SHORT COMMUNICATIONS

The Rearrangement of 2-Hydroxy-3,4-bis(diphenylmethylene)-cyclobutanone to the Enolizable Cyclobutenedione, 3,4-Bis(diphenylmethyl)-3-cyclobutene-1,2-dione *via* Methylenecyclobutenone Intermediate

Fumio Toda, Nobuhiro Ooi, Yoshikazu Takehira, and Katsuhiko Akagi
Department of Chemistry, Faculty of Engineering, Ehime University, Matsuyama

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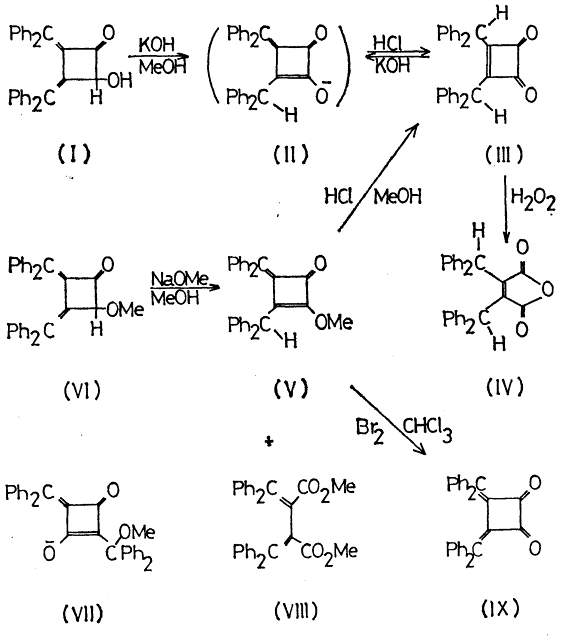
In the course of our studies of the reactions of 2,3-dimethylenecyclobutanones with a base, we have found that the title cyclobutanone (I)[1] dissolves in aqueous KOH easily and that the acidification of the solution affords the title cyclobutenedione (III) as colorless prisms in a 62% yield, mp 130—131°C. The structure of III was determined by means of the spectral data: λ_{max} (CH_3CN) 258 sh (8200), 265 sh (6600) and 271 sh nm (ε, 5300); ν_{max} (Nujol) 1790 and 1770 (unsplit doublet, CO) and 1580 cm^{-1} (C=C); NMR ($CDCl_3$) 2.5—3.0 (m, Ph, 20H), and 4.73 τ (s, CH, 2H). The oxidation of III with neutral H_2O_2 afforded the corresponding anhydride, bis(diphenylmethyl)maleic anhydride (IV), in a 71% yield, mp 171—172°C. It is well established that cyclobutenediones undergo a Bayer-Villiger-type oxidation with neutral H_2O_2 to give the corresponding maleic anhydrides.[2]

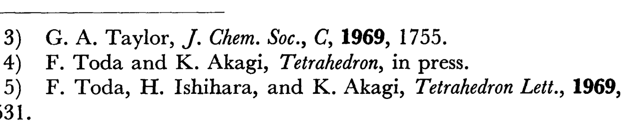


The dione III also dissolved in aqueous KOH and even in aqueous $NaHCO_3$, from which III was recovered quantitatively by acidification. Since the electronic spectrum of an alkaline solution of III (or of I) showed an absorption band at 330 nm (ε, 21700) which is comparable to that of the analogous anion VII obtained by dissolving 2,4-bis(diphenylmethylene)cyclobutanedione in MeOH-KOH, 324 nm (ε, 24600),[3] the structure in the alkaline media may be said to be II. The acidification of a solution of III (or of I) in KOD-D_2O-MeOD (prepared by the addition of D_2O to MeONa in MeOD) with DCl-D_2O afforded III-d_2, which showed no methine proton signal in the NMR spectrum. Under neutral conditions, however, neither I nor III exchanged its methine hydrogen with deuterium by recrystallization from MeOD.

The rearrangement of I into II is likely, since the treatment of VI[4] with NaOMe in MeOH at room temperature afforded the rearranged product, V, as colorless prisms in a 30% yield, mp 126—127°C, in addition to the diester, VIII, as yellow needles in a 43% yield, mp 233—234°C. The structure of V was identified by means of the spectral data: λ_{max} (EtOH) 293 nm (ε, 17600); ν_{max} (Nujol) 1760 (CO), 1650 (*exo* C=C), and 1590 cm^{-1} (*endo* C=C); NMR ($CDCl_3$) 2.6—3.2 (m, Ph, 20H), 5.53 (s, CH, 1H), and 5.95 τ (s, OMe, 3H). The structure of V was further identified by the following reactions. The treatment of V in $CHCl_3$ with bromine afforded IX[5] in a 30% yield. The treatment of V in MeOH with hydrogen chloride afforded III in a 64% yield.

The cyclobutenediones which have been reported to date are all sensitive to the base and all undergo ring-cleavage.[2] The enolization of III in alkaline media without decomposition differs widely from these facts.

When the reaction of VI with NaOMe in MeOH was carried out under a nitrogen atmosphere, the major product was V (65%), and the minor one was VIII (1%). On the other hand, the treatment of V with NaOMe under an oxygen atmosphere afforded VIII in a 40% yield. On the basis of these results and the observation that 1,2-bis(diphenylmethylene)cyclobutene reacts with oxygen to afford 2,3-bis(diphenylmethylene)-butanedial quantitatively,[6] a possible reaction path leading to VIII is as follows:



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[1] F. Toda, N. Ooi, and K. Akagi, unpublished data.

[2] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York and London (1967), pp. 128—156.

[3] G. A. Taylor, *J. Chem. Soc., C*, **1969**, 1755.

[4] F. Toda and K. Akagi, *Tetrahedron*, in press.

[5] F. Toda, H. Ishihara, and K. Akagi, *Tetrahedron Lett.*, **1969**, 2531.

[6] F. Toda, M. Higashi, and K. Akagi, *Chem. Commun.*, **1969**, 1219.