# Attempted Synthesis of Diphenylmethylenecyclobutanetrione and the Anomalous Behavior of Its Monoacetal, 4,4-Dimethoxy-2-diphenylmethylenecyclobutane-1,3-dione

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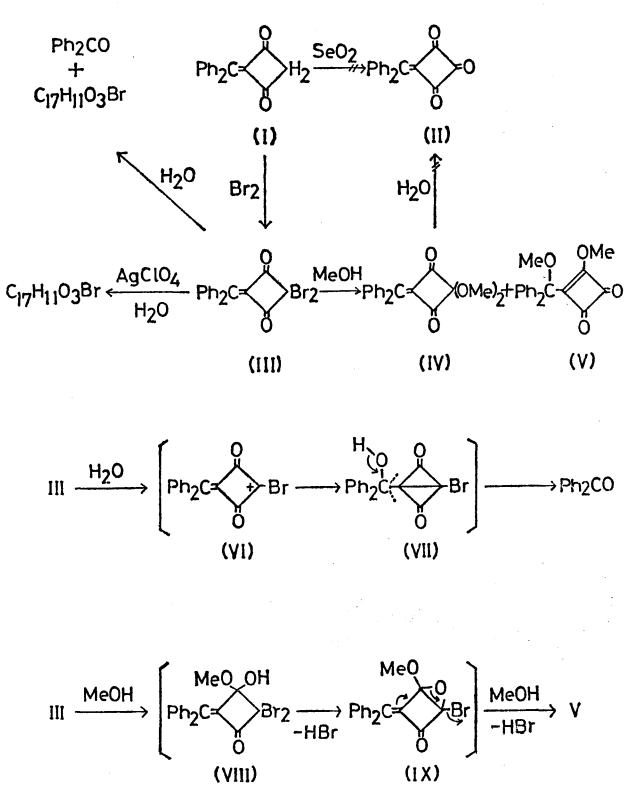
Neither the oxidation of 2-diphenylmethylenecyclobutane-1,3-dione (I) with $SeO_2$ nor the hydrolysis of 4,4-dibromo- (III) and 4,4-dimethoxy-2-diphenylmethylenecyclobutane-1,3-dione (IV) afforded the title cyclobutanetrione (II). The title acetal (IV) was dissolved in concd HCl–MeOH without hydrolysis, probably in the protonated form (X) on its carbonyl oxygen. The basification of a solution of IV in concd HCl–MeOH-$d_4$ recovered the IV undeuterated. On the other hand, IV was dissolved in KOH–MeOH in the form of the enolate anion (XII). The acidification of a solution of IV in KOH–MeOH-$d_4$ afforded the deuterated acetal (IV-$d_6$).

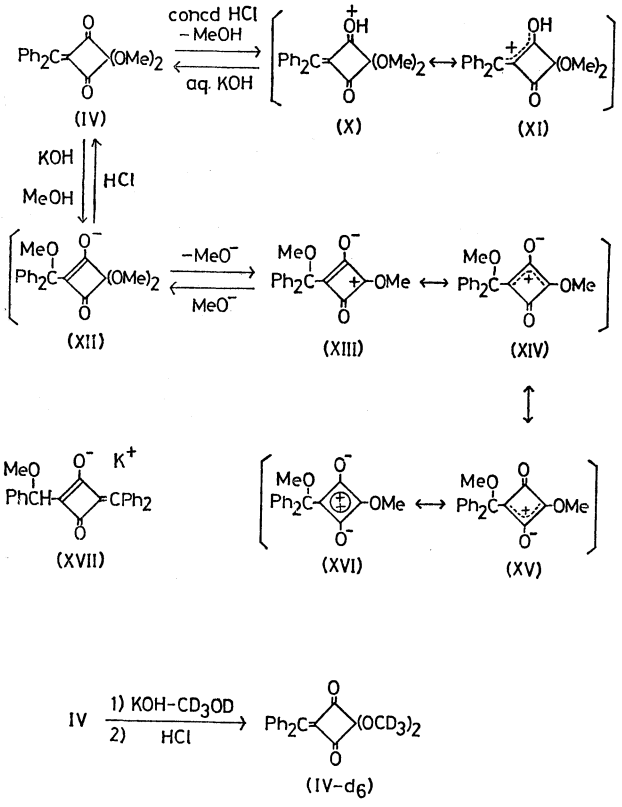
No derivative of methylenecyclobutanetrione has yet been reported, even though derivatives of 3,4-dimethylenecyclobutane-1,2-dione,[1] 2,4-dimethylenecyclobutane 1,3-dione,[2] and trimethylenecyclobutanone[3] have been prepared. All our attempts to prepare diphenylmethylenecyclobutanetrione (II) by the oxidation of 2-diphenylmethylenecyclobutane-1,3-dione (I) and by the hydrolysis of 4,4-dibromo- (III) and 4,4-dimethoxy-2-diphenylmethylenecyclobutane-1,3-dione (IV) failed. During the course of these attempts, however, we have found some anomalous behavior of IV in reaction to acid and base.

The treatment of I[2] with two molar amounts of $Br_2$ in $CHCl_3$ at room temperature afforded III in a 92% yield. The heating of III in MeOH under reflux for 2 hr afforded IV and 4-diphenylmethoxymethyl-3-methoxycyclobut-3-ene-1,2-dione (V) in 39 and 10% yields respectively. Because the reaction of III with MeOH in the presence of pyridine afforded IV in a 52% yield, but no any detectable amount of V, the HBr initially evolved by the methanolysis of III, thus leading to IV, is essential for the production of V. Therefore, a plausible pathway of the formation of V is as follows: a HBr-catalyzed addition of MeOH to the carbonyl of III gives VIII. The ketonization, accompanied by the attack of the methoxide ion on the diphenylmethyl carbon of the epoxide intermediate (IX) which is derived from VIII, affords V (Scheme 1).

The oxidation of I with $SeO_2$ in dioxane gave only a resinous material. The hydrolysis of III in boiling aqueous MeCN afforded benzophenone and an unidentified carboxylic acid ($C_{17}H_{11}O_3Br$) in 30 and 31% yields respectively. The formation of the benzophenone can be interpreted by assuming such an interme-



Scheme 1.



Scheme 2.

diate bearing diphenylhydroxymethyl moiety as VII. The formation of VII can be formulated by a homoallylic rearrangement across the four-membered ring (1,3-interaction), accompanied by the attack of the hydroxy ion on the diphenylmethyl carbon of VI initially produced from III (Scheme 1). The treatment of III with $AgClO_4$ in aqueous THF afforded the carboxylic acid in a 50% yield, but no II.

In contrast with usual acetals, IV was dissolved in concd HCl–MeOH without hydrolysis into the ketone (II), and the basification of the solution recovered the IV quantitatively. Because IV is almost insoluble in MeOH at room temperature, it is clear that HCl has a role in dissolving IV in MeOH. Because the basification of a solution of IV in concd HCl–MeOH-$d_4$ recovered the IV undeuterated, and because the UV spectral data of IV in concd HCl–MeOH are comparable to those of IV in MeOH (Table 1), the form of IV in the acidic media must be one derived by a protonation on its carbonyl oxygen (X). The contribution of XI to the resonance of X is considerable. However, it is not clear why the $\varepsilon$ decreases as the concentration of concd HCl increases.

Table 1. The UV spectra of IV

| Solvent | $\lambda_{max}$ nm ($\varepsilon \times 10^{-2}$) | | |
|---|---|---|---|
| MeOH | 247 (94) | 330 (69) | 392 (128) |
| 5% concd HCl-MeOH | | 331 (67) | 393 (127) |
| 20% concd HCl-MeOH | | 332 (39) | 394 (83) |
| 50% concd HCl-MeOH | | 332 (25) | 400 (54) |
| 5% KOH-MeOH | 241 (107) | | |

In a similar manner, IV was dissolved in KOH–MeOH, and the acidification of the solution recovered the IV quantitatively. However, the UV spectrum of IV in 5% KOH–MeOH differs widely from that of IV in MeOH (Table 1). The IR spectrum of IV in 5% KOH–MeOH showed a very strong $\nu$(C–O$^-$) band at such lower frequencies (1560 cm$^{-1}$) as does the carboxylate ion (1600—1540 cm$^{-1}$). The data are comparable to those of the potassium salt of the analogous enolate anion (XVII), which has been prepared by the reaction of 4-diphenylmethylene-2-benzylidenecyclobutane-1,3-dione with KOH–MeOH,[2] thus showing

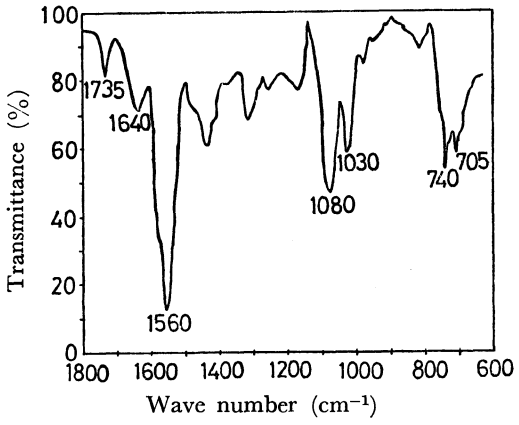



Fig. 1. The IR spectrum of IV in 5% KOH-MeOH (polyethylene-film window cell).

a very strong $\nu$(C–O$^-$) band at 1580—1540 cm$^{-1}$. Therefore, it is reasonable to consider that the enolate anion (XII) is formed when the IV is dissolved in KOH–MeOH.

Nevertheless, the acidification of a solution of IV in KOH–MeOH-$d_4$ afforded the fully deuterated acetal (IV-$d_6$). The exchange of the two MeO with the $CD_3O$ of the solvent can be interpreted by assuming an equilibrium between XII and XIII (Scheme 2). If the presence of XIII in the media is correct, the contribution of XIV and XV to its resonance is considerable. However, the contribution of the cyclobutadiene dication (XVI) to the resonance is doubtful, because even the tetraphenylcyclobutadiene dication is unstable and has been observed only at temperatures below −40 °C.[4]

## Experimental

*Reaction of I with $Br_2$.* Into a solution of I (2.48 g) in $CHCl_3$ (100 ml), $Br_2$ (3.2 g) was stirred over a period of 10 min under cooling with an ice bath. The subsequent evaporation of the solvent left crude crystals. Recrystallization from acetone afforded III as red-prisms; 3.74 g (92%); mp 191 °C. IR (Nujol): 1790 (m), 1710 (vs), and 1505 cm$^{-1}$ (vs); $\lambda_{max}^{CHCl_3}$: 246 sh (6300), 336 (9800), 407 (20700), and 425 sh nm ($\varepsilon$, 19600); NMR ($CDCl_3$): 2.45 $\tau$ (s, Ph).

Found: C, 50.54; H, 2.54%. Calcd for $C_{17}H_{10}O_2Br_2$: C, 50.29; H, 2.46%.

*Reaction of III with MeOH.* A solution of III (2.03 g) in MeOH (20 ml) was heated under reflux for 2 hr. The subsequent evaporation of the solvent left a mixture of purple rhombs and colorless needles, which were separated mechanically. The recrystallization of the purple rhombs from MeOH afforded IV; 0.6 g (39%); mp 129—130 °C. IR (Nujol): 1790 (m), 1700 (vs), 1085 (s), and 1040 cm$^{-1}$ (vs); NMR ($CDCl_3$): 2.50 (s, Ph, 10H) and 6.36 $\tau$ (s, OMe, 6H).

Found: C, 73.88; H, 5.00%. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23%.

The recrystallization of the colorless needles from MeOH afforded V; 0.15 g (10%); mp 209—210 °C. IR(Nujol): 1790 (s), 1750 (m), 1585 (s), and 1360 cm$^{-1}$ (s); $\lambda_{max}^{MeOH}$: 230 nm ($\varepsilon$, 23700); NMR ($CDCl_3$): 2.63 (s, Ph, 10H), 5.45 (s, OMe, 3H), and 6.87 $\tau$ (s, OMe, 3H).

Found: C, 73.87; H, 5.26%. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23%.

When the reaction of III (1.15 g) with MeOH (10 ml) was carried out in the presence of pyridine (0.1 g) by the same procedure as above, 0.4 g (52%) of IV was obtained.

*Hydrolysis of III.* A solution of III (0.406 g) in 5% aqueous MeCN (10 ml) was heated under reflux for 1 hr. After cooling, the reaction mixture was diluted with ether (100 ml). The ether solution was washed with dil KOH and water, and then dried over anhydrous $Na_2SO_4$. The evaporation of the solvent left benzophenone; 0.55 g (30%). The crude crystals obtained by the acidification of the alkaline extract were recrystallized from MeOH to afford an unidentified compound ($C_{17}H_{11}O_3Br$) as colorless needles; 0.106 g (31%); mp 189—190 °C. Mass spectrum *m/e*: 344 and 342 ($M^+$); IR (Nujol): 1690 (vs), 1625 (m), 1530 (m), and 1175 cm$^{-1}$ (m); $\lambda_{max}^{CHCl_3}$: 330 nm ($\varepsilon$,←12100); NMR ($CDCl_3$): 2.5—2.9 $\tau$ (m, Ph).

Found: C, 59.56; H, 3.28%. Calcd for $C_{17}H_{11}O_3Br$: C, 59.50; H, 3.23%.

*Reaction of III with $AgClO_4$.* A mixture of III (0.406 g), $AgClO_4$ (0.45 g), and 10% aqueous THF (10 ml) was

kept at 0 °C for 5 min. Aqueous NaCl was then added to the reaction mixture. After the precipitates had been filtered off, the filtrate was diluted with ether (50 ml). The ether solution was washed with water and dried over anhydrous $Na_2SO_4$. The recrystallization from MeOH of the crude crystals left by the evaporation of the solvent afforded an unidentified compound ($C_{17}H_{11}O_3Br$): 0.17 g (50%).

*The Formation of IV-*$d_6$. The addition of dil HCl to a solution of IV (0.1 g) in 5% KOH-MeOH (10 ml) afforded IV-$d_6$; 0.1 g (100%). IR (Nujol): 2100 (w), 1790 (m), 1700 (vs), and 1525 $cm^{-1}$ (vs); NMR ($CDCl_3$): 2.5 $\tau$ (s, Ph).

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