



Photochemical Dichloromethylation of Methylarenes

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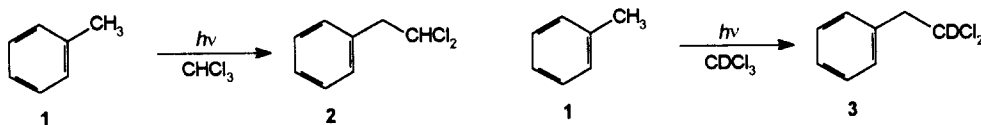
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Abstract: The irradiation of methylarenes in chloroform gave in good yields the corresponding dichloromethyl analogues. Copyright © 1996 Elsevier Science Ltd

Recently we reported that the irradiation of alkylbenzenes in chloroform in the presence of oxygen gave the corresponding carboxylic acid in high yields.¹ In that paper, we justified the obtained products considering that CHCl_3^* , CCl_3^* , or CHCl_2^* can be formed during the irradiation *via* an electron transfer process, or *via* a homolytic fission of the C-H or C-Cl bond.

In this communication we want to report our results obtained irradiating alkylbenzenes in chloroform without the presence of oxygen. In fact, whether CHCl_3^* or CCl_3^* or CHCl_2^* can react with aromatic compounds.

In a typical experimental procedure the alkylbenzene (200 mg), dissolved in chloroform (100 ml), was irradiated in an immersion apparatus with a 125 W high-pressure mercury arc (Helios-Italquartz) surrounded by a quartz water-jacket in a nitrogen atmosphere. After 2 h the mixture was washed with 0.1 M potassium bicarbonate. The organic layer was washed with a saturated solution of NaCl and then dried over Na_2SO_4 . Removal of the solvent yielded a crude product that was chromatographed on silica gel. The elution with *n*-hexane gave pure products (Table 1).



All the substrates tested showed the same trend. We used as substrate some methylnaphthalenes and 3- and 4-methylanisole (Table 1). The same reaction can be performed with good yields using as substrate ethylbenzene (Table 1, entry 2). On the contrary, the use of other alkylbenzenes did not allow us to obtain interesting products. We used *n*-propyl, *n*-butyl, and *n*-pentylbenzene but we obtained the dichloromethylation

Table 1 - Photochemical Reactions of Alkylarenes with Chloroform.

Entry	Substrate	Irradiation time (h)	Product	Yields (%) ^a
1	Toluene	2	(2,2-Dichloro-1-ethyl)benzene	85
2	Ethylbenzene	2	(1,1-Dichloro-2-propyl)benzene	72
3	1-Methylnaphthalene	4	1-(2,2-Dichloro-1-ethyl)naphthalene	55
4	2-Methylnaphthalene	4	2-(2,2-Dichloro-1-ethyl)naphthalene	53
5	3-Methylanisole	4	3-(2,2-Dichloro-1-ethyl)anisole	60
6	4-Methylanisole	4	4-(2,2-Dichloro-1-ethyl)anisole	65

a) All the yields refer to isolated chromatographically pure products.

products without selectivity. In fact, we obtained a complex mixture of products where the CHCl_2 group was bound to all the methylenes on the side chain of the substrate.

The above described reaction seems to be related to the known photo-Reimer-Tiemann reaction.²⁻⁴ In that case, phenols, irradiated in chloroform, gave, probably through an electron transfer process, the corresponding dichloromethyl derivatives. However, the obtainment of product mixtures when alkylbenzenes were used as substrates does not seem in agreement with an electron transfer process able to generate the radical cation of the aromatic compound, and, then, after the loss of a proton, a benzyl radical, selectively. Therefore, the reaction can start through the homolytic fission of the C-H or the C-Cl bond. The formation of CCl_3^\bullet via the homolytic fission of the C-H bond seems to be in agreement with the observed formation of hexachloroethane as a by-product in some reactions. Furthermore, when toluene (1) was irradiated in CDCl_3 , the deuterated product 3 was obtained. This datum seems to be in agreement with a mechanism involving the homolytic fission of the C-H or the C-Cl bond in chloroform to give CCl_3^\bullet or CHCl_2^\bullet . These radicals can interact with the aromatic compounds, through a hydrogen abstraction reaction, to give a radical on the side chain of the aromatic compound that then reacts with CDCl_3 to give the product.

In conclusion, we have described an efficient photochemical dichloromethylation of methylarenes that can be a useful method to introduce a C_1 -synthon in the side chain of a methylarene.

References

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