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AROMATIC $S_{RN}1$ REACTIONS STIMULATED BY SUNLIGHT - PHENYLATION OF DIMSYL ANION

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Bunnett and his coworkers[1] have successfully carried out many nucleophilic substitution reactions on simple halobenzenes under stimulation either by ammoniated electrons or light (around 300-380 nm). These reactions according to them proceed via $S_{RN}1$ mechanism[2]. Very recently Bunnett[3] reported a variety of solvents that can be used for carrying out $S_{RN}1$ reactions which include DMF, DMSO, HMPT and Sulfolane among many others. We also reported the use of aqueous t-butyl alcohol as a possible solvent for $S_{RN}1$ reactions[4].

Because of the high temperatures that prevail in Madras during summer it is decided to carry out organic reactions under the stimulation by sunlight. We report here that $S_{RN}1$ reactions can be initiated by sunlight. We have successfully phenylated the anion of dimethylsulfoxide in DMSO solvent. The temperature in Madras when these reactions were carried out varied between 38-40°C (100-104°F). Halobenzenes are used as substrates. The anion of DMSO was made by utilising $NaNH_2$ as base in DMSO.

Details on a number of reactions are given in Table 1. The reaction mixture is homogeneous before exposure to light. The products obtained are mostly benzyl methyl sulfoxide and unreacted halobenzenes. The yields are by glpc and the products are characterised by glpc retention times with known samples. In all runs, glpc shows the presence of another compound (maximum yield 5%) which may be 1,1-diphenyl dimethylsulfoxide. Similar diphenylated derivatives were found to be formed in the phenylation of acetone enolate anion[5]. No attempts were made to identify this compound, as the yields are very low. In spite of assiduous search, no aniline was found to be formed (possibly by the reaction of excess NH_2^- ion with the phenyl radical).

Out of the three possible mechanisms available, two are easily rejected while the third one explains our results satisfactorily. The possibility that this is a light-induced S_NAr reaction is rejected because this reaction exhibits radical characteristics, such as inhibition by oxygen. The possibility that phenyl radicals are generated by a homolytic cleavage of halobenzenes (equation 1) is rejected, because under identical conditions, the homolysis of iodobenzene requires long exposure to sunlight; other halobenzenes still longer exposure[6].

$$PhX \xrightarrow{\text{Sunlight}} Ph\cdot + X\cdot \tag{1}$$

We sketch Scheme I to explain the formation of the products; this in its general sense is a $S_{RN}1$ mechanism.

SCHEME I

$$\text{Electron donor} + PhX \longrightarrow [PhX]^{\dot{-}} + \text{residue} \tag{2}$$

$$[Ph\text{-}X]^{\dot{-}} \longrightarrow Ph\cdot + X^- \tag{3}$$

$$Ph\cdot + CH_3SOCH_2^- \longrightarrow [Ph\text{-}CH_2\text{-}SO\text{-}CH_3]^{\dot{-}} \tag{4}$$

$$[Ph\text{-}CH_2\text{-}SOCH_3]^{\dot{-}} + Ph\text{-}X \longrightarrow Ph\text{-}CH_2SOCH_3 + [PhX]^{\dot{-}} \tag{5}$$

Termination steps

Sunlight is necessary for provoking the reaction as suggested by run 1. Halide ions are released according to this scheme which are identified qualitatively. The qualitative order of reactivity of halobenzene follows $I > Br > Cl$, as indicated by the time required for the reaction. This order parallels the earlier report of Bunnett[5]. Oxygen inhibits the reaction as is shown in run 5. It possibly interferes with propagation of the reaction chain by trapping the phenyl radicals, or by abstracting electrons

TABLE 1

Reactions of halobenzenes with dimsyl anion in DMSO stimulated by sunlight

Run	Substrate	Substrate concn.(M)	Dimsyl anion (M)	Time of exposure to sunlight (mts.)	Results Products & yields[a]
1.	Ph-Br	0.1028	0.211	Nil	Ph-Br (98)
2.	Ph-I	0.0897	0.211	20	Ph-I (8); Ph-CH_2SOCH_3(87); b (5)
3.	Ph-Br	0.0952	0.211	60	Ph-Br(18); Ph-CH_2SOCH_3(78); b(4)
4.	Ph-Cl	0.0900	0.211	120	Ph-Cl (24); Ph-CH_2SOCH_3(74); b(2)
5.	Ph-Br[c]	0.0952	0.211	100	Ph-Br (79)

a. The products are identified by glpc and the percentages are by glpc unless otherwise stated; no internal standard is used.

b. The product may be 1,1-diphenyl dimethylsulfoxide; no attempts were made to identify it as the yields are very low.

c. The reaction is carried out in the presence of oxygen.

from the radical anion, $[Ph\text{-}CH_2\text{-}SOCH_3]^{\dot{-}}$, forming $O_2^{\dot{-}}$. The identity of electron source in equation 2 is not clear. A good possibility is the demsyl anion itself. Further research is planned on this line.

This is the first paper to our knowledge that describes the radical anion intermediates in reactions carried out under stimulation by sunlight. This is also the first report on the phenylation of sulfoxide anions in the $S_{RN}1$ sense. Phenylation of other sulfoxide and related anions are in progress.

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