Photodimerization. II. The Structure and Isomerization of the Photodimer of Crystalline *trans*-Benzalacetone

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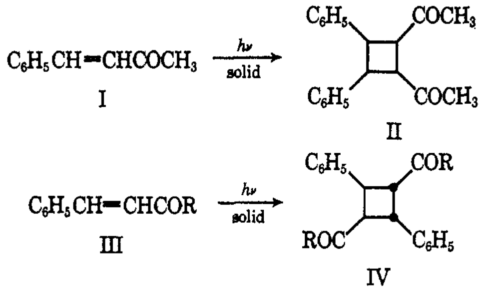
Butenandt reported[1] that the light-induced dimerization of solid benzalacetone (I) proceeded in a head-to-head fashion, leading to II. It is known, however, that various crystalline α,β-unsaturated carbonylic compounds (III, R = OH,[2] OCH_3,[3] C_6H_5[4]) produce photodimers of the α-truxillic type (IV, R = OH, OCH_3, C_6H_5).



I

II

III

IV

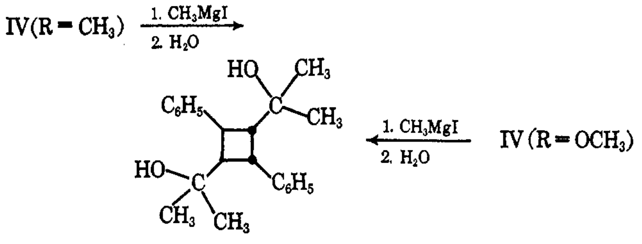
Although one cannot predict the course of a solid-state photodimerization without information concerning the crystal lattice geometry, one may expect that I should dimerize similarly in a head-to-tail fashion. We, therefore, decided to reinvestigate the structure of the photodimer of I.

Upon irradiation of a thin-layer of crystalline I for 8-hours at 10°, by means of a medium pressure ultraviolet lamp, a crystalline dimeric product, which melts at 142–143° (lit.[1] mp 142–143°), was obtained. The infrared spectrum of this dimer, compared to that of I, showed typical saturated carbonylic absorption at 1696 cm^{-1}, and the total absence of olefinic absorption.

On treating the benzalacetone dimer with sodium hypobromite at 38–40° and subsequent acidification of the reaction mixture, α-truxillic acid (IV, R = OH) was obtained, indicating that the benzalacetone dimer should have structure IV (R = CH_3).

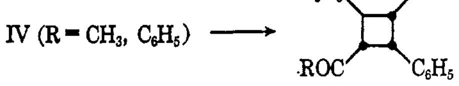
$$\mathrm{I} \xrightarrow[\text{solid}]{h\nu} \mathrm{IV}\ (\mathrm{R}=\mathrm{CH_3}) \xrightarrow[2.\ \mathrm{H^+}]{1.\ \mathrm{NaOBr}} \mathrm{IV}\ (\mathrm{R}=\mathrm{OH})$$

Further unambiguous proof of the correctness of structure IV (R = CH_3) was obtained by treating IV (R = CH_3) with methyl magnesium iodide. Hydrolysis of the reaction mixture led to the isolation of the crystalline derivative V (mp 114–115°). Compound V was additionally synthesized by treating dimethyl α-truxillate[5] (IV, R = OCH_3) with methyl magnesium iodide, followed by hydrolysis of the reaction mixture. Microanalysis showed V to have a molecular formula $C_{22}H_{28}O_2$. Further support for the proposed structure of V was given by its mass spectrum, which showed the molecular ion at *m/e* 324. The infrared spectrum displayed typical hydroxylic absorption (3553 cm^{-1}) and the total absence of carbonyl groups.



V

The benzalacetone dimer (IV, R = CH_3) appeared to be very unstable in acid or alkaline media. When IV (R = CH_3) was refluxed in ethanol containing hydrochloric acid or sodium hydroxide, complete isomerization to a crystalline product (mp 160–162°) took place. A comparison of the infrared spectra of IV (R = CH_3) and its isomer showed that the 753 and 771 cm^{-1} bands (associated with the aromatic out-of-plane C–H deformation vibration) in the spectrum of IV (R = CH_3) appeared as three bands (738, 761, and 770 cm^{-1}) in the spectrum of its isomer. This splitting is ascribed to steric interference in the isomer.[6,7] The splitting of the carbonylic absorption band (1700, 1709 cm^{-1}) in the spectrum of the isomer and the shift to higher frequency (1696 to 1709 cm^{-1}), can only be brought about by intercarbonylic electrostatic interaction.[7,8] From the spectroscopic data it seems evident that the isomer of IV (R = CH_3) must have the γ-truxillic structure VI (R = CH_3), *i.e.*, a rearrangement analogous to that of bischalkone B(IV, R = C_6H_5) to bischalkone D(VI, R = C_6H_5)[3] must have taken place.



VI

The nmr spectra of the benzalacetone dimer IV (R = CH_3) and its isomer (VI, R = CH_3) both revealed the presence of ten phenyl, six acetyl, and four cyclobutyl protons. A comparison of these two spectra with those of the corresponding truxillic acids (IV, R = OH and VI, R = OH) gave evidence for the correctness of structures IV (R = CH_3) and VI (R = CH_3). Due to the chemical equivalence of the two phenyl groups in both IV (R = CH_3) and α-truxillic acid (IV, R = OH), the signal for the phenyl protons was re-

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[1] A. Butenant, *et al.*, *Ann.*, **575**, 123 (1951).

[2] H. Stobbe, *Ber.*, **52**, 666 (1919).

[3] H. Stobbe and K. Bremer, *J. Prakt. Chem.*, **123**, 44 (1929).

[4] C. Liebermann and M. Zsuffa, *Ber.*, **44**, 841 (1911); A. W. K. de Jong, *ibid.*, **56**, 818 (1923).

[5] C. Liebermann, *ibid.*, **21**, 2347 (1888).

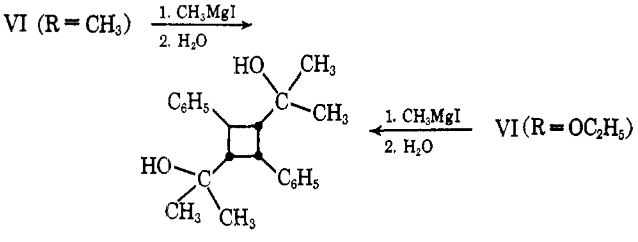
[6] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1959, p 77.

[7] J. Dekker, P. Janse van Vuuren, and D. P. Venter, *J. Org. Chem.*, **33**, 464 (1968).

[8] R. N. Jones, P. Humphries, and K. Dobriner, *J. Amer. Chem. Soc.*, **72**, 956 (1950).

corded in each case as a sharp singlet. The splitting of the signal for the phenyl protons in the spectrum of VI (R = CH_3) and VI (R = OH) confirmed the γ-truxillic type structure of the isomer (VI, R = CH_3). The patterns of the signals for the cyclobutyl protons of IV (R = CH_3) and of VI (R = CH_3) were typical of A_2B_2 and ABX_2 systems respectively, resembling those of the corresponding α- and γ-truxillic acids (IV, R = OH and VI, R = OH).

Various attempts to convert VI (R = CH_3) into γ-truxillic acid (VI, R = OH) by means of sodium hypobromite failed, probably on account of steric hindrance. The structural and stereochemical relationship between the isomer (VI, R = CH_3) and γ-truxillic acid (VI, R = OH) was proved unambiguously by converting both the isomer (VI, R = CH_3) and diethyl γ-truxillate (VI, R = OC_2H_5)[9] by means of methyl magnesium iodide into a common crystalline derivative (VII, mp 125–126°). The mass spectrum of VII, of which the microanalysis corresponds with $C_{22}H_{28}O_2$, showed the molecular ion at *m/e* 324. The infrared spectrum exhibited typical hydroxylic absorption (3576 cm^{-1}) and the total absence of carbonyl groups.



VII

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer. Mass spectra were obtained on a M.S. 9 mass spectrometer. Nmr spectra were recorded on a Varian A60 apparatus. Melting points were determined on a Gallenkamp (design no 889339) apparatus and are uncorrected.

A. Photodimerization of Crystalline I.—Molten benzalacetone (I, 1 g) was allowed to solidify in a thin layer in a Duran 50 test tube and irradiated for 8 hr, at 10°, by means of a medium pressure uv lamp. The reaction mixture was fractionally recrystallized from ethanol, yielding colorless needles (0.13 g) of IV (R = CH_3): mp 142–143° (lit.[1] 142–143°); ir (KBr), 3053 w, 3026 w, 2949 m, 2914 w, 1696 s, 1599 w, 1491 m, 1446 m, 1419 w, 1368 s, 1360 s, 1338 w, 1261 m, 1230 w, 1180 m, 1169 s, 1127 w, 1087 w, 1030 w, 789 w, 771 m, 753 s, 717 m, and 700 s cm^{-1}; nmr ($CDCl_3$), τ 8.37 (6 H), 6.27–5.2 (m, 4 H), and 2.7 (s, 10 H); mass of molecular ion, *m/e* 292.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.17; H, 6.896. Found: C, 81.79; H, 6.98.

B. Reaction of IV (R = CH_3) with Sodium Hypobromite.—A solution of NaOBr (0.42 g of NaOH, 0.44 g of Br_2, 2 ml of water) was added to a solution of IV (R = CH_3, 0.1 g) in dioxane (1.5 ml) over a period of 30 min. The reaction temperature was kept between 38 and 40°. The reaction mixture was stirred for a further period of 15 min, followed by the addition of 10 ml of water; 5 ml of solvent was distilled off under diminished pressure (18 mm). The reaction mixture was filtered. Acidification of the filtrate with dilute HCl led to a white precipitate. Recrystallization from aqueous ethanol yielded 0.017 g of α-truxillic acid, mp 270–273° (lit.[2] mp 273°); identification was by ir spectroscopy.

C. Isomerization of IV (R = CH_3). 1. In Acidic Medium.—Compound IV (R = CH_3, 0.1 g) was refluxed for 2 hr in ethanolic HCl (0.5 *N*, 6 ml). The reaction mixture was diluted with water (30 ml) and extracted with benzene. The extract was washed successively with 5% $NaHCO_3$ and water, and dried (Na_2SO_4). On evaporation of the solvent, a solid residue was obtained. Recrystallization from benzene–petroleum ether (bp 60–80°) yielded colorless needles of VI (R = CH_3, 0.07 g): mp 160–162°; ir (KBr), 3052 w, 3018 w, 2993 w, 2947 w, 2895 w, 1709 s, 1700 s, 1597 w, 1490 s, 1450 w, 1442 m, 1420 w, 1361 s, 1332 w, 1218 w, 1186 s, 1086 w, 1031 w, 949 w, 770 s, 761 m, 738 m, 717 w, and 698 s cm^{-1}; nmr ($CDCl_3$), τ 8.38 (6 H), 6.52–5.0 (m, 4 H), and 2.78 (d, 10 H); mass of molecular ion, *m/e* 292.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.17; H, 6.896. Found: C, 82.01; H, 7.124.

2. In Alkaline Medium.—Compound IV (R = CH_3, 0.15 g) was refluxed for 2 hr in ethanolic KOH (5%, 6 ml). The reaction mixture was diluted with water (30 ml), acidified with 1 *N* HCl, and extracted with benzene. The extract was washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and chromatographed over alumina. Evaporation of the solvent produced a solid, which was recrystallized from benzene–petroleum ether (bp 60–80°) as colorless needles (mp 160–162°, 0.1 g). The ir spectrum was identical with that of VI (R = CH_3).

D. Preparation of V. 1. From IV (R = CH_3).—A mixture of IV (R = CH_3, 0.1 g) and a concentrated solution of CH_3MgI in ether (4.1 *M*, 5 ml) was stirred magnetically in a glass-stoppered 25-ml, round-bottom flask until a clear solution was obtained[10] (usually within 30 min). The reaction mixture was treated carefully with excess 0.5 *N* HCl (10 ml) and extracted with ether. The extract was washed successively with 5% $NaHCO_3$, 5% $Na_2S_2O_3$, and water and dried (Na_2SO_4). Evaporation of the solvent yielded a crystalline product (V, 0.104 g) which was recrystallized from petroleum ether (bp 50–70°) as colorless needles: mp 114–115°; ir (KBr), 3553 s, 3063 w, 3030 w, 3002 m, 2980 s, 2970 s, 2932 m, 2914 m, 1600 m, 1580 w, 1491 m, 1460 w, 1448 m, 1380 m, 1365 m, 1337 w, 1310 w, 1260 w, 1228 m, 1211 m, 1189 m, 1166 m, 1121 s, 1077 w, 1031 m, 1000 w, 958 m, 945 m, 906 m, 856 m, 827 w, 798 w, 764 s, 730 w, 700 s, and 653 w cm^{-1}; mass of molecular ion, *m/e* 324.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.57; H, 8.69.

2. From IV (R = OCH_3).—A mixture of IV (R = OCH_3, 0.1 g) and a solution of CH_3MgI in ether (4.1 *M*, 7 ml) was treated as above to yield 0.093 g of product, mp 114–115°. The ir spectrum was identical with that of the product found in procedure D-1.

E. Preparation of VII. 1. From VI (R = CH_3).—A mixture of VI (R = CH_3, 0.1 g) and a solution of CH_3MgI in ether (4.1 *M*, 5 ml) was treated as above. Recrystallization of the product (0.105 g) from petroleum ether (bp 50–70°) yielded colorless needles: mp 125–126°; ir (KBr), 3576 s, 3065 w, 3032 w, 2977 s, 2938 m, 1600 m, 1582 w, 1490 m, 1450 m, 1364 m, 1313 w, 1271 w, 1232 w, 1201 w, 1172 m, 1125 m, 1100 w, 1083 w, 1065 w, 1045 w, 958 m, 926 w, 891 w, 851 w, 831 s, 761 s, 701 s, and 698 s cm^{-1}; mass of molecular ion, *m/e* 324.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.65; H, 8.62.

2. From VI (R = OC_2H_5).—A mixture of VI (R = OC_2H_5, 0.1 g) and a solution of CH_3MgI (4.1 *M*, 7 ml) was treated as above to yield 0.087 g of product, mp 125–126°. The ir spectrum was identical with that of the product found in procedure E-1.

F. The nmr spectra (DMSO) of the α- and γ-truxillic acids (IV, R = OH, and VI, R = OH) showed signals at τ 6.28–5.44 (m, 4 H) and 2.62 (s, 10 H) and at τ 6.53–5.28 (m, 4 H) and 2.63 (d, 10 H), respectively. In neither case was any signals for hydroxylic protons observed.

Registry No.—IV (R = OH) 16607-21-9; IV (R = CH_3) 16607-22-0; V, 16607-23-1; VI (R = OH) 16607-24-2; VI (R = CH_3) 16607-25-3; VII, 16607-26-4.

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(9) C. Liebermann, *Ber.*, **22**, 2243 (1889).

(10) The reaction in which concentrated Grignard reagents are employed at room temperature (in contrast to the conventional method, in which the Grignard reaction is carried out under reflux in dilute solution) proceeds fast and practically quantitatively. This modified method was developed in our laboratory and finds its most valuable application in the case of highly insoluble substrates. The development of a clear solution indicates completion of the reaction.