Methylene Analogs of Cyclobutenedione. VIII.[1] The Oxidation of 1-Halo- and 1,2-Dihalo-3,4-bis(diphenylmethylene)cyclobut-1-enes

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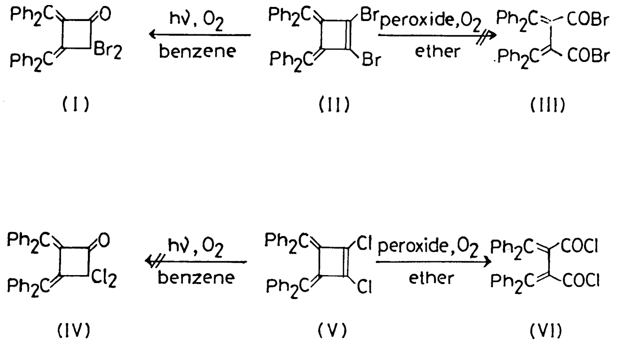
The ether peroxide-catalyzed oxidation of 1-chloro- (X) and 1,2-dichloro-3,4-bis(diphenylmethylene)cyclobut-1-enes (V) afforded two ring-opened products, XI and VI respectively. However, neither X nor V was oxidized by photooxidation. By the photooxidation, 1-bromo- (XVI) and 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobut-1-enes (II) were converted to cyclobutanones, XIII and I respectively. Although II was inert to the peroxide-catalyzed oxidation, XVI was oxidized by this procedure. Nevertheless, the main product of the latter reaction was the cyclobutanone (XIII). The mechanisms of these reactions were described.

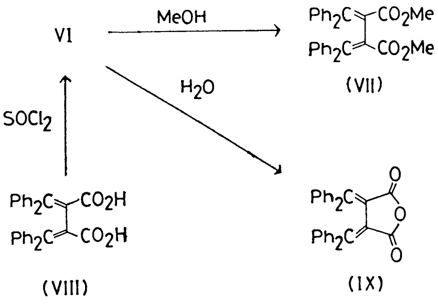
We have previously reported[2] a photooxidation of 1,2-dibromo-3,4-bis(diphenylmethylene) cyclobut-1-ene (II) in benzene affording 2,2-dibromo-3,4-bis(diphenylmethylene)cyclobutane-1-one (I) in a 78% yield. It was found, however, that the dichloro-analog of II (V) was inert to the photooxidation and did not afford the dichloro-analog of I (IV). On the other hand, V was oxidized in ether containing its peroxide to afford 2,3-bis(diphenylmethylene)succinoyl chloride (VI), while the ether peroxide-catalyzed oxidation of II did not afford any product, II being recovered (Scheme 1).



Scheme 1.

These facts suggest that the behavior in response to oxidation reactions varies with the halogen bonded to the 1,2-positions of 3,4-bis(diphenylmethylene)cyclobut-1-ene (XXII). The study was extended to the oxidations of 1-monohalo derivatives of XXII and the Br-Cl-analog (XIX).

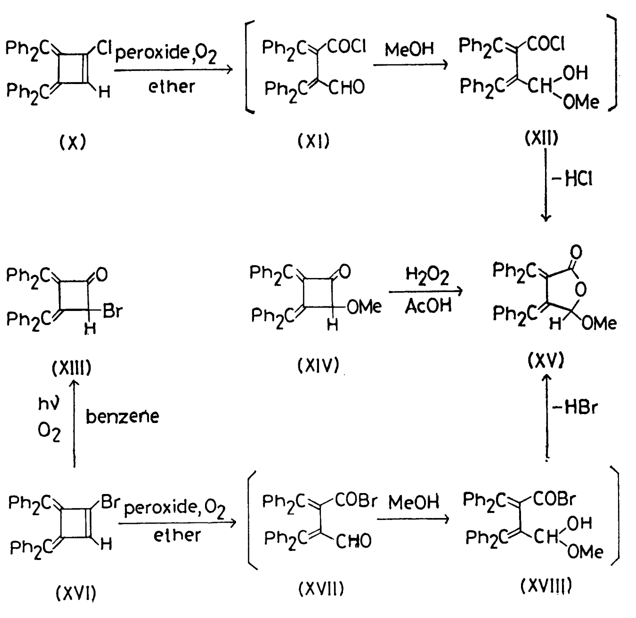
The stirring of a solution of V in commercial ether under an oxygen atmosphere at room temperature for 3 hr afforded VI in a 62% yield. The structure of VI was determined by studying its reactions with methanol and with water, which afforded dimethyl 2,3-bis(diphenylmethylene)succinate (VII) and 3,4-bis(diphenylmethylene)succinic anhydride (IX) respectively. Finally VI was identified by a comparison of its spectral data with those of an authentic sample prepared by the reaction of 2,3-bis(diphenylmethylene)succinic acid (VIII) with $SOCl_2$ (Scheme 2).



Scheme 2.

Although X was inert to the photooxidation in benzene, it underwent the peroxide-catalyzed oxidation; 5-methoxy-3,4-bis(diphenylmethylene)-γ-butyrolactone (XV) (33%) was isolated after the treatment of the reaction mixture with MeOH. The structure of XV was identified by a comparison of its spectral data with those of an authentic sample prepared by the oxidation of 2-methoxy-3,4-bis(diphenylmethylene)-cyclobutane-1-one (XIV) with H_2O_2 in AcOH. The formation of XV can be interpreted in terms of an intramolecular esterification of the hemiacetal (XII) produced by the reaction of the oxidation product (XI) with MeOH (Scheme 3).

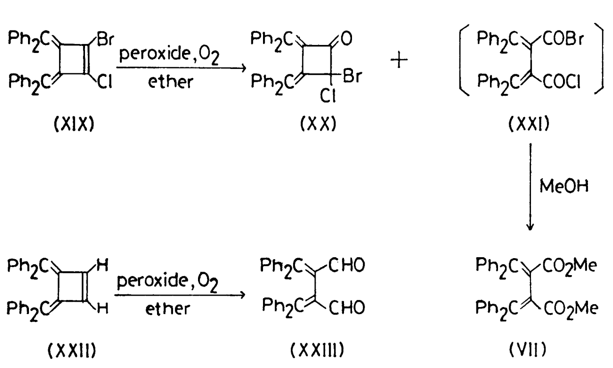
The photooxidation of XVI afforded 2-bromo-3,4-bis(diphenylmethylene)cyclobutane-1-one (XIII) in an 81% yield. XVI was also oxidized by the peroxide-



Scheme 3.

catalyzed method to afford, after treatment with MeOH, XIII and XV in 48 and 15% yields respectively. Since the same result was obtained when the oxidation was carried out in the dark, the pathway of the formation of XIII may not be a photochemical one. The mechanism of the formation of XV is probably the same as that of the conversion of X to XV (Scheme 3).

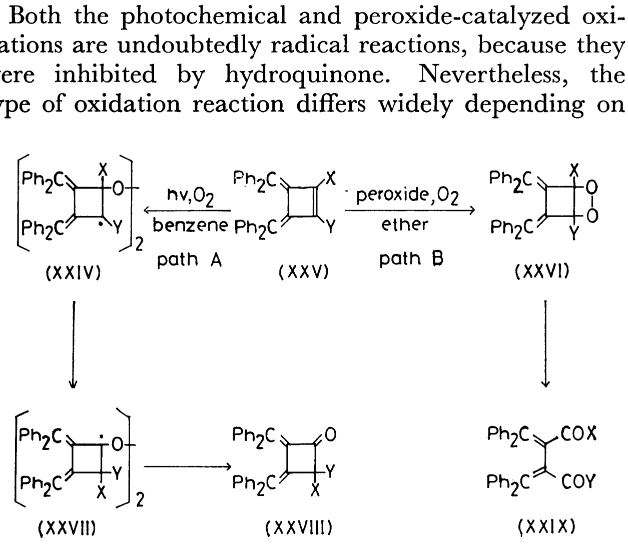
The chloro-derivatives (V and X) were oxidized by the peroxide-catalyzed procedure, but not photochemically. On the contrary, the bromo-derivative (II) was oxidized by the photochemical procedure, but not by the peroxide-catalyzed one. This rule, however, was not applicable to the peroxide-catalyzed oxidation of XVI, even though the main product (XIII) was the same as the photooxidation product of XVI.



Scheme 4.

The photooxidation of XIX[1] afforded only a resinous material. The peroxide-catalyzed oxidation of XIX afforded, after treatment with MeOH, 2-bromo-2-chloro-3,4-bis(diphenylmethylene)cyclobutane-1-one (XX) and VII in 24 and 12% yields respectively. The acid halide (XXI) may be an initial oxidation product and a precursor of VII (Scheme 4). The peroxide-catalyzed oxidation of XXII in ether afforded 2,3-bis(diphenylmethylene)butanedial (XXIII) in a quantitative yield, whereas the photooxidation of XXII in benzene did not afford any product, XXII being recovered.[3]

Both the photochemical and peroxide-catalyzed oxidations are undoubtedly radical reactions, because they were inhibited by hydroquinone. Nevertheless, the type of oxidation reaction differs widely depending on whether the halogen bonded to the cyclobutene is Br or Cl. The reason for the difference is not clear, but one plausible interpretation is as follows: the photooxidation proceeds *via* Path A, which includes a 1,2-shift of the halogen atom (X·) in the intermediate (XXIV) initially produced by an intermolecular oxygenation of XXV. The ketonization of XXVII affords XXVIII. The peroxide-catalyzed oxidation proceeds *via* Path B, which includes the ketonization of XXVI initially produced by an intramolecular oxygenation of XXV (Scheme 5). It is understandable that only the cyclobutenes containing Br can be oxidized to cyclobutanone derivatives, because the elimination of the Br atom from a radical species is easier than that of the Cl atom.[4] The formation of XX, which was not contaminated with its dibromo-(I) and/or dichloro-analog (IV), in the oxidation of XIX suggests that the 1,2-shift of X· is an intramolecular one. Because it has been established that 1,2-shifts of hydrogen do not occur to any detectable extent during the lifetime of radicals,[4] the oxidation reaction of XXII to afford XXIII, but not any cyclobutanone derivative, is also understandable. An intermediate similar to XXVI has been postulated for the reaction of tetraphenylcyclobutadiene with oxygen to afford dibenzoyl-*cis*-stilbene.[5]



Scheme 5.

Experimental

All the melting points are uncorrected. Photooxidation was carried out at room temperature under an oxygen atmosphere in purified dry benzene, using 100-W high-pressure mercury lamp (Riko Kagaku Sangyo Co.). Peroxide-catalyzed oxidation was carried out at room temperature under an oxygen atmosphere in commercial ether. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$ respectively.

Peroxide-catalyzed Oxidation of V. A solution of V (0.2 g) in ether (30 ml) was stirred under an oxygen atmosphere at room temperature for 3 hr. The recrystallization from dry AcOEt of the crystals formed when the reaction mixture was allowed to stand for 10 hr afforded VI as pale yellow prisms; 0.133 g (62%); mp 164—165 °C. IR: 1790 and 1770 (C=O) and 1540 cm^{-1} (C=C); λ_{max}: 356 (14000), 306 (13000), and 249 nm (ε, 20000); NMR: 2.8 τ (m, Ph).

Found: C, 74.88; H, 4.09%. Calcd for $C_{30}H_{20}O_2Cl_2$: C, 75.00; H, 4.17%.

Reactions of VI with MeOH and H_2O. A solution of VI (0.1 g) in MeOH (30 ml) was heated under reflux for 1 hr. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded VII as yellow needles; 0.095 g (97%); mp 233—234 °C (lit,[6] mp 233—234 °C).

A solution of VI (0.1 g) in wet THF (5 ml) was heated under reflux for 1 hr. Recrystallization from AcOEt of the crude crystals obtained by the evaporation of the solvent afforded IX as red rhombs; 0.08 g (90%); mp 230 °C (lit,[2] mp 230 °C).

Preparation of an Authentic Sample of VI. A mixture of VIII (1 g) and $SOCl_2$ (5 ml) was heated at 70 °C for 5 hr. The residue left after the evaporation of the excess $SOCl_2$ was recrystallized from dry AcOEt to afford VI; 0.42 g (38%); mp 164—165 °C.

Peroxide-catalyzed Oxidation of X. A solution of X (0.49 g) in ether (50 ml) was stirred under an oxygen atmosphere at room temperature for 3 hr. The oily material left by the evaporation of the solvent was crystallized by the addition of MeOH. Recrystallization from AcOEt afforded XV as orange prisms; 0.17 g (33%); mp 212.5—214 °C. IR: 1770 (C=O), 1550 (C=C), and 1080 cm^{-1} (MeO-); λ_{max}: 380 (9600) and 258 nm (ε, 21600); NMR: 3.0 (m, Ph, 20 H), 4.7 (s, CH, 1H), and 6.5 τ (s, OCH_3, 3H).

Found: C, 83.63; H, 5.30%. Calcd for $C_{31}H_{24}O_3$: C, 83.76; H, 5.40%.

Preparation of an Authentic Sample of XV. A solution of XIV[2] (0.1 g) and 30% H_2O_2 (0.4 ml) in AcOH (40 ml) was heated at 60 °C for 7 hr. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded XV; 0.047 g (45%); mp 212.5—214 °C.

Photooxydation of XVI. A solution of XVI (1 g) in benzene (100 ml) was irradiated under an oxygen atmosphere at room temperature for 3 hr. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded XIII as orange red hexagonals; 0.84 g (81%); mp 202—203 °C (lit,[2] mp 202—203 °C).

Peroxide-catalyzed Oxidation of XVI. A solution of XVI (0.193 g) in ether (30 ml) was stirred for 3 hr under the same conditions as were used for X. The subsequent evaporation of the solvent left crude oil. Treatment with a small amount of MeOH afforded a mixture of orange red and orange crystals, which were then separated mechanically. The recrystallization of the former from AcOEt afforded XIII; 0.085 g (48%). The recrystallization of the latter from AcOEt afforded XV; 0.027 g (15%).

Peroxide-catalyzed Oxidation of XIX. A solution of XIX (1 g) in ether (100 ml) was stirred for 5 hr under the same conditions as were used for X. The subsequent evaporation of the solvent left an oil, which was crystallized by the addition of a small amount of MeOH to afford a mixture of red prisms and yellow prisms. They were separated mechanically. The recrystallization of the red prisms from AcOEt afforded XX; 0.248 g (24%); mp 169.5—171 °C. IR: 1775 (C=O) and 1540 cm^{-1} (C=C); λ_{max}: 463 (15600), 344 (9200), and 273 nm (ε, 20200).

Found: C, 70.68; H, 3.63%. Calcd for $C_{30}H_{20}OBrCl$: C, 70.40; H, 3.94%.

The recrystallization of the yellow prisms from AcOEt afforded VII; 0.119 g (12%).

Peroxide-catalyzed Oxidation of XXII. A solution of XXII (1 g) in ether (100 ml) was stirred for 3 hr under the same conditions as were used for X. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded XXIII as pale yellow rhombs; 1.08 g (100%); mp 208.5 °C (lit,[3] mp 208.5 °C). The spectral data were identical with those recorded for XXIII.[3]

References

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2) F. Toda and K. Akagi, *Tetrahedron*, **27**, 2801 (1971).

3) In a preliminary communication (F. Toda, M. Higashi, and K. Akagi, *Chem. Commun.*, **1969**, 1219.), we have reported that XXII was oxidized into XXIII photochemically.. This oxidation reaction, however, should be corrected to read "by a peroxide-catalyzed process."

4) C. Walling, "Molecular Rearrangements," Vol. 1, ed. by P. de Mayo, Interscience Publishers, New York (1963), Chap. 7.

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6) F. Toda, and J. Fujita, This Bulletin, **45**, 1928 (1972).