

PHOTOCHEMICAL OXIDATION AND DIMERIZATION OF ALKYL BENZENES.
SELECTIVE REACTIONS OF THE ALKYL SIDE GROUPS

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Abstract: Irradiations of alkylbenzene compounds in an oxygen atmosphere result exclusively in oxidation reactions, while in a less oxidative environment dimerization processes predominate. Under all conditions studied, the reactions took place only at one benzyl position.

Recently there has been an interest in photooxidation of alkylbenzene derivatives related to air pollution, whereby harmful oxidants are produced by nitrogen oxides and alkylbenzene compounds.¹ Similarly, some industrial research efforts have been directed towards the prevention of undesirable photooxidations by the development of new photostabilizers and antioxidants.² However, less attention has been directed towards the application of photooxidations in synthetic organic chemistry. We now wish to report new results of alkylbenzene photoconversions which demonstrate high versatility and good selectivity under various oxidation atmospheres. Noteworthy is the mildness of the photochemical reaction conditions, in contrast to rather drastic ones for similar catalytic oxidations.³

Monosubstituted alkylbenzenes (methyl, ethyl, i-propyl, n- and s-butylbenzenes) as well as multisubstituted derivatives (di-, tri- and tetra-methylbenzenes) were irradiated at $\lambda > 280\text{nm}$ and $\lambda > 330\text{nm}$ in the presence and absence of acetone (acetone/alkylbenzene 0.5 mole ratio).⁴ Two main processes were observed: oxidation and dimerization solely dependent on reaction atmosphere.

The photooxidations conducted by bubbling oxygen through the medium yielded mainly the corresponding alcohols and aldehydes (ketones), irregardless of the presence of acetone. Irradiation in sealed non deaerated tubes, so that after the initial oxygen was consumed the photolysis proceeded essentially in a nitrogen atmosphere, resulted in photodimerization to form bibenzyl derivatives⁵. This reaction occurred only in the presence of acetone. The following scheme demonstrates product profile and ratio observed from neat alkylbenzene (20mM) irradiations at $\lambda > 280\text{nm}$. All reactions were run under identical conditions with the photoconversion ratio listed relative to toluene (actual photoproduct yield 0.15%).

SCHEMEOXIDATIONPRODUCTS
(PRODUCT RATIO, %)PHOTOCONVERSION
(RELATIVE RATES)

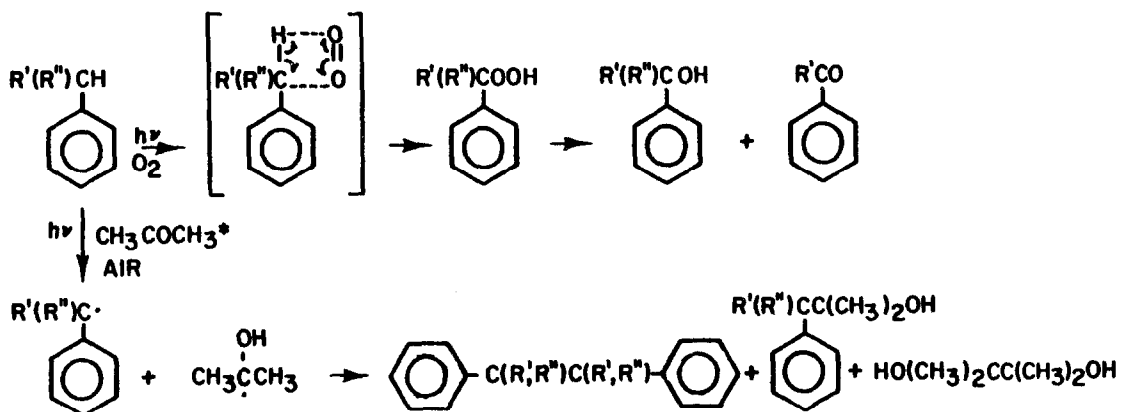
$R_1 = R_2 = R_3 = R_4 = H$ $R_3 = CH_3, R_1 = R_2 = R_4 = H$ $R_2 = R_4 = CH_3, R_1 = R_3 = H$ $R_1 = R_3 = R_4 = CH_3, R_2 = H$	25 26 29 42	75 74 71 58
		1.0 5.2 3.3 2.2
$R' = CH_3, R'' = H$ $R' = CH_3, R'' = CH_3$ $R' = C_2H_5, R'' = CH_3$ $R' = C_3H_7, R'' = H$	53 100 100 58	47 — — 42
		16.7 19.9 8.9 10.1

DIMERIZATION*

$R_1 = R_2 = R_3 = R_4 = H$ $R_3 = CH_3, R_1 = R_2 = R_4 = H$ $R_2 = R_4 = CH_3, R_1 = R_3 = H$ $R_1 = R_3 = R_4 = CH_3, R_2 = H$	57 53 55 52	1.0 1.9 1.6 1.4
$R' = CH_3, R'' = H$ $R' = CH_3, R'' = CH_3$ $R' = C_2H_5, R'' = CH_3$ $R' = C_3H_7, R'' = H$	65 62 63 53	11.5 10.0 7.1 6.8

* Acetone adducts were also detected in these reactions.

The mechanism of these processes seems to involve an initial reaction at the benzyl hydrogen. This reaction is believed to be a charge transfer 4-center reaction in the case of the photooxidations and a hydrogen abstraction reaction in the photodimerizations. Without an oxygen atmosphere or in the absence of hydrogen abstraction catalysts no reaction takes place, even though adequate energy is absorbed by the system to accomplish benzyl C-H scission ($E_{280-300\text{nm}} = 102-95\text{kcal/mol}$ vs $E_{\text{PhCH}_2-\text{H}} = 85\text{kcal/mol}$). In high oxygen concentration, photooxidation to yield only oxygenated products occur with or without acetone (no alkylbenzene dimers or acetone adducts were detected), precluding a hydrogen transfer process. Direct photooxidation of these alkylbenzenes at $\lambda > 330\text{nm}$ above their absorption range indicates the existence of additional absorption bands extending above 330nm, which is reasonably attributed to charge transfer complexes between alkylbenzenes and oxygen.⁶ Moreover, substantial amounts of benzylperoxides were observed in these less energetic irradiations, whereas only trace quantities accompanied the more energetic $\lambda > 280\text{nm}$ irradiations. These results led us to conclude that the photooxidation process involves an excited charge transfer complex to form benzylperoxides via a 4-center reaction which later dissociate photochemically mainly in the low λ region to yield alcohols and aldehydes (ketones) by a free radical mechanism. Similar photooxidations at $\lambda > 400\text{nm}$ with and without methylene blue (MB) resulted in the same product yields of oxygenated compounds. These results indicate that even in the presence of MB (a singlet oxygen sensitizer) the excitation of the charge transfer complex is the determinant factor in the overall reaction irrespective of a singlet oxygen presence.⁷ In an air atmosphere photodimerization of the alkylbenzenes proceed only in the presence of acetone or similar hydrogen abstraction agents which further react to form photoaddition adducts (2-butanone and acetophenone demonstrate the same hydrogen abstraction catalysis under these conditions).



Finally, the high selectivity seems to be the most impressive feature of these photoconversions. All mono alkylbenzene compounds with up to C_4 open chain alkyl substituents underwent the same course of photoreaction at the

α -position to the aromatic ring. Similarly, multisubstituent derivatives^{7,8} with up to four groups selectively reacted only at one methyl group.⁹ No attack on the aromatic ring was detected under these circumstances with any of the alkylbenzene compounds.

Comparing mono and multi derivatives with the same number of alkyl carbons indicates that the size rather than the number of the alkyl side groups increases the photoconversion rate either by affecting the absorption efficiency of the alkylbenzene oxygen charge transfer complexes, or by forming more stable radical intermediates. Yet, steric hindrance seems to decrease the photoformation rate of the more bulky products both in mono and multi alkylbenzene compounds.

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4. Irradiations were carried out in an immersion well assembly with absorption sleeves (pyrex $\lambda > 280\text{nm}$, uranium salt $\lambda > 330\text{nm}$, soda lime $\lambda > 400\text{nm}$) and a 450 Watt medium pressure mercury-vapor lamp.
5. Products were identified and measured by GC and GCMS. Alkylbenzenes were irradiated for 24 hours at room temperature. Control experiments indicate that these reactions do not proceed in the absence of light.
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9. This exclusiveness was further verified when p-methylbenzylalcohol (oxidation product of p-xylene) was exposed to photooxidative conditions yielding only the p-methylbenzaldehyde and the corresponding acetal. No attack on the second methyl group was detected.

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