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Synthetic Photochemistry. II.[1] The Cycloaddition Reaction of Dehydroacetic Acid with Olefins

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As a part of the study of the photochemical cycloaddition reactions of α,β-unsaturated ketones bearing functional substituents, we have recently reported the reaction of methyl acetopyruvate with olefins.[1] According to the results thus obtained, the photoadducts have been directly formed by a reaction with the tautomer which exists in the ground state by means of remarkable regiospecific control. Dehydroacetic acid (I) possesses several tautomeric forms because of different orientations of enolization; this, from the preparative point of view, aroused our interest in examining the cycloaddition reaction with olefins.

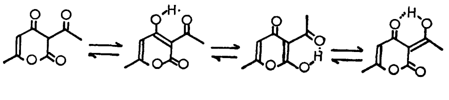

Chart 1.

During the course of our investigations, Kumamoto *et al.*[2] reported their results on the photochemical reactions of I with cyclohexene, acrylonitrile, and trimethylethylene. Our observations contain some novel features which we want to record in this brief paper.

The irradiation of I and cyclohexene in an ethyl acetate solution through a Pyrex glass filter by means of a 450 W high-pressure mercury lamp afforded several products, but the reaction could not be completed because of the production of a resious material. The products isolated by chromatography were II (pale yellow liquid (2%)), III(colorless needles, mp 85.5—87°(20%)), IV(colorless liquid (20%)), and V(colorless crystals, mp 215—216° (2.5%)).

Among these, III and V were identified, by comparisons of their physical data, as the 1 : 1 adduct previously obtained by Kumamoto,[2] and as the dimer formed by the solid-phase irradiation of I by Sugiyama,[3] respectively. The structure of II was deduced to be 3-(2-acetylcyclohexyl)-4-hydroxy-6-methyl-α-pyrone on the basis of NMR and IR spectral analyses, since the disappearance of the tricarbonyl-methane chromophore and the presence of a vinylic-methyl group and an olefinic proton were evident.

The structure of III has already been proposed by Kumamoto to be the *cis-cis-cis* isomer, mainly on the basis of his analysis of the NMR spectrum but his assignment of the stereochemistry seems unconvincing. The IV we obtained revealed physical properties very similar to those of III and was deduced to be a stereoisomer of III; therefore, the inspection of the NMR spectra of the two compounds might provide information on the point. When the NMR spectrum was measured in a benzene solution, the signal attributable to the C-5 methin proton clearly appeared as a doublet ($J=9.3$ Hz) at δ 2.35 indicating that the vicinal protons in the cyclobutane ring were in a *cis*-relationship. On the other hand, the NMR signal of the corresponding proton of IV had the same magnitude of the coupling constant, with a still-smaller spin-spin splitting (δ 3.09 dd, $J=9$, 2.5 Hz) in a carbon tetrachloride solution also showing a *cis*-relationship. In addition, the occurrence of only the long range coupling in IV would represent the *W*-letter-type relation for both the protons, and the *cis-cis*-configuration for three hydrogens at the A/B/C ring junctures. Therefore, III must be the *trans-cis* isomer. Moreover, the configuration of the methyl group and the hydrogen at the B/C ring should be a thermodynamically stable *cis*-configuration. Thus, the stereochemistry of III and IV has been deduced.

A few other products were isolated, but because of the limited quantity available for characterization and because of the instability to the isolation conditions, no further work was attempted.

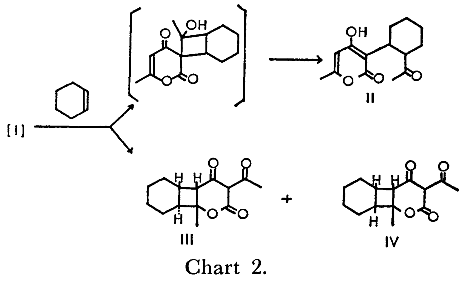

Chart 2.

A similar reaction of I with vinyl acetate also resulted in several products; among those fractionated from a complex mixture were VI (pale yellow liquid (21% as an isomeric mixture)), VII (pale yellow liquid (4.1%)), and VIII (colorless needles, mp 90.5—91°C (5.2%)).

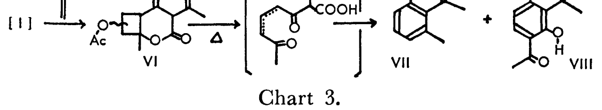

Chart 3.

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[1] Previous paper; H. Takeshita and S. Tanno, This Bulletin, in press (1973).

[2] S. Kumamoto, K. Somekawa, and A. Tsuchida, Abstract Papers of 23rd Annual Meeting of Chemical Society of Japan(Apr., 1070, Tokyo), [III], 1300.

[3] N. Sugiyama, T. Sato, H. Kataoka, and C. Kashima, This Bulletin, **44**, 555 (1971). In this paper, the authors described however I did not cause any photochemical change in solutions.

Although VI appeared as a single spot on thin-layer chromatograms, the NMR spectrum indicated it to be a mixture of all four of the possible stereo- and regio-isomers of the 1 : 1 adducts. Intensive efforts to separate them failed, except that the least polar component (VIa) could be obtained in an 80% purity, according to the NMR spectral analysis. VIa has shown a characteristic NMR signal for the tricarbonyl system, like I, indicating that a reaction has taken place at the C-5,6 position. The rest of the isomers also have very similar NMR spectral data for this reason.

The structure of VII was deduced to be 2-acetyl-3-cresol on the basis of the NMR and the other spectral properties. VIII was also identified as 2,4-diacetylresorcine.[4] Obviously, VII and VIII were formed by the aromatization of VI during the work-up. In fact, when a methanolic solution of VI was refluxed for a while, considerable amounts of VII and VIII were obtained.[5]

Thus, our results agree, in general, with those of Kumamoto. However, the formation of II shows a bi-functional nature in the photochemical cycloaddition.[6]

Experimental

Photochemical Reaction of Dehydroacetic Acid (I) and Cyclohexene. I (3.5 g) was dissolved in cyclohexene (70 ml) and ethyl acetate (80 ml), and then the solution was internally irradiated by means of a 450 W high-pressure mercury lamp through a Pyrex glass filter in a nitrogen atmosphere. The solution soon become dark brown and a polymeric material has deposited on the wall; therefore, irradiation was terminated after 5 hr. The reaction mixture was heated under reduced pressure to remove the solvent, and the residue was washed with a small amount of ligroin to recover the unreacted I, which weighed 0.63 g (22%) after collection. Then, the product mixture in ligroin was distilled *in vacuo* to give a yellow, viscous oil (2 g). This was fractionated by silica gel (200 g) column chromatography with benzene. After the elution of unidentified crystals (6 mg), II was isolated as a faintly colored liquid (bp 130°/0.5 mmHg (bath temp.), 80 mg). This sample showed a single spot on thin-layer chromatograms. (Found: C, 67.25; H, 7.40%). $\lambda_{\max}^{\mathrm{MeOH}}$ 230 nm(sh.), 281 nm (6300). $\nu_{\mathrm{C=O}}$ 1715 cm^{-1}(v. strong). $\delta_{\mathrm{CCl_4}}$ 1.5(9H, m), 2.05(3H, s), 2.12 (3H, s), 2.86(1H, br.), and 5.50(1H, s).

Next several fractions containing a crystalline material were collected to give III (colorless needles; mp 85.5—87° (from ether-cyclohexane)(lit.[2] 88—89°C); weight, 120 mg). (Found: C, 67.83; H, 7.40%). $\delta_{\mathrm{CCl_4}}$ 1.43(3H, s), 2.65 (3H, s), and 2.72(1H, d, J=9 Hz); $\delta_{\mathrm{C_6H_6}}$ 1.03 (3H, s), 2.55(3H, s), and 2.35(1H, d, J=9.3 Hz).

Further elution with benzene–ethyl acetate gave on oily mixture of III and IV(1.87 g), which additionally yielded some crystalline III; repeated silica-gel chromatography with petroleum ether–benzene and preparative thin-layer chromatography finally yielded an enriched fraction of IV, together with some crystalline III. The NMR assay of the fraction still indicated the presence of III(*ca.* 5—10%), but a further attempt at its purification was not made. This specimen (colorless liquid, bp 120°C/0.5 mmHg(bath temp.)) showed an IR spectrum almost undistinguishable from that of III. (Found: C, 67.41; H, 7.44%). $\delta_{\mathrm{CCl_4}}$ 1.53(3H, s), 2.67(3H, s), and 3.09(1H, dd, J=9, 2.5 Hz). The estimated yields of III and IV was both about 20% respectively.

Subsequent elution with benzene–ether gave mainly V and some unidentified compounds, from which V was isolated by fractional crystallization with cyclohexane as colorless needles(mp 215—216°C(from cyclohexane)(lit,[3] 214.5—215.5°C); weight, 75 mg).

Photochemical Reaction of I and Vinyl Acetate. I (3.5 g) was dissolved in vinyl acetate (35 ml) and ethyl acetate (250 ml), and the mixture was irradiated much as in the preceding reaction; again, the formation of a polymeric material prevented the completion of the reaction. The reaction mixture was evaporated under reduced pressure to remove most of the solvent and the unreacted vinyl acetate; the residue was washed with cold ligroin to separate the unreacted I (510 mg) and the products, which were distilled *in vacuo* to give a pale yellow liquid(bp 155—165°C/3 mmHg(bath temp.), 2.9 g) and separated by silica gel chromatography. The first fraction, eluted with benzene, contained VII, which was obtained in a pure form through preparative thin-layer chromatography as a pale yellow liquid(110 mg). (Found: C, 71.70; H, 6.87%). $\delta_{\mathrm{CCl_4}}$ 2.59(3H, s), 2.64(3H, s), 6.72(1H, dd, J=7.5, 1.2 Hz), 6.83(1H, dd, J=7.8, 1.2 Hz), 7.28(1H, dd, J=7.8, 7.5 Hz), and 12.15(1H, OH).

The next fraction yielded VIII (colorless needles; mp 90.5—91°C(from ethyl acetate)(lit.[4] 88—90°C); weight, 189 mg). The following fraction, eluted with benzene-ether, contained VI and unidentified compounds; after repeated chromatography, VI(950 mg) was obtained as a colorless liquid(bp 120—130°C/1.5 mmHg(bath temp.)), whose least polar fraction, VIa, was obtained in a purity of *ca.* 80%. (Found: C, 56.69; H, 5.55%). $\delta_{\mathrm{CDCl_3}}$ 1.58(3H, s), 2.00 (3H, s), 2.60(3H, s), 2.2—2.9(3H), and 4.87(1H, dd, J=5.5, 3.5 Hz).

Aromatization of VI in Methanol. VI(30 mg, as a mixture of isomers) was heated in a methanol(10 ml) solution under reflux. The VI disappeared within 30 min, and after the removal of the solvent, VII(9 mg) and VIII(3 mg) were isolated by preparative thin-layer chromatography.

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4) G. Witting, *Ann. Chem.*, **446**, 155 (1926).

5) In this treatment, colorless needles (mp 87.5—87.5°) were obtained, and the structure was considered to be a monomethyl ether of VIII. However, no further characterization was attempted.

6) The formation of II can be regarded as another example of the cycloaddition reaction of α-acyl-β-diketone. The photochemical reaction of such a system has been successfully employed in the total synthesis of loganin; *cf.* G. Büchi, J. A. Carlson, J. F. Powell, Jr., and L. F. Tietze, *J. Amer. Chem. Soc.*, **92**, 2165 (1970).