

Photochemical Oxidation of Benzyl Alcohol

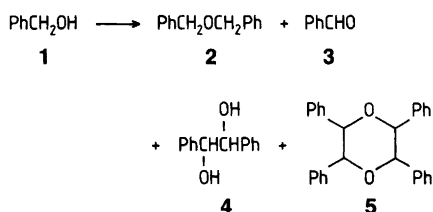
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Hansen, S. H. and Sydnæs, L. K., 1989. Photochemical Oxidation of Benzyl Alcohol. – Acta Chem. Scand. 43: 395–398.

Irradiation of neat, pure benzyl alcohol through Pyrex gives mainly 1,2-diphenyl-1,2-ethanediol, 1,2-diphenylethanol, benzaldehyde, benzoic acid, and benzaldehyde dibenzyl acetal. The product composition is sensitive to the presence of contaminants. The course of reaction is different in dichloromethane.

During studies of the photooxidation of toluene we noticed that the predominant primary oxidation product, benzyl alcohol (**1**), gave rise to several compounds upon direct irradiation through Pyrex.¹ Later we discovered that the same compounds were formed, albeit in different relative amounts, when **1** was irradiated through quartz. This observation seemed, at first, to be in keeping with the results of Balsells and Frasca;² they reported that irradiation of **1** in the presence or absence of oxygen with quartz-filtered light from a high-pressure mercury lamp gave minor quantities of dibenzyl ether (**2**), small amounts of benzaldehyde (**3**) and the *dl* and *meso* isomers of 1,2-diphenyl-1,2-ethanediol (**4**), and large amounts (88 %) of two diastereoisomers of 2,3,5,6-tetraphenyl-1,4-dioxane (**5**).



When the structures of our products were elucidated, however, it became apparent that our results deviated considerably from those summarized above. Our findings are therefore reported here.

Results and discussion

In all our experiments **1** was photolyzed in the presence of air at 20 °C using Pyrex-filtered light ($\lambda > 285$ nm) from a medium-pressure mercury lamp (125 or 400 W) which was immersed into the liquid. A number of different samples of benzyl alcohol was used, but despite the fact that the purity in all cases was proved to be better than 98 %, all the samples contained minor amounts of several unknown contaminants which were observed to influence the photooxidation rather extensively. Thus, some of the products that

were formed from one sample of **1**, were not detected when other samples of the same alcohol were employed. Therefore, the course of reaction is extremely sensitive to the quality of the starting material. All the samples of the alcohol were therefore thoroughly distilled, but the purity of most of the samples did not improve very much. However, one sample gave benzyl alcohol with a purity of at least 99.9 % upon being thoroughly distilled; these lots gave reproducible results and were used in all the experiments reported here.

The alcohol was first irradiated neat using a 125 W, internal lamp and maintaining a slow flow of air through the liquid. The course of reaction was conveniently monitored by GLC provided an inert column was used; if the column contained active sites decomposition of several of the products took place and erroneous results were obtained. After 12 h of irradiation six products were present, viz. **3**, *dl*-**4**, *meso*-**4**, benzoic acid (**6**), 1,2-diphenylethanol (**7**), and benzaldehyde dibenzyl acetal (**8**), all of which were identified by comparison of their retention times and spectroscopic and spectrometric properties with those of authentic samples. At least one of the products was, to some extent, present as the corresponding peroxide, as borne out by a positive KI/starch test of an aliquot of the photolysate. When the irradiation was continued the absolute yields of products **3**, **4**, and **6–8** gradually increased (Table 1), but concomitant secondary reactions also took place. As a result, a number of minor products were formed and the total relative yield of the primary products dropped from 96 % after 24 h to 88 % after 96 h (Table 1).

The only minor product identified was benzyl benzoate, which incidentally was a minor product from one of the impure samples of **1**. However, the 1,4-dioxane **5**, the major product obtained by Balsells and Frasca,² was not detected in any of our experiments.

When external irradiation of neat **1** was carried out, the course of reaction did not change significantly; however, owing to the fact that only a part of the emitted light actually reached the reacting solution, the total efficiency of the reaction dropped considerably. As expected the

compound with a *dl/meso* ratio close to 1.0 whereas they report² only a 2% yield and a *dl/meso* ratio of 0.14. Two of these disagreements are actually interrelated since Balsells and Frasca state that **4** is easily converted into a mixture of stereoisomeric dioxanes (**5**) in an efficient thermal reaction.² A corollary of this is that more than 95% of the diol formed during the photolysis of benzyl alcohol has to be converted thermally to dioxanes, but this is not the case; Balsells and Frasca themselves report that only 7.5% of the diol actually reacts when **4** is subjected to the conditions prevailing during the irradiation.²

A further point that should be made is related to the influence of the solvent on the product distribution. When neat benzyl alcohol and a dichloromethane solution of benzyl alcohol were irradiated under identical conditions Balsells and Frasca obtained very similar results.² This is somewhat surprising since the viscosity difference between CH₂Cl₂ (0.393 cP at 30°C)⁷ and benzyl alcohol (5.8 cP at 20°C)⁷ should be large enough to influence at least the efficiency of the bimolecular reactions. In fact, when we irradiated dilute CH₂Cl₂ solutions of benzyl alcohol for up to 24 h, our reaction mixtures were totally different from those obtained during the photolysis of neat benzyl alcohol. The acetal **8** was not obtained, and the lower the concentration of **1** the lower the yield of diol **4**, conceivably because the benzoyloxy radical forms benzoic acid before the transient undergoes other bimolecular reactions.⁸ The high yield of benzoic acid under dilute conditions (up to 39%) is in accordance with this reasoning as is the absence of benzyl benzoate, a secondary product from **8**, under the same conditions.

Another new product formed from **1** under our reaction conditions is 1,2-diphenylethanol (**6**). How **6** is formed is far from clear, although one conceivable route involves trapping of the 1-hydroxybenzyl radical by the benzyl radical, both of which are generated during the photolysis (Schemes 1 and 2).^{1,3,5}

Experimental

General. Most of the equipment has been described elsewhere.⁹ In addition, a Carlo Erba HRGC 5300 Mega Series gas chromatograph, equipped with a Chrompack CP-Sil 8 CB fused silica capillary column (25 m, ID 0.32 mm) and an FID, was employed. Helium (2 ml min⁻¹) was used as the carrier gas and the oven temperature was programmed as follows: 80°C for 2 min then rising at a rate of 20°C min⁻¹ to 240°C (10 min). Benzoin was used as an internal standard and its response ratio to benzaldehyde, benzoic acid, 1,2-diphenylethanol, *meso*-1,2-diphenyl-1,2-ethanediol, and *dl*-1,2-diphenyl-1,2-ethanediol was 1.20, 1.34, 0.88, 1.05, and 1.05, respectively. The response ratio to benzaldehyde dibenzyl acetal was assumed to be 1.0. A Chrompack CP-Sil 5 CB fused silica capillary column (50 m, ID 0.22 mm) was used for the GC/MS analyses.

Samples of benzyl alcohol from Aldrich, BDH, Fluka and Merck were used. The purity of all the samples was

above 98% (GLC) and the alcohol was therefore distilled. The sample from Aldrich gave alcohol of highest purity.

Photolysis. Most of the quantitative experiments were carried out using a Pyrex 150 ml immersion well reactor from Applied Photophysics, England, equipped with a 125 W medium-pressure lamp and cooled with tap water (4–6°C). The cut-off of the Pyrex glass was approximately 290 nm. Air was bubbled through the solution at controlled speed during the photolysis. External irradiations were carried out using 125 and 400 W medium-pressure mercury lamps which were surrounded by a Pyrex sleeve (cut-off 290 nm). Borosilicate vials were used as containers and were placed 10 cm from the lamp. The lamp and the vials were kept in a shelter where the ambient temperature reached 30–35°C. The vials were loosely covered with aluminium foil to reduce evaporation.

The photolysates were diluted with dichloromethane (1:10) and mixed with the internal standard prior to GLC analysis.

The following samples were irradiated: unpurified samples from most of the suppliers, purified (distilled) samples from all suppliers, a mixture of pure benzaldehyde and a purified sample of benzyl alcohol, a purified sample of benzyl alcohol and hydrogen chloride, and solutions (0.4 and 1.0% v/v) of pure benzyl alcohol in dichloromethane.

Synthesis of 1,2-diphenyl-1,2-ethanediol (4**).** A mixture of *dl*-**4** and *meso*-**4** was prepared by adding a slurry of lithium aluminium hydride (0.48 g, 12 mmol) in dry ether (50 ml) to a stirred solution of benzil (1.26 g, 6.0 mmol) in dry ether (25 ml) under nitrogen. The mixture was refluxed for 2 h, then cooled and hydrolyzed with water (100 ml). The hydrolysate was treated with 3 M sulfuric acid until a clear solution was obtained and then extracted with ether (3×50 ml). The combined extracts were washed (aqueous sodium hydrogencarbonate) and dried (sodium sulfate). Evaporation of the solvent gave 0.94 g (73%) of **4**¹⁰ which was a 13:87 *dl/meso* isomeric mixture. The ratio was determined by GLC and ¹H NMR analyses and the *meso* isomer was identified by independent synthesis.¹¹ MS [70 eV, *m/z* (% rel. int.)] (*dl*-**4**): 196 (3, *M*⁺–H₂O), 195 (2), 180 (9), 179 (9), 178 (7), 167 (51), 165 (24), 152 (13), 108 (70), 107 (100), 105 (60), 91 (8), 90 (8); (*meso*-**4**): 196 (1, *M*⁺–H₂O), 195 (0.5), 180 (4), 179 (4), 178 (3), 167 (20), 165 (11), 152 (5), 108 (70), 107 (100), 105 (49), 91 (5), 90 (4).

Benzaldehyde dibenzyl acetal (8**)** was obtained by azeotropic removal of the water formed by condensing benzaldehyde (3.0 g, 25 mmol) and benzyl alcohol (6.1 g, 50 mmol) in refluxing benzene (500 ml). Strongly acidic ion-exchange resin (2 spatulas, Dowex 50W-X8, 20–40 mesh) was added as a catalyst. After 4 h, the reaction mixture was cooled, the catalyst was removed by filtration, and the solvent was evaporated under reduced pressure to give a slightly yellow oil which was subjected to Kugelrohr distillation (150°C/9 mmHg) to remove unchanged starting ma-

terial. At 220 °C/9 mmHg 4.25 g (56 %) of **8** was obtained as a clear liquid (lit.,⁵ 150–155 °C/0.05 mmHg). IR (CCl₄): 3050 (m), 3030 (m), 2860 (m), 1190 (m) cm⁻¹. ¹H NMR (60 MHz, CCl₄): δ 4.58 (4H, s, 2 × CH₂), 5.76 (1H, s, CH), 7.18–7.67 (15H, m).

Acknowledgements. Financial support from the Norwegian Research Program for Marine Arctic Ecology, administered by the Norwegian Research Council for Science and the Humanities, is gratefully acknowledged.

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Received November 4, 1988.