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(7) Similar identification has been reported: N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 9228 (1972).

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Photochemistry of Dispiro-1,3-cyclobutanediones in Methylene Chloride and Methanol Solutions

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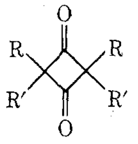
Received March 18, 1974

The photolysis of dione **3** ($n = 4$) in methylene chloride leads mainly to the isomeric, photolabile enol lactone **6**. Diones **3** ($n = 5$, 6, or 7) on irradiation in methylene chloride solutions lead to 20, 50, and 40% yields of **4** ($n = 5$, 6, or 7), respectively. Pentamethyleneketene and hexamethyleneketene were also formed from diones **3** ($n = 6$ or 7). Little cycloelimination occurs in the case of dione **3** ($n = 5$). Small amounts of cycloalkanones are also formed from diones **3** ($n = 5$, 6, or 7) (less than 10%). Dione **3** ($n = 4$) could not be photolyzed in methanol because of its facile ring opening in this solvent to yield **7**. The photolysis of **3** ($n = 5$) in a methanol solution leads to α-methoxydicyclopentyl ketone (**8**), methyl cyclopentanecarboxylate, cyclopentanone, and several other unidentified products. The photolysis of **3** ($n = 6$ or 7) in methanol leads to the unstable hemiketals of the dispirocyclopropanones **12** ($n = 6$ or 7), the corresponding methyl cycloalkanecarboxylates, and cycloalkanones (small amounts). On work-up the β-peroxy esters **11** ($n = 6$ or 7) were isolated from these photolyses in 43 and 25% yields, respectively. The β-peroxy esters **11** ($n = 6$ or 7) on treatment with base form the β-peroxy lactones **15** ($n = 6$ or 7), respectively. Thermolyses of **15** ($n = 6$ or 7) lead to the spiranones **14** and **17**, respectively, in nearly quantitative yields.

The photolysis of tetramethyl-1,3-cyclobutanedione **1** (R = R′ = Me) in inert solvents such as benzene or methylene chloride produces tetramethylethylene. A competitive cycloelimination also occurs to yield some dimethylketene.[2,3] A low yield of the isomeric enol β-lactone **2** has been obtained when **1** (R = R′ = Me) is irradiated in ether, dioxane, or tetrahydrofuran.[4] The irradiation of this dione in dioxane containing some acetic acid or in propionic acid leads to α-acyloxy ketones.[5]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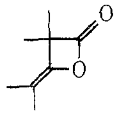
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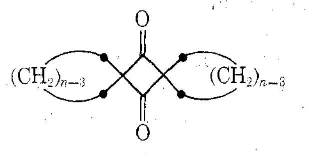
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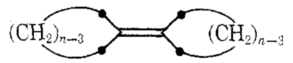
The intermediacy of tetramethylcyclopropanone in the photolysis of **1** (R = R′ = Me) has been supported by its isolation,[2d] its trapping on photolysis of the dione in furan,[3,6] and the isolation of hemiketals of the cyclopropanone when the photolysis is performed in alcohols as solvents.[2,6,7] The irradiation of **1** (R = R′ = Me) or **2** in methanol leads to similar products and the dione and lactone **2** were not measurably interconverted under the conditions utilized.[7d]

Diones **1** (R = R′ = Et) and **1** (R = R′ = n-Pr) also yield the corresponding olefins on photolysis in inert solvents.[2a] The dispiro-1,3-cyclobutanedione **3** ($n = 6$) on irradiation in methylene chloride yields **4** ($n = 6$) (50%) along with the cycloelimination product pentamethyleneketene.[2b,8] Irradiation of **5** in aqueous THF yields bicyclo[2.2.1]heptane-7-carboxylic acid (53%).[9]

In connection with another study,[10] it was of interest to study the effect of ring size on the products of the photolysis of a series of dispiro-1,3-cyclobutanediones **3** ($n = 4$, 5, 6, or 7) in inert solvents. Since the photolysis of **3** ($n = 6$) leads to **4** ($n = 6$),[2b,8] a similar double decarbonylation of the other diones would be a useful synthetic route to cycloalkylidenecycloalkanes of various ring size. In addition the photolysis of **3** ($n = 4$, 5, 6, or 7) in a reactive solvent such as methanol would be of interest in order to hopefully isolate and investigate the stabilities of the hemiketals of the dispirocyclopropanones which might be produced in the photolysis.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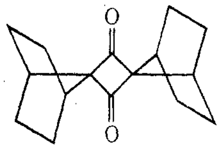
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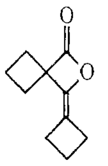
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Syntheses of the Diones 3 (n = 4, 5, 6, and 7). The diones **3** ($n = 4$, 5, 6, and 7) can readily be prepared by dehydrohalogenation of the cycloalkanecarbonyl chlorides of the proper ring size with triethylamine.[10,11]

Spectral Characteristics of the Tetrasubstituted 1,3-Cyclobutanediones. The ultraviolet spectrum of dione **1** (R = R′ = Me) exhibits two distinct n-π^* transitions.[2a,12] The ultraviolet spectra for diones **1** (R = R′ = Me) and **3** ($n = 4$, 5, 6, and 7) are tabulated in Table I. All diones except **3** ($n = 4$) exhibit two n-π^* transitions. These two bands can be attributed to 1,3-π interactions in the excited states of these diones.[2c]

Results and Discussion

All irradiations were performed through Pyrex or by use of a Pyrex filter to ensure that the initial absorption was restricted to n-π^* excitation. Photolyses were performed using a Rayonet RPR-208 reactor or a Hanovia medium-pressure lamp (see Experimental Section).

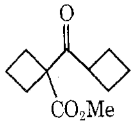
A. Dispiro[3.1.3.1]decane-5,10-dione (3, n = 4). (a) Methylene Chloride. A 0.08 M solution of **3** ($n = 4$) in methylene chloride was irradiated (Rayonet) and the progress of the photolysis was periodically monitored by ir analysis of aliquots. The original carbonyl absorption peak

Table I
Ultraviolet Spectra of the Tetrasubstituted 1,3-Cyclobutanediones

Dione	λ, nm (ε)	Solvent
1 (R = R′ = Me)	227 (173), 302 (30), 345 (18)	Ethanol[a]
3 (*n* = 4)	239 (153), 313 (46),[b]	Methanol
3 (*n* = 5)	233 (157), 299 (44), 350 (26)	Methanol
3 (*n* = 6)	239 (150), 303 (40), 340 (24)	Methanol[c]
3 (*n* = 7)	238 (171), 307 (46), 342 (28)	Methanol

[a] F. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **83,** 4867 (1961). [b] No defined absorption in the 340–350-nm region. [c] Reference 9 reports values of 233 (194), 301 (39), and 341 (20) in ethanol as solvent.

at 1735 cm^{-1} decreased over a 10-hr period and a peak at 1870 cm^{-1} appeared and increased in intensity. No bands attributable to the fragmentation product trimethyleneketene (about 2100 cm^{-1})[2c] or to a dispirocyclopropanone (about 1840 cm^{-1})[2d,f] were detectable. After 24 hr of irradiation strong bands at 1870 and 1740 cm^{-1} were present. These bands are attributable to the isomeric enol lactone **6**.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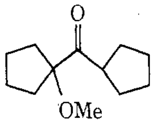
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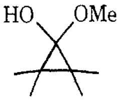
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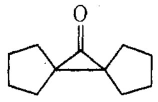
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A 0.03 *M* solution of dione **3** (*n* = 4) was irradiated for 1 hr (Hanovia). Microdistillation of the concentrated residue led to a 30% isolated yield of **6**. This lactone is thermally unstable and some product was lost during decomposition on distillation. It also forms a viscous liquid on standing in air. Longer irradiations of methylene chloride solutions produce substantial amounts of a high-melting solid which could not be characterized. Enol lactone **6** is also photolabile and on overirradiation is readily destroyed.

(b) Methanol. Initial attempts to photolyze solutions of **3** (*n* = 4) in MeOH led to a complex mixture of products. However, it then became evident that dione **3** (*n* = 4) undergoes a facile ring opening on solution in methanol to quantitatively produce **7**. It has previously been reported that diones **3** (*n* = 4, 5, or 6) on treatment with ethanol (catalytic amount of NaOEt present) undergo ring openings to produce the corresponding β-keto esters.[11a,13] Undoubtedly the facile ring opening of **3** (*n* = 4) in methanol is due to the release of internal ring strain. Diones **3** (*n* = 5, 6, or 7) are stable in refluxing methanol. In fact **3** (*n* = 6 or 7) can nicely be recrystallized from methanol.

B. Dispiro[4.1.4.1]dodecane-6,12-dione. (a) Methylene Chloride. A 0.07 *M* solution of **3** (*n* = 5) was photolyzed (Rayonet) and the progress of the reaction was monitored periodically by ir. After 3 hr of irradiation the original carbonyl absorption at 1735 cm^{-1} diminished in intensity and a very weak peak appeared at about 2100 cm^{-1} (tetramethyleneketene). After 10 hr the 2100-cm^{-1} peak did not change in intensity but the 1735-cm^{-1} peak diminished in intensity. After 20 hr no absorption was present at 2100 cm^{-1} and very weak absorptions appeared in the 1650–1750-cm^{-1} region.

Dione **3** (*n* = 5) (0.022 *M* solution) in methylene chloride was photolyzed for 3 hr (Hanovia). The crude photolysate did not contain any tetramethyleneketene (ir analysis). Glpc analysis indicated the presence of about 40% **4** (*n* = 5), cyclopentanone [ratio of **4** (*n* = 5) to cyclopentanone of 8:1], and four unidentified components in 2, 5, 12, and 33% yields. Column chromatography led to a 20% isolated yield of **4** (*n* = 5) and a viscous material which was not further characterized.

(b) Methanol. A 0.022 *M* solution of dione **3** (*n* = 5) in methanol was irradiated for 1.5 hr (Hanovia). Concentration on a rotary evaporator yielded a crude photolysate which exhibited absorption peaks at 1748 (cyclopentanone), 1735 (methyl cyclopentanecarboxylate and starting dione), and 1704 cm^{-1} (**8**). Glpc indicated the presence of cyclopentanone (22%), methyl cyclopentanecarboxylate (20%), unidentified peak A-3 (4%), **8** (20%), starting dione (16%), and two unidentified components in 6 and 11% yields, respectively. Several additional overlapping peaks were also detectable in the glpc trace. On longer irradiation the third peak A-3 was present in a larger amount and was tentatively identified as dicyclopentyl ketone by a retention time comparison. This ketone presumably arises from irradiation of the α-methoxydicyclopentyl ketone (**8**). Product analyses were complicated by the volatility of the methyl cyclopentanecarboxylate and cyclopentanone and these components may have been partially lost on concentration. Pure ketone **8** was separated by glpc and identified by ir and nmr analyses. Distillation of the crude photolysate led to an overall isolated yield of 10% cyclopentanone and 5% methyl cyclopentanecarboxylate.

Ring openings of tetramethylcyclopropanone hemiketals have been previously reported.[2e,f,7,14] The major product which is formed when **9** is heated in MeOH is 2-methoxy-2,4-dimethylpentan-3-one and the minor product is methyl 2,2,3-trimethylbutyrate.[7b,14]

The α-methoxy ketone **8** would appear to arise from the small equilibrium concentration of the dispirocyclopropanone **10** which is present.[2e,7b,14a] This process would appear to be favorable in this case in cold methanol because of the higher internal ring strain in **10** in comparison to tetramethylcyclopropanone and the other dispirocyclopropanones mentioned below.

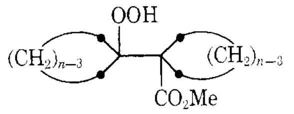
C. Dispiro[5.1.5.1]tetradecane-7,14-dione (3, ***n*** **= 6). (a) Methylene Chloride.** This dione has been previously photolyzed[2c,8] and has been studied here for direct comparison with the other dispiro systems. A 0.07 *M* solution of dione **3** (*n* = 6) was irradiated (Rayonet) and the progress of the reaction was periodically monitored by ir analysis. The dione carbonyl peak at 1735 cm^{-1} commenced to decrease after 1 hr and a strong peak appeared at 2100 cm^{-1} (pentamethyleneketene, about 0.75 times the intensity of the 1735 cm^{-1} absorption peak). After 10 hr of irradiation the 2100-cm^{-1} band was equal in intensity to the CH stretching absorption while the 1735-cm^{-1} peak was about 0.75 times the intensity of the 2100-cm^{-1} peak. After 20 hr the ketene peak had decreased in intensity (0.75 times the CH peak) and the 1735-cm^{-1} absorption was weak (very weak absorptions appeared at 1800 and 1705 cm^{-1}).

Photolysis of a 0.022 *M* solution of **3** (*n* = 6) (Hanovia, 3 hr) led to a yellow oil which had a strong ketene band at 2100 cm^{-1} (equal in intensity to the CH absorption). On addition of water the yellow color disappeared. Glpc chromatography of the crude product which was washed with a NaHCO$_3$ solution indicated the presence of cyclohexanone and **4** (*n* = 6) in a 1:4 ratio, respectively. Chromatography of the oil over alumina with pentane as eluent led to a 50% isolated yield of **4** (*n* = 6). Cyclohexanone

(6% isolated yield) along with an uncharacterized viscous oil was eluted from the column with ether.

A duplicate run was performed as above and methanol was added to the solution on termination of the irradiation. Glpc analysis of the photolysate indicated the presence of cyclohexanone (18%), methyl cyclohexanecarboxylate (10%), 3 (n = 6) (60%), and three unidentified components in 1, 3, and 3% yields, respectively. Treatment of the crude product with methanol followed by cooling led to a 45% isolated yield of 3 (n = 6).

(b) Methanol. Photolysis of a 0.022 M suspension of 3 (n = 6) for 2 hr (Hanovia) followed by concentration on a rotary evaporator (3 hr), addition of pentane and stirring in air led to the isolation of the β-hydroperoxy ester **11** (n = 6) in a 43% yield and ethyl cyclohexanecarboxylate (about 20%). Cyclohexanone (4% overall conversion) and a trace amount of 4 (n = 6) could be detected in the crude photolysate by glpc analysis. Glpc analysis was complicated by the thermal decomposition of the β-peroxy ester **11** (n = 6).



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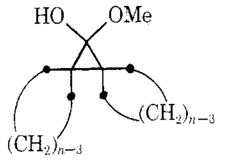

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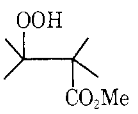

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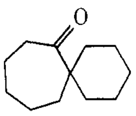

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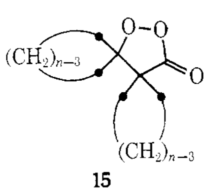
It has recently been reported that the methyl hemiketal of tetramethylcyclopropanone (**9**) in a hexane solution reacts with atmospheric oxygen to yield the β-hydroperoxy ester **13**.[7c] The β-hydroperoxy ester **11** (n = 6) undoubtedly arises in a similar fashion from the methyl hemiketal **12** (n = 6) during the concentration process of the crude photolysate. The ester **11** (n = 6) is stable at its melting point (97°) but at about 125° it undergoes decomposition to yield spiranone **14** in a 56% yield. Cyclohexanone (20%) and three other unidentified products are also produced in 3, 3, and 21% yields.



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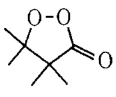

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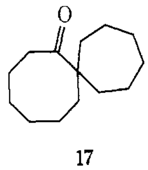

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Treatment of **11** (n = 6) with an aqueous THF solution of sodium hydroxide produced the β-peroxy lactone **15** (n = 6). Thermolysis of **15** (n = 6) at 110° yields the spiranone **14**.[15]

The peroxy lactone **16** was prepared following the procedure of Gibson and DePuy.[7c] It was found that **16** on heating to about 125° leads to pinacolone as the only isolable product. Undoubtedly this peroxy lactone or the β-peroxy ester **13** is the pinacolone precursor which was reported to be formed when **9** was heated in the presence of oxygen.[7b]

D. Dispiro[6.1.6.1]hexadecane-8,16-dione. (a) Methylene Chloride. A 0.07 M solution of dione 3 (n = 6) was irradiated (Rayonet) and the progress of the reaction was monitored by ir analysis. The starting dione exhibits strong absorption at 1730 cm^{-1}. After 3 hr an absorption peak appeared at 2090 cm^{-1} (hexamethyleneketene). After 9 hr the ketene absorption was as intense as the CH absorption while the 1730-cm^{-1} peak was about 0.5 times the intensity of the 2090-cm^{-1} peak. After 24 hr the 2090-cm^{-1} absorption was 0.75 times the intensity of the CH absorption. After 30 hr the 2090-cm^{-1} peak was still present and weak absorptions appeared in the 1600–1800-cm^{-1} region.

Irradiation of a 0.021 M solution of dione 3 (n = 7) for 3 hr (Hanovia) followed by concentration led to a crude yellow oil which showed a medium-intensity ketene absorption at 2090 cm^{-1} (about 0.5 times the intensity of the CH absorption). Treatment of the crude product with water and a solution of $NaHCO_3$ removed the hexamethyleneketene. Glpc of the product indicated the crude product to contain cycloheptanone (20%), 4 (n = 7) (56%), and three unidentified components in 3, 2, and 16% yields. Chromatography over alumina led to 4 (n = 7) (40%) and cycloheptanone (7%).

(b) Methanol. Photolysis of dione 3 (n = 7) for 3 hr (Hanovia) followed by concentration leads to the β-hydroperoxy ester **11** (n = 7), methyl cycloheptanecarboxylate (about 20%), and cycloheptanone (5%). Although **11** (n = 7) could not be isolated, it was found that on allowing the crude photolysate to stand for several days a new peak appeared in the ir spectrum at 1782 cm^{-1} and crystals slowly formed. Treatment of the crude photolysate with an aqueous THF sodium hydroxide solution produced the β-peroxy lactone **15** (n = 7), which could be isolated in a 25% yield.

The thermolysis of **15** (n = 7) leads to spiranone **17**.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 237-B grating spectrophotometer. Ultraviolet spectra were determined on a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Nmr spectra were taken on a Jeolco JNM-MH-100 spectrophotometer and are reported as parts per million values relative to internal TMS. Glpc analyses were performed on a Gow-Mac 69-100 chromatograph using a 4 ft × 0.25 in. Carbowax PEG 20M Chromosorb column. All percentage data for the glpc analyses are raw data and are uncorrected for variations in detector response. The data for the glpc analyses are listed in the order in which the compounds eluted from the column. Microanalyses were performed by Robertson Laboratories, Florham Park, N. J. 07932.

Materials. Methanol (Certified ACS) was treated with Mg and distilled. Methylene chloride was predried over $MgSO_4$ and distilled.

Irradiation Procedures. External photolyses were performed using a Rayonet RPR-208 photoreactor which was fitted with 8 RUL-300 nm lamps (85 W). Solutions were placed in Pyrex tubes, degassed with N_2 for 5–10 min, and cooled with an internal cold finger. A mercury bubbler was attached to prevent entrance of air and escape of gas. Aliquots could be periodically withdrawn for ir analyses.

Preparative photolyses were performed in an internally water-cooled (5–7°) reactor (quartz) with a Hanovia Type L-679A-36, 450-W, medium-pressure arc. A cylindrical Pyrex filter sleeve was employed to surround the lamp to restrict the initial excitation to the n-π^* bands of the dione. All solutions were degassed with N_2 for 5–10 min and the system was purged with N_2 before the irradiation was commenced. A mercury bubbler was attached to the apparatus.

A. Photolysis of Dispiro[3.1.3.1]decane-5,10-dione (3, n = 4). (a) CH_2Cl_2. Dione 3 (n = 4) (0.61 g, 3.7 mmol) was dissolved in 170 ml of dry CH_2Cl_2 and the solution was irradiated for 1 hr (Hanovia). The solution was concentrated with a rotary evaporator. Glpc (165°) indicated the presence of a small amount of starting dione and one major volatile product. Ir analysis showed strong absorption peaks at 1745 and 1875 cm^{-1} (neat).[16] Distillation using a Kontes micro apparatus gave 0.20 g (30%) of **6**: nmr ($CDCl_3$) δ 1.8–2.7 (m, 8 H) and 2.9 ppm (slightly deformed quartet, 4 H, allylic CH_2).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.96; H, 7.41.

(b) Preparation of 7. Dione 3 (n = 4) (100 mg) was added to 15 ml of methanol. The solution was allowed to stand at room temperature for 1 hr. The methanol was removed on a rotary evaporator to produce a quantitative yield of **7**: bp (oil bath temperature 40°, 0.02 mm) using a Kontes micro distillation apparatus; ir (neat) 1735 and 1700 cm^{-1} (both strong); nmr ($CDCl_3$) δ 1.7–2.8 (complex m, 12 H, $-CH_2-$), 3.4 (m, 1 H, -CHCO), and 3.7 ppm (s, 3 H, CO_2CH_3).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.63; H, 8.14.

B. Photolysis of Dispiro[4.1.4.1]dodecane-6,12-dione (3, *n* = 5). (a) CH_2Cl_2. Dione **3** (*n* = 5) (0.71 g, 3.7 mmol) in 170 ml of dry CH_2Cl_2 was irradiated for 3 hr (Hanovia). Concentration of the photolysate yielded 0.60 g of a thick oil. Ir analysis indicated no ketene absorption peak. Glpc analysis showed the presence of cyclopentanone (5%), **4** (*n* = 5) (40%), and four unidentified components in 2, 5, 12, and 33% yields, respectively. Chromatographic separation over aluminum oxide (neutral, Brockmann No. 1) using pentane as eluent gave 0.1 g (20%) of pure **4** (*n* = 5): nmr ($CDCl_3$) δ 1.6 (m, 8 H) and 2.0 (m, 8 H).[17] Elution with ether gave 0.4 g of a viscous material which was not characterized.

(b) Methanol. Dione **3** (*n* = 5) (0.75 g, 4.0 mmol) in 170 ml of MeOH was irradiated for 1.5 hr (Hanovia). Concentration on a rotary evaporator yielded 0.64 g of a pleasant-smelling liquid which showed ir absorptions at 1748, 1735, and 1705 cm^{-1}. Distillation at 25° (0.02 mm) and collection of the volatile material using a Dry Ice–acetone bath gave a mixture of cyclopentanone (10% isolated yield) and methyl cyclopentanecarboxylate (5%). Pure **8** was isolated by glpc (10-ft column of 20% SE-30, Chromosorb W at 175°) (15% isolated yield): ir (neat) 1705 cm^{-1}; nmr ($CDCl_3$) δ 1.7 (m, 16 H), 2.5 (m, 1 H), and 3.0 ppm (s, 3 H, $-OCH_3$).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.47.

C. Photolysis of Dispiro[5.1.5.1]tetradecane-6,12-dione (3, *n* = 6). (a) CH_2Cl_2. Run 1. Dione **3** (*n* = 6) (0.85 g, 3.9 mmol) in 175 ml of dry methylene chloride was irradiated for 3 hr (Hanovia). On concentration a yellow, pungent oil was obtained (ir 2100 cm^{-1}). Water and a dilute sodium bicarbonate solution were added to the photolysate. The products were extracted into methylene chloride. Concentration of this extract yielded 0.7 g of an oil which solidified. Glpc indicated the presence of **4** (*n* = 6) and cyclohexanone in a 1:4 ratio. Chromatography over alumina using pentane as eluent gave 0.32 g (50%) of **4** (*n* = 6). Elution with ether led to a 0.05 g (6%) of cyclohexanone along with an uncharacterized viscous oil.

Run 2. The reaction was performed as in run 1. At the end of the irradiation period methanol was added to the photolysate. Concentration yielded 0.6 g of crude product. Glpc analysis indicated the presence of cyclohexanone (10%), methyl cyclohexanecarboxylate (10%), **4** (*n* = 6) (77%), and three unidentified products in 1, 3, and 3% yields, respectively. Pure **4** (*n* = 6) (0.3 g, 47%) was isolated by crystallization from methanol.

(b) Methanol. The dione (0.82 g, 3.7 mmol) in 170 ml was irradiated for 2 hr (Hanovia). Initially not all the dione was in solution and a blue coloration appeared on the undissolved solid. The dione dissolved as the irradiation progressed. The photolysate was transferred to a 500-ml round-bottom flask and the photolysis apparatus was rinsed with 10 ml of pentane. The solution was concentrated by use of a rotary evaporator. Pentane was added to the residue and the solution was allowed to stir overnight. On concentration, followed by cooling and filtration, 0.41 g (43%) of **11** (*n* = 6) was obtained. The analytical sample was crystallized from pentane: mp 97–98°; ir (CCl_4) 3400 and 1705 cm^{-1}; nmr ($CDCl_3$) δ 0.7–2.5 (broad m, 20 H), 3.7 (s, 3 H, $-CO_2CH_3$), and 8.4 ppm (s, 1 H, -OOH).

Anal. Cacld for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.36; H, 9.73.

After removal of **11** (*n* = 6) the filtrate was analyzed by glpc. Analysis showed the major component to be methyl cyclohexanecarboxylate (65%). Cyclohexanone (10%), spiro[5.6]dodecan-7-one (15%), and two unidentified components were present in 7 and 2% yields, respectively. A trace amount of **4** (*n* = 6) was also present. Methyl cyclohexanecarboxylate was obtained in a 20% overall yield while cyclohexanone was formed in a 4% overall yield.

D. Photolysis of Dispiro[6.1.6.1]hexadecane-8,16-dione. (a) CH_2Cl_2. Dione **3** (*n* = 7) (0.92 g, 3.7 mmol) was dissolved in 170 ml of dry methylene chloride and the solution was irradiated for 3 hr (Hanovia). The yellow solution was concentrated using a rotary evaporator to a yellow oil. Ir analysis of the crude photolysate showed an absorption peak at 2100 cm^{-1} (hexamethyleneketene). Cold water and a dilute $NaHCO_3$ solution were added to the crude photolysate. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated to yield 0.7 g of crude product. Glpc analysis indicated the following approximate composition: cycloheptanone (20%), **4** (*n* = 6) (56%), and three unidentified components in 3, 2, and 16% yields. No starting dione was detectable. Chromatography of the sample (aluminum oxide, neutral, Brockmann No. 1) using pentane gave 0.28 g (40%) of **4** (*n* = 4).[17] Elution with ether gave 0.06 g (7%) of cycloheptanone.

(b) Methanol. Dione **3** (0.091 mmol) in 180 ml of methanol was irradiated for 3 hr (Hanovia). About 1 g of crude photolysate was obtained on concentration using a rotary evaporator. Ir analysis of this crude product showed a broad absorption at 3400 cm^{-1} [OOH of **11** (*n* = 7)], a peak at 1735 cm^{-1} (ester of methyl cycloheptanecarboxylate), a shoulder 1710 cm^{-1} [ester of **11** (*n* = 7)], and a shoulder at 1700 cm^{-1} (carbonyl of cycloheptanone). Nmr analysis showed peaks at δ 8.8 (broad, OOH), and singlets at 3.7 (CO_2CH_3 of methyl cycloheptanecarboxylate) and 3.6 ppm [CO_2CH_3 of **11** (*n* = 7)].

On addition of pentane to the crude product followed by stirring overnight, an absorption peak at 1782 cm^{-1} appeared [peroxy lactone **15** (*n* = 7)]. The oil was dissolved in 4 ml of THF and a solution of 0.1 g of NaOH in 2 ml of water was added. The mixture was stirred overnight and then concentrated under vacuum. Water was added and the mixture was extracted with pentane. On concentration and cooling 0.25 g (25%) of **15** (*n* = 7), mp 65–67°, was obtained. The analytical sample was crystallized from pentane: mp 67–68° (dec 80°); ir (CCl_4) 1782 cm^{-1}; nmr ($CDCl_3$) δ 1.2–2.4 (m).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.60; H, 9.89.

The filtrate after removal of **15** (*n* = 7) still showed the presence of some of this peroxy lactone on ir analysis. The major component was methyl cycloheptanecarboxylate along with a small amount of cycloheptanone. Glpc analysis was complicated by the thermal decomposition of the residual peroxy lactone **15** (*n* = 7). The ratio of the methyl cycloheptanecarboxylate to cycloheptanone was about 4:1. Distillation using a Kontes macro apparatus yielded 0.3 g (bp 60–65°, 1 mm) of a product which was about 85% methyl ester (overall conversion estimated to be 22%) and 15% cycloheptanone (overall yield of about 5%). A solid collected in the cold finger and was identified as spiranone **17** [from thermal decomposition of the β-peroxy lactone **15** (*n* = 7), 0.05 g, 7% yield].

β-Peroxy Lactone 15 (*n* = 6). The β-hydroperoxy ester **11** (*n* = 6) (0.256 g, 10 mmol) was dissolved in 8 ml of THF. To this solution was added a solution of 0.19 g (4.7 mmol) of NaOH in 6 ml of water. Two layers formed and the mixture was allowed to stir at room temperature for 16 hr. The reaction mixture was poured into ice water and the solid was collected, 0.20 g (90%), mp 94–96°. The product was crystallized from pentane: 0.15 g; mp 99–100° (dec at about 120°); ir (CCl_4) 1780 cm^{-1}; nmr (CCl_4) δ 1.0–2.0 ppm (broad multiplet pattern).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 70.01; H, 9.40.

Thermolysis of β-Peroxy Lactone 15 (*n* = 6). A sample of **11** (*n* = 6) (0.089 g, 0.4 mmol) was heated under a N_2 blanket in an oil bath the temperature of which was gradually raised. After about 0.5 hr (oil bath temperature 110°) a vigorous evolution of CO_2 occurred. The temperature rose to 150° over a 35-min period. The residue showed only one component on glpc analysis on a DC 200 column (210°). The product was readily identified as spiranone **14** by an ir and nmr comparison with those of an authentic sample.[18]

Thermolysis of β-Peroxy Lactone 15 (*n* = 7). A sample of **15** (*n* = 7) (0.033 g) was heated in an oil bath under a N_2 blanket. At about 80° gas evolution was brisk and the temperature of the bath was raised to 135° over a total of 0.5 hr. On cooling, the melt solidified and **17** (0.26 g, quantitative yield) was obtained, mp 72–73° (lit. mp 71–72°). The ir and nmr spectra were identical with those of an authentic sample.[18]

Registry No.—**1** (R = R′ = Me), 933-52-8; **3** (*n* = 4), 4893-00-9; **3** (*n* = 5), 5011-61-0; **3** (*n* = 6), 950-21-0; **3** (*n* = 7), 6558-10-7; **4** (*n* = 5), 16189-35-8; **4** (*n* = 6), 4233-18-5; **6**, 51593-63-6; **7**, 51593-64-7; **11** (*n* = 6), 51593-65-8; **11** (*n* = 7), 51593-66-9; **15** (*n* = 6), 51593-67-0; **15** (*n* = 7), 51593-68-1; **16**, 23438-10-0; **17**, 13169-19-2.

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Electrophilic Additions to Dienes. VI.[1] Halogenation of Phenylallene

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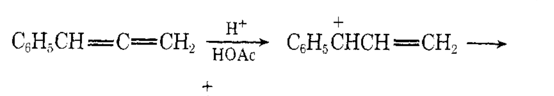
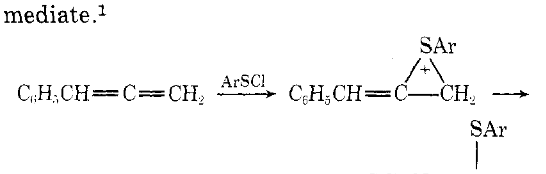
Received January 2, 1974

Electrophilic bromination, iodination, and chlorination of phenylallene and its derivatives were carried out under various reaction conditions. Products were exclusively monoadducts and the ratios of 1,2 to 2,3 adducts were determined by pmr spectroscopy. Bromination in methanol gave exclusively a 1,2-bromomethoxide at −70° while it resulted in the formation of the 2,3 adduct as well at 0°. Bromination in carbon disulfide yielded both 1,2- and 2,3-dibromides at −70° but the former rearranged completely to the latter at 0°. The fraction of a 1,2 adduct decreased with the electron-donating ability of a substituent of phenylallene derivatives in the bromination in methanol at 0°. Iodination tended to give more 1,2 adduct and chlorination less 1,2 adduct. The former reaction gave exclusively a 1,2 adduct in methanol even at 0°. The product ratios are considered to be determined by the stability of the initially formed 1,2-halonium ion and the reactivity of a nucleophile.

We have previously investigated the hydrochlorination[2] and the sulfenyl chloride addition[1] of phenylallene and its derivatives. It was concluded that the hydrochlorination involves the rate-determining protonation at the central carbon to form a perpendicularly twisted vinylbenzyl cation which easily leads to a conjugated cinnamyl cation by the bond rotation.[2] That is, the reaction takes place *via*


$$C_6H_5CH{=}C{=}CH_2 \xrightarrow[HOAc]{H^+} C_6H_5\overset{+}{C}HCH{=}CH_2 \longrightarrow C_6H_5CH\overset{\cdot\cdot}{-}CH\overset{\cdot\cdot}{-}CH_2 \xrightarrow{Cl^-} C_6H_5CH{=}CHCH_2Cl \qquad (1)$$

the internal bond addition to form a terminal bond adduct. By contrast, 2,4-dinitrobenzenesulfenyl chloride proved to add directly (kinetically) to the terminal double bond of phenylallene through an episulfonium ion intermediate.[1]


(2)

These contrasting behaviors exhibited by the typical electrophiles in the addition to phenylallene prompted us to examine those to be shown by halogen ions, which are generally considered to be intermediate in nature between the above two extremes of electrophiles.

On the other hand, the intermediacy of a cyclic halonium ion is widely considered in the halogenation of olefins.[3] Bromination of optically active allenic compounds has recently been studied in the interest of scrutiny as to whether it takes place through a cyclic bromonium ion or through an open allylic cation. Caserio, *et al.*,[4] found that the bromination of optically active 1,3-dimethylallene gives an optically active product *via* a stable bromonium ion, while Jacobs, *et al.*,[5] observed the loss of optical activity during the bromination of active 2,2-dimethyl-3,4-hexadien-1-ol. The former authors concluded that there was intervention of a stable bromonium ion during the reaction while the latter considered that it was not stable enough to maintain stereochemistry. The direct observation of allenic halonium ions has recently been made in a superacid at lower temperatures.[6]

The present investigation has proved to provide useful information on the intermediacy of cyclic halonium ions and their stabilities.

Results

Bromination. Bromination of phenylallene (1) was investigated under various reaction conditions. We first carried out the reaction in methanol at 0°. A pmr spectrum of the reaction products revealed the formation of a 1,2