Bromodemetallation of β-Methoxyphenethylthallium(III) Diacetate and β-Methoxyphenethylmercury(II) Acetate with Copper-(I) and -(II) Bromide, Direct Evidence for Alkyl Radicals in Bromodethallation by the Spin Trapping Technique

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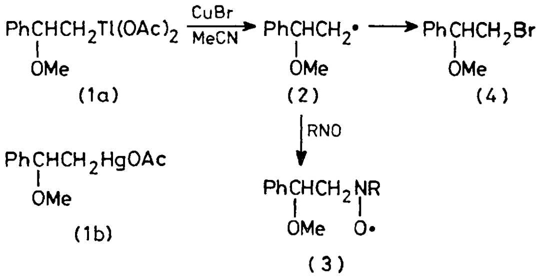
Summary Free alkyl radicals have been observed by a spin trapping technique in the bromodethallation of β-methoxyphenethylthallium diacetate with copper(I) bromide; the species have been shown to be involved in the main course of the reaction.

Halogenodemetallation of organic compounds with various copper-(II) or -(I) salts is of current interest.[1–4] In some cases free alkyl radical species have been proposed as intermediates. We now report the first example of the direct observation of an alkyl radical by the spin trapping technique[5] in a halogenodemetallation, namely, in the reaction of the thallium salt (**1a**) with copper(I) bromide in acetonitrile.



In the reaction of (**1a**) and copper(I) bromide in deoxygenated acetonitrile at 50 °C for 5 min in the presence of the spin trap perdeuterionitrosodurene, followed by immediate measurement of the e.s.r. spectrum at −35 °C, a spectrum consisting of two sets of doublets (0·311 and 1·44 mT) further split into a 1 : 1 : 1 triplet (1·32 mT), *g* factor 2·0059, was observed. The same spectrum was obtained during photolysis of a mixture of β-methoxyphenethyl bromide (**4**), triethylsilane, di-t-butyl peroxide, and the spin trap in acetonitrile at −35 °C. No e.s.r. signal was observed in a control experiment between (**1a**) and perdeuterionitrosodurene without copper(I) bromide. The *g* factor of 2·0059 and the magnitude of the nitrogen splitting constant of 1·32 mT are reasonable for an adduct of the alkyl radical and the nitrosodurene.[6] Two sets of large doublets (1·44 and 0·311 mT) show that the alkyl radical is primary and that internal rotation around the methylene–nitrogen bond of the nitroxide is hindered, suggesting that a bulky group is attached to the carbon atom of the methylene group.[7] We attribute this spectrum to the nitroxide [**3**; $R = 2,3,5,6\text{-}C_6H(CD_3)_4$]. When the same system was examined with Bu^tNO as spin trap, a spectrum consisting of a 1·51 mT nitrogen triplet further split into three sets of doublets (1·19, 0·71, and 0·08 mT) was observed (*g* 2·0061). This spectrum is ascribed to (**3**; $R = Bu^t$), the smallest doublet being assigned to the methine proton.

TABLE. Reaction of (**1a**) (1 mmol) with CuBr in acetonitrile[a]

CuBr (mmol)	Additive (mmol)	Yield (%) (4)	(5)	(6)
4	—	83	0	6
4	PhNO (4)	32	–[b]	–[b]
4	4-t-Butylcatechol (4)	3	–[b]	–[b]
4	Bubbling O_2	18	–[b]	–[b]
1	—	33	9	14

[a] Acetonitrile 30 ml, at reflux for 2 h, in the presence of atmospheric oxygen. [b] Not determined.

In order to examine whether the detected radical is involved in the main reaction course, several experiments were carried out with the addition of various radical scavengers (see Table). Addition of nitrosobenzene, 4-t-butylcatechol, or oxygen decreased the yield of (**4**) considerably. In the reaction with equimolar amounts of (**1a**) and copper(I) bromide, the amounts of 1-methoxyphenylethane (**5**) and styrene (**6**) increased with a corresponding decrease in the amount of (**4**). This may be due to a decrease in the extent of bromine transfer to the alkyl radical compared to the case where 4 mol. equiv. of copper (I) bromide were used, (**5**) probably being formed from the alkyl radical by hydrogen abstraction. These data clearly show that the main course of the reaction proceeds by a radical mechanism.

The mercury analogue (**1b**) of (**1a**) hardly reacted at all with copper(I) bromide, whereas it reacted smoothly with copper(II) bromide.† Mercury–copper exchange giving an alkyl–copper compound followed by C–Cu bond fission to give an alkyl radical has been proposed as a mechanism for bromodemercuration.[3,4] We examined the (**1b**)–$CuBr_2$ system by a spin trapping technique using Bu^tNO as spin trap in acetonitrile as solvent. This system did not give a spectrum analogous to that observed in the (**1a**)–CuBr system, but only weak triplet signals (0·81 mT) with a *g* factor of 2·0067 were observed.‡ We therefore suggest that in the bromodemercuration of (**1b**) with copper(II) bromide, the steady-state concentration of alkyl radicals may be quite low or the radicals may not be completely free, in contrast to the radicals involved in the bromodethallation of (**1a**) with copper(I) bromide.

We thank Dr. G. van Koten of University of Amsterdam for helpful discussions and Drs. S. Terabe and R. Konaka of Shionogi and Co. Ltd. for perdeuterionitrosodurene. This work was supported in part by a grant from the Ministry of Education, Japan.

(*Received, 4th August* 1977; *Com.* 812.)

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† Yields of (4) under the various conditions were as follows: 2% (CuBr, MeCN, reflux, 20 h), 1% (CuBr, KBr, dimethylformamide, 90 °C, 5 h), 22% ($CuBr_2$, MeCN, 20 °C, 2 h), and 60% ($CuBr_2$, KBr, dimethylformamide, 90 °C, 5 h).

‡ The abnormally small nitrogen splitting constant and the somewhat large *g*-factor of 2·0067 suggest (ref. 5) that the observed radical is an adduct of an acyl radical and Bu^tNO, although acyl radicals are not expected to be involved in the main course of the reaction.

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