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

Preliminary communication

An ESR study of arsenanyl radicals, $As^{\bullet}X_4$, in solution

ALWYN G. DAVIES, D. GRILLER and B.P. ROBERTS

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H OAJ (Great Britain)

(Received March 9th, 1972)

The ESR spectra of some phosphoranyl radicals, $P^{\bullet}X_4$, [t-BuOP$^{\bullet}$Me$_n$H$_{3-n}$[1] and t-BuOP$^{\bullet}$(OEt)$_3$[2]] have recently been observed for the first time in solution, but the corresponding arsenic species have never been reported. We now report the detection by ESR spectroscopy of a series of arsenanyl radicals, $As^{\bullet}X_4$.

When a mixture of di-t-butyl disulphide and trimethylarsine in isopentane was irradiated with UV light in an ESR cavity, the spectrum shown in the figure was observed. This spectrum is assigned to the radical t-BuSAs$^{\bullet}$Me$_3$, and the four lines (of equal intensity but unequal width) are produced by coupling with the ^{75}As nucleus (100% abundance; $I = \frac{3}{2}$); no further fine structure was resolved.

$$\text{t-BuSSBu-t} \longrightarrow 2\ \text{t-BuS}^{\bullet} \qquad (1)$$

$$\text{t-BuS}^{\bullet} + \text{AsMe}_3 \longrightarrow \text{t-BuSAs}^{\bullet}\text{Me}_3 \qquad (2)$$

Similar spectra were obtained from the photolysis of other disulphides or of alkanethiols in the presence of trimethylarsine, and the results are collected in Table 1. The hyperfine splittings and *g*-values were calculated from the observed line positions and the microwave frequency using the Breit–Rabi formula.

TABLE 1

SPECTROSCOPIC PARAMETERS FOR TRIMETHYL(ALKYLTHIO)ARSENANYL RADICALS, RSAs$^{\bullet}$Me$_3$, IN ISOPENTANE

Source of RS$^{\bullet}$	*R*	*Temp. (°)*	*a(^{75}As) (G)*	*g*
Disulphide	Me	–97	651.9	2.017
Disulphide	Et	–100	651.3	2.016
Disulphide	t-Bu	–100	648.4	2.018
Thiol	t-Bu	–100	649.5	2.018
Thiol	n-Bu	–100	653.0	2.016

UV irradiation of a mixture of di-t-butyl peroxide and trimethylarsine in isopentane gave a strong spectrum of the methyl radical, and a 1/1/1/1 quartet whose intensity increased with the duration of the photolysis. We tentatively assign this spectrum to the dimethyl(di-t-butoxy)arsenanyl radical, $Me_2As^{\bullet}(OBu\text{-}t)_2$ [$a(^{75}As)$ 766.7 G; g 2.010 at −80°], formed by reactions (3) and (4)[★].

$$t\text{-}BuO^{\bullet} + AsMe_3 \longrightarrow t\text{-}BuOAsMe_2 + Me^{\bullet} \tag{3}$$

$$t\text{-}BuO^{\bullet} + t\text{-}BuOAsMe_2 \longrightarrow (t\text{-}BuO)_2As^{\bullet}Me_2 \tag{4}$$

The behaviour of the corresponding phosphorus systems presents an interesting comparison, and supports the identification of the arsenanyl radicals.

Although no intermediate phosphoranyl radical could be detected when di-t-butyl disulphide was photolysed in the presence of trialkyl-phosphines or -phosphites, we were able to detect the radicals $MeSP^{\bullet}\text{-}n\text{-}Bu_3$ [$a(^{31}P)$ 635.5 G; g 2.009] and $MeSP^{\bullet}(OEt)_3$ [$a(^{31}P)$ 748.1 G; g 2.008] during photolysis of mixtures of dimethyl disulphide and the appropriate phosphorus compound in isopentane at −93°.

When di-t-butyl peroxide was photolysed in the presence of triethylphosphine an ESR spectrum (the intensity of which increased with the duration of the photolysis) was observed in addition to that of the ethyl radical[3]; we assign this spectrum to the radical $(t\text{-}BuO)_2P^{\bullet}Et_2$ [$a(^{31}P)$ 705.1 G; g 2.003 at −80° in cyclopentane]. This contrasts with the behaviour of trimethylphosphine under similar conditions when the spectrum of $t\text{-}BuOP^{\bullet}Me_3$ was detected[1].

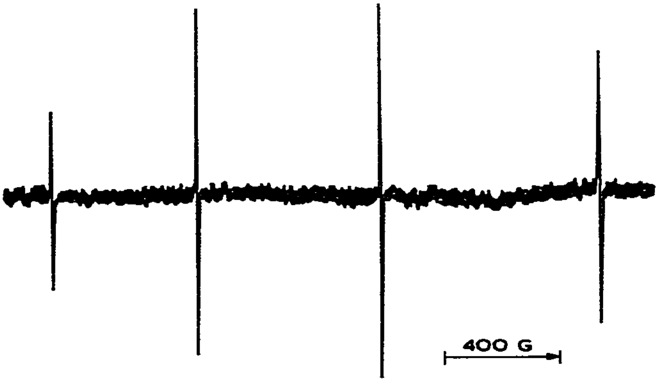

Fig. 1. ESR spectrum of the radical $Me_3As^{\bullet}SBu\text{-}t$ in isopentane at −100°.

Thiols react readily with trialkyl-phosphines and -phosphites by a radical chain process to give alkane and phosphorus(V) sulphide, by reactions (5) and (6), (X = R′ or OR′)[4].

[★] When azomethane was photolysed in the presence of trimethylarsine no arsenanyl radicals were detected, although a strong spectrum of the methyl radical was obtained.

$$RS^{\bullet} + PX_3 \longrightarrow R^{\bullet} + SPX_3 \qquad (5)$$

$$R^{\bullet} + RSH \longrightarrow RS^{\bullet} + RH \qquad (6)$$

Trialkyl-stibines and -bismuthines also react homolytically with alkanethiols, but now the alkylthiyl radical displaces an alkyl radical from the metal (eqns. 7 and 8; M = Sb or Bi)[5].

$$RS^{\bullet} + MR'_3 \longrightarrow RSMR'_2 + R'^{\bullet} \qquad (7)$$

$$R'^{\bullet} + RSH \longrightarrow R'H + RS^{\bullet} \qquad (8)$$

In contrast, tributylarsine could not be induced to react with thiols under similar conditions, even in the presence of a source of free radicals[6]. If reactions (5) and (7) involve, respectively, the β-scission and α-scission of an intermediate of the type $RSM^{\bullet}X_3$, the unreactivity of the arsine probably reflects the reluctance of the arsenanyl radical $RSAs^{\bullet}R'_3$ to undergo any type of scission, apart from the loss of $RS^{\bullet}$.

REFERENCES

1 J.K. Kochi and P.J. Krusic, *J. Amer. Chem. Soc.*, 91 (1969) 3944; *Chem. Soc. Spec. Pub.*, 24 (1970) 147.
2 A.G. Davies, D. Griller and B.P. Roberts, *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 738.
3 R.W. Dennis, unpublished work.
4. J.I.G. Cadogan, *Advan. Free Radical Chem.*, 2 (1968) 203.
5 A.G. Davies and S.C.W. Hook, *J. Chem. Soc. B*, (1970) 735.
6 S.C.W. Hook, unpublished work.