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Photochemistry of Non-enolizable β-Diketones Containing Cyclopropane Ring in Conjugation

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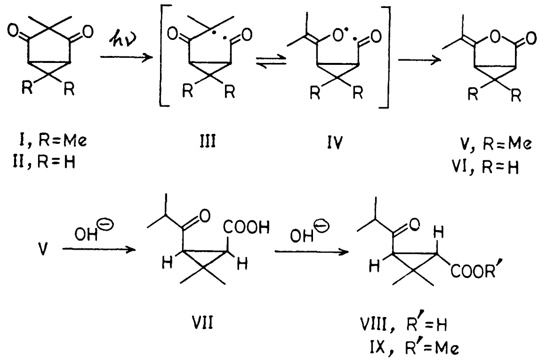
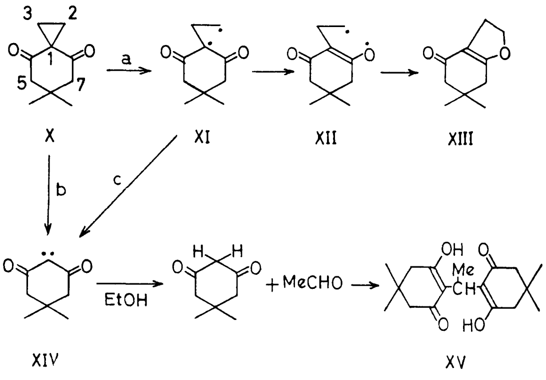
Irradiation of bicyclo[3.1.0]hexane-2,4-diones affords isomeric enol lactones retaining the cyclopropane ring. In contrast, photoreaction of 6,6-dimethylspiro[2.5]octane-4,8-dione in ethanol results in the formation of an isomeric benzofuran derivative and dimedone-acetaldehyde condensation product. Cleavage of the cyclopropane ring is characteristic of the behavior of the latter β-diketone.

A compound with a cyclopropane ring in close proximity to a carbonyl group is expected to be photoreactive on account of the unsaturated nature of the three-membered ring. In fact, the photochemical reactions of conjugated cyclopropyl ketones are well-known.[1] In continuation of photochemical studies on non-enolizable β-diketones,[2] we have examined the behavior of two types of this class of compound containing a cyclopropane ring in conjugation of both ketone chromophores, in which the cyclopropane ring is in a different environment with respect to carbonyl groups. One is bicyclo[3.1.0]hexane-2,4-diones (I and II) and the other spiro[2.5]octane-4,8-dione (X). A remarkable difference in the stability of cyclopropane ring has been observed.

Irradiation of I[*1] in a benzene solution by means of a Pyrex-filtered mercury arc lamp afforded a single volatile product V in a 98% isolation yield. The structure assigned to V was consistent with spectral data and analyses. Alkaline hydrolysis of V gave a known keto-acid VIII,[3],[*2] which was transformed into the known keto-ester IX[3] by means of diazomethane. Epimerization of the *cis*-isomer VII into a thermodynamically stable *trans*-isomer VIII must have occurred during the alkali treatment.[*3] UV irradiation of the diketone II[4] also induced the same





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1) a) A. Padwa, "Organic Photochemistry," Vol. 1, ed. by O. L. Chapman, Marcel Dekker Inc., New York, N. Y. (1967), p. 35. b) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967). c) W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, **1967**, 4415. d) A. Sonoda, I. Moritani, J. Miki and T. Tsuji, *ibid.*, **1969**, 3187.

2) H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori and M. Kawanisi, *Tetrahedron*, **23**, 3993 (1967). Similar types of rearrangement have been disclosed: R. C. Cookson, A. G. Edwards, J. Hudec and M. Kingsland, *Chem. Commun.*, **1965**, 98; H. U. Hostettler, *Tetrahedron Lett.*, **1965**, 1941; J. Rigaudy and P. Derible, *Bull. Soc. Chim. Fr.*, **1965**, 3047, 3055, 3061; N. J. Turro, W. B. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **87**, 2775 (1965).

[*1] Synthesis and reaction of I are described in Experimental.

3) M. Matsui, H. Yoshioka and H. Hirai, *Agr. Biol. Chem.* (Tokyo), **28**, 456 (1964).

[*2] Matsui *et al.* have recently reported the synthesis of *trans*-chrysanthemic acid from VIII in three steps.[3]

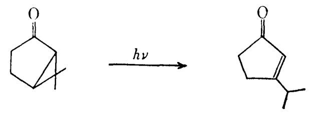
[*3] *Cf.* Ref. 3, footnote in p. 456.

4) H. Stetter and H.-J. Sandhagen, *Chem. Ber.*, **100**, 2837 (1967).

type of rearrangement to afford lactone VI in an 85% isolation yield. This kind of transformation reminds us of the photochemical rearrangement of 2,2-dimethyl-1,3-cyclohexanediones.[2] The intermediacy of the diradicals III and IV is to be considered.

Irradiation of X[5] was conducted in an ethanolic solution by means of a high pressure mercury arc (quartz vessel). Chromatographic separation on a silica gel column afforded two products, which were found to be 4-oxo-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzofuran (XIII, 31%) and a dimedone-acetaldehyde condensation product (XV, 5%). Both products were identified by comparison with authentic samples.

Conjugated cyclopropyl ketones such as XVI gives the primary photoproduct XVII under cleavage of the cyclopropane ring.[1a] If the cyclopropane ring is held in a rigid conformation with respect to the carbonyl π system so as to construct optimum geometry for an overlap with the π electrons of the carbonyl group, excitation of an electron into π* orbital appears to lead to rupture of the cyclopropane bond. Absence of cyclopropane ring cleavage is rather unexpected in the reaction of I and II. Inspection of the molecular model shows the existence of considerable conjugation between cyclopropane ring and carbonyl group. *Gem*-dimethyl groups in the cyclopropane ring should be expected to contribute to the conjugation. However, α-fission is preferred to cyclopropane ring cleavage in the case of I and II. This is because the diradical(s) III and/or IV are stabilized on account of allylic conjugation.



XVI XVII

Cleavage at C$_1$–C$_2$ position of X affords the diradical XI (path a), which isomerizes to the O-radical XII followed by cyclization to form the furan XIII. As the conversion of X to XIII was also observed thermally (>120°), the precursor of XIII would be either the electronically excited state of X or the vibronically excited one. The formation of XV is rationalized by assuming the intermediacy of cyclic diketocarbene XIV.[*4] Carbene XIV abstracts hydrogen from the solvent ethanol to afford dimedone and acetaldehyde, which subsequently condense to form XV. It is not certain whether XIV is derived from X in one step in a concerted manner (path b) or from X by a stepwise mechanism *via* XI (path c). Thus, α-fission is not observed in the case of X. This can be accounted for by the fact that the bond order of C$_1$–C$_4$ or C$_1$–C$_8$ increases on account of conjugation between the cyclopropane ring and both the carbonyl groups. Cyclopropane ring cleavage is the only observed process, although the result differs greatly from that obtained in the case of XVI.

Experimental

All melting points and boiling points were uncorrected. The IR spectra were obtained in a neat liquid film or in Nujol mull on a Shimadzu IR-27-G spectrophotometer. The NMR spectra were taken with a JEOL C-60-H spectrometer with CCl$_4$ as a solvent, and chemical shifts are reported in δ values relative to TMS as an internal standard. The NMR data are given in the order of multiplicity (s=singlet, d=doublet, t=triplet, q=quartet and m=unresolved multiplet), integration and assignment. The UV spectra were taken in EtOH on Hitachi EPS-2 recording spectrophotometer. The mass spectra were obtained with a Hitachi RMU-6D spectrometer with a direct inlet (200°) and at 80 eV. Plates of Silica gel G were used for TLC and the spots were visualized with iodine vapor.

Preparation of 4-Bromo-2,2,5,5-tetramethyl-1,3-cyclohexanedione. The method was essentially based on the bromination procedure.[4] A solution of 2,2,5,5-tetramethyl-1,3-cyclohexanedione[7] (40.0 g, 240 mmol) in carbon tetrachloride (150 m*l*) was treated with *N*-bromosuccinimide (50.0 g, 280 mmol), which afforded a bromide (43.0 g, 73%), mp 91°C (from ether). IR (Nujol): 1710 (C=O) and 1685 cm^{-1} (C=O). NMR: δ 1.05 (s, 3, CH$_3$), 1.20 (s, 3, CH$_3$), 1.37 (s, 3, CH$_3$), 1.46 (s, 3, CH$_3$), 2.77 (s, 1, CH$_2$), 2.85 (s, 1, CH$_2$) and 4.75 ppm (s, 1, CH).

Preparation of 3,3,6,6-Tetramethylbicyclo[3.1.0]-hexane-2,4-dione (I). The method was essentially based on the one reported by Stetter in the preparation of 3,3-dimethylbicyclo[3.1.0]hexane-2,4-dione (II).[4] A solution of bromide (15.0 g, 61 mmol) in dry dioxane (150 m*l*) was dropwise added with a solution of potassium *t*-butoxide (*f*=1.3) (20.0 g, 178 mmol) in *t*-butyl alcohol (50 m*l*) with stirring at reflux. Evaporation

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5) K. Ichikawa, O. Itoh and T. Kawamura, This Bulletin, **41**, 1240 (1968).

[*4] We have independently found that diketocarbene XIV in triplet state, generated by the benzophenone-sensitized photolysis of 2-diazo-5,5-dimethyl-1,3-cyclohexanedione, abstracts hydrogen from the medium to form dimedone.[6] When ethanol was used as a solvent, dimedone-acetaldehyde condensation product XV was obtained, but in 2-propanol dimedone and acetone were isolated, which do not condense under that condition. In view of these behaviors of diketocarbene XIV, the formation of XV in the photolysis of X reminds us of the intermediacy of XIV.

6) Y. Hayasi, T. Okada and M. Kawanisi, This Bulletin, **43**, 2506 (1970).

7) T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, **1956**, 2431, 2438.

8) H. E. Simmons, E. P. Blanchard and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

[*5] The sample of II was kindly supplied by Professor H. Stetter, Technische Hochschule Aachen. The measurement of NMR spectrum was performed in our laboratory (Fig. 2).

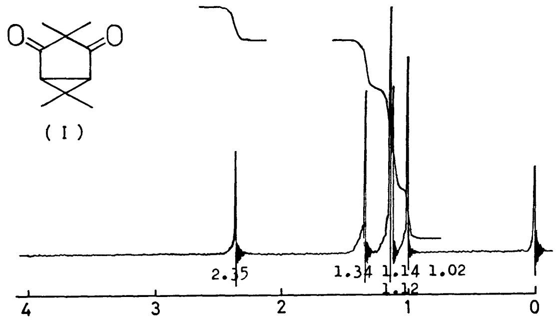

Fig. 1. NMR spectrum of I.

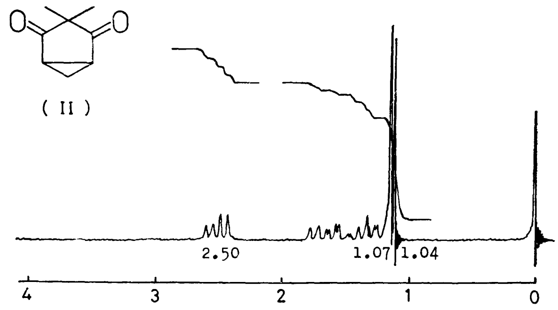

Fig. 2. NMR spectrum of II.

of the solvent, ether extraction, drying ($MgSO_4$), concentration *in vacuo* followed by distillation afforded I (4.50 g, 44%), bp 75°C/5 mmHg, n_D^{20} 1.4681. IR (neat): 3060 (C–H stretching in cyclopropane ring),8) 1710 (C=O) and 1040 cm^{-1} (cyclopropane ring).8) NMR: δ 1.02 (s, 3, CH_3), 1.12 (s, 3, CH_3), 1.14 (s, 3, CH_3), 1.34 (s, 3, CH_3) and 2.35 ppm (s, 2, CH). The NMR spectrum of I is shown in Fig. 1. Each methyl signal can be assigned by comparing the spectrum of I with II.[*5] UV: λ_{max} (EtOH) 281 nm (log ε 2.01). Mass spectrum consisted of parent peak at *m/e* 166.

Found: C, 72.1; H, 8.2%. Calcd for $C_{10}H_{14}O_2$: C, 72,3; H, 8.5%.

Acid-catalyzed Isomerization of I. A solution of I (4.5 g, 27 mmol) in 18 N hydrochloric acid (120 m*l*) was heated under reflux for 3 hr. After cooling the reaction mixture was extracted twice with ether, and the combined extracts were washed with aqueous sodium carbonate solution and subsequently with water and dried ($MgSO_4$). Removal of the solvent *in vacuo* followed by distillation at 90—92°C/20 mmHg afforded a greenish yellow oil (2.7 g, 60%), which was established to be 1,1-dimethyl-3-isopropyl-3-cyclopentene-2,5-dione, n_D^{20} 1.4667. NMR: δ 0.90 (s, 6, CH_3), 1.04 (d, 6, CH_3), 2.67 (septet, 1, CH) and 6.55 ppm (s, 1, -CH). UV: λ_{max}(EtOH) 232 nm (log ε 4.12).

Found: C, 72.5; H, 8.6%. Calcd for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5%.

Irradiation of 3,3,6,6-Tetramethylbicyclo[3.1.0]-hexane-2,4-dione (I). A solution of I (1.40 g, 8.4 mmol) in benzene (43 m*l*) was irradiated by means of 200 W high pressure mercury arc (Pyrex filter) for 9 hr under nitrogen at room temperature. The progress of the reaction was followed by vpc analysis of the aliquots. Evaporation of the solvent and single distillation afforded 2,2-dimethyl-3-*cis*-(1′-hydroxy-2′-methyl-1′-propenyl)cyclopropanecarboxylic acid γ-lactone (V) (1.37 g, 98%), bp 115—117°C/20 mmHg, n_D^{20} 1.4793. IR (neat): 3050 (C–H stretching in cyclopropane),8) 1785, 1720 (enol lactone) and 995 cm^{-1}. NMR: δ 1.10 (s, 3, CH_3), 1.23 (s, 3, CH_3), 1.70 (broad s, 6, olefinic CH_3), 2.05 (d, 1, J=6 Hz, CH) and 2.47 ppm (d, 1, J=6 Hz, CH). The NMR spectrum of V is shown in Fig. 3. UV: λ(EtOH) 220 nm (log ε 3.66) and λ(EtOH) 280 nm (log ε 2.42). The mass spectrum consisted of parent peak at *m/e* 166.

Found: C, 72.2; H, 8.3%. Calcd for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5%.

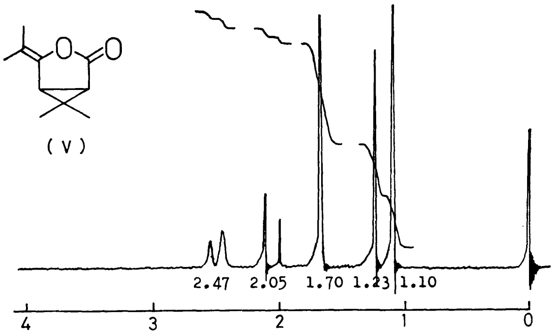

Fig. 3. NMR spectrum of V.

Hydrolysis of the Enol Lactone V. A solution of V (332 mg, 2 mmol) in alcoholic aqueous potassium hydroxide solution (20 m*l*) was heated under reflux for 2 hr. Work-up afforded 2,2-dimethyl-3-*trans*-isobutyrylcyclopropanecarboxylic acid (VIII) (250 mg, 68%), mp 88—89°C (from *n*-hexane) (lit,3) mp 86—87.5°C). The IR spectrum was superimposable with that of the authentic spectrum.[*6] (Found: C, 65.0; H, 8.6%). 2,4-Dinitrophenylhydrazone of VIII melted at 186—187°C (lit,3) mp 184—186°C).

Esterification of VIII by means of excess ethereal diazomethane afforded methyl 2,2-dimethyl-3-*trans*-isobutyrylcyclopropanecarboxylate (IX), bp 118—120°C/22 mmHg (lit,3) bp 126—131°C/38 mmHg). The IR spectrum was superimposable with that of the authentic sample.[*6] (Found: C, 65.9; H, 9.0%).

Irradiation of 3,3-Dimethylbicyclo[3.1.0]hexane-2,4-dione (II). A solution of II (100 mg, 0.72 mmol) in benzene (15 m*l*) was irradiated by means of 200 W high pressure mercury arc (Pyrex filter) for 1 hr

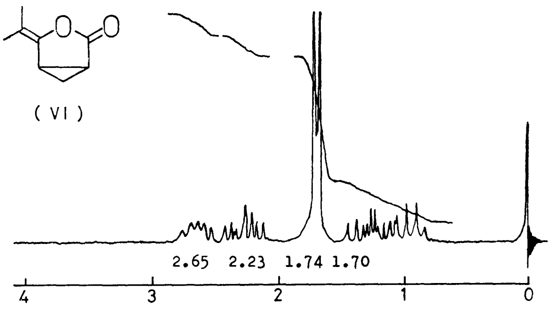

Fig. 4. NMR spectrum of VI.

[*6] The IR spectra of VIII and IX were kindly supplied by Professor M. Matsui, The University of Tokyo.

at room temperature. The progress of the reaction was followed by vpc analysis of the aliquots. After the complete disappearance of II, the reaction mixture was concentrated *in vacuo* and the single distillation at 123—125°C/25 mmHg afforded 2-*cis*-(1′-hydroxy-2′-methyl-1′-propenyl)-cyclopropanecarboxylic acid γ-lactone (VI) (85 mg, 85%), n_D^{24} 1.4958. IR (neat): 3100 (C–H stretching in cyclopropane ring),[8] 1795, 1720 cm^{-1} (enol lactone). NMR: δ 0.80—1.50 (m, 2, CH_2), 1.70 (s, 3, CH_3), 1.74 (s, 3, CH_3), 2.23 (m, 1, CH) and 2.65 ppm (m, 1, CH). The NMR spectrum is shown in Fig. 4. UV: λ(EtOH) 220 nm (log ε 3.62) and λ(EtOH) 280 nm (log ε 2.12). The mass spectrum consisted of parent peak at *m/e* 138.

Found: C, 69.5; H, 7.4%. Calcd for $C_8H_{10}O_2$: C, 69.5; H, 7.3%.

Irradiation of 6,6-Dimethylspiro[2.5]octane-4,8-dione (X). A solution of X[5] (1.3 g, 8.2 mmol) in EtOH (20 m*l*) was irradiated by means of 200 W high pressure mercury arc (quartz vessel) for 16 hr under nitrogen at room temperature. The reaction mixture was concentrated *in vacuo* and taken up in benzene (5 m*l*). Polymeric amorphous material undissolved in benzene was removed by filtration and the filtrate was chromatographed on silica gel. The following compounds were isolated: 4-oxo-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzofuran (XIII) (210 mg, 31%), bp 125—128°C/15 mmHg (lit,[5] bp 109—113°C/4 mmHg). IR (neat): 1630 (broad), 1407, 1223 and 1035 cm^{-1}. The IR spectrum was superimposable with that of the authentic specimen.[*7] The NMR spectrum of XIII was quite similar to the one given in literature.[5] Mass spectrum consisted of parent peak at *m/e* 166. 2,2′-Ethylidenebis(5,5-dimethyl-1,3-cyclohexanedione) (XV) (33 mg, 5%), mp 139—140°C (from H_2O) (lit,[9] mp 140°C). The IR spectrum was superimposable with that of the authentic specimen, which was prepared from dimedone and acetaldehyde.[9] NMR: δ 1.06 (s, 12, CH_3), 1.50 (d, 3, J=7.5 Hz, CH_3), 2.30 (s, 8, CH_2), 4.15 (q, 1, J=7.5 Hz, CH) and 11.45 ppm (broad s, 2, enolic protons). X (638 mg, 50%) was recovered in addition.

Thermal Reaction of X. Neat X (50 mg) was heated at 120°C in a sealed tube for 1 hr. Vpc analysis indicated the formation of XIII (60%) accompanied with the recovered X and unidentified products.

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[*7] The IR spectrum of XIII was kindly supplied by Professor K. Ichikawa, Kyoto University.

9) W. Weinberg, *Ind. Eng. Chem. Anal. Ed.*, **3**, 365 (1931).