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

Preliminary communication

Bimolecular homolytic substitution by tert-butoxy radicals at metal atoms

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(Received August 4th, 1969)

It is now established that the autoxidation of organometallic compounds involves the rapid bimolecular homolytic substitution by an alkylperoxy radical at a metal M (eq.1; *e.g.* M = Mg, Zn, Cd, B, Al)[1].

$$\mathrm{ROO^{\bullet} + MR \rightarrow ROOM + R^{\bullet}} \qquad (1)$$

We have recently shown that a similar S_H2 displacement can be brought about by tert-butoxy radicals (eq.2; M = B), and that the alkyl radicals which are liberated can be observed by ESR spectroscopy[2].

$$\mathrm{t\text{-}BuO^{\bullet} + MR \rightarrow t\text{-}BuOM + R^{\bullet}} \qquad (2)$$

We have now established by the same ESR technique that tert-butoxy radicals will react in the same way with a variety of other organometallic compounds, as shown in Table 1; similar results (M = B, Al, Ga, P) have recently been reported independently by Kochi and Krusic[3].

The tert-butoxy radicals were usually generated by photolysis of di-tert-butyl peroxide, in the presence of the organometallic compound at room temperature[2]. Alternatively, when the organometallic compound itself was photosensitive (*e.g.* Me_2Cd and Et_3Bi), the tert-butoxy radicals were generated by the thermolysis of di-tert-butyl hyponitrite at *ca.* 80°.

Signals of approximately equal intensity were obtained for the radicals derived from trialkylboranes, R_3B, and the corresponding alkylboronic anhydrides, $(RBO)_3$; for the tert-butyl radical from tert-butylboronic anhydride, eight of the ten first-order lines could be observed, each showing the appropriate second-order fine structure.

Triethylaluminium could not be used because it reacted vigorously directly with di-tert-butyl peroxide at room temperature. By the photolytic method, diethylbutoxyaluminium gave initially a strong spectrum of the ethyl radical, but, after about 30 min, this was replaced by a more complex unidentified spectrum.

Buckler[4] reported that the thermal decomposition of di-tert-butyl peroxide in the presence of tributylphosphine at 130° gave tert-butyl dibutylphosphinite (Bu_2POBu-t) and tributylphosphine oxide (Bu_3PO) in the ratio of 4/1; implying that, under these conditions, the S_H2 displacement at phosphorus occurs four times as fast as the β-scission of the intermediate phosphoranyl radical, $Bu_3(t\text{-}BuO)P^{\bullet}$. By the photolytic technique, we obtained only the spectrum of the ethyl radical from triethylantimony and triethylbismuth, and

TABLE 1

REACTION OF TERT-BUTOXY RADICALS WITH ORGANOMETALLICS

RM	Source of t-BuO•[a]	Solvent[b]	R• observed by ESR
Et_2Zn	*hν*	T	Et•
Me_2Cd	Δ	B	Me•
Bu_3B	*hν* and Δ	O or P	Bu•
s-Bu_3B	*hν*	O or P	Bu^{s}•
$(BuBO)_3$	*hν*	P	Bu•
(s-$BuBO)_3$	*hν*	P	Bu^{s}•
(t-$BuBO)_3$	*hν*	P	Bu^{t}•
Me_3Al	*hν*	O	Me•
Et_2AlOBu	*hν*	O	Et•
Et_3Sb	*hν* and Δ	O or P	Et•
Et_3Bi	Δ	B	Et•

[a] *hν*, photolytic; Δ, thermolytic.
[b] T, tetrahydrofuran; B, t-butylbenzene; O, isooctane; P, di-tert-butyl peroxide.

there was no evidence for the formation of the t-butylradical. Kochi[3] has similarly detected only radicals R• from the photolysis of di-tert-butyl peroxide in the presence of the phosphines R_3P, and Adams' work[5] on the same system can be reinterpreted in similar terms.

Photolysis of di-tert-butyl peroxide in tetrahydrofuran gave the spectrum of the 1-tetrahydrofuryl radical, but an 0.5*M* solution of diethylzinc showed only the ethyl radical. Similarly an 0.84*M* solution of tributylborane in cyclohexane showed initially only the butyl radical, and the spectrum of the cyclohexyl radical became apparent only after most of the organoborane had reacted. This demonstrates that the rate of the S_H2 reaction by the tert-butoxy radical at zinc or at boron, under these conditions, must be much greater than that for the abstraction of a hydrogen atom from tetrahydrofuran or from cyclohexane respectively.

Butyl radicals could also be observed during the photolysis of biacetyl in the presence of tributylborane in benzene, supporting Grotewold and Lissi's suggestion that (in the gas phase), acetyl radicals will bring about an S_H2 reaction at boron[6]. Kochi[3] has observed by ESR the radical R• formed by displacement by the butylthio radical at phosphorus in a phosphine, R_3P, and many other examples of S_H2 displacements at metal centres can be inferred from information in the literature. Clearly this type of process will turn out to be of major importance in organometallic chemistry.

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