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Free-Radical Intermediates in the Reactions of Organolithium Reagents with Alkyl Halides[1]

Sir:

It is recognized that the reaction of numerous organometallic reagents with alkyl halides can proceed by electron transfer (reaction 1).[2] Among the experimental observations supporting these conclusions are

$$R^-M^+ + R'X \longrightarrow R\cdot + R\cdot' + MX \qquad (1)$$

(a) the formation of 2,3-dimethyl-2,3-diphenylbutane in the presence of cumene,[3] (b) the formation of trityl radical from trityl chloride,[4] (c) nuclear polarization in the olefinic products[5] or in the alkyl halide,[6] and (d) the formation of the expected coupling and disproportionation products of R· and R·'.[3,7] Evidence for radical intermediates is particularly compelling for the reactions of organolithium reagents,[3–7] even though an analysis of the reaction products is complicated by the occurrence of metal–halogen interchange,[8] a process that may itself occur *via* radical intermediates.

We now present direct evidence for radical formation in the reaction between alkyl halides and alkyllithium reagents. We have found that free radicals are easily detected by esr spectroscopy in the reaction between organolithium reagents and bromine, iodine, alkyl bromides, or alkyl iodides in benzene solutions containing ether or tetramethylethylenediamine at a concentration approximately equal to that of the lithium reagent.[9] Detection of radicals was possible in a standard flow system approximately 0.03 sec after mixing solutions of the alkyl halide (0.2 *M*) and lithium reagent (0.1 *M*). The reaction of *n*-butyllithium with ethyl, *n*-propyl, *n*-butyl, *n*-octyl, isopropyl, or *t*-butyl iodide furnished the spectrum of the alkyl radical derived from the iodide (Figure 1). Free radicals are therefore detected before an appreciable amount of metal–halogen interconversion has occurred. In the reaction with bromine or iodine the *n*-butyl radical was detected from *n*-butyllithium only after the color of the halogen had been discharged, and the radical observed quite likely reflects the subsequent reaction between the organolithium reagent and the first-formed alkyl halide.

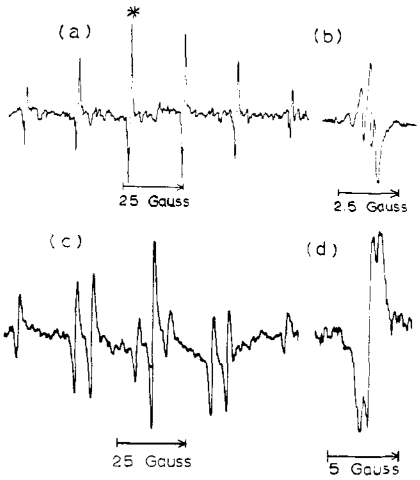

Figure 1. (a) *t*-Butyl radical prepared by the reaction of *n*-butyllithium with *t*-butyl iodide. Only the central six lines of a ten-line pattern are shown, $a^H = 22.8$ G; (b) second-order splitting of the starred peak in (a); relative intensities are roughly 1:8:27:48:42 (see R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962)); (c) *n*-butyl radical prepared by the reaction of *n*-butyllithium with *t*-butyl bromide, $a_{C-1}^H = 21.7$, $a_{C-2}^H = 27.6$ g; (d) central line of (c) under higher resolution, $a_{C-3}^H \approx 0.5$ G.

Isobutyl and *t*-butyl bromides, ethylene dibromide, or benzyl chloride reacted with *n*-butyllithium to give only the esr spectrum of the *n*-butyl radical (Figure 1); *sec*-butyllithium and ethyl bromide yielded a mixture of the two radicals.

The results obtained from our studies of the reaction of alkyl halides with organolithium reagents suggest a simple rationalization in terms of reactions 1–4.[10] We presume that the ether or amine is required to increase the rate of reaction 1 and therby increase the steady-state concentration of radicals.

$$R\cdot + R'X \longrightarrow RX + R\cdot' \qquad (2)$$

$$R\cdot' + RLi \longrightarrow R'Li + R\cdot \qquad (3)$$

$$R\cdot + R\cdot' \longrightarrow \text{alkanes and alkenes} \qquad (4)$$

The effect of the cosolvent may be to dissociate the polymeric organolithium reagent by functioning as a Lewis base. Alternately, the cosolvent may be more intimately involved in the electron-transfer reaction.[9] The nature of the radicals that we have observed seems to be correlated by the relative rates of the atom-transfer reactions 2 and 3. When X = iodine, R = *n*-butyl, and R' = ethyl, propyl, butyl, etc., the relative rates of reactions 2 and 3 lead to $[R\cdot']/[R\cdot] > 20$. On the other hand, when X = bromine or chlorine, either R· or a mixture of R· and R·' was observed. These results apparently reflect the fact that k_2 is much greater for alkyl iodides than for alkyl bromides or chlorides.[11] The factors controlling

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(1) Electron Transfer Processes. X. This work was supported by a grant from the National Science Foundation.

(2) See G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964), for pertinent references.

(3) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

(4) J. Schmidlin, *Chem. Ber.*, **43**, 1137 (1910); F. S. D'yachkovskii, N. N. Bubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **123**, 870 (1958).

(5) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(6) A. R. Lepley, *Chem. Commun.*, 64 (1969); A. R. Lepley and R. L. Landau, *J. Amer. Chem. Soc.*, **91**, 748 (1969); H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969).

(7) R. C. Fuson, *ibid.*, **48**, 2681 (1926); C. S. Marvel, F. D. Hager, and D. D. Coffman, *ibid.*, **49**, 2323 (1927); F. S. D'yachkovskii and A. E. Shilov, *Russ. Chem. Rev.*, **35**, 300 (1966); D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963).

(8) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

(9) See J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965); **88**, 5668 (1966).

(10) Additional intermediates such as $RI\cdot^-$, $R_nLi_{n-1}\cdot$, RIR, can be imagined. Our results do not require these intermediates since the radicals we observe have hfsc similar to those reported for radicals formed by the radiolysis of alkanes: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(11) For example, the methyl radical at 65° abstracts the halogen atom from methyl iodide 7000 times more readily than from methyl bromide: F. W. Evans and M. Szwarc, *Trans. Faraday Soc.*, **57**, 1905 (1961). The difference in energy of activation for attack on iodine or bromine is approximately one-half the difference in bond dissociation energies: M. Szwarc, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 91.

the rate of reaction 3, or even the enthalpy change in reaction 3, are not easily approximated. The stabilities of the organometallic reagents $(RLi)_n$ are involved as well as the stabilities of the radicals R· and R·′. Apparently (3) occurs readily for R·′ = *t*-butyl in the presence of excess *n*-butyllithium.

As a further test of the above rationalization, the results with methyl iodide and allyl bromide are of particular interest. The reactivity of methyl iodide in reaction 2 would be expected to be orders of magnitude less than for the other acyclic alkyl iodides. Experimentally in this case we observed (with *n*-butyllithium) a mixture of methyl and *n*-butyl radicals. One interpretation is that the rates of reactions 2 and 3 are now approximately equal. Allyl bromide would be expected to be much more reactive in bromine atom transfer than the simple alkyl bromides. Experimentally, we observed (with *n*-butyllithium) that only the allyl radical is detected by esr.

Reactions 2 and 3 provide a reasonable mechanism for metal–halogen interchange.[6] However, extensive metal–halogen interchange under our reaction conditions would be expected to give rise to mixtures of radicals, particularly in cases such as R′ = *n*-propyl, R = *n*-butyl. With the exception of methyl iodide–*n*-butyllithium, we have never observed mixtures of radicals in reactions of alkyl iodides even when the reaction had proceeded to much higher conversions than required for the optimum esr signals.

A possible explanation to this dilemma is that the concentration of RI never reaches an appreciable fraction of the R′I concentration under conditions where the esr signal can be detected, *i.e.*, the consumption of R′I must be much faster than the rate of formation of RI. Thus, by the time that an appreciable fraction of the unreacted alkyl iodide has been converted into RI, the rate of process 1 has decreased to such a value that radicals can no longer be easily detected. Since steps 2 and 3 must be fast compared to steps 1 and 4 to yield the observed ratios of [R·′]/[R·], it follows that only a small fraction of the R′I (or RLi) consumed is being converted to free radicals observable by esr spectroscopy.[12] Presumably the same conclusion applies to alkyl bromides and chlorides.

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(12) Some retention of configuration in the reaction of 2-iodooctane with butyllithium [R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950)] is probably the result of an ionic or cage process; see also H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966).

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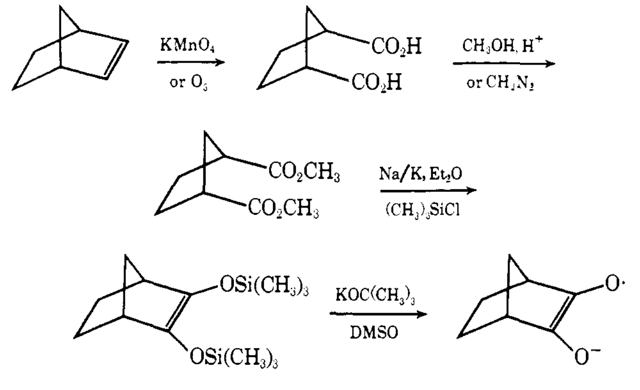
Stereochemistry of the Reaction of the 7-Norbornenyl Radical with Tri-*n*-butyltin Deuteride[1]

Sir:

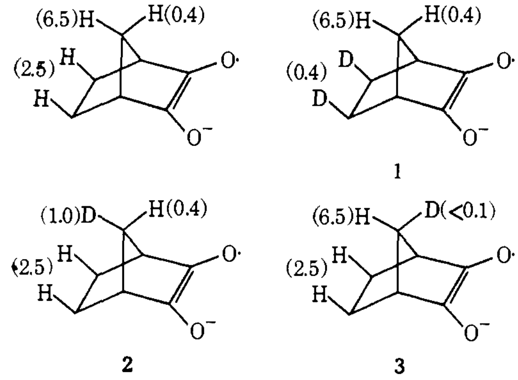
It was recently reported that the reaction of tri-*n*-butyltin deuteride with *syn*- or *anti*-7-bromonorbornene yielded exclusively *anti*-7-deuterionorbornene.[2] The analysis was performed by pmr spectroscopy. Since we had already demonstrated that *exo,exo*-5,6-dideuterionorbornene[3] could be converted into the semidione **1** without rearrangement, we have applied the sequence of reactions in Scheme I[4] to the product of the reaction of tri-*n*-butyltin deuteride with 7-*syn*- and 7-*anti*-bromonorbornene.

Scheme I



The semidiones produced were analyzed by esr spectroscopy. The spectrum (Figure 1) obviously was a mixture of two semidiones (**2** and **3**) with *syn* and *anti* deuterium atoms with the hyperfine splitting constants as assigned in Chart I at 25° in DMSO solution.[5] Analysis was performed by comparison of the height of the wing peaks of **3** ($^1/_{32}$ of total intensity) with the fourth peaks of **2** ($^1/_{96}$ of total intensity).[6] The intensity ratios indicate a ratio of **2**/**3** = 4.9 ± 0.1. The same ratio was obtained from both the *syn*- and *anti*-7-bromonornene.[7,8] Although there is some stereospecificity in the reaction of tri-*n*-butyltin deuteride with the 7-norbornenyl radical, it does not appear necessary to invoke a

Chart I



[a] Bridgehead hfsc = 2.5 G in all cases.

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(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XVI. This work was supported by a grant from the National Science Foundation.

(2) J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968).

(3) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965).

(4) G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

(5) See also G. A. Russell and K.-Y. Chang, *ibid.*, **87**, 4381 (1965).

(6) It is assumed that the line widths of **2** and **3** are the same, *i.e.*, that any unresolved hfs is the same in **2** and **3**. Since **3** contains an unresolved *syn*-7-deuterio hyperfine splitting, we expect that the line width of **3** may be slightly greater than **2** and the ratio of **2**/**3** of 4.9 is a maximum limit; *e.g.*, the yield of **3** may be greater than 16%.

(7) H. Kwart and L. Kapan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

(8) The *anti*-7-bromonorbornene was prepared by the action of hydrobromic acid on 7-*anti*-norborneol: P. Story, *J. Org. Chem.*, **26**, 287 (1961). Solvolysis of this *anti*-7-bromonorbornene in the presence of sodium borodeuteride yielded *anti*-7-deuterionorbornene: H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968). Conversion to the semidione yielded only **2**; the wing peaks from **3** (Figure 1) were completely missing from the esr spectrum.