One-electron Transfer in Reactions of the Perfluoro-t-butyl Anion with Triarylmethyl Halides

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Summary Free triarylmethyl radicals are formed in reactions of triphenylmethyl chloride and tri-(*p*-nitrophenyl)methyl bromide with perfluoroisobutene and caesium fluoride.

The perfluoro-t-butyl anion (I), generated from $(CF_3)_2$-$C{=}CF_2$ and CsF in polar aprotic solvents, reacts readily with Ph_3CCl (II) giving compounds (III) in high yield.[1]

$$\underset{}{(CF_3)_2C{=}CF_2} \xrightarrow{F^-} \underset{(I)}{(CF_3)_3C^-} \xrightarrow{(II)} \underset{(III)}{p\text{-}(CF_3)_3{\cdot}C_6H_4{\cdot}CHPh_2}$$

An e.s.r. investigation of this process in diglyme showed the formation of free trityl radicals, the concentration of which varied with time in the case of the excess of (II) as shown in curve 1 in the Figure. The general reaction sequence is as in the Scheme.

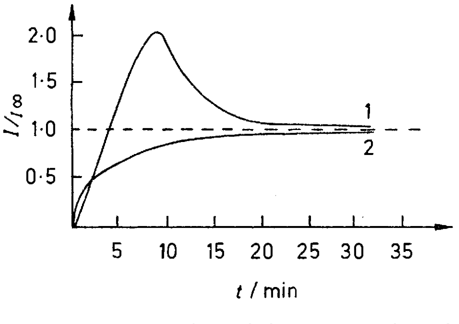
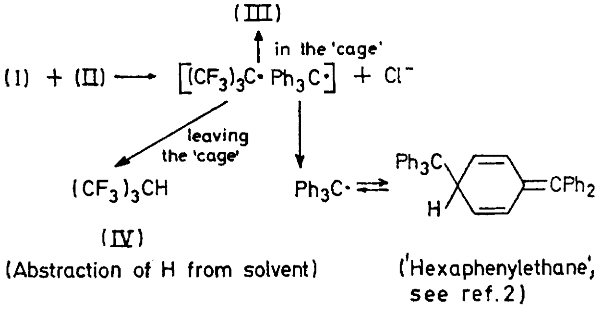


Figure. *Variation with time of the concentration of the radicals* $Ph_3C\cdot$ (*curve* 1) *and* $(p\text{-}O_2N{\cdot}C_6H_4)_3C\cdot$ (*curve* 2) *in the reactions of* $(CF_3)_3C^-Cs^+$ *with* Ph_3CCl *and* $(p\text{-}O_2N{\cdot}C_6H_4)_3CBr$, *respectively.* (*I is current concentration of the radical;* I_∞ *is concentration extrapolated at* $t \rightarrow \infty$.



Scheme

One-electron transfer is also observed in the reaction of (I) with $(p\text{-}O_2NC_6H_4)_3CBr$ (V), radicals $(p\text{-}O_2NC_6H_4)_3C\cdot$ and $(CF_3)_3C\cdot$ being formed, which both leave the 'cage.' Tris-(trifluoromethyl)methane (IV) is the only organofluorine product. The concentration variation with time of the corresponding free triarylmethyl radical is shown by curve 2 in the Figure, (V) being in excess. With excess of anion (I), the free triarylmethyl radicals were rapidly destroyed, presumably as a result of further reactions with (I). In a separate experiment it was shown that 'hexaphenylethane' reacts with (I) giving a very complex mixture of products, including (III) and Ph_3CH, identified by g.l.c. and t.l.c. The main reaction leading to (III), even with (I) in excess, is, however, the geminate recombination of the radicals in the 'cage' as shown in the Scheme.

The one-electron transfer stage in nucleophilic substitution reactions is a general problem.[3] The reactions discussed are, as far as we know, the first proved examples of this stage for perfluoroalkyl carbanions. The oxidation of (I) by the $F_2N\cdot$ radical was suggested earlier[4] to occur in the reaction of $(CF_3)_2C{=}CF_2$ + KF with N_2F_4 but this supposition could not be verified experimentally in view of the forcing conditions necessary and the explosion hazards of the reaction.

(*Received, 28th February* 1973; *Com.* 279.)

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