The Preparation of Capto-dative Radicals by Homosolvolysis

By HARI SINGH and JOHN M. TEDDER
(*Department of Chemistry, The University, St. Andrews, Fife* KY16 9ST, *Scotland*)

Summary Alkyl bromides R^1R^2CHBr in which R^1 is an electron acceptor and R^2 is an electron donor, when treated with di-t-butyl nitroxide, undergo extremely rapid homosolvolysis to yield unreactive 'capto-dative' free radicals.

VIEHE and his co-workers have developed the concept of 'capto-dative' free radicals.[1,2] These are radicals in which the carbon atom with the unpaired electron is flanked by both an electron donor group and an electron acceptor group. Viehe has shown that radicals of this type are very unreactive, but not persistent, because unlike persistent radicals they can combine with each other. If the concept of a 'capto-dative' radical is correct, *i.e.* if the presence of adjacent donor and acceptor groups greatly stabilises a radical, then an alkyl halide, which on homosolvolysis[3,4] yields a 'capto-dative' radical, should undergo homosolvolysis with particular ease. We report that we have strong evidence that this is so.

The Table shows the compounds which have been treated with a deficiency of di-t-butyl nitroxide (DTBNO) in benzene solution and for which the disappearance of the nitroxide signal in the e.s.r. spectrum has been monitored. The first two compounds (**1**) and (**2**) with a single acceptor group do not undergo detectable homosolvolysis when treated with DTBNO at 60 °C for three weeks. Compound (**3**) (diethyl bromomalonate), with two acceptor groups, reacts slowly with DTBNO but after two weeks at 60 °C all the starting nitroxide has been consumed and a new nitroxide radical (A) has been formed. The three compounds (**4**), (**5**), and (**6**) all yield 'capto-dative' radicals on homosolvolysis. These reactions are very rapid, so much so that all the nitroxide has been consumed before the reaction mixture can be inserted into the cavity of the e.s.r. spectrometer. When nitrosobenzene is added to the alkyl bromide before the nitroxide, the 'capto-dative' radicals which are insufficiently reactive to abstract a hydrogen atom from the unchanged nitroxide, or even to add to 2-methyl-2-nitrosopropane, add to nitrosobenzene to form a new nitroxide, (B).

$$\mathrm{BrCH(CO_2Et)_2 + Bu^t_2NO\cdot \rightleftharpoons \dot{C}H(CO_2Et)_2 + Bu^t_2NOBr}$$

$$\mathrm{\dot{C}H(CO_2Et)_2 + Bu^t_2NO\cdot \rightarrow CH_2(CO_2Et)_2 + Bu^tNO + CH_2{=}CMe_2}$$

$$\mathrm{\dot{C}H(CO_2Et)_2 + Bu^tNO \rightarrow (EtO_2C)_2CHN(\dot{O})Bu^t}$$

(A)

$$\mathrm{MeO\dot{C}HCO_2Me + PhNO \rightarrow (MeO_2C)(MeO)CHN(\dot{O})Ph}$$

(B)

TABLE. The homosolvolysis of some alkyl bromides.

Compound		Radical type[a]	Rate of homolysis	Hydrogen abstraction from nitroxide	Couples with PhNO
$BrCH_2CO_2Et$	(**1**)	A	Nil	—	—
$BrCH(Me)CO_2Et$	(**2**)	A	Nil	—	—
$BrCH(CO_2Et)_2$	(**3**)	A + A	2 weeks at 60 °C	As fast as is formed	—
$BrCH(OMe)CO_2Me$	(**4**)	A + D	Instantaneous	Nil	Yes
$BrCH(OMe)COPh$	(**5**)	A + D	Instantaneous	Nil	Yes
$BrCH(OMe)COMe$	(**6**)	A + D	Instantaneous	Nil	Yes
$BrCH_2OMe$	(**7**)	D	7 h at room temp.	Nil	Yes

[a] A = acceptor; D = donor.

Bromomethyl methyl ether (**7**), possessing just a donor group, undergoes fairly rapid homosolvolysis, not as rapid as the incipient 'capto-dative' compounds (**4**), (**5**), and (**6**), but very much more rapidly than the compounds containing one adjacent (or even two adjacent) acceptor groups. Unfortunately, dimethoxybromomethane (MeOCHBrOMe), *i.e.* with two donor groups, could not be prepared pure.[5]

The results we have obtained show that a bromine atom attached to a carbon atom flanked by both electron-donor and -acceptor groups undergoes extremely rapid homosolvolysis. A single donor group, although much less activating than the combined 'capto-dative' groups, enhances homosolvolysis more than two acceptor groups. This may be a polar effect, for although the reaction is clearly a homolysis, electron-withdrawing acceptor groups would be expected to resist the solvolysis of an electronegative halogen atom.

All the reactions were carried out using degassed solutions. The reactants were in the molar proportions nitroxide : bromide 1 : 10 and the co-solvent was benzene, except for 1-bromo-1-methoxypropan-2-one (**6**), where chloroform was the co-solvent. The e.s.r. spectra were observed using a Decca X3 spectrometer.

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