Notes

Structure of the Hemihydrates of Phenylglyoxals[1,2]

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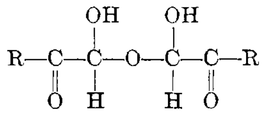
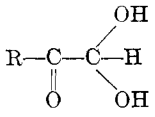
The literature contains a reference to hemihydrates of phenylglyoxals for which structure I has been presumed.[4] Prior to this publication the hemihydrates (I) and the normal hydrates (II) had often been confused. Evidence for structure I was based mainly on elemental analysis.[4] We have prepared the hemihydrate of p-methoxyphenylglyoxal and obtained proof for structure Ia.



$R-\underset{\underset{O}{\|}}{C}-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-O-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-R$

I

Ia, $R = p\text{-}CH_3OC_6H_4-$

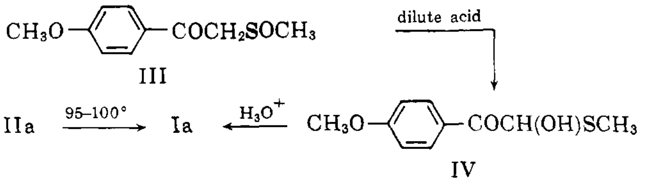


$R-\underset{\underset{O}{\|}}{C}-C(OH)_2-H$

II

IIa, $R = p\text{-}CH_3OC_6H_4-$

In connection with a study of the formation of β-keto sulfoxides and their acid-catalyzed rearrangement into the hemimercaptals of α-ketoaldehydes,[5] we have found that, while treatment of the condensation product (III) of dimethyl sulfoxide and methyl p-anisate with dilute hydrochloric acid gives the hemimercaptal (IV), the use of more concentrated acid leads to a sulfur-free compound proved to be Ia. In separate experiments Ia was also formed from IV in the presence of strong acid or by heating of the glyoxal hydrate (IIa).



On the basis of elemental analysis, molecular weight determination, and infrared and integrated n.m.r. spectra we have been able to verify the bis(p-anisoylhydroxymethyl) ether structure for Ia. The n.m.r. spectrum of Ia is particularly instructive and conclusively supports structure Ia. In addition to the singlet for the methoxy group ($\tau = 6.15$, area $= 6.0$ units) and the a_2b_2 system of the benzene ring protons at $\tau = 1.85$, area $= 4$, and $\tau = 3.06$, area $= 4$, $J = 8.95$ c.p.s., the spectrum contains a pair of doublets representing the H_a–C–OH_b group in Ia.[6] Deuterium exchange with deuterium oxide proved H_a absorbs at $\tau = 3.68$, area $= 2$ and H_b absorbs at $\tau = 4.88$, area $= 2$ with a coupling constant J_{ab} of 10.3 c.p.s. Similar absorption has been found for the H–C–OH group in the hemimercaptals of phenylglyoxals.

The hydrate of p-methoxyphenylglyoxal had been prepared by Karrer and v. Segesser[7a] as well as by Sisido and Nozaki.[7b] The melting point as given by Sisido and Nozaki (110–114°) is close to the melting point we observed for the hemihydrate (107–109°). We, therefore, prepared p-methoxyphenylglyoxal hydrate by the literature method.[7b] Its infrared spectrum was entirely different from that of Ia. Moreover, as reported,[7b] the hydrate (IIa) melted at about 70°, resolidified at about 75°, and melted again at 107–108°. The resolidified product did not depress the melting point of Ia.[8] When IIa was kept at 95–100° for four hours it was converted into Ia in good yield. It can, therefore, be stated that the melting point reported for IIa is actually that of its dehydration product, Ia.

Experimental

Preparation of Ia from III.—A few minutes after dissolving 250 mg. of III (1.18 mmoles), m.p. 101°, in 2.5 ml. of 18% hydrochloric acid, the initially clear solution turned cloudy and an oil separated. The mixture was kept in an open beaker at room temperature for 6 days during which time the aqueous phase evaporated to leave a crystalline residue. Washing with ether gave 89 mg. (43%) of Ia as colorless, ether-insoluble crystals, m.p. 107–109°, with a strong infrared absorption at 2.93 and 5.98 μ.

Anal. Calcd. for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24; mol. wt., 346. Found: C, 62.55; H, 5.24; mol. wt., 301 (dioxane).[9]

Preparation of Ia from IV.—A solution of 85 mg. of IV (0.4 mmole), m.p. 89–92°, in a mixture of 3 ml. of ethanol and 1.2 ml. of 18% hydrochloric acid was kept on a steam bath for 1 hr. Evaporation of solvent during this period left an oily substance which was kept in an open beaker for 4 days. Upon washing with ether 47 mg. (67%) of Ia was obtained as insoluble crystals, m.p. 107–109°. The infrared absorption spectrum was identical with that of Ia prepared from III.

Preparation of Ia from IIa.—Heating of 200 mg. of IIa (m.p., *ca.* 70°), prepared according to the directions of Sisido and Nozaki,[7b] at 95–100° for 4 hr. in a test tube gave a solid mass which, when treated with a few drops of ethanol at room temperature, yielded a yellowish crystalline substance. Washing with ether gave 180 mg. (95%) of insoluble Ia, m.p. 107–109°, which did not depress the melting point of Ia from III or IV and had an infrared absorption spectrum identical with that of Ia from III or IV.

Phenylosazone of p-Methoxyphenylglyoxal from Ia.—The hemihydrate Ia (25 mg.) was dissolved by heating in a solution of 0.5 ml. of ethanol, 0.2 ml. of water, and 1 drop of concentrated hydrochloric acid. After addition of 0.1 ml. of phenylhydrazine the reaction mixture was kept on a steam bath for 2 hr. A yellow solid was filtered off to yield the osazone of p-methoxyphenylglyoxal; m.p. 190° (lit.[10] m.p. 190°).

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[1] Reactions of Resonance Stabilized Carbanions, part VI. For part V see G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

[2] Supported in part by a grant from the Alfred P. Sloan Foundation.

[3] Alfred P. Sloan Foundation Fellow, 1959–1963.

[4] R. B. Moffett, B. D. Tiffany, B. D. Aspergren, and R. V. Heinzelman, *J. Am. Chem. Soc.*, **79**, 1687 (1957).

[5] G. A. Russell and H.-D. Becker, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 3Q.

[6] The spectrum was measured for a saturated solution of Ia in chloroform-*d* at 60 Mc./sec.

[7] (a) P. Karrer and A. v. Segesser, *Helv. Chim. Acta*, **18**, 273 (1935); (b) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 3326 (1948).

[8] Melting points are uncorrected and were obtained using a Fisher-Johns melting point block.

[9] Determined by a thermoelectric osmometric measurement, Schwarzkof Microanalytical Laboratories, Woodside, N. Y.

[10] C. Weygand, *Ann.*, **459**, 99 (1927).