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Methylene Analogs of Cyclobutenedione. V.[1] The Reactions of 3,4-Bis-(diphenylmethylene)cyclobutanedione with Water, Alcohol, and Amine in the Presence of Bromine. The Approach to a Bisketene

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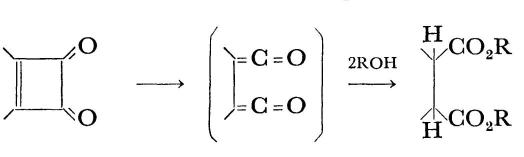
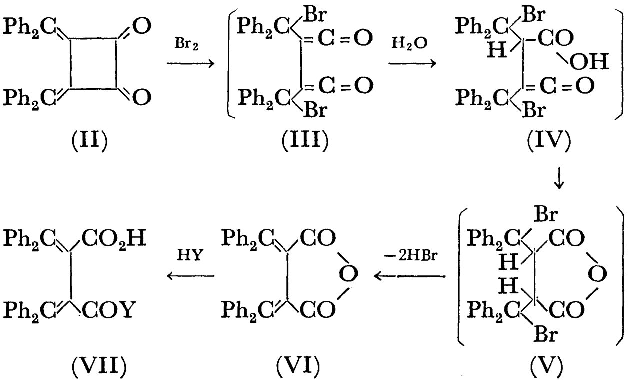
The approach to the bisketene (I) is an interesting subject. Evidence for the formation of I as an intermediate has been reported by several investigators. Both the ethanolysis of diphenylcyclobutenedione[2] and the photolysis of phenylcyclobutenedione[3] in methanol to afford diethyl 2,3-diphenylsuccinate and dimethyl 2-phenylsuccinate respecitvely have been interpreted as proceeding *via* the corresponding bisketene intermediate (I). A similar photochemical transformation of benzocyclobutenedione to a bisketene intermediate has also been reported.[4,5]



(I)

On the contrary, 3,4-bis(diphenylmethylene)-cyclobutanedione (II)[6] was stable in methanol for 24 hr, whereas under the same conditions diphenyl cyclobutenedione was completely destroyed within 12 hr[2]. The stability of II is probably the result of the impossibility of its transformation into a bisketene intermediate. If this assumption is correct, a reagent which localizes the π-electrons of the diene system of II will promote the transformation of II into a bisketene intermediate. This expectation was confirmed using bromine, and II was converted, probably *via* a bisketene intermediate into various products depending on the nucleophiles added.



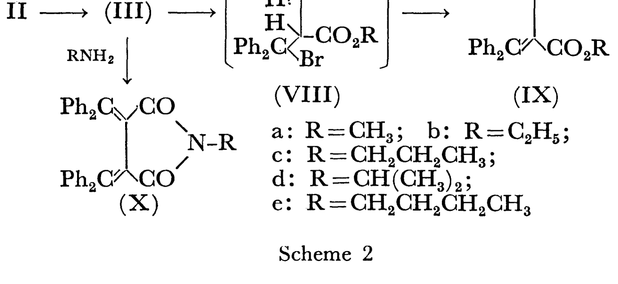
a: $R=OH$, b: $R=OC_2H_5$, c: $R=NH_2$

Scheme 1

The heating of a solution of II in wet carbon tetrachloride containing about 2.5 molar amounts of bromine under reflux for 30 min afforded VI. VI was identified by a comparison of its IR spectrum with that of an authentic sample prepared accroding to a previously-reported method[6]. The structure of VI was further confirmed by its hydrolysis, ethanolysis, and ammonolysis, which afforded VIIa, VIIb, and VIIc respectively.

The formation of VI can be well interpreted by assuming the bisketene (III) as an intermediate, even though it is not clear whether or not the C–Br bond of III is a real σ-bond. A possible reaction mechanism of the formation of VI from III is an intramolecular cyclization of the IV initially produced by the addition of water to III, accompanied by dehydrobromination, as is shown in Scheme 1, even though it is again not clear whether or not the intramolecular cyclization of IV into V precedes the dehydrobromination of IV.

The reactions of II with alcohol and amine in the presence of bromine to afford the diester IX and the succinimide X respectively can also be interpreted by assuming the bisketen III as an intermediate. The heating of a solution of II in dry carbon tetrachloride containing methanol and bromine under reflux for 30 min afforded IXa in a 68% yield. By a similar procedure, IXb was obtained in a 71% yield. IX was identified by means of the spectral data described in the Experimental section. The reaction of II with *n*-propyl-, isopropyl-, and *n*-butylamine in dry carbon tetrachloride containing a small amount of bromine at room temperature for 30 min afforded three succinimides, Xc, Xd, and Xe, in 63, 58, and 59% yields respectively. X was identified by means of the spectral data described in the Experimental section.



a: $R=CH_3$; b: $R=C_2H_5$;
c: $R=CH_2CH_2CH_3$;
d: $R=CH(CH_3)_2$;
e: $R=CH_2CH_2CH_2CH_3$

Scheme 2

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[1] Part IV: F. Toda and N. Ooi, This Bulletin, **45**, 1820 (1972).

[2] A. T. Blomquist and E. A. LaLancette, *J. Amer. Chem. Soc.*, **83**, 1387 (1961).

[3] J. D. Roberts and F. B. Mallory, *ibid.*, **83**, 393 (1961).

[4] R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, **1966**, 169.

[5] H. A. Staab and J. Ipaktaschi, *Chem. Ber.*, **101**, 1457 (1968).

[6] F. Toda and K. Akagi, *Tetrahedron*, **27**, 2801 (1971).

Experimental

The Reaction of II with Water. A solution of II (0.5 g) and bromine (0.3 g) in wet carbon tetrachloride (50 m*l*) was refluxed for 30 min. The crude crystals obtained by the subsequent evaporation of the solvent were recrystallized from acetonitrile to afford VI as red rhombs; 0.385 g (74%); mp 230—231°C (lit,[6] mp 230°C). IR (Nujol), 1795 and 1755 (C=O) and 1545 cm^{-1} (C=C). The IR spectrum was identical with that of an authentic sample prepared according to a previously-reported method.[6]

The Hydrolysis, Ethanolysis, and Ammonolysis of VI. A mixture of VI (0.25 g), KOH (0.04 g), and acetone (25 m*l*)-water (5 m*l*) was refluxed for 2 hr. The reaction mixture was concentrated to *ca.* 10 m*l* and was acidified with hydrochloric acid. The solid thus formed was collected by filtration, washed with water, and recrystallized from ethanol to leave VIIa as pale yellow needles; 0.165 g (63%); mp 233—234°C. IR (Nujol), 1695 and 1670 cm^{-1} (C=O); UV (EtOH), 228 (20300), 266 (11700), and 320 sh nm (ε, 6800).

Found: C, 80.40; H, 4.76%. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%.

A mixture of VI (0.15 g), KOH (0.05 g), and ethanol (3 m*l*) was refluxed. The solid obtained by the same treatment of the reaction mixture as that employed for the hydrolysis of VI was recrystallized from cyclohexane to afford VIIb as colorless needles; 0.12 g (68%); mp 188—189°C. IR (Nujol), 1735 and 1665 (C=O) and 1230 cm^{-1} (ester); UV (EtOH), 232 (22300), 267 (13300) and 320 nm (ε, 7600).

Found: C, 81.10; H, 5.65%. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52%.

Through a solution of VI (0.1 g) in chloroform (30 m*l*), ammonia was bubbled for 30 min. The crude product which remained after the evaporation of the solvent was recrystallized from acetone to afford VIIc as colorless needles; 0.07 g (67%); mp 243—244°C. IR (Nujol), 3320 and 3200 (NH) and 1675 cm^{-1} (C=O); UV (EtOH), 232 (11600), 265 (6500) and 320 sh nm (ε, 4100).

Found: C, 80.65; H, 5.31%. Calcd for $C_{30}H_{23}O_3N$: C, 80.88; H, 5.20%.

The Reaction of II with Alcohol. A solution of II (0.5 g) and bromine (0.3 g) in carbon tetrachloride (dried over P_2O_5) (50 m*l*)-methanol (5 m*l*) was heated under reflux for 30 min. The crude product obtained by the evaporation of the solvent was recrystallized from acetone to yield IXa as yellow needles; 0.39 g (68%); mp 233—234°C. IR (Nujol), 1700 (C=O), and 1240 and 1270 cm^{-1} (ester); UV (CHCl$_3$), 246 (22700), 272 (14500), and 330 nm (ε, 8600).

Found: C, 81.22; H, 5.56%. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52%.

The heating of a solution of II (0.25 g) and bromine (0.2 g) in carbon tetrachloride (dried over P_2O_5) (30 m*l*)-ethanol (5 m*l*) under reflux for 30 min afforded IXb as pale yellow prisms; 0.22 g (71%); mp 210—211°C. IR (Nujol), 1690 (C=O), and 1245 and 1270 cm^{-1} (ester); UV (CHCl$_3$), 245 245 (21400), 270 (14400), and 326 nm (ε, 7400); NMR (CDCl$_3$), 2.8—3.2 (m, Ph, 20H), 6.13 (q, CH$_2$, 4H), and 9.18 τ (t, CH$_3$, 6H).

Found: C, 81.37; H, 5.99%. Calcd for $C_{34}H_{30}O_4$: C, 81.24; H, 6.02%.

The Reaction of II with Amine. A mixture of II (0.3 g), bromine (0.2 g), carbon tetrachloride (dried over P_2O_5) (30 m*l*) and *n*-propylamine (1 g) was stirred at room temperature for 30 min. After the removal of the amine salt by filtration, the mother liquor was concentrated to dryness. The crude product which remained was recrystallized from acetone to afford Xa as yellow needles; 0.215 g (63%); mp 249—250°C. IR (Nujol), 1740 and 1685 cm^{-1} (C=O); UV (CHCl$_3$), 258 (20800), 310 (14600), and 400 nm (ε, 8700).

Found: C, 84.14; H, 5.57%. Calcd for $C_{33}H_{27}O_2N$: C, 84.40; H, 5.80%.

By the same treatment of II with isopropylamine as above, Xb was obtained as yellow needles in a 58% yield; mp 256—257°C. IR (Nujol), 1747 and 1685 cm^{-1} (C=O); UV (CHCl$_3$); 258 (22100), 310 (15600), and 400 nm (ε 9500).

Found: C, 84.12; H, 5.58%. Calcd for $C_{33}H_{27}O_2N$: C, 84.40; H, 5.80%.

By the same treatment of II with *n*-butylamine as above. Xc was obtained as yellow needles in a 59% yield; mp 234—235°C. IR (Nujol), 1750 and 1690 cm^{-1} (C=O); UV (CHCl$_3$); 258 (21600), 310 (15200) and 400 nm (ε, 9000).

Found: C, 84.36; H, 5.81%. Calcd for $C_{34}H_{29}O_2N$: C, 84.44; H, 6.04%.