Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Homolytic displacement at a metal centre by the dimethylamino radical

ALWYN G. DAVIES, S.C.W. HOOK, and B.P. ROBERTS
Department of Chemistry, University College London, 20 Gordon Street, London W.C. 1 (Great Britain)

(Received February 12th, 1970)

Organometallic reactions which involve bimolecular homolytic substitution (S_H2) at a metal centre appear to comprise an important mechanistic type, and by stereochemical, kinetic, or ESR methods, reactions have been established which follow equation (1) where X is an oxygen-[1-3] or sulphur-centred radical[4,5] and M represents a variety of non-transition metals from Group I–V.

$$X\cdot + MR_n \rightarrow XMR_{n-1} + R\cdot \qquad (1)$$

No reactions of this type appear to be known, however, where X· is a nitrogen-centred radical. We have now established that dimethylamino radicals, $Me_2N\cdot$, generated photolytically or, in all probability, thermally from tetramethyltetrazene, will bring about the S_H2 displacement of an alkyl radical from an alkylborane (and from certain other organometallic compounds) forming a dimethylaminoborane. In the case of tributylborane, this is represented by equation (3).

$$Me_2N{-}N{=}N{-}NMe_2 \xrightarrow{h\nu} 2Me_2N\cdot + N_2 \qquad (2)$$

$$Me_2N\cdot + BBu_3 \rightarrow Me_2N{-}BBu_2 + Bu\cdot \qquad (3)$$

Ultraviolet irradiation at room temperature of a mixture of tributylborane (0.033 moles) and tetramethyltetrazene (0.021 moles) ultimately caused complete disappearance of the ^1H NMR signal of the tetrazene, and the appearance of the signal due to the Me_2N group of dibutyl(dimethylamino)borane. Only a trace of dimethylamine, which would form a complex with residual tributylborane, was formed. No reaction occurred at room temperature in the absence of irradiation. Distillation of the photolysis product gave pure dibutyl(dimethylamino)borane[6,7] (68% yield on BBu_3) and n-octane.

When a mixture of tributylborane and tetramethyltetrazene was photolysed in the cavity of an ESR spectrometer (*cf.* refs. 2*b* and 2*c*), the spectrum of the n-butyl radical was observed. The best spectra were obtained with both reagents 1*M* in toluene at −81°, when $a_\alpha^H = 22.1$G, $a_\beta^H = 29.3$G, $a_\gamma^H = 0.75$G.

A weaker signal due to the butyl radical was observed when the tetrazene was photolysed in the presence of dibutyl(dimethylamino)borane and although, when the tetrazene was omitted the signal was still detectable, it was extremely weak and it appears probable that a second butyl group can be displaced by a dimethylamino radical to give butylbis(dimethylamino)borane. Under similar conditions the ESR spectra of the appropriate displaced alkyl radicals were observed when tri-s-butylborane, oxybis(di-n-butylborane) ($Bu_2B{-}O{-}BBu_2$), tri-s-butylboroxine [$(s\text{-}BuBO)_3$] triethylantimony, or triethylaluminium replaced the tri-n-butylborane. However, the signals were not so intense, nor does the method appear to be so generally applicable as when di-t-butyl peroxide is used in place of the tetrazene.

The ultraviolet spectrum[8] of the tetrazene in the presence of an excess of triethylaluminium indicated that complete complexation had occurred, in agreement with previous work[9]. During photolysis, the signal of the ethyl radical was overlain by another, more intense signal, which was selectively broadened at lower temperatures. No complexation between the tetrazene and tributylborane was indicated by ultraviolet spectroscopy; although a small amount of complex may have been present at the higher concentrations used in the ESR experiments, most of the radiation must still have been absorbed by the free tetrazene.

We propose, however, that a small amount of complexation is responsible for the thermal reaction which occurs between tetramethyltetrazene and tributylborane. When a benzene solution of tetrazene (1 *M*) and borane (2 *M*) was refluxed under nitrogen, the NMR spectrum showed that the tetrazene reacted to form an equivalent amount of dibutyl(dimethylamino)borane (67% conversion in 16.5 h), whereas the tetrazene is stable in the absence of the borane★. This reaction is analogous to the decomposition of 2-tetrazenes catalysed by acids or acid anhydrides, which has recently been shown to occur homolytically[10].

The facile S_H2 displacement of alkyl radicals from organoboranes by dimethylamino radicals, coupled with the fact that an alkyl radical will rapidly extract chlorine from a dialkylchloramine, suggests that the reported reaction of dialkylchloramines with trialkylboranes[11] may involve a free radical chain process. This possibility is being investigated.

REFERENCES

1 (*a*) A.G. Davies and B.P. Roberts, *J. Chem. Soc., B*,(1969) 317 and earlier papers; (*b*) K.U. Ingold, *Chem. Commun.*, (1969) 911; (*c*) A.G. Davies, K.U. Ingold, B.P. Roberts and R. Tudor, unpublished work.
2 (*a*) R. Tudor, unpublished results; (*b*) A.G. Davies and B.P. Roberts, *Chem. Commun*, (1969) 699; (*c*) A.G. Davies and B.P. Roberts, *J. Organometal. Chem.*, 19 (1969) P17.
3 P.J. Krusic and J.K. Kochi, *J. Amer. Chem. Soc.*, 91 (1969) 3942, 3944.
4 A.G. Davies and S.C.W. Hook, *J. Chem. Soc., B*, in the press.
5 A.G. Davies and B.P. Roberts, unpublished results.
6 J.K. Ruff, *J. Org. Chem.*, 27 (1962) 1020.
7 K. Niedenzu, D.H. Harrelson, W. George and J.W. Dawson, *J. Org. Chem.*, 26 (1961) 3037.
8 W.E. Bull, J.A. Senton and L.F. Andreith, *J. Amer. Chem. Soc.*, 80 (1958) 2516.
9 N. Fetter and B. Bartocha, *Canad. J. Chem.*, 40 (1962) 342.
10 S.F. Nelsen, R.B. Metzler and M. Iwamura, *J. Amer. Chem. Soc.*, 91 (1969) 5103.
11 J.G. Sharefkin and H.D. Banks, *J. Org. Chem.*, 30 (1965) 4313.

★The thermal reaction of tetramethyltetrazene with the aluminium compounds R_3Al, R_3Al,NMe_3, or H_3Al,NMe_3 has been shown to yield products containing an $Me_2N{-}Al$ bond. Homolytic substitution by the dimethylamino radical may be inferred in these reactions, but this possibility does not appear to have been considered[9].