blum[11,12] and Russell[13] who have demonstrated that a radical anion chain mechanism operates in oxidation of 2-nitropropane lithium salts by compounds such as *p*-nitrocumyl chloride and *α,p*-dinitrocumene.[11]

The question arises whether diphenylmethyl halides react in a similar manner with triphenylmethyl carbanion?

Treatment of triphenylmethyllithium with benzhydryl bromide (3.55 g, 0.0143 mol) produced pentaphenylethane, **5** (5.58 g, 95%).[14] Use of benzhydryl chloride also produced pentaphenylethane in 91% yield. These reactions appear to involve either simple nucleophilic displacement[19] or formation of a pair of radicals in a cage,[1h] from which benzhydryl and trityl radicals do not escape, for if any free benzhydryl or trityl radicals were formed, *sym*-tetraphenylethane and **1** would have been produced.

In order to show that cross coupling products would form from mixtures of benzhydryl and trityl radicals, competition experiments using 1 equiv of equimolar benzhydryl and trityl halides solution with 1 equiv of lithium naphthalenide were run. After discharge of the aromatic radical anion color, oxygen was bubbled through the mixture to convert residual trityl radicals into bis(triphenylmethyl) peroxide (18% isolated). Pentaphenylethane (36%) and tetraphenylethane (32%) were isolated.

Comparison of the competition experiments with naphthalenide ion with the triphenylmethyllithium–diphenylmethyl halide reactions leads us to conclude that diphenylmethyl halides do not oxidize triphenylmethyl carbanion by a single-electron transfer process that produces free trityl and benzhydryl radicals.

The question of whether trityl halides react with diphenylmethyllithium to produce radical intermediates was studied. Diphenylmethyllithium was titrated with benzhydryl chloride (6.19 g, 0.0305 mol), to give *sym*-tetraphenylethane (10.2 g, 97.2%).

Reaction of diphenylmethyllithium and triphenylmethyl chloride was followed by quenching with oxygen and gave predominantly **5** (60%) together with **3** (6.%), bis(triphenylmethyl) peroxide (6.6%) and benzhydryl and trityl chlorides. These results are in harmony with rapid establishment of a halogen–metal interconversion equilibrium. This equilibrium lies well to the right as judged by the low yields of peroxide and **3**. If single-electron transfer oxidation of the primary reactants was occurring to any significant extent the yields of **3**, **5**, and peroxide should be comparable not only in absolute amounts but also to the results from the naphthalenide ion competition experiments. The fact that they are not statistically equivalent leads to the conclusion that coupling of free radical intermediates is not the mechanism for formation of **3** and **5** from diphenylmethyllithium. This conclusion finds experimental support in the work of Sommer who has shown that benzhydryllithium reacts with (−)-*α*-phenylethyl chloride with 100% inversion of configuration to give (−)-1,1,2-triphenylpropane.[19]

The most surprising result in Table I is that a threefold molar excess of lithium naphthalenide reacting with benzhydryl halide does not completely suppress the formation of **3** either by reducing benzhydryl radicals to carbanions faster than they can couple or by cleaving **3** after it is formed. The implication is that benzyhydryl radical is not reduced by naphthalenide ion at diffusion-controlled rates or that benzhydryl anion reacts with benzhydryl halide at a rate competitive with that of lithium naphthalenide. It is hard to imagine an SN2 displacement by benzhydryl anion on benzhydryl halide which can operate at a rate competitive with reduction by naphthalenide. Perhaps oxidation of benzhydryl anion by the halide can produce two radicals with the same speed as naphthalenide ion reduction of a radical.

The other significant result reported here is that naphthalenide ion reacts indiscriminately with an equimolar mixture of trityl chloride and benzhydryl chloride to produce mixtures of radicals which couple statistically forming **3** and **5**.

Acknowledgments. This investigation was supported in part by Undergraduate Science Education Program Grants GY-7540 and GY-9960 of the National Science Foundation. It is a pleasure to acknowledge the philanthropy of Mr. Wilbur E. Zieger.

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(11) R. C. Kerber, G. W. Urry and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 5420 (1965); (b) R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **86**, 3904 (1964).

(12) Also see later references, N. Kornblum, *et al.*, *ibid.*, **89**, 725, 5714 (1967); **90**, 6219, 6221 (1968).

(13) (a) G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964); (c) G. A. Russell and D. W. Lamson, *ibid.*, **95**, 3967 (1969).

(14) Satisfactory microanalysis, mass spectral, and pmr data support this structure. Furthermore, this sample is identical with that obtained following Bachmann's procedure[15] for **5** from triphenylmethylmagnesium bromide and benzhydryl bromide in ether–benzene. The melting points of **5** vary from 145–148° to 178–179° with decomposition in general agreement with literature values[15,16] and the known thermal instability of **5**.[17] Molecular oxygen was bubbled through a benzene solution of **5** for 3 hr at 25° and **5** was recovered quantitatively. The reported reaction[18] of O_2 with **5** at 80° probably depends upon prior thermal decomposition of **5**.

(15) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 2135, 3005 (1933).

(16) (a) M. Gomberg and Cone, *Ber.*, **39**, 1466 (1906); (b) A. Tschitschibabin, *ibid.*, **40**, 367 (1907).

(17) W. E. Bachmann, R. Hoffmann, and F. Whitehead, *J. Org. Chem.*, **8**, 320 (1943); (b) W. E. Bachmann and F. Y. Wiselogle, *ibid.*, **1**, 354 (1936).

(18) J. Coops, G. Galenkamp, J. Haantjes, H. L. Luirink, and W. Th. Nauta, *Recl. Trav. Chim. Pays-Bas*, **67**, 469 (1948).

(19) L. H. Sommer and W. D. Korte, *J. Org. Chem.*, **35**, 22 (1970).

(20) National Science Foundation Undergraduate Research Participant: (a) 1970–1971; (b) 1971–1972.

(21) Presented in Part at the 164th National Meeting of the American Chemical Society, Aug 27–Sept 1, New York, Abstract No. 12-0.

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Evidence for an Electron-Transfer Component in a Typical Nucleophilic Displacement Reaction

Sir:

Whereas electron-transfer has been noted in a variety of nucleophilic reactions,[1] it has not always been clear what driving forces are operative[1d,e,f] nor in what way electron processes contribute to a nonbiased, typical

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(1) (a) For leading references see K. A. Bilevich and O. Yu Okhlobystin, *Russ. Chem. Rev.*, **37**, 12 (1968); (b) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5662 (1966); (c) G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); (d) H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969); (e) G. A. Russell and D. W. Lamson, *ibid.*, **91**, 3967 (1969); (f) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969); (g) M. Barreau and M. Julia, *ibid.*, 1537 (1973).

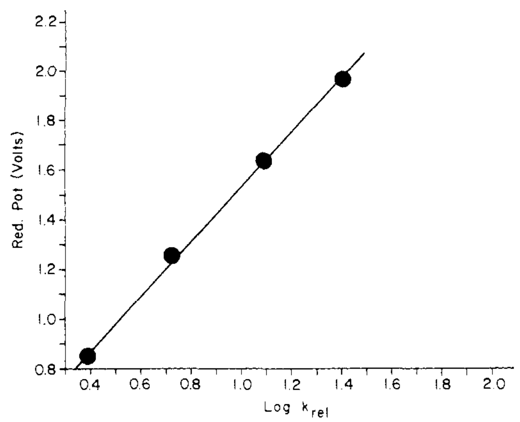

Figure 1. Correlation between the half-wave reduction potentials of methyl-substituted compounds and the log of the relative rates of the primary and secondary butyl compounds.

SN2 reaction.[2] We have investigated the reaction of thiophenoxide ion with primary and secondary alkyl substrates. This system is a bias-free, typical SN2 reaction; the reactions are first order in each component and only substitution products are obtained. We are pleased to report evidence for an electron-transfer component.

We investigated the relative rates of displacement on primary and secondary alkyl compounds by thiophenoxide ion as a function of the leaving group, with the expectation that a classical displacement favors the primary[3] whereas electron transfer favors the secondary.[4] As shown in Table I, the trend for leaving groups is RBr > RI > ROMs ≅ ROTs > RONs. As the ease of reduction of the substrate is increased correlated by the half-wave potentials of the methyl derivatives, the rate ratio of primary to secondary decreases. The plot (Figure 1) reveals a linear free energy relationship. These data are consistent with a one electron transfer, although permissive of other interpretations such as a classical displacement reaction with increasing amounts of bond breaking.[5]

Table I. Relative Rates of Displacement of *n*-Butyl and *sec*-Butyl Compounds with Thiophenoxide[a]

Leaving group	Relative rates[b]	Half reduction potential of methyl compounds, V[d]
Bromide	25.7 ± 0.5[c]	−1.96[e]
Iodide	12.8 ± 0.4[f]	−1.63[g]
Tosylate[j]	5.3 ± 0.1[c]	−1.25[h]
Mesylate[j]	5.9 ± 0.1[f]	
Nosylate[j]	2.5 ± 0.1[f]	−0.847[i]

[a] In 87% ethanol at 25°. [b] k_n/k_s, defined by the equations: rate of primary = $k_n[\text{1-Bu-X}][C_6H_5S^-]$, rate of secondary = $k_s[\text{2-Bu-X}][C_6H_5S^-]$. [c] Reference 5. [d] At 25° with a saturated calomel electrode. [e] F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966). [f] This work determined by competition experiments using a 50-fold excess of both 1- and 2-butyl substrates. [g] M. von Stackleberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949). [h] P. Yousefzadeh and C. K. Mann, *J. Org. Chem.*, **33**, 2716 (1969). [i] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961). [j] Tosylate, mesylate, and nosylate are common names for the esters of *p*-tolyl-, methane-, and *p*-nitrobenzenesulfonic acids.

Independent evidence for electron-transfer species was obtained.[6] Reaction of 2-butyl nosylate with lithium thiophenoxide in the presence of the spin trap, phenyl-*tert*-butylnitrone[7] (PBN), in tetrahydrofuran (THF) solution gave the 2-butyl spin adduct nitroxide. The esr hyperfine coupling constants of $A_n = 14.64$ and $A_{\beta H} = 3.19$ agree with the independently prepared spin adduct.[8] Control experiments of THF and PBN, THF, PBN, and 2-butyl nosylate, and THF, PBN, and lithium thiophenoxide gave no detectable concentration of nitroxide. The phenylthiyl radical was detected by the styrene polymerization technique.[9] Lithium thiophenoxide and 2-butyl nosylate were allowed to react in the presence of styrene. From the several high-boiling products, a compound $C_{36}H_{38}S$, mol wt 527, was isolated and identified as a four styrene–thiophenol oligomer.[10] This same compound was obtained when authentic phenylthiyl radicals were generated in the same media from the oxidation of thiophenol and cerium(IV).[11] There were no high-boiling products when 2-butyl nosylate or lithium thiophenoxide were independently subjected to the reaction conditions in the presence of styrene.

The stereochemistry of the displacement reaction was studied with the expectation that participation of radical species would lead to extensive racemization. However, the reaction of *S*-2-octyl nosylate[12] (88.9 ± 2.0% optically pure) with lithium thiophenoxide yielded *R*-2-octylphenyl sulfide (89.3 ± 2.0% optically pure) and hence proceeded with complete inversion. There are three possible explanations for this apparent contradiction.

First, the reaction might involve the following sequence.[13]

$$\text{PhS}^- + \text{RONs} \longrightarrow \text{PhS}\cdot + \text{RONs}\cdot^- \tag{1}$$

$$\text{PhS}\cdot + \text{RONs}\cdot^- \longrightarrow \text{PhSR} + \text{ONs}^- \tag{2}$$

$$\text{RONs}\cdot^- \longrightarrow \text{R}\cdot + \text{ONs}^- \tag{3}$$

$$\text{R}\cdot + \text{PhS}\cdot \longrightarrow \text{RSPh} \tag{4}$$

Reaction 2, displacement by the phenylthiyl radical, is favored over reaction 3. Since it is not clear what stereochemistry is demanded from reaction 2 and inversion is a viable possibility, the absence of extensive racemization rules out only significant contributions from reaction 4. The products of the reaction and of styrene polymerization arise from reactions 1 and 2 whereas the highly sensitive probe of spin-trapping detects the species from the small contribution of reactions 3 and 4.

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(2) E. G. Janzen, Ph.D. Thesis, Iowa State University, 1963.

(3) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 11-13; *Chem. Rev.*, **56**, 571 (1956).

(4) An example of this is the reinterpretation of the data in G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 5363 (1966), as discussed in ref 1f.

(5) E. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1959).

(6) Only 2-butyl nosylate was investigated.

(7) (a) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971), and references cited therein. (b) The concentrations were: 2-BuNOS, 0.025 *M*; LiSPh, 0.033 *M*; PBN, 0.037 *M*.

(8) Prepared by the reaction of PBN with 2-butylmagnesium chloride in THF followed by air oxidation as outlined in ref 7.

(9) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 182.

(10) Satisfactory analyses and spectral data were obtained to confirm the structure.

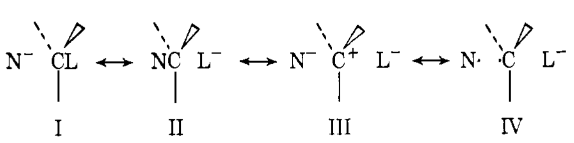
(11) (a) E. L. Jenner and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **83**, 1911 (1961); (b) W. S. Trahanovsky, *ibid.*, **91**, 7184 (1969).

(12) Prepared from commercially available (Aldrich) *S*-2-octanol and *p*-nitrobenzene sulfonyl chloride. Reactions were conducted in 87% ethanol–water.

(13) An esr run during the reaction denotes the presence of para-substituted nitrobenzene radical anions. Attempts to characterize these species have not been successful.

The second consideration is a two-path reaction, an electron-transfer process in competition with a favored S_N2 process. Since the reaction involves complete inversion, the classical mechanism has a $\Delta G^{\ddagger}$ of at least 2.7 kcal/mol lower.[14] This model is incomplete in that it does not attempt to explain anomalous behavior discussed below.

Finally, the reaction can be formulated as proceeding through an intermediate that is a resonance hybrid of forms including a one-electron transfer.



N is the nucleophile, L is the leaving group, forms I, II, and III are contributions from a two-electron bond formation, and IV is the contribution from a one-electron transfer. An analogous formulation has been used for proton transfer to aromatic radical anions and accounts for the rate dependence upon both the reduction potential and the localization energy.[15] The extension of this concept to nucleophilic reactions has significant value in that the successful two-term rate equation includes a term for basicity and one for the reduction potential of the nucleophile.[16,17] Similarly, the model can account for the observation that both electron-withdrawing and electron-donating groups increase the rate of nucleophilic substitution in meta- and para-substituted benzyl halides.[18] Additional systems that include polar forms as well as the expected one-electron form are polarographic reductions[19] and relative reactivities of free radicals.[20]

Our results and rate data for other nucleophilic substitution reactions suggest that electron transfer contributes to these reactions and that one-electron forms should be included along with the generally accepted two-electron forms.

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(14) In this explanation, the highly sensitive probe of spin trapping detects the presence of a small amount (<0.01%) of reaction from reduction of the nosylate.

(15) S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jap.*, **44**, 2046 (1971).

(16) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(17) R. E. Davis, *J. Amer. Chem. Soc.*, **87**, 3010 (1965).

(18) (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 172. (b) Electron-withdrawing substituents in both the meta and para positions are known to stabilize benzyl radicals; see ref 19 and L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

(19) A. Streitwieser, Jr., and C. Perrin, *J. Amer. Chem. Soc.*, **86**, 4938 (1964).

(20) See ref 9, p 135 ff.

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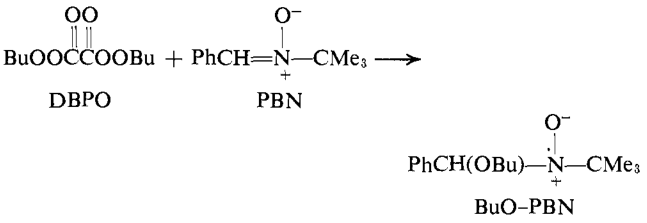
Rate Constants for Spin Trapping *tert*-Butoxy Radicals as Studied by Electron Spin Resonance

Sir:

It has recently been shown that certain free radicals can be quantitatively detected[1] by the method of spin trapping.[2] Thus the thermal decomposition of benzoyl peroxide can be followed by trapping all of the benzoyloxy radicals produced by using phenyl *N-tert*-butyl nitrone (PBN) in benzene at ambient temperatures. Since the rate of production of the spin adduct α-benzoyloxybenzyl *tert*-butyl nitroxide is first order in benzoyl peroxide and zero order in PBN, spin trapping appears to provide a useful method for counting short-lived reactive free radicals (spin counting[1]).

The spin trapping technique could become more useful if absolute rate constants for trapping radicals were available. We previously reported two estimates of the absolute rate constant for trapping benzoyloxy radicals.[1] One of these was based on DeTar's estimates of certain rate constants. Subsequent work on trapping phenyl radicals allows us to improve these estimates and these results will be described in a following communication. In this paper we report on a study of the rate constant for trapping *tert*-butoxy radicals produced by thermal decomposition of di-*tert*-butyl peroxalate.

Di-*tert*-butyl peroxalate (DBPO) decomposes in the presence of PBN to produce the *tert*-butoxy spin adduct (BuO–PBN). The hyperfine splitting constants in benzene at room temperature are: $a^{N} = 14.22$, $a_{\beta}{}^{H} = 1.95$ G. The reaction is first order in DBPO and zero order in PBN over the range of concentrations studied: [DBPO] = 0.001–0.1 *M*, [PBN] = 0.02–0.2 *M*. If the following mechanism is assumed, $d[BuO\text{–}PBN]/dt = 2k_1[DBPO]$ (see eq 1 and 2′).



$$\underset{\text{DBPO}}{\text{BuOO}\overset{\text{O}}{\overset{\|}{\text{C}}}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OOBu}} + \underset{\text{PBN}}{\text{PhCH}{=}\overset{\text{O}^-}{\overset{|}{\underset{+}{\text{N}}}}\text{—CMe}_3} \longrightarrow \underset{\text{BuO–PBN}}{\text{PhCH(OBu)—}\overset{\text{O}^-}{\overset{\cdot|}{\underset{+}{\text{N}}}}\text{—CMe}_3}$$

$$\text{DBPO} \longrightarrow 2\text{BuO}\cdot + 2\text{CO}_2 \qquad (1)$$

$$\text{BuO}\cdot + \text{PBN} \longrightarrow \text{BuO–PBN} \qquad (2')$$

Rate constants obtained by a method previously described[1] compare well with the values of Bartlett, *et al.*:[3] *e.g.* at 35° $k_1 = 6.8 \times 10^{-5}$ sec^{-1} by spin counting and 7.1×10^{-5} sec^{-1} by observing the disappearance of DBPO by ir.[3] An Arrhenius plot of the data obtained by esr over a 16° temperature range (23–39°) gives an energy of activation of 30 kcal/mol. Bartlett, *et al.*, report 26 kcal/mol. All the data available give a value of 27 kcal/mol.

Since the absolute rate constant for hydrogen atom abstraction by *tert*-butoxy radicals from toluene and cyclohexane is known,[4] it should be possible to obtain the absolute rate constant for spin trapping *tert*-butoxy radicals by simultaneously monitoring the build-up of the *tert*-butoxy and the alkyl radical spin

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(1) E. G. Janzen, C. A. Evans, and Y. Nishi, *J. Amer. Chem. Soc.*, **94**, 8236 (1972).

(2) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(3) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

(4) (a) see J. A. Howard, *Advan. Free Rad. Chem.*, **4**, 49 (1971); (b) K. U. Ingold, "Free Radicals," J. K. Kochi, Ed., Vol. 1, Wiley, New York, N. Y., 1973, p 74.