

Photochemical Oxidation of Toluene and Xylenes. Concurrent Formation of Products Due To Photooxygenation and Photodimerization

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Irradiation through pyrex of toluene and *o*-, *m*- and *p*-xylene in the liquid phase in the presence of air gave product mixtures which mainly contained alcohols, aldehydes, acids, and various dimers.

During the preparation of 9,10-dimethylanthracene-9,10-endoperoxide by photolysis of the corresponding hydrocarbon in toluene with pyrex-filtered light in the presence of oxygen, several minor products originating from toluene were detected.¹ We therefore became interested in studying the photochemical properties of toluene which turned out to be relatively little investigated. Thus, a few papers have dealt with the photochemistry of toluene in the gas phase²⁻⁴ and on solid support⁵ and some reports on the photochemical properties of toluene in the liquid state have appeared.⁶⁻¹¹ Most of the irradiations involving the liquid state have been performed with high-energy light ($\lambda \leq 265$ nm) from lasers and medium-pressure mercury lamps.⁶⁻¹⁰ One exception is a study by Pasternak and Morduchowitz¹¹ who employed pyrex-filtered light ($\lambda > 280$ nm) from a medium-pressure mercury lamp to investigate the photoreactivity of neat toluene in the presence of oxygen. They found that benzyl alcohol and benzaldehyde were the only products formed, but in contrast to this, we have found several other products as well under comparable conditions.

RESULTS AND DISCUSSION

The photolyses were carried out by irradiating neat liquid toluene (*1a*) with pyrex-filtered light ($\lambda > 285$ nm) from a medium-pressure mercury lamp. The total time of irradiation was 96 h, but the reaction mixture was analyzed every 24th h. As expected¹¹ illumination of deoxygenated toluene gave no product. Irradiation of *1a* in the presence of air gave a complex mixture which consisted mainly (>90 %) of 5 products, viz. benzyl alcohol (*2a*), benzaldehyde (*3a*), benzoic acid (*4a*), 1,2-diphenylethane (*5a*), and 1,2-diphenylethanol (*6a*) (Scheme 1). The products were identified by comparing their retention times and mass spectra with those of authentic samples. In agreement with the work of Pasternak¹¹ but in contrast to the report of Wei and Adelman⁸ benzyl hydroperoxide was not observed; this is attributed to photodissociation of the hydroperoxide, the primary photochemical product (*vide infra*), whose 0–0 absorption band extends well above 300 nm.¹²

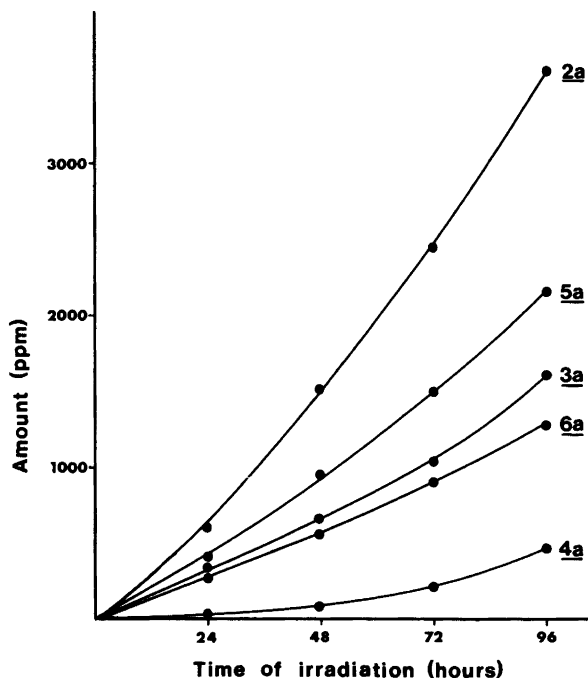
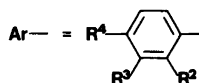
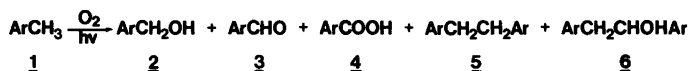


Fig. 1. The distribution of the products formed during photooxidation of toluene as a function of time.

The amount of the various photolysis products was determined by gas chromatography. Results are compiled in Table 1, entry 1, and depicted in Fig. 1. Benzoic acid was formed in the lowest yield, but with increasing time of irradiation the relative amount of this compound increased. This is clearly demonstrated in Fig. 2 which shows the yields of the photolysis products relative to the yield of 1,2-diphenylethanol. Figure 2 also shows that the relative amounts of the other main photolysis products remain constant after a period of time as long as the conversion is kept low.

The formation of 1,2-diphenylethane (5a) and 1,2-diphenylethanol (6a) in our reactions is particularly noteworthy. Indeed, 5a has previously been described as a photooxidation product of toluene, but only in the presence of a hydrogen abstractor like acetone,¹¹



- a R² = R³ = R⁴ = H
- b R² = CH₃, R³ = R⁴ = H
- c R² = R⁴ = H, R³ = CH₃
- d R² = R³ = H, R⁴ = CH₃

Scheme 1.

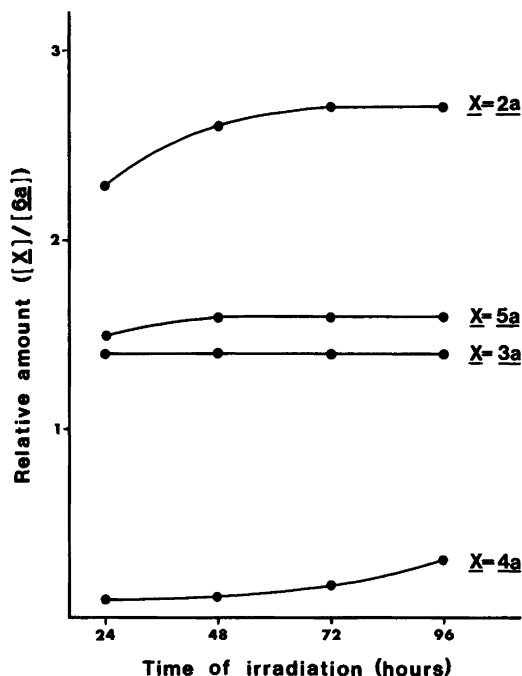
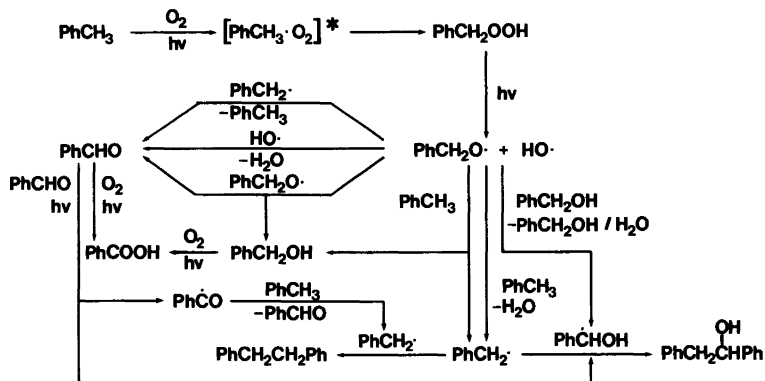


Fig. 2. The amount of oxidation products from photooxidation of toluene relative to 1,2-diphenylethanol (*6a*).

although the radiation energy at about 290 nm (~ 100 kcal/einstein) is sufficient to cleave a benzylic C–H bond (85 kcal/mol). Since triplet oxygen is not a good hydrogen abstractor, dimer *5a* conceivably results from secondary processes involving decomposition species of benzyl hydroperoxide (*vide infra*).

Alcohol *6a* has previously not been detected as a product from photooxidation of toluene. This is somewhat surprising considering the significant yield of the compound even after 24 h of irradiation. One tentative explanation for this escape of detection^{8,11} might be that *6a* decomposed in the gas chromatograph before reaching the detector. Thus, we found



Scheme 2.

Table 1. The amount of the main products from irradiation of toluene (1a) and various toluene solutions at room temperature for 72 h.

Entry	Sample	Yield/ %					Other products
		2a	3a	4a	5a	6a	
1	1a	36	17	3	23	14	7
2	1a ^a	23	31	28	2	2	14
3	1a+2a (25 %, w/v)	—	5	2	1	15	77
4	1a+5a (3 %, w/v)	42	22	2	—	18	16
5	1a+6a (0.3 %, w/v)	41	16	4	30	—	9
6	1a+6a (3 %, w/v)	31	6	9	25	—	29

^a A stream of air was passed continuously over the toluene surface during the irradiation.

that alcohol 6a survived neither an injector temperature in excess of 240 °C nor various contaminated columns.

The distribution of the photooxidation products from toluene was considerably influenced if the amount of certain compounds present during the irradiation was changed. The most notable changes were observed when oxygen was supplied in large excess; this resulted in a significant increase in the benzylic oxidation products 2a, 3a, and 4a and concomitantly, a drastic reduction in the amount of the dimerization products 5a and 6a (Table 1, entry 2). This clearly indicates that the precursors of 5a and 6a are consumed by oxygen and subsequently converted into oxygenated products, viz. 2a, 3a, and 4a. Addition of benzyl alcohol (2a) had similar effects; thus, the reactions demanding 2a directly (oxidation to benzoic acid) and indirectly (dimerization to 1,2-diphenylethanol) to form a product became more efficient at the expense of the competing reaction, i.e. dimerization of benzyl radicals to form 1,2-diphenylethane (Table 1, entry 3). It should be noted that compounds 3a–6a altogether constitute only 23 % of the product mixture in this case (Table 1) because a number of new products, originating from benzyl alcohol, was formed. The photochemical properties of benzyl alcohol are presently under study to elucidate the structures of these products. Addition of 1,2-diphenylethane (5a), on the other hand did not change the product composition (Table 1, entry 4); consequently, 5a is a final product which is not involved in any of the dynamic processes leading to products. Finally, it should be mentioned that photolysis of toluene which contains 1,2-diphenylethanol, leads to formation of more benzoic acid at the expense of benzaldehyde, although the total amount of these two compounds is not altered (Table 1, entries 5 and 6). The explanation of these puzzling results is not clear, but work in progress will hopefully illuminate the problem.

It should also be mentioned that when toluene was irradiated for a much longer time than 96 hours a variety of other products were formed in quantities. Although a thorough structure elucidation of these products has not been performed some of the mass spectra indicate that the compounds, e.g. benzoin, are photooxidation products from benzaldehyde, a compound known to be easily photooxidized to a variety of products.^{13–17}

Most of our results can be accommodated by the reaction scheme depicted in Scheme 2. On the basis of the work of Chien⁷ the initial step is supposed to involve the excitation of a toluene:oxygen charge transfer complex which is converted into benzyl hydroperoxide, perhaps via a 4-centre transition state.¹¹ Subsequent decomposition of this peroxide gives the benzyloxy and hydroxyl radicals which can yield the final products as outlined in Scheme

Table 2. Product distribution in photolysis of *o*-, *m*- and *p*-xylene at room temperature for 72 hours.

Compound	Yield/ %					Other products
	2	3	4	5	6	
<i>o</i> -Xylene (<i>Ib</i>)	28	7	3	18	4	40
<i>m</i> -Xylene (<i>Ic</i>)	30	30	11	11	7	11
<i>p</i> -Xylene (<i>Id</i>)	31	11	1	31	16	10

2. It should also be noted that benzyl and phenylhydroxymethyl radicals can be formed from benzaldehyde.^{13,15}

Pasternak and Morduchowitz found that the photochemical properties of various alkylbenzenes were similar to those of toluene.¹¹ For comparison we therefore studied the reactivity of the three xylenes under our experimental conditions. It turned out that photolysis under those conditions gave oxidation products analogous to those described for toluene. The relative product distribution of compounds 2–6 varied to some extent (Table 2), but with the exception of *o*-xylene these five products amounted to approximately 90 % of the reaction mixture. For *o*-xylene these five products constituted only 61 % of the product mixture which was more complex than those obtained from the *meta* and *para* isomers. This reduction in the total yield of compounds 2–6 seems to be due to side reactions which are facilitated by the proximity of the two methyl groups.¹⁸ Thus, one of the other products, formed in 5 % yield, was identified as phthalide on the basis of its mass spectrum.¹⁹ This compound has been observed as a product from vanadiumcatalyzed oxidation of *o*-xylene.^{20,21} Further studies of the photochemical properties of *o*-xylene are under way.

EXPERIMENTAL

The equipment employed has been described elsewhere.²² All chemicals used were of *p.a.* quality.

Photolysis. The photolyses were carried out at 35 °C in borosilicate vials (30 ml) with irradiation from a 400 W medium pressure mercury lamp. The vials were loosely covered with aluminium foil in order to avoid excessive evaporation, and arranged circumferentially around the lamp at a distance of 8.0 cm. When neat toluene was irradiated the product mixture was analyzed after 24, 48, 72, and 96 h; in all other cases the photolysis was terminated and the analysis performed after 72 hours of irradiation. The products were identified by comparison of retention times and mass spectra with those of authentic samples, and the amount was determined with 1,8-dimethylnaphthalene as internal standard.

In addition to photolysis (three parallels of each experiment) of neat toluene and neat *o*-, *m*- and *p*-xylene, the following samples were irradiated: highly aerated toluene, toluene under nitrogen, toluene and benzyl alcohol (75:25 %), toluene and 1,2-diphenylethane (97:3 %), and toluene and 1,2-diphenylethanol (97:3 % and 99.7:0.3 %).

Synthesis of oxidation products. All synthetic work was carried out at 20 °C in dry glassware under nitrogen.

1,2-Diarylethanes, general procedure. Grignard reagents were synthesized by adding 25 mmol of the appropriate benzyl chloride in 25 ml of dry ether to magnesium shavings (12.5 mmol) in 50 ml of dry ether. When necessary, a crystal of iodine was added to initiate the reaction. After generation of the Grignard reagent, a catalytic amount of CuBr was added to

the solution. The reaction mixture was stirred for 12 h, then poured on ice and extracted with ether (3×25 ml). The combined extracts were washed with water (2×20 ml) and dried with CaCl₂ (24 h) before evaporation of the solvent. The solid residue was recrystallized from ethanol.

1,2-Diphenylethane (5a) was synthesized from benzyl chloride in 60 % yield, IR²³, NMR²⁴, MS²⁵, m.p. 50.8 °C (lit.²⁶ 52.2 °C).

1,2-Di-o-tolylolethane (5b) was synthesized from *o*-methylbenzyl chloride in 16 % yield, IR, NMR,²⁷ MS *m/e* (rel. intensity): 210 (16), 105 (100), m.p. 66.3 °C (lit.²⁷ 65–66 °C).

1,2-Di-m-tolylolethane (5c) was synthesized from *m*-methylbenzyl chloride in 18 % yield, IR, NMR, MS.^{28,29}

1,2-Di-p-tolylolethane (5d) was synthesized from *p*-methylbenzyl chloride in 25 % yield, IR, NMR, MS,²⁸ m.p. 82.5 °C (lit.³⁰ 82 °C).

1,2-Diarylethanol, general procedure: The alcohols were synthesized by adding the appropriate benzaldehydes (25 mmol) in dry ether (50 ml) to stirred solutions of the corresponding benzylmagnesium chloride (25 mmol) in 50 ml of dry ether. Stirring was continued for 12 h and the reaction mixture was then worked up as described above and dried with MgSO₄ (24 h). The solvent was removed under reduced pressure before the residue was recrystallized from hexane.

1,2-Diphenylethanol (6a) was synthesized from benzylmagnesium chloride and benzaldehyde in 65 % yield, IR, NMR, MS,³¹ m.p. 64.7 °C (lit.²⁶ 67–68 °C).

1,2-Di-o-tolylolethanol (6b) was synthesized from *o*-methylbenzylmagnesium chloride and *o*-methylbenzaldehyde in 18 % yield, IR: 3600, 1175 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 1.90 (1H, br s, OH), 2.22 (3H, s, CH₃), 2.29 (3H, s, CH₃), 2.98 (2H, d, *J* 6.6 Hz, CH₂), 5.11 (1H, br t, CH), 7.10–7.62 (8H, m); MS [70 eV, *m/e* (% rel. int.)]: 226 (1, M⁺), 208 (3), 193 (3), 178 (3), 121 (76), 106 (100), 93 (44), 91 (42); m.p. 53.2 °C. Anal. C₁₆H₁₈O: C, H.

1,2-Di-m-tolylolethanol (6c) was synthesized from *m*-methylbenzylmagnesium chloride and *m*-methylbenzaldehyde in 15 % yield, IR: 3600, 1150 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 2.19 (1H, s, OH), 2.32 (3H, s, CH₃), 2.34 (3H, s, CH₃), 2.87–2.96 (2H, m, AB part of an ABX system), 4.58–4.89 (1H, m, X part of an ABX system), 7.03–7.24 (8 H, m); MS [70 eV, *m/e* (% rel. int.)]: 226 (0.5, M⁺), 208 (1), 193 (1), 178 (1), 121 (51), 106 (100), 93 (33), 91 (32). The compound was an oil which was not pure enough for elemental analysis.

1,2-Di-p-tolylolethanol (6d) was obtained in 21 % yield from *p*-methylbenzylmagnesium chloride and *p*-methylbenzaldehyde, m.p. 76.6 °C (lit.⁵ 77 °C); IR: 3595, 1170 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 1.92 (1H, d, *J* 2.7 Hz, OH), 2.31 (3H, s, CH₃), 2.33 (3H, s, CH₃), 2.94 (2H, dd, *J* 1.7 and 6.5 Hz, CH₂), 4.72–4.89 (1H, m, CH), 7.08–7.30 (8H, m); MS [70 eV, *m/e* (% rel. int.)]: 226 (0.2, M⁺), 208 (5), 193 (2), 178 (2), 121 (73), 106 (100), 93 (27), 91 (31). Anal. C₁₆H₁₈O: C, H.

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