Photochemically Induced Nucleophilic Aromatic Substitution

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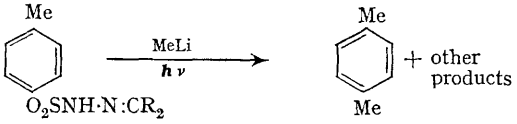
DURING investigations on the reaction of toluene-*p*-sulphonyl hydrazones with alkyl-lithium reagents,[1] we observed a unique example of a photochemically induced nucleophilic aromatic substitution. Upon reaction with an excess of methyl-lithium in the presence of u.v. light (2537 Å), the toluene-*p*-sulphonylhydrazones of camphor and acetone yield a significant amount of *p*-xylene (45%) in addition to small amounts of toluene and ethylbenzene as well as the expected aliphatic hydrocarbons. The reaction does not occur in the absence of light or in the presence of black light.



Other examples of photochemically induced nucleophilic aromatic substitutions in which a mono-anionic group is displaced have been reported,[2] but there have been no reports of a dianion acting as a leaving group under these conditions. However, a recent communication describes the ground state displacement of sulphite anion from sodium toluene-*p*-sulphonate with sodium hydrazide.[3]

Since toluene-*p*-sulphinate salts are produced in the dark reaction of the hydrazones with various bases, the photochemical reaction was attempted with sodium toluene-*p*-sulphinate and methyl-lithium. Again the major product obtained from this reaction was *p*-xylene. The sulphoxylate anion (SO_2^{2-}) is reported to be stable as its disodium salt.[9] In addition, toluene does not give *p*-xylene under equivalent reaction conditions. Therefore this process represents the first example of photochemically induced nucleophilic displacement of a dianionic species from an aromatic ring.

Butyl-lithium reacts photochemically with sodium toluene-*p*-sulphinate to give *p*-n-butyltoluene (10%).

The reaction of methyl-lithium with sodium toluene-*p*-sulphonate in the presence of high-energy light yields only a small yield (4·5%) of the substitution product. However, the light does, in fact, have an effect on the efficiency of the reaction, since in its absence the yield of *p*-xylene is reduced to <1%. Thus it appears that under photochemical conditions the sulphoxylate anion is a better leaving group than the sulphite anion.

We thank the National Science Foundation for financial support.

(*Received, February* 27*th*, 1968; *Com.* 238.)

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