August, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (8), 2017—2020 (1977) 2017

Photochemical Reaction of Diphenylcyclobutenedione Derivatives. Formation and Reaction of Conjugated Bisketene and Its *N*-Analog*

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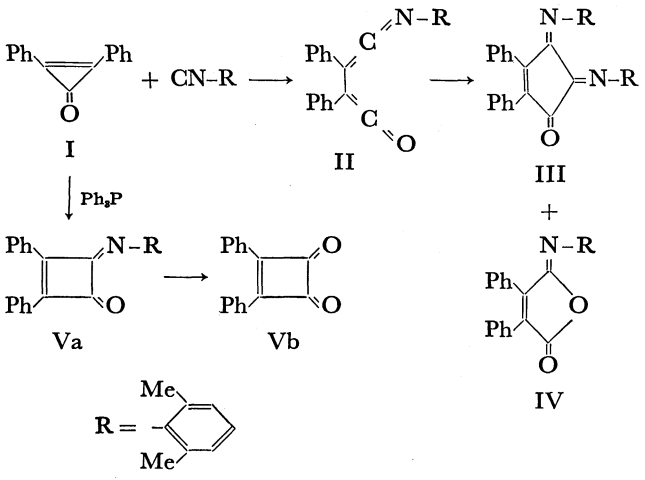
(Received January 12, 1977)

The photolysis of diphenylcyclobutenedione derivatives (Va, b) under N_2 and that in the presence of substrate, O_2 or isocyanide, have been studied. The former resulted in the recovery of a large amount of V and the fragmentation; the latter gave the insertion products into V, diphenylmaleic anhydrides and iminocyclopentenones in good yield. The intermediates, bisketene and ketene-ketenimine as primary photo products were confirmed by the photolysis of Va in methanol to give succinates and by low-temperature IR-technique. Structural aspects of bisketene intermediate were discussed.

In a previous paper,[1)] we reported facile ring-enlargement reactions of diphenylcyclopentenone (I) with 2,6-xylyl isocyanide to give cyclopentenetrione (III) together with a small amount of isomaleimide (IV), and cyclobutenedione (Va) in the presence of catalytic amount of triphenylphosphine. Since Va did not react further with the isocyanide in the dark, we proposed a tentative mechanism *via* ketene-ketenimine intermediate (II) rather than that of stepwise insertion of isocyanide into carbon-carbon bond of I *via* Va.

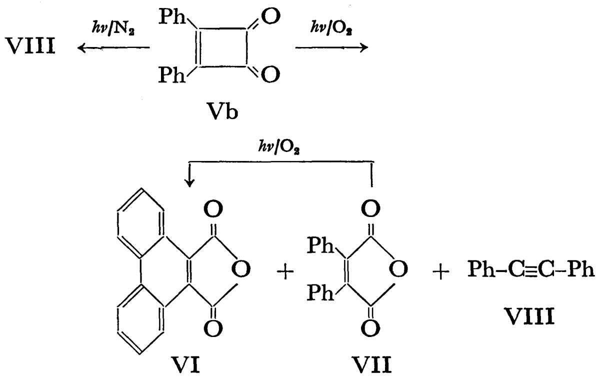


Scheme 1.

We found that diphenylcyclobutenedione (Vb) obtained from the hydrolysis of Va readily undergoes photochemical reaction to give a yellow solid on exposure to direct sunlight in the air. The same phenomenon to give a tan solid was observed by Blomquist and LaLancette[2b)] who assumed it was a dimer of Vb. However, details of the photochemical reaction and the structure of the products have remained unsolved. A few photochemical reactions of cyclobutenedione derivatives were reported,[2,3)] in which bisketene derivatives were only postulated as an intermediate. In view of the possible isolation of bisketenes under certain photochemical reactions, the photolysis of cyclobutenediones Va and Vb with and without O_2 or isocyanide were investigated.

Result and Discussion

Vb in benzene was irradiated with a high-pressure mercury lamp for 6 h under a slow stream of O_2 at room temperature. The reaction products were chromatographed on silica gel. 9,10-Phenanthrenedicarboxylic anhydride (VI, in 52% yield), diphenylmaleic anhydride (VII, in 4% yield), and diphenylacetylene (VIII, in 4% yield), were obtained together with the recovery of Vb in 30% yield. These compounds could not be obtained without light under O_2. Photolysis of VII under the same conditions as above gave VI in good yield *via* oxidative cyclization.[4)]



Scheme 2.

The structures of VI, VII, and VIII were confirmed by elemental analysis, molecular weight determination, spectroscopic data, and direct comparison with the samples prepared by the authentic route.[5,6)] The mp and IR spectrum of VI agreed with those of the compound assumed to be a dimer of Vb.[2b)]

Irradiation of Vb in benzene under N_2 stream for 6 h at room temperature gave VIII in 28% yield as the sole product accompanied by the recovery of Vb in 69% yield.

Photolysis of Va under O_2 stream gave *N*-(2,6-dimethylphenyl)diphenylisomaleimide (IV, in 25% yield), 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one (III, in 5% yield), and VIII in 8% yield.

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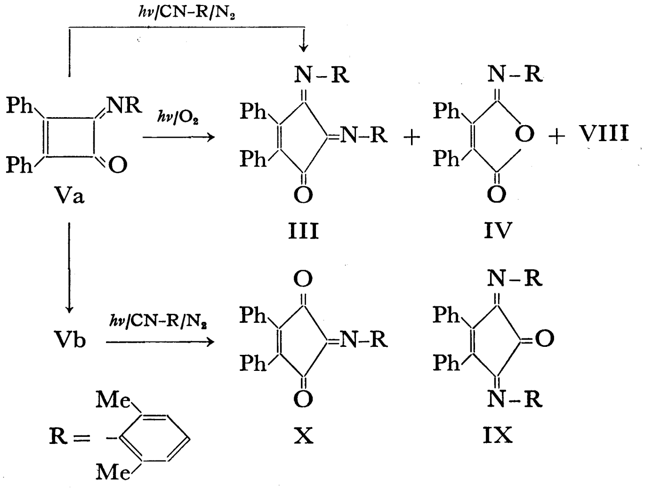
* A part of this work has been published: N. Obata and T. Takizawa, *Chem. Commun.*, **1971**, 587. It was also presented at the 23rd National Meeting of the Chemical Society of Japan, Tokyo, April 1970.



Scheme 3.

The molecular formula for III was found to be $C_{33}H_{28}ON_2$ on the basis of elemental analysis and molecular weight. In the IR spectrum, III showed characteristic two peaks at 1640 and 1710 cm^{-1} due to νC=N and νC=O on cyclopentene skeleton. In the NMR spectrum, III showed multiplets at 2.40—2.90 τ(10H) and 3.10—3.40 τ(6H), and two singlets at 7.95 τ(6H) and 8.25 τ(6H) due to 2,6-disubstituted methyl group on phenyl ring, suggesting that III is not symmetrical 2,5-bis(2,6-dimethylphenylimino)-3,4-diphenylcyclopenten-1-one (IX).

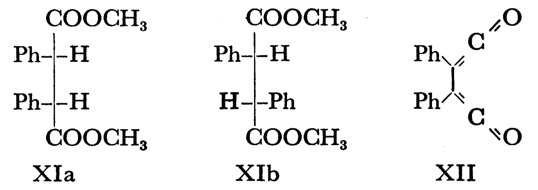
IV, the molecular formula $C_{24}H_{19}O_2N$, showed characteristic IR bands at 1710 and 1800 cm^{-1} due to νC=N and νC=O on cyclopentene ring, and UV spectrum in ethanol at 230 nm (log ε 4.26), 253 nm (4.12) and 330 nm (3.98). All these data were similar to those of *N*-substituted isomaleimide reported.[7] Treatment of IV with dil. HCl in methanol gave *N*-substituted diphenylmaleimide, which was prepared by a modification of the reaction by Reimer[6] and characterized.

The structures of III and IV were further confirmed by comparison with those obtained from the reaction of I with 2,6-xylyl isocyanide.[8] In contrast to the photolysis of VII in O_2, IV was not further photooxidized to phenanthrene derivatives upon prolonged irradiation.

III might be produced by the insertion of 2,6-xylyl isocyanide eliminated from Va with concomitant formation of VIII and CO during the course of photolysis. The isocyanide eliminated so far was also detected by thin-layer chromatography on silica gel and UV spectrum. Photolysis of Va in the presence of the isocyanide under N_2 gave III in 80% yield. However, no reaction of Va with the isocyanide in benzene at 80 °C was observed in the dark.

The photolysis of Vb in the presence of the isocyanide gave 5-(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1,4-dione (X, in 86% yield). The structure of X was established by elemental analysis, molecular weight determination and spectral data. IV as well as VI and VII could be formed as a result of the insertion of O_2[9] into Va and Vb in a similar way to that for III.

In order to trap the intermediate in the photochemical reactions of Va, Vb with O_2 and isocyanide to give their insertion products, photolysis of Va and Vb in methanol at room temperature was carried out.[10] When Vb in methanol was irradiated at room temperature, dimethyl *meso*-diphenylsuccinate (XIa, in 67% yield) and dimethyl *dl*-isomer (XIb, in 17% yield) were obtained.



Scheme 4.

The photolysis of Vb in THF–methanol at −78 °C gave the same products in about the same ratio. The structures of XIa and XIb were confirmed by direct comparison with samples prepared by an authentic route.[11]

A solution of Va or Vb in THF was irradiated under N_2 at −78 °C (10 h for Va: 2 h for Vb). Addition of 2,6-xylyl isocyanide to both solution at −78 °C in the dark gave III and X in 78 and 82% yield, respectively. When O_2 was bubbled into the solution obtained from the photolysis of Vb at −78 °C in the dark, VII was obtained in 42% yield. Addition of cold methanol to the solution gave succinate XIa (39%) and XIb (14%) along with a trace amount of VIII. All these results indicate that the primary intermediacy of the photolysis of Va and Vb would be bisketene (XII) and keteneketenimine (II) which are stable at −78 °C.

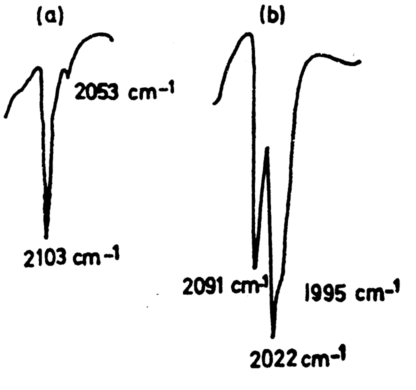


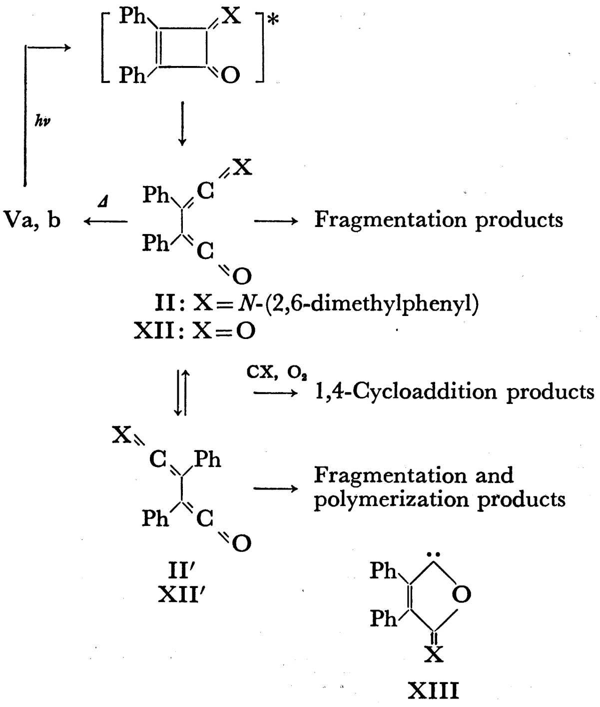
Fig. 1. IR spectra (tetrahydrofuran solution) of (a) XII at −50°C and (b) II at −46°C.

For direct observation of the intermediates II and XII, IR spectra of the solution irradiated at low temperature (−46 °C for II: −50 °C for XII) were determined using a Nihon-Bunko DS-403G IR spectrophotometer equipped with a low-temperature solution cell.[12] The results are shown in Fig. 1. The band at 2103 cm^{-1} for XII is readily assigned to the νC=O of the ketene. It follows that the 2091 and 2022 cm^{-1} bands of II are attributable to ketene νC=O and ketenimine νC=N, respectively.

II and XII in THF are stable in the dark for several days at −78 °C, but on warming slowly the THF solution of XII to above 0 °C, the characteristic peak at

2103 cm^{-1} disappears completely. When methanol was added to the THF solution of XII after the solution had been warmed to room temperature, no more succinate was obtained. However, Vb was recovered in 15% yield together with a small amount of VIII and a large amount of glassy material, while no Vb was recovered on addition of methanol to the solution at −78 °C following the work-up at room temperature.

These results seems to indicate that by photolysis at room temperature under N_2, primary photo products II and XII come to equilibrium with Va and Vb, which is responsible for the retardation of the photochemical fragmentation *via* II and XII to give VIII, CO and/or isocyanide. This is in marked contrast to the photolysis at low temperature which is very effective in the transformation of Va and Vb into II and XII.



Scheme 5.

On the other hand, the ratio (4: 1) of XIa and XIb isolated on the direct photolysis of Vb in methanol at room temperature and in THF–methanol at −78 °C differs a great deal from that (3: 2) on addition of cold methanol to a THF solution at −78 °C after photolysis. This indicates that II and XII in high concentration at low temperature might be equilibrated with geometrical isomers II′ and XII′, warming of which to room temperature might favor the formation of polymeric glassy materials for reverting to the starting ketones.

In conclusion, the superficial insertion of the substrate CX (*e.g.*, isocyanide) or O_2 into V in the present photolysis might take a route of 1,4-cycloaddition reaction of the substrate with primary photo products II and XII which might be equilibrated with starting ketones Va, Vb and their geometrical isomers II′, XII′, although some other mechanism, *e.g.*, *via* carbene (XIII)[2b,13] cannot be excluded completely.

Experimental

All the melting points were uncorrected. IR spectra were determined using a Nihon-Bunko DS-402G infrared spectrophotometer. UV spectra were obtained with a Carry 11 recording spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. The molecular weight was determined by use of a Hitachi 105 vapor pressure osmometer.

Photolysis of Diphenylcyclobutenedione (Vb) under O_2 Stream. A solution of Vb (0.4 g, 1.7 mmol) in dry benzene (40 ml) was irradiated with a high-pressure mercury lamp for 6 h under O_2 stream at 15 °C. Yellow crystals precipitated gradually. Recrystallization from THF gave 9,10-phenanthrenedicarboxylic anhydride (VI, 0.16 g, 52%), mp 320—322 °C (lit,[5]) 321—322 °C). The mother liquor was concentrated and the residue was chromatographed on silica gel. Diphenylacetylene (VII, 0.03 g, 14%) was obtained from the eluent with hexane. Elution with hexane–benzene (1: 1) gave diphenylmaleic anhydride (VII, 0.01 g, 4%), mp 156—158 °C (lit,[6]) 155—156 °C). The structures of VI and VII were established by direct comparison of the melting point and spectral data with those of the authentic samples.[5,6]) The starting ketone Vb (0.21 g, 30%) was recovered from the eluent with benzene.

Photolysis of VII under O_2 Stream. A solution of VI (0.1 g, 0.4 mmol) in dry benzene (10 ml) was irradiated under similar conditions to those given above. Chromatography on silica gel gave VI (0.08 g, 78%).

Photolysis of Vb under N_2 Stream. Vb (0.3 g, 1.3 mmol) was dissolved in dry benzene (30 ml) and irradiated with a 500 W high-pressure mercury lamp for 6 h under N_2 stream at 15 °C. After removal of the solvent, the residue was subjected to silica gel chromatography. Elution with hexane gave VIII (0.066 g, 28%) and elution with benzene resulted in the recovery of Vb (0.21 g, 69%).

Photolysis of Iminocyclobutenone (Va) under O_2 Stream. A solution of Va (0.5 g, 1.5 mmol) in dry benzene (40 ml) was irradiated with a high-pressure mercury lamp for 15 h under O_2 stream at 15 °C. After removal of the solvent under reduced pressure, the residue was subjected to silica gel chromatography. Elution with hexane gave VIII (0.022 g, 8%) and from the eluent with hexane–benzene (7: 3), *N*-(2,6-dimethylphenyl)diphenylisomaleimide (IV, 0.13 g, 25%), mp 172—173 °C was obtained.

Found: C, 81.57; H, 5.42; N, 4.31%; mol wt: 353 (by MS). Calcd for $C_{24}H_{19}O_2N$: C, 81.56; H, 5.42; N, 3.96%; mol wt: 353.4. IR (KBr): 1710 (νC=N) and 1800 cm^{-1} (νC=O). NMR (CCl_4): 2.65 (m, 10H), 3.10 (m, 3H), and 7.85τ (s, 6H). UV (Ethanol) max: 230^{sh} (log ε 4.26), 253 (4.12), and 330 nm (3.98).

Further elution with benzene gave a small amount of 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one (III, 0.005 g, 5%), mp 184 °C and unidentified substances.

Found: C, 84.62; H, 5.98; N, 6.06%; mol wt: 468 (by MS). Calcd for $C_{33}H_{26}ON_2$: C, 84.58; H, 6.02; N, 5.98%; mol wt: 468.7. IR (KBr): 1640 (νC=N) and 1710 cm^{-1} (νC=O). NMR (CCl_4): 2.4—2.9 (m, 10H), 3.1—3.4 (m, 6H), 7.95 (s, 6H), and 8.25 τ (s, 6H), UV (Ethanol) max: 240 (log ε 4.4) and 330 nm (4.18).

Hydrolysis of IV. IV (0.05 g, 0.14 mmol) in methanol containing a catalytic amount of HCl was refluxed for 2 h. Recrystallization from methanol gave *N*-(2,6-dimethylphenyl)-diphenylmaleimide (0.035 g, 72%), mp 191—192 °C. The compound was rigorously characterized by comparison with a sample prepared by the reaction of diphenylmaleic anhydride with 2,6-dimethylaniline, a modification of reported reaction.[6)]

Found: C, 81.66; H, 5.55; N, 4.24%; mol wt: 340 (by osmometer). Calcd for $C_{24}H_{19}O_2N$: C, 81.56; H, 5.42; N, 3.96%; mol wt: 353.4. IR (KBr): 1770 and 1710 cm^{-1} (νC=O). NMR ($CDCl_3$): 2.60 (m, 10H), 2.8 (m, 3H), and 7.75 τ (s, 6H).

Photolysis of Va in the Presence of 2,6-Xylyl Isocyanide. A solution of Va (0.3 g, 0.9 mmol) and 2,6-xylyl isocyanide (0.13 g, 1 mmol) in dry benzene (30 ml) was irradiated with a high-pressure mercury lamp under N_2 at 15 °C. After removal of the solvent, recrystallization of the residue from hexane–benzene gave III (0.34 g, 80%).

Photolysis of Vb in Methanol. A solution of Vb (0.3 g, 1.3 mmol) in dry methanol (30 ml) was irradiated with a high-pressure mercury lamp at 15 °C. While crystals precipitated within 10 min and yellow solution was completely decolorized in 40 min. Filtration and repeated recrystallization from hexane–CH_2Cl_2 gave dimethyl *meso*-diphenylsuccinate (XIa, 0.26 g, 67%), mp 220—221 °C (lit,[11)] 219—220 °C). The mother liquor was concentrated. Repeated recrystallization from hexane gave dimethyl *dl*-diphenylsuccinate (XIb, 0.065 g, 17%), mp 171—172 °C (lit,[11)] 173.5—174 °C). NMR ($CDCl_3$) for XIa: 2.70 (m, 10H) and 6.6 (s, 6H); for XIb: 3.0 (m, 10H) and 6.35 τ (s, 6H).

Photolysis of Va at Low Temperature (−78 °C) Followed by Addition of Methanol. A solution of Vb (0.30 g, 1.3 mmol) in dry THF (30 ml) was irradiated with a high-pressure mercury lamp at −78 °C under N_2 stream. After irradiation for 1.5 h, the lamp was turned off and cold methanol was added to the solution at −78 °C in the dark. The solution was then warmed slowly to room temperature. After removal of the solvent, recrystallization of the residue from hexane–CH_2Cl_2 gave XIa (0.11 g, 29%). The mother liquor was concentrated and the residue was subjected to silica gel chromatography. Elution with hexane gave a trace amount of VIII. Elution with benzene gave additional XIa (0.03 g, 8%). XIb (0.05 g, 13%) and a small amount of unidentified high-melting compound were obtained from the eluent with benzene–CH_2Cl_2 (1:1). When the irradiated solution was allowed to warm slowly to room temperature, starting Vb was recovered in 15% yield and a large amount of glassy material was obtained by chromatography on silica gel.

Photolysis of Vb at Low Temperature (−78 °C) Followed by the Reaction with O_2. A solution of Vb (0.2 g, 0.86 mmol) in dry THF (20 ml) was irradiated for 1.5 h under N_2 stream at −78 °C. The lamp was turned off and O_2 gas was bubbled into the solution in the dark to warm it to room temperature. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel. Elution with hexane gave VIII (0.01 g, 7%) and elution with hexane–benzene gave VII (0.09 g, 42%). Elution with benzene–CH_2Cl_2 gave unidentified glassy materials.

Photolysis of Vb in the Presence of 2,6-Xylyl Isocyanide. A solution of Vb (0.3 g, 1.3 mmol) and 2,6-xylyl isocyanide (0.17 g, 1.3 mmol) in dry benzene (10 ml) was irradiated with a high-pressure mercury lamp under N_2 at room temperature for 1.5 h. After removal of the solvent, the residue was recrystallized from hexane–benzene to give 5-(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1,4-dione (X, 0.41 g, 86%), mp 142—143 °C.

Found: C, 81.88; H, 5.35; N, 3.94%; mol wt: 362 (by osmometer). Calcd for $C_{25}H_{19}O_2N$: C, 82.17; H, 5.24; N, 3.83%; mol wt: 365.4. IR (KBr): 1780, 1770, 1745, and 1700 cm^{-1} (νC=O and νC=N). UV (Ethanol) max: 230^{sh} (log ε 4.39), 280^{sh} (4.00), 332 (4.23), and 535 nm (2.84). NMR (CCl_4): 2.70 (broad s, 10H), 3.20 (broad s, 3H), and 8.00 τ (s, 6H).

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