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PHOTOSUBSTITUTION OF BENZYL HYDROGENS WITH ALCOHOLIC MOIETIES. SELECTIVE FORMATION OF ALKYLBENZENE CARBINOLS

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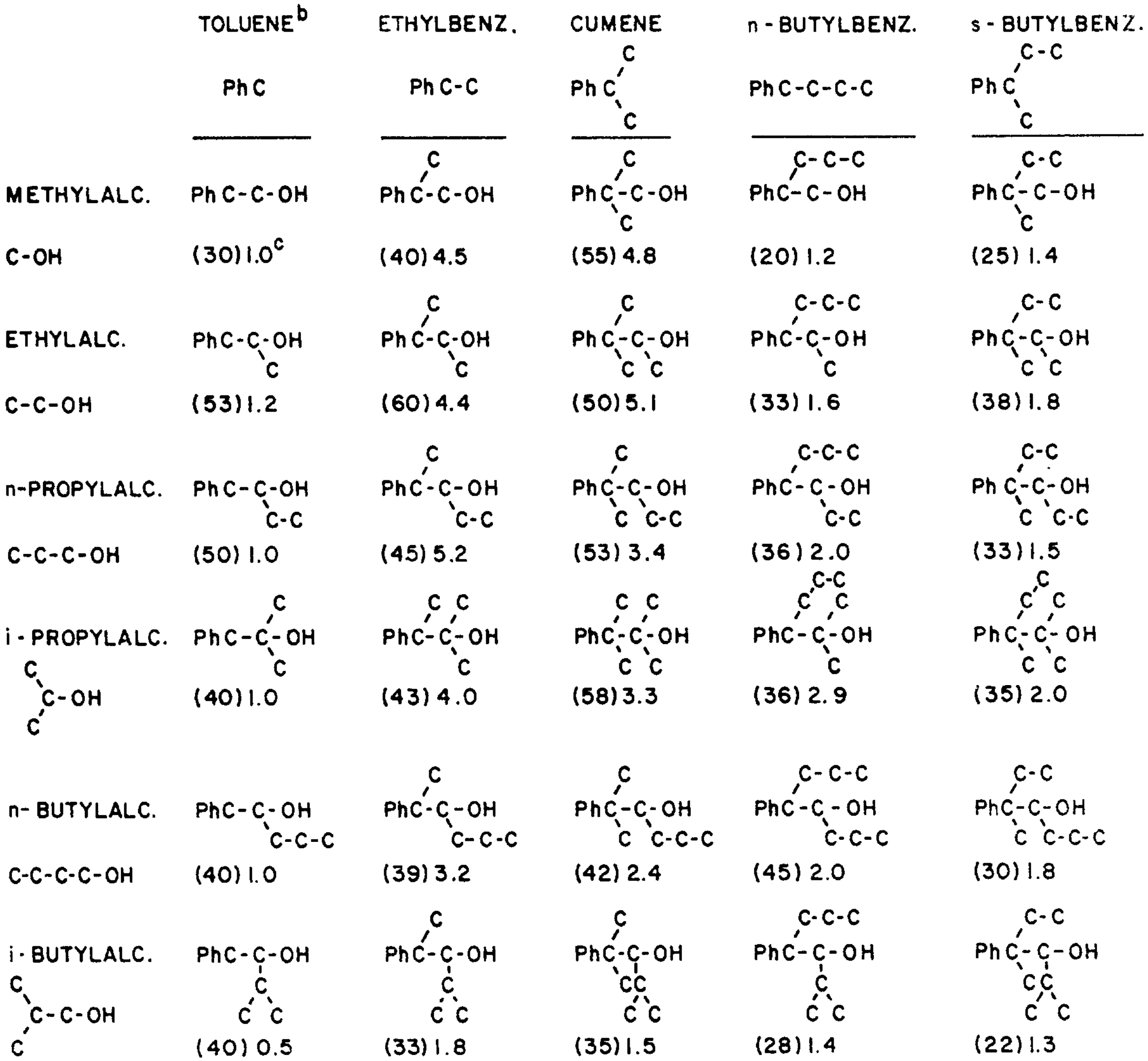
Abstract: Irradiations of alkylbenzene compounds with various alcohols in an air atmosphere, resulted in substitution of the benzyl hydrogens with alcoholic moieties in a very selective mode.

Recently we have been investigating some photoconversion processes of alkylbenzene compounds which were accompanied to some extent by photoaddition of the acetone catalyst to the alkyl side chains.[1] Similar photochemical formations of carbinols by addition of both ketones and aldehydes to allyl methylene groups or benzyl type protons have been explored for some time.[2] However, no efforts have been directed toward photochemical substitution of activated methylene hydrogens with alcoholic moieties to form homologous carbinol compounds. The following communication describes such a photosubstitution process, which resulted in the replacement of benzyl hydrogens with -CH(R)OH (R=alkyl group) fragments in a very selective mode.

To establish the generality of this photosubstitution reaction, various mono-substituted alkylbenzenes (methyl, ethyl, i-propyl, n- and s-butylbenzenes) as well as multisubstituted derivatives (di-, tri- and tetra-methylbenzenes) were irradiated in alcoholic media in the presence of acetone. Similarly, six aliphatic alcohols with up to C_4 alkyl chains (methyl, ethyl, n- and i-propyl, n- and i-butylalcohols) were also investigated in order to reveal the alcohol's role in the reaction course. Photosubstitution was the main process observed under these circumstances, forming the appropriate alkylbenzene carbinols.

Alkylbenzenes (10mM) and acetone (10mM) were irradiated in a neutral alcoholic medium (50mM) at $\lambda > 280$nm[3] to yield mainly alkylbenzene carbinol products and smaller amounts of alkylbenzene and alcohol dimers accompanied by their acetone photoaddition adducts.[4]

SCHEME[a]



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[a] Carbon skelton structures are given for the sake of simplicity.

[b] Di-,tri-and tetra-methylbenzenes reacted similarly to toluene only at one methyl group.

[c] (30) = % in product mixture, 1.0=photoconversion rate.

The alkylbenzene carbinol structures are depicted in the attached scheme. All reactions were run under identical conditions with the photoconversion ratio listed relative to toluene and methanol photosubstitution reaction yield (actual photoproduct yield 0.1%).

The mechanism of the photosubstitution reactions seems to be similar to that of the photodimerization process[1]. The reaction proceeds only in the presence of acetone, even though adequate energy is absorbed by the system (E 280-300nm = 102-95kcal/mol) to accomplish both $PhCH_2$-H bond scission (85kcal/mol) or $HOCH_2$-H bond dissociation (95.9kcal/mol)[5]. The initial step is apparently hydrogen abstraction by excited acetone at the benzyl position of the alkylbenzenes, and α to the hydroxylic group in the alcohol molecules. Analysis of the minor products in the reaction mixtures revealed the existence of these two hydrogen abstraction modes to yield radicals, which further react to form bibenzyl derivatives (alkylbenzene dimers) and pinacols (alcohol dimers)[6] accompanied by acetone photoaddition adducts[1,7]. A bimolecular combination of alkylbenzene and alcohol radicals accounts for alkylbenzene carbinol formation.

Similar to other alkylbenzene photoreactions (oxidation and dimerization)[1] steric hindrance in the more bulky alkylbenzenes decrease both the total photoconversion rate and the alkylbenzene carbinol yield. In addition, both reaction medium and atmosphere affect the reaction course. Higher alcohol concentrations (100mM) increase alkylbenzene carbinol formation, to some extent. Oxygen saturation quenched all non oxidative processes, yielding only oxidation products of the alkylbenzenes.

To summarize, these photosubstitution reactions, albeit their low photoconversion rates relatively to other alkylbenzene photoconversions (oxidation and dimerization)[1] demonstrate high selectivity. All mono alkylbenzene compounds with up to C_4 open chain alkyl substituents underwent photosubstitution at the α -position to the aromatic ring[8]. With multisubstituent derivatives (e.g. xylene, mesitylene and durene) the reaction only afforded one substituted product irrespective of the number of benzyl hydrogens. No attack on the aromatic ring was detected under these circumstances with any of the alkylbenzene compounds . The aliphtic alcohol molecules also demonstrated high selectivity in the reaction course as all of them reacted exclusively at the α position to the hydroxyl group.

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REFERENCES and NOTES

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2. A. Schonberg in "Preparative Organic Photochemistry," Springer-Verlay New York Inc., 1968, p. 198 and references therein.

3. Irradiations were carried out in an immersion well assembly with pyrex absorption sleeve ($\lambda > 280$nm) and a 450 Watt medium pressure mercury-vapor lamp.

4. 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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6. R. E. Balsells and A. R. Frasca, Tetrahedron, 38, 2525 (1982).

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8. Supporting evidence for exclusive benzyl hydrogen reactivity under these circumstances was provided by the fact that t-butylbenzene was inert to similar irradiations.

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