

PHOTOCHEMICAL REACTIONS OF BENZENE WITH ACIDS

by

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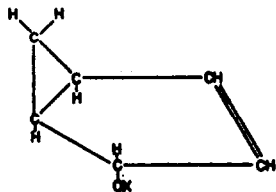
(Received 15 September 1966)

A recent publication by Kaplan et al. (1) prompts us to present our results on the photochemical interaction of benzene and acids. These photo-reactions were observed by irradiation in a cell and measuring the change in the absorption spectrum. Experiments on a preparative scale were performed with benzene and acetic acid, with benzene and aqueous phosphoric acid, and with tert-butylbenzene and acetic acid. In addition to polymeric material, mixtures of 1:1 addition products of benzene and acid were obtained.

Benzene (0.31 mole) dissolved in glacial acetic acid (2.4 l) was irradiated with a submerged Philips TUV 15W low-pressure mercury vapour lamp for 480 hours at 20 °C. Distillation yielded 8.14 g of a product boiling at 65 °C/15 mm, and about 20 g of polymeric residue. Mass spectrum and elemental analysis indicated the distillate to be an addition product $C_6H_6 \cdot CH_3COOH$ (mass peak at 138; elemental analysis: found 69.2% C, 7.36% H, 23.6% O; calc. for $C_8H_{10}O_2$: 69.5, 7.25, 23.2%). Preparative GLC allowed separation into two fractions, one of which (M) consisted of two as yet unidentified isomers. After two passages the other fraction could be identified by NMR as 4-acetoxy-bicyclo [3.1.0]hex-2-ene (Ia), the acetoxy group occupying the exo-position.

Fig. I

, Ia X = COCH₃
Ib X = H



The purest product contained 94% Ia and 4% M; $n_D^{20} = 1.4653$; elemental analysis: C = 69.0%, H = 7.3%. The NMR spectrum was taken with benzene as internal reference. Besides the methyl protons of the acetate group ($\delta = 1.87$), two protons were observed at $\delta = 1.6-1.9$, and five single protons at $\delta = -0.1, 0.9, 5.4, 5.5$ and 6.2 . In the ultraviolet, only end absorption was observed, beginning at 2350 \AA .

The proportion of Ia to the mixture M varied from 2:1 to 3:2 in batch irradiations. However, upon refluxing a mixture of benzene and acetic acid in a fractionating column and irradiating the downcoming top liquid, this proportion changed to at least 10:1, while only a small quantity of polymeric material was formed. Thus, the polymeric products are almost certainly due to over-irradiation. The isomers M may also be products of secondary photoreactions, although thermal decomposition of M in preference to Ia during refluxing cannot be excluded.

Aqueous phosphoric acid (0.1 molar) saturated with benzene was irradiated with a submerged Philips TUV 30 W lamp. During irradiation (300 hours) the products were continuously extracted with benzene. Upon distillation two fractions were obtained. The first, bp $34^\circ\text{C}/13 \text{ mm Hg}$, consisted of a mixture of products; NMR, mass and IR spectra as well as elemental analysis suggest that two different aldehydes $\text{C}_6\text{H}_8\text{O}$ are the main components. Their structures are under investigation. The second fraction, bp $59^\circ\text{C}/13 \text{ mm Hg}$, consisted mainly of one component; $\text{C}_6\text{H}_7\text{OH}$: mass peak at 96; elemental analysis: 74.2% C, 8.52% H, 17.3% O; (Calc. for $\text{C}_6\text{H}_7\text{OH}$: 75.0, 8.34, 16.7%); IR and NMR spectra revealed the presence of a hydroxyl group; a small quantity of aldehydes was also present. In the UV only end absorption below 2300 \AA occurred. In the NMR spectrum the alcoholic proton signal shifted from $\delta = 5.0$ at 35°C to 4.3 at 60°C ; two proton signal appeared at $\delta = 1.6-2.1$, single protons at $\delta = -0.16, 0.92, 4.4, 5.5$ and 6.15 . This confirms the structure Ib for the water adduct, also with the hydroxyl group in the exo-position.

Hydrolysis of Ia did not lead to formation of Ib; however, both in weakly acid medium (0.1 molar phosphoric acid) and in alkaline aqueous solutions (sodium bicarbonate, carbonate and hydroxide) yellow discoloration was observed together with formation of polymeric products. Only the formation of fulvene could be ascertained by its characteristic absorption spectrum(2).

Apparently, the products Ia and Ib are analogous to the 4-substituted bicyclo [3.1.0]hex-2-enes obtained by Kaplan et al. (1). So far it is not certain whether the other acetates (M) obtained by us are analogous to the 6-substituted bicyclo [3.1.0]hex-2-enes described by these authors(1).

In the photoaddition of acetic acid onto tert-butylbenzene no polymeric material was formed. The product, bp 103 °C/13 mm Hg, was a mixture of 1:1 adducts: mass peak at 194; elemental analysis: 74.0% C, 9.4% H and 16.7% O; calc. for $C_6H_5C(CH_3)_3 \cdot CH_3COOH$: 74.3, 9.3 and 16.5%. Although during GLC considerable decomposition occurred, the presence of four different compounds, presumably isomeric adducts, could be demonstrated. It should be noted that during thermal decomposition a product of retention time slightly different from that of tert-butylbenzene was formed together with tert-butylbenzene, and that the former seems to have been spontaneously converted into tert-butylbenzene. This behaviour seems to indicate the formation of a valence tautomer of tert-butylbenzene.

Irradiation of benzene dissolved in ethereal hydrochloric acid (0.3 N) gave 2,3-diethoxybutane as the main product, which suggests intermediate formation of 1-ethoxy-1-ethyl radicals(3,4). The occurrence of a free radical type photoreaction of benzene even in the presence of acid may be of some mechanistic importance.

In a separate communication (5) we suggested that different photo-reactions of benzene may be interpreted by assuming a common highly reactive intermediate, viz. a Möbius type isomer (cf. ref. 6), and we gave a detailed discussion of the formation of valence tautomers. The formation of products of type I can be explained along similar lines. However, the data available do not yet allow us to indicate a detailed mechanistic pathway.

References

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