; distilled from CaH_2) was placed in a Vycor tube (2 mm thick, 3 cm i.d.; $T_{254} = 29{\cdot}5\%$; $T_{280} = 63\%$). Irradiation was carried out using 2537 Å lamps in a Rayonet reactor at room temp. No attempt was made to remove O_2 as it was found in exploratory experiments that more triene may be obtained when degassing is avoided. After 1 h the MeOH was removed, without warming, in a high vacuum. The yellow oily residue showed the pres-

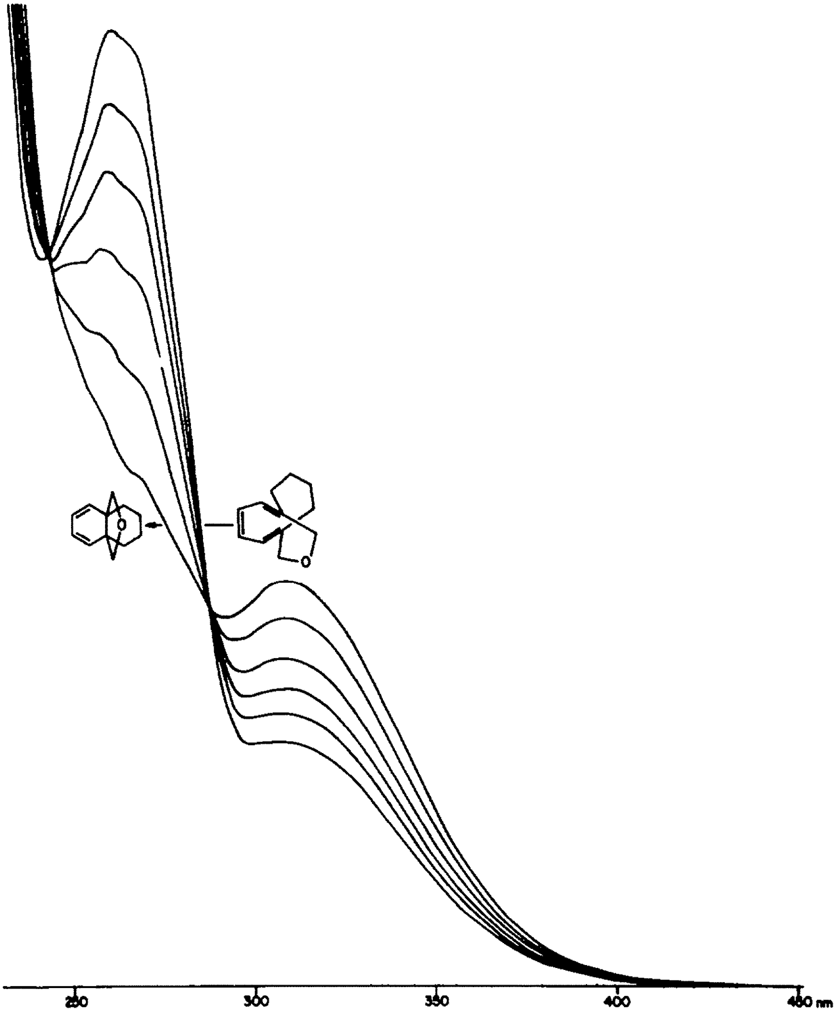

Fig 5. Photochemical reversion of **5** into **1**.

ence of *ca* 60% triene (integration in region of protons adjacent to ether oxygen in NMR spectrum). Preparative TLC on basic alumina plates (20 × 20 cm) including elution twice with light petroleum (4): CH_2Cl_2 (1) afforded two bands. The one with higher R_f corresponded to the triene. This could be observed also by irradiation with 366 nm light. Extraction with CH_2Cl_2—MeOH gave the yellow triene (47·5 mg of >95% purity by NMR). IR (liq film): 1020, 825, 745, 735, 705 cm^{-1}; NMR (CCl_4): τ 3·80–4·30 (m, 2 vinylic H); 4·35–4·80 (m, 2 vinylic H); 274, 268, 261, 259, 242, 233, 228, 214 Hz ($4C\underline{H}_2O$); 7·30–8·80 (m, $8C\underline{H}_2$). The $C\underline{H}_2O$ protons were recorded in an expanded scale and gave the following data: τ $A_1 = 5{\cdot}55$ (d, $J_{A_1B_1} = 12{\cdot}4$ Hz, 1H); $B_1 = 6{\cdot}32$ (d, $J_{A_1B_1} = 12{\cdot}4$ Hz, 1H); $A_2 = 5{\cdot}62$ (d, $J_{A_2B_2} = 9{\cdot}2$ Hz, 1H); $B_2 = 6{\cdot}03$ (d, $J_{A_2B_2} = 9{\cdot}2$ Hz, 1H). UV (methylcyclohexane): λ_{max} 309 nm (ϵ_{max} 716).

Thermal reversion of triene. The soln of triene in CCl_4 was kept in the NMR tube at room temp in the dark. The relative amounts of **5** and **1** were determined by integration in the $C\underline{H}_2O$ region.

t(h)	% triene	% diene
0	*ca* 93	*ca* 7
5·3	75	25
18·3	50	50
44·4	27	73
68·6	*ca* 10	*ca* 90

$t_{1/2} = 18 \pm 2$ h at room temp (25°). A similar value was obtained from observation of the disappearance of the triene in the UV spectrum of the crude irradiation mixture in methanol.

Proof of photochemical reversibility $\mathbf{1} \xrightleftharpoons[313\,nm]{254\,nm} \mathbf{5}$. Irradiations were conducted in spectroscopic grade methylcyclohexane. Irradiation at 254 nm was effected with a low pressure Philips 93109E lamp and at 313 nm with a Philips medium pressure 125 watt mercury lamp using an interference filter. A soln of **1** (2 ml) with an initial absorbance of 0·93 at 263 nm was irradiated at 254 nm during 55 min. The absorbance at 263 nm fell to 0·70 whilst that at 313 nm rose from 0 to 0·08. Two isosbestic points were observed at 243 and 288 nm (Fig 5). The end product soln from the previous irradiation was then irradiated at 313 nm (the diene does not absorb at this wavelength) for longer and longer periods up to a total of 75 min. At the endpoint of this irradiation the absorbance at 313 nm fell by 0·06 units and that at 263 nm rose by 0·15 units. The same isosbestic points were maintained. After alternate irradiations for a long period it was possible to estimate that the equilibrium mixture is roughly **1**:**5** = 1:4.

Reaction of **5** *with 4-phenyl-1,2,4-triazoline-3,5-dione.* Freshly isolated **5** (36 mg) was dissolved in CH_2Cl_2 (3 ml) and treated at −30° with a CH_2Cl_2 soln of the dienophile until the red color persisted. After the soln had warmed up to room temp the solvent was removed in a vacuum without external warming. After workup the Diels-Alder adduct was obtained, identical to that obtained from **1** and the same dienophile.[3]

Determination of thermodynamic parameters for thermal reversion **5**→**1**. Aliquots (3 ml) of the soln of freshly-prepared **5** in methylcyclohexane (spectroscopic grade), with an absorbance of 0·78 at 309 nm were placed in quartz cells (10 × 10 mm) with a ground joint and pyrex sidearm. The solns were subjected to a 7 stage degassing sequence including freezing, pumping and thawing, and they were then sealed in a vacuum. They were stored in liquid air until each measurement was carried out.

The kinetic measurements were conducted using a Cary 15 spectrophotometer. Temperature was maintained by circulating water at the desired temp from a thermostat maintained at that temp ±0·05° through the cell jacket. Each sample had undergone thermal equilibration of 15 min before measurement. The rate constant was obtained from the curve for in A_0/A *vs* t, A being measured at 315 nm. The thermodynamic parameters were obtained from ln k/T *vs* 1/T.

t (°C)	k (sec^{-1})
19·4 ± 0·05	$0{\cdot}52 \times 10^{-5} \pm 0{\cdot}01 \times 10^{-5}$
30·0 ± 0·05	$1{\cdot}71 \times 10^{-5} \pm 0{\cdot}02 \times 10^{-5}$
40·2 ± 0·05	$4{\cdot}88 \times 10^{-5} \pm 0{\cdot}02 \times 10^{-5}$
50·1 ± 0·05	$14{\cdot}58 \times 10^{-5} \pm 0{\cdot}05 \times 10^{-5}$

$$\Delta H\ddagger = 19{\cdot}4 \pm 0{\cdot}2\ \text{Kcal/mole};\ \Delta S\ddagger = -16\ \text{e.u.}$$

Irradiation of **2**

(a) Irradiation was carried out at 254 nm in the same Vycor tube as described for **1** with the same lamps in the Rayonet reactor at room temp. Dry oxygen-free nitrogen was passed through the soln of **2** (200 mg) in spectral grade methylcyclohexane (150 ml). Progress of the reaction was controlled by withdrawing aliquots (80 μl), adding spectral grade methylcyclohexane (2 ml) and measuring the UV spectrum. Aliquots removed after 25, 60 and 90 min showed 7, 18 and 26% conversion, respectively. The samples were injected into a Varian aerograph gas chromatograph using a glass column (5′ × ⅛″) with 1% XE-60 on gaschrom Q, 100–120 mesh at 140°, 4 ml/min (16 psi) N_2. The retention times are **2** (9·6 min), **10** (13%; 10·5 min), **12** (20%; 11·6 min), **11** (26%; 13·0 min), **13** (33%; 16·3 min) and X (7%; 17·5 min). This ratio was checked at 7, 18 and 26% conversion and no significant dependence upon conversion was found. Since **2** and **10** differed so little in retention time the exact concentration of **10** was determined by first adding 4-phenyl-1,2,4-triazoline-3,5-dione to remove **2** and then injecting into the gas-chromatograph. (It was found that **13** being a vinylcyclopropane, reacts slowly with this dienophile.)

The crude soln was concentrated at the water pump. After replacement of the removed solvent by CCl_4 the NMR spectrum showed a similar ratio of the above products **10**–**13** by integration in the region τ 5·5–6·9. Preparative TLC was carried out as above but elution was effected with light petroleum (40–60°)–ethyl acetate, 4:1. In addition to decomposition products at the plate bottom, two bands were obtained. The one with higher R_f gave after extraction with CH_2Cl_2—MeOH **12** (7·5 mg; 15% based upon reacted **2**). Removal of solvent gave solid **12**, m.p. 50–51°. IR (KBr): 1710, 1670, 780, 705 cm^{-1}; NMR (CCl_4); τ 3·56 (t, J = 7 Hz, 1 vinylic H); 4·00 (m, 2 vinylic H); 5·80 (further split t, J_1 = 7 Hz, J_2 = 2 Hz, 1 doubly allylic H); 7·10 (s, 3 $NC\underline{H}_3$); 7·30–7·80 (m, 2 allylic $C\underline{H}_2$); 7·8–8·9 (m, 6 $C\underline{H}_2$). $Eu(fod)_3$ (20 mg) was added to **12** (14 mg). The following chemical shifts were observed: τ 0·95 (further split t, J_1 = 7 Hz, J_2 = 2 Hz, 1 doubly allylic H); 2·10 (t, J = 7 Hz, 1H); 2·50 (br, d, J = 7 Hz, 1H); 2·82 (further split d, J_1 = 7 Hz, J_2 = 2 Hz, 1H). Irradiation at 0·95 converted to 2·10 triplet into a doublet and the 2·50 doublet into a broad singlet. The finely split doublet at 2·82 disappeared. Irradiation of the 2·10 triplet converted the 0·95 triplet into a doublet; UV (MeOH): λ_{max} 245 (ϵ_{max} 685). MS:M^+ 217, 133, 117, 105.

After standing in CCl_4 soln for several weeks **12** affords an oxide, m.p. 149–153° (M^+, 233); IR (CCl_4) exhibits imide absorption at 1785, 1710 cm^{-1}.

The second band in the preparative plate was extracted with CH_2Cl_2—MeOH and gave a mixture of **2** and all of the other products (120 mg). The mixture was dissolved in light petroleum 40–60° (2 ml) and refrigerated. After 24 h **2** (50 mg) which had crystallized was removed by filtration. The mother liquor was evaporated and the residue was taken up in CH_2Cl_2. The diene **2** still present was "titrated" with a CH_2Cl_2 solution of 4-phenyl-1,2,4-triazoline-3,5-dione and the mixture was then subjected to preparative gas-chromatographic separation, 5′ × ¼″ glass column, 10% XE-60 on gaschrom Q, 60–80 mesh, 145°, 100 ml/min He. inj. 145–150°. The following retention times were obtained: **10** (11·5 min), **11** (14·0 min), **13** (18·0 min). The Diels-Alder adduct was retained by the column.

Compound **10**. IR (liq film): 1780, 1710, 1560, 780, 740, 720 cm^{-1}; NMR (CCl_4): τ 3·76 (narrow m, 2 vinylic H); 6·70 (narrow m, 2 allylic H); 7·08 (s, 3 $NC\underline{H}_3$); 7·8–8·8 (m, 8 $C\underline{H}_2$). Irradiation at 6·70 converted the 3·76 multiplet into a sharp singlet and *vice versa*; UV: end absorption at 220 nm; M.S. M^+, 217.

Compound **11**. IR (liq film): 1780, 1710, 1560, 780, 740, 720 cm^{-1}; NMR (CCl_4): τ 3·46 (narrow m, 2 vinylic H); 6·67 (narrow m, 2 allylic H); 6·98 (s, 3 $NC\underline{H}_3$); 7·8–9·2 (m, 8 $C\underline{H}_2$). Irradiation at 6·67 converted the 3·46 multiplet into a sharp singlet and *vice versa*; UV: end absorption at 220 nm; M.S. M^+, 217.

Compound **13**. IR (liq film): 1710, 1680, 1010, 790 cm^{-1}; NMR (CCl_4): τ 3·90 (m, $-CH{=}C\underline{H}\ \Delta$); 4·50 (dd, J_1 = 6 Hz, J_2 = 2 Hz, $-C\underline{H}{=}CH\ \Delta$); 6·47 (br s, 1 $COC\underline{H}C{=}C$); 6·94 (s, 3 $NC\underline{H}_3$); 7·77 (d, J = 2 Hz, 1 allylic cyclopropyl H); 7·7–8·8 (m, 8 $C\underline{H}_2$). Irradiation at 3·90 converted the 7·77 doublet into a broad singlet and caused sharpening at 6·47. Irradiation at 4·50 sharpened the 6·47 signal. Irradiation at 6·47 caused the 2 Hz splitting at 4·50 to disappear; UV (95% EtOH): 220 (39200), 260 nm (4300); M.S. M^+, 217, 132.

The configurations of **10** and **11** were determined by addition of Eu(fod)$_3$ to the mixture containing **10**:**11** in the ratio 1:4·5. From measurement of the respective chemical shifts the ratio $\Delta\delta$(allylic)/$\Delta\delta$(vinylic) was determined. This was 1·86 for **10** in which the cyclobutene is *syn* to the imide ring and 2·95 for **11** in which the cyclobutene ring is *anti* with respect to the imide ring.

(b) Irradiation of **2** at longer wavelength was carried out under conditions identical to those described above under (a) except that Rayonet RPR 3000 Å lamps were used. These lamps emit down to 270 nm. The workup and analytical methods were as above. Aliquots were removed after 40, 100 and 160 min corresponding to 7, 17 and 29% conversion. The products were **10** (15·5%), **11** (67·5%), **12** (10·5%), **13** (6%) and **X** (trace). The NMR spectrum also showed that the cyclobutenes **10** and **11** formed more than 80% of the product mixture. Preparative TLC carried out after the Diels-Alder adduct of **2** had been formed as above gave after elution with a 1:1 mixture of CH_2Cl_2 and light petroleum 40–60° two fractions, one containing the photo-products (52 mg) and the other the Diels-Alder adduct (108 mg). NMR analysis of the former confirmed the gas chromatographic ratios by integration in the vinylic region. The Diels-Alder adduct of **2** (90 mg), had m.p. 259–261° (MeOH) and was identical with the authentic specimen to be described elsewhere.[3]

(c) Irradiation of **2** at −180°C (Fig 6) was carried out in a methylcyclohexane–isohexane glass. A soln of **2** was prepared in this solvent mixture 2:1 v/v. Its initial absorbance was 0·85 at 263 nm. Aliquots (3 ml) were placed in quartz cells (10 × 10 mm, x-section). Each was subjected to degassing through 7 cycles of freezing, pumping (1 μ) and thawing. The cells were then sealed in a vacuum. Cooling to −180° gave a transparent glass affording a spectrum exhibiting absorption bands at 243 (sh), 254 (max), 261 (highest max), 272 (max), 282 nm (max). Irradiation was effected at 254 nm using a low pressure Philips 93109E lamp. Irradiation for 92 min caused a lowering of the spectrum above 254 nm by 0·15 absorbance units and a strong rise at shorter wavelength. At 254 nm a point almost approximating an isosbestic point was observed. The increase in absorbance at 230 nm was 297% of the decrease at 282 nm. After warming to room temp this increase was only 50% of the decrease at the maximum.

Irradiation above 275 nm was carried out with a Mazda 250 watt lamp using a Jena WG 284 filter. After 77 min of irradiation a more or less proportional decrease by 0·15 absorbance units was obtained for the whole spectrum accompanied by only a slight increase at shorter wavelength. The increase at 230 nm was 50% of the decrease at 282 nm. In neither of these irradiations was an increase corresponding to triene observed at longer wavelength.

Irradiation of **3**

(a) Freshly sublimed **3**, m.p. 78–79°,[1] (150 mg) was dissolved in spectral grade hexane (150 ml) and the soln was irradiated in a Vycor tube (as above) in a Rayonet reactor with 3000 Å lamps (i.e. 270–300 nm) at room temp. Dry

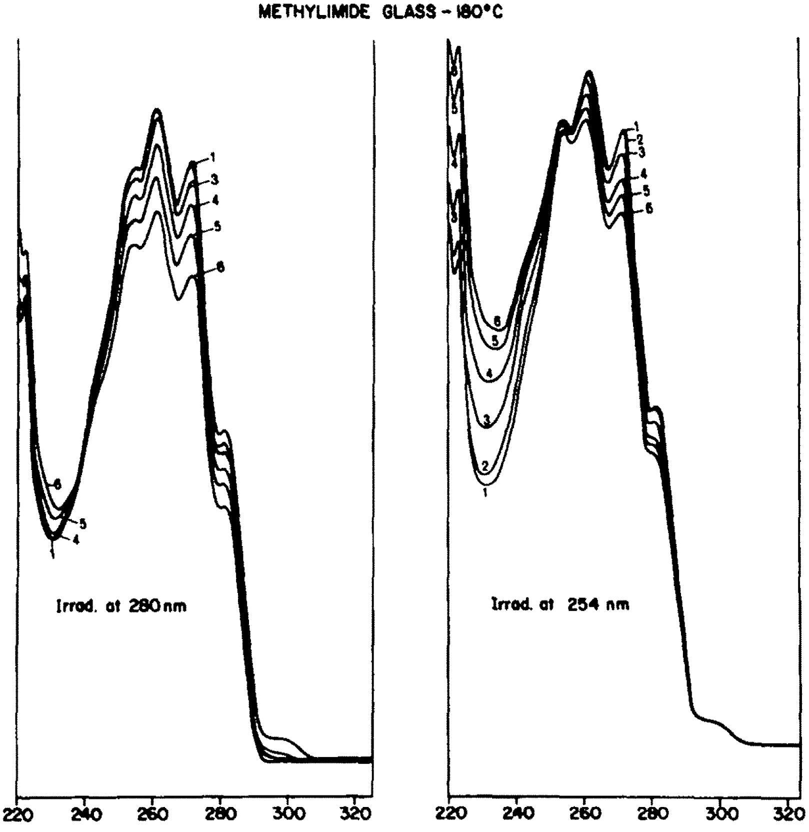

Fig 6. UV spectra of **2** at −180°.

oxygen-free nitrogen was passed through the soln for 30 min preceding irradiation and during irradiation. Control of the progress of reaction was conducted by diluting aliquots and measuring the UV spectrum. After 13·5 h, 66% of **3** had disappeared and an isosbestic point appeared at 219 nm. After this time the soln was filtered and evaporated to dryness in a vacuum without application of external heat. The residue (135 mg) was an oily solid. The NMR spectrum of this crude material showed the presence of the *anti*-cyclobutene **15** (40%), the *syn*-cyclobutene **16** (8%), tetralin **17** (17·5%) and starting material **3** (34%). Gas chromatography using a $5' \times \frac{1}{8}''$ glass column, 1% XE-60 on gaschrom Q 100–120 mesh, 150°, 5 ml/min N_2 flow gave retention times for tetralin (1·5 min), **3** (8·1 min) and the two cyclobutenes together (12·3 min). A trace (< 1%) of a further product could be observed (10·3 min). The tetralin was identical by GLC and NMR with an authentic specimen.

The crude mixture was dissolved in CH_2Cl_2 and the Diels-Alder adduct of **3** was prepared to avoid interference of the starting material in the separation of products. It was retained by the $5' \times \frac{1}{4}''$ glass column using 10% XE-60 on gaschrom Q 60–80 mesh, 150°, 100 ml/min He flow. The tetralin was removed after 0·8 min, a trace of **3** after 5·2 min and the cyclobutenes after 7·7 min. By repeated injections a crystalline mixture (15 mg) of the two cyclobutenes, m.p. 80–95°, was collected. IR (KBr): 1840, 1780, 780 cm^{-1}; NMR (CCl_4): τ 3·46, 3·60 (2 finely split m, 2 vinylic H); 6·46, 6·62 (2 finely split m, 2 allylic H); 7·6–9·2 (br m, 8 $C\underline{H}_2$). Irradiation at 3·46 converted the 6·46 multiplet into a sharp singlet and *vice versa*. Irradiation at 3·60 converted the 6·62 multiplet into a sharp singlet and *vice versa*; M.S.: M^+, 204; M^+ —CO—CO_2, 132; 105, 91.

The signals for the two isomers were sorted out by employing NMR and adding $Eu(fod)_3$ to the 1 : 3 mixture of the two cyclobutenes in CCl_4.

τ 6·46 allylic bridgehead H in *anti*-isomer **15**.

τ 3·46 vinylic H in *anti*-isomer **16**. Δδ allylic/Δδ vinylic = 3·0. τ 6·62 allylic bridgehead H in *syn*-isomer. τ 3·60 vinylic H in *syn*-isomer. Δδ allylic/Δδ vinylic = 1·05.

(b) Irradiation of **3** at 254 nm was carried out exactly as described under (a) except for the lamps: 2537 Å lamps were used in the Rayonet reactor. After 2 h irradiation the solvent was removed in a vacuum without external heating and the NMR spectrum of the residue dissolved in CCl_4 was measured. Integration in the region τ 3·0–6·8 showed the presence of **3** (69%), *anti*-cyclobutene **15** (10%), *syn*-isomer **16** (5%), tetralin (16%).

Irradiation of **4**

A soln of **4**[9] (80 mg) in MeOH (distilled from CaH_2; 100 ml) was irradiated in a Vycor tube as above without N_2 using 2537 Å lamps in a Rayonet reactor at room temp. After 40 min the MeOH was removed in a vacuum. A pale yellow oil was obtained (80 mg). Its NMR spectrum in CCl_4 showed by integration in the $C\underline{H}_2S$ region that conversion was *ca* 50%. Preparative TLC as above on basic alumina plates (20 × 20 cm) and elution with light petroleum 40–60° (4): CH_2Cl_2 (1) gave a band whose composition after extraction with CH_2Cl_2—MeOH was shown to contain *ca* 1 : 1-mixture of **4** and the resulting triene **18**. The triene signals (CCl_4) which were not hidden by those of the diene appeared at τ 4·7 (m, vinylic H); 231, 227, 221, 213, 201, 181 Hz ($C\underline{H}_2S$), 7·6–8·6 (m, $C\underline{H}_2$). A soln of this mixture was used for determination of the activation energy.

The mixture (12 mg) was separated on an analytical silica gel plate (20 × 20 cm). After eluting twice with light petroleum 60–70° two bands were obtained. From the one with higher R_f (this could also be observed by shining 366 nm light), extraction with CH_2Cl_2—MeOH afforded pure triene (1·4 mg). UV (methylcyclohexane): 265 (sh, ε 685); 310 nm (sh, ε 385).

Thermal reversion of triene into **4**. A soln of the triene in methylcyclohexane with absorbance of 0·75 at 330 nm was placed in square quartz cells (10 × 10 mm) as above as 3 ml aliquots. After 6 cycles of degassing as above the vacuum-sealed cells were stored in liquid air until the measurement was carried out. Observation of disappearance of triene was conducted at 330 nm. The following data were collected:

t (°C)	k (sec^{-1})
60·4 ± 0·05	0·39 × 10^{-5}
70·8 ± 0·05	1·30 × 10^{-5}
80·1 ± 0·05	2·86 × 10^{-5}

ΔH‡ = 23·8 ± 1·8 Kcal/mole
ΔS‡ = − 12 e.u.

Irradiation of **19**. A soln of the sulfone[9] (90 mg) in MeOH (from CaH_2; 100 ml) was irradiated in a Vycor tube as above with 2537 Å lamps in a Rayonet reactor at room temp without removal of O_2. After 60 min the MeOH was removed in a vacuum without external heating. A yellow oil was obtained (90 mg). Its NMR spectrum in CCl_4 showed the presence of *ca* 1 : 1-mixture of starting material and triene (by integration in the τ 5·0–8·0 region). Preparative TLC on basic alumina plates (20 × 20 cm) using 2 elution stages with light petroleum (40–60°) CH_2Cl_2, 3 : 1 gave two bands. The upper one, (observable also by using 366 nm light) contained the triene. The lower one (diene) was observed only with 254 nm light. Extraction of triene with CH_2Cl_2 and MeOH gave *triene* (16 mg; > 95% pure by NMR) as a yellowish oil. IR (liq film): 1290, 1110 (SO_2), 890, 760, 700 cm^{-1}; NMR (CCl_4): τ 3·90–4·50 (complex m, 4 vinylic H); 5·21 (A_1, d, J = 14 Hz, 1H), 6·76 (B_1, d, J = 14 Hz, 1H), 5·82 (A_2, d, J = 12·5 Hz, 1H), 6·24 (B_2, d, J = 12·5 Hz, 4 $C\underline{H}_2SO_2$); 7·0–8·3 (m, 8 $C\underline{H}_2$); UV (hexane): 322 nm (ε 735). A tail from 322 nm beyond 400 nm is responsible for the yellowish color of the triene.

Thermal reversion of triene **20** *into diene* **19**. The NMR tube containing the triene in CCl_4 soln was kept in the dark at room temp and from time to time the spectrum was measured. After 6 days the NMR spectrum was that of pure diene–sulfone. After 7 days the solvent was removed and replaced by $CHCl_3$. The IR spectrum was identical to that of pure diene sulfone.

Measurement of thermodynamic parameters. A soln of triene in spectral grade methylcyclohexane with an initial absorbance of 0·8 at 322 nm was separated into 3 ml aliquots and degassed in 6 cycles as above in quartz cells (10 × 10 mm), sealed in vacuum and stored in liquid air until use. Disappearance of triene was observed at 330 nm. The rate constants were obtained from the curve ln A_0/A *vs* t.

t(°C)	k(sec^{-1})
30·0 ± 0·05	0·626 × 10^{-5}
40·3 ± 0·05	2·037 × 10^{-5}
50·1 ± 0·05	5·446 × 10^{-5}
59·8 ± 0·05	14·444 × 10^{-5}

ΔH‡ = 20·4 ± 0·2 Kcal/mole
ΔS‡ = − 15 e.u.

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