

ON THE REACTIVITY OF DIMSYL ANION WITH ARYL RADICALS

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ABSTRACT - We demonstrated that 1-iodoadamantane, iodobenzene and 2-chloroquinoline do not react with dimsyl anion in DMSO, in sharp contrast with results previously reported.

Recently we described the photostimulated reaction of 1-haloadamantanes with several nucleophiles in liquid ammonia by the  $S_{RN}1$  mechanism of nucleophilic substitution.<sup>1-3</sup> However, carbanionic nucleophiles, such as acetone enolate ion, cyanomethyl anion, etc. failed to react with 1-adamantyl radicals in liquid ammonia.<sup>2</sup> The lack of reactivity of carbanionic nucleophiles with 1-adamantyl radicals contrasts with the behaviour of aromatic  $\sigma$  radicals which reacted very easily with these and other carbanionic nucleophiles.<sup>4</sup>

We are studying the photostimulated reaction of 1-haloadamantanes with different nucleophiles in DMSO as solvent by the  $S_{RN}1$  mechanism and found that under irradiation, 1-iodoadamantane reacts with diphenylphosphide and benzenethiolate ions giving good yields of the substitution product by the  $S_{RN}1$  mechanism.<sup>5</sup> On the other hand, we also found that 1-adamantyl radicals failed to react with carbanionic nucleophiles such as the acetone enolate anion.<sup>5</sup>

It has been reported that dimsyl anion in DMSO reacts with halobenzenes by irradiation to give good yields of benzylmethylsulfoxide by the  $S_{RN}1$  mechanism<sup>6</sup> so we decided to study the photostimulated reactions of 1-iodoadamantane and iodobenzene with dimsyl anion in DMSO, but no reaction occurred in sharp contrast with results previously reported under similar experimental conditions.<sup>6</sup>

Electrochemical reduction of haloarenes to arenes and halide ions is a two electron reduction. However, quantitative yields of arenes are not always obtained. In a detailed study of electrolysis of 4-bromobenzophenone in DMSO several other products besides benzophenone were formed. It was suggested that some products arise from fragmentation of the p-benzoylbenzylmethylsulfoxide radical anion intermediate proposed.<sup>7</sup>

Other examples of the fragmentation of radical anion intermediates formed by the coupling of radicals with nucleophiles are the radical anion formed by coupling of phenyl radicals with a cyanomethyl anion<sup>3</sup> or alkane thiolate ions.<sup>9</sup> But when these nucleophiles couple with an aromatic

$\sigma$  radical with lower LUMO than phenyl radicals, such as 1-naphthyl radicals, only the substitution products are formed without fragmentation of the radical anion intermediate.<sup>10</sup> If dimethyl anion couples with the phenyl radical to produce a radical anion which fragments, it is possible in principle to avoid the fragmentation with a radical with lower LUMO than phenyl radical such as 2-quinolyl radicals.<sup>10</sup> In the photostimulated reaction of 2-chloroquinoline with dimethyl anion we did not find any reaction under our experimental conditions with it.

We conclude that if there is a coupling of phenyl, 4-benzoylphenyl and 2-quinolyl radicals with dimethyl anion, a radical anion which fragments is produced. This fragmentation process is a termination step in the  $S_{RN}1$  mechanism of the photostimulated reaction. These results agree with those previously reported electrochemical studies<sup>7</sup> and with the well known tendency of DMSO to produce methyl radicals upon dissociative electron capture,<sup>11</sup> and by the action of light on carbanions in DMSO,<sup>12</sup> but they are opposite to those in the previous report.<sup>6</sup>

## REFERENCES AND NOTES

- Rossi, R.A., Palacios, S.M., Santiago, A.N., *J.Org.Chem.*, **47**, 4654 (1982).
- Palacios, S.M., Santiago, A.N., Rossi, R.A., *J.Org.Chem.*, **49**, 4609 (1984).
- Palacios, S.M., Alonso, R.A., Rossi, R.A., *Tetrahedron*, in press.
- For reviews see: a) Bunnett, J.F., *Acc.Chem.Res.*, **11**, 413 (1978).  
b) Rossi, R.A., de Rossi, R.H., "Aromatic Substitution by the  $S_{RN}1$  Mechanism", (1983), ACS Monograph 178.
- Bornancini, E.R., Alonso, R.A., Rossi, R.A., unpublished results.
- Rajan, S., Muralimohan, *Tetrahedron Lett.*, 433 (1978).
- M'Halla, F., Pinson, J., Savéant, J.M., *J.Electroanal.Chem.*, **89**, 347 (1978).
- a) Bunnett, J.F., Gloor, B.F., *J.Org.Chem.*, **38**, 4156 (1973).  
b) Rossi, R.A., de Rossi, R.H., Pierini, A.B., *J.Org.Chem.*, **44**, 2662 (1979).
- a) Bunnett, J.F., Creary, X., *J.Org.Chem.*, **40**, 3740 (1975).  
b) Rossi, R.A., Palacios, S.M., *J.Org.Chem.*, **46**, 5300 (1981).
- For a review see: Rossi, R.A., *Acc.Chem.Res.*, **15**, 164 (1982).
- a) Chung, Y.J., Nishikida, K., Williams, F., *J.Phys.Chem.*, **78**, 1882 (1974).  
b) Cooper, T.K., Walker, D.C., Gillies, H.A., Klassen, N.V., *Can.J.Chem.*, **51**, 2195 (1973).
- Tolbert, L.M., *J.Am.Chem.Soc.*, **102**, 3531, 6808 (1980).

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