BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 555—556 (1971)

The Photoreaction of Dehydroacetic Acid

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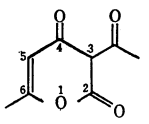
(Received May 14, 1970)

Since dehydroacetic acid (DHA)[1] shows strong antifungal and antibacterial activity, it has been widely used as a fungicide and bactericide in food. The present authors are interested in the photoreaction of DHA in the solid state from the points of view of photochemistry and biochemistry.



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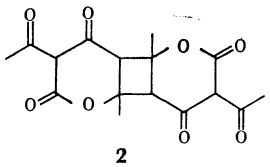

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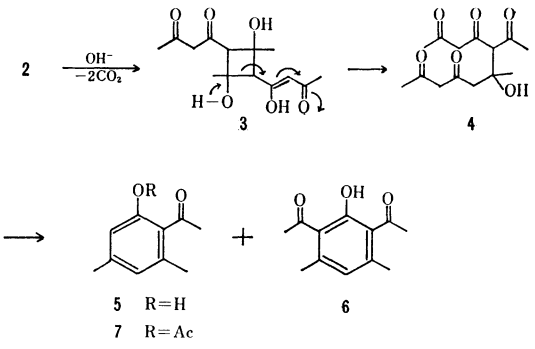
DHA (**1**) was irradiated for a week in the solid state in thin layers by means of a high-pressure mercury lamp. After removing the cold, acetone-soluble fraction from the irradiated material, the residue was recrystallized from acetone to give colorless needles (**2**) in a yield of 4%. The elemental analysis, the thermal decomposition to a monomer at the melting point, and the mass spectrum fragment (*m/e* 239 M^+-COCH_3 and *m/e* 168, which is equivalent to a monomer) all show a dimeric structure. The UV,[2] IR,[2] and NMR spectra supported the idea of the presence of the $(2+2)\pi$ dimer at the 5 and 6-positions. The NMR spectrum, which showed a singlet signal at τ 6.60, indicated a cyclobutane methine proton instead of a vinyl proton in a monomer. The head-to-tail form was suggested by the following reactions. The hydrolysis of the dimer **2** with aqueous sodium hydroxide gave 2-acetyl-3,5-xylenol (**5**) and 2,6-diacetyl-3,5-xylenol (**6**) in a yields of 46 and 42% respectively. The formation of **5** and **6** may be explained by assuming the intermediates **3** and **4**, which have been postulated by Yates[3] in the hydrolytic formation of 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene from the 2,6-dimethyl-4-pyrone cage dimer. In the case of the hydrolysis of **2**, the reaction conditions are stronger than these of the cage dimer of Yates, so two deacetyl-



1) Physical data are listed in E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **30**, 1255 (1965).

2) Methyl 2-acetylacetoacetate has a closely similar structure. IR: 1711(s), 1559(braod), 1441(s) 1240, 1086(s), 918 cm^{-1}. UV: 277 nm (log ε, 4.08). T. Motoda and Y. Yoshida, *Kogyo Kagaku Zasshi*, **68**, 1669 (1965).

3) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963).

ated compounds, **5** and **6**, might be produced. The compound **5** was identical with the authentic specimen of 2-acetyl-3,5-xylenol,[4] while **6** was identical with the authentic specimen of 2,6-diacetyl-3,5-xylenol prepared by the Fries rearrangement of the acetate **5** (**7**).

Although whether the structure of **2** is of a syn or anti form is at present uncertain, the formation of this head-to-tail, four-membered dimer is the first such example in any photodimer of 4-pyrones[3,5] and 2-pyrones[6,7] except for the case of 2,6-diphenyl-4*H*-thiopyran-4-one.[8]

Experimental

Photoreaction of Dehydroacetic Acid (**1**). The inner surface of the wall of the irradiation vessel (cylindrical, 10×25 cm) was covered with solid DHA film by rotating and warming the vessel. In the vessel we placed a concentrated acetone solution of 1 g of DHA. The DHA film thus formed was irradiated with a 125-W, high-pressure mercury lamp at room temperature for a week. After irradiation, the solid was triturated with acetone to dissolve the unchanged starting material. The sparingly-soluble, colorless solid was collected and washed with cold acetone. This material, the crude photodimer (**2**), was obtained in a yield of about 4%. Recrystallization from acetone gave colorless needles; mp 214.5—215.5°C.

Found: C, 57.39; H, 4.90%. Calcd for $C_{16}H_{16}O_8$: C, 57.14; H, 4.80%. Mass: *m/e* 293(4%), 169(82%, base), 153(base), 125(33%), 85(62%), 69 (33%), 43(118%). UV: λ_{max}^{EtOH} nm (ε) 279 (27800). IR (KBr): 1706(s), 1555 (broad), 1445(s), 1240, 1080(s), 910 cm^{-1}. NMR (in $CDCl_3$): τ 8.46 (s, 6H), 7.31(s, 6H), 6.60(s, 2H), −7.91(s, 2H).

The irradiation of 1-g protions of DHA solutions in 5 m*l* of acetone, 6 m*l* of benzene, or 20 m*l* of methanol in a Pyrex tube under a nitrogen atmosphere with a high-pressure mercury lamp for 5 days showed no change.

Hydrolysis of the Dimer **2** *to 2-Acetyl-3,5-xylenol* (**5**) *and 2,6-Diacetyl-3,5-xylenol* (**6**). A mixture of 40 mg of **2**, 12.5 m*l* of saturated aqueous sodium bicarbonate, and 2.5 m*l* of aqueous 5% sodium hydroxide was heated under reflux for 4.5 hr. After cooling, the reaction mixture was extracted with chloroform. The aqueous layer was acidified with dilute sulfuric acid and then again extracted with chloroform. Treating both chloroform extracts separately in the usual manner gave **5** (9 mg; 46%) and **6** (10 mg; 42%) respectively; they were purified by silica-gel-column chromatography using benzene. No change was observed upon the same treatment of DHA.

Preparation of 2-Acetyl-3,5-xylenol (**5**) *and 2,6-Diacetyl-3,5-xylenol* (**6**). Compound **5** was prepared by Smith's method[4]; mp 56—58°C (lit, 57—58.5°C). To a pyridine solution of 290 mg of **5** we added an excess of acetic anhydride. After the reaction mixture had stood overnight, it was poured into cold water and extracted with chloroform. Treating the chloroform extract in the usual manner gave 2-acetoxy-4,6-dimethylacetophenone (**7**) (370 mg; 100%); bp 164—167°C /13 mmHg.

Found: C, 69.81; H, 6.95%. Calcd for $C_{12}H_{14}O_3$; C, 69.88; H, 6.95%. UV: λ_{max}^{EtOH} nm(ε) 246(20600), 285(3000) sh. IR (KBr): 1770, 1695 cm^{-1}. NMR(in $CDCl_3$): τ 7.77, 7.74, 7.70, 7.58 (all s, 3H each), 3.23 (s, 1H), 3.12 (s, 1H).

A mixture of 370 mg of **7** and 720 mg of anhydrous aluminum chloride was heated on a steam bath for 2.5 hr, and then it was mixed with *ca.* 5 m*l* of water. The mixture was extracted with chloroform. The chloroform extract was treated in the usual manner, the chloroform was evaporated, and the residue was chromatographed on silica gel. The fraction which was eluted with benzene gave **5** (96 mg; 33%) and **6** (175 mg; 42%), mp 108—109.5°C.

Found: C, 69.87; H, 6.97%. Calcd for $C_{12}H_{14}O_3$; C, 69.88; H, 6.84%. UV: λ_{max}^{EtOH} nm 243 (12900), 267 (9500) sh. IR (KBr): 1687, 1615 cm^{-1}. NMR (in $CDCl_3$): τ 7.60(s, 6H), 7.41(s, 6H), 3.42(s, 1H), −2.10(s, 1H).

4) L. I. Smith and J. W. Opie, *J. Org. Chem.*, **6**, 427 (1941).
5) P. Yates and D. J. Macgregor, *Tetrahedron Lett.*, **1969**, 453.
6) P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, **1964**, 84.
7) W. H. Pirkle and L. H. Mckendry, *Tetrahedron Lett.*, **1968**, 5279.
8) N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima, and K. Yamada, This Bulletin, **42**, 3005 (1969).