Radical Formation from the Intermediates of S_N1 Reacions. A One-Electron Transfer Reaction between a Carbonium-ion Type Intermediate and Nucleophiles

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The recent work of Kerber et al.[1] on the transient formation of a radical anion, probably of E. Weitz's molecular-complex type,[2] during the course of the reaction of *p*-nitrobenzyl halides with a salt of 2-nitropropane prompts us to report on some of our previous work.[3] It has been found that reactions of benzhydryl halides with hindered nucleophiles, e. g., potassium 2, 6-di-*t*-butyl-4-methylphenoxide (I) and tri-*n*-butylamine, afford not the products anticipated for nucleophilic substitution, but rather products derived from benzhydryl radicals, i. e., *sym*-tetraphenylethane, diphenylmethane, and 1-(3′, 5′-di-*t*-butyl-4′-hydroxyphenyl)-2, 2-diphenylethane (II). The results are illustrated in Table I.

The structure of II, m. p. 113.0—115.0°C, was assigned on the basis of its elementary composition and spectral data (Found: C, 87.07; H, 8.76; mol. wt., 386 (cryoscopic measurements in benzene). Calcd. for $C_{28}H_{34}O$: C, 86.99; H, 8.87%; mol. wt., 386.6). Spectral peaks appeared at: infrared spectrum λ_{max} (KBr pellet) 2.70 μ (OH, monomeric), no polymeric OH; 60 Mc. NMR (carbon tetrachloride):[4] 1.28 p.p.m. (18-proton singlet, *t*-butyl methyls), 3.20 p.p.m. (2-proton doublet, methylene, $J=7.7$ c.p.s.), 3.93 p.p.m. (1-proton triplet, methine, $J=7.7$ c.p.s.), 4.78 p.p.m. (1-proton singlet, hydroxyl), 6.52 p.p.m. (2-proton singlet, tetra-substituted phenyl) and 7.10 p.p.m. (10-proton, mono-substituted phenyl).

For purposes of comparison the results of the reaction of benzhydryl chloride and potassium phenoxide in acetonitrile are also presented in Table I.

Despite their second-order kinetics (Table I), the S_N1 ionization character of the initiation of these reactions of hindered nucleophiles is supported by the following facts and considerations: (1) The reaction of unhindered potassium phenoxide displays characteristics typical of an S_N1 reaction with respect to the reaction-order and the products (Table I). Consequently, there would exist an S_N1 intermediate produced from a benzhydryl halide in acetonitrile in all reactions with hindered nucleophiles. (2) The nature of the reaction products can not be explained by the S_N2 mechanism. (3) The rates of these second-order reactions are sensitive to the natures of the solvents and of the leaving groups. The reaction of benzhydryl chloride and tri-*n*-butylamine proceeds more than 68% at about 150°C for 6.5 hr. (Table I), whereas the same reaction in decalin yields chloride ions less than 4% of the starting chloride under identical reaction conditions. Furthermore, it is estimated that bromide is about 5—30 times as reactive as the chloride (Table I) (4) These second-order reactions of benzhydryl chloride proceed with rates which do not exceed the rate of a typical S_N1 reaction of the chloride and potassium phenoxide (Table I).

On the basis of the above facts, (1)—(4), these reactions can be explained as a limiting case of an S_N1 reaction where the condition, $k_{-1} \gg k_2[Y]$, is satisfied in the following rate expression, which correspondes to the general reaction scheme of the S_N1 reaction:

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (R^{\delta+}\cdots X^{\delta-}) \xrightarrow{k_2[Y]} RY$$

$$\text{Rate} = \frac{k_1 k_2 [RX][Y]}{k_{-1} + k_2[Y]}$$

Namely, for hindered nucleophiles,

$$\text{Rate} = \frac{k_1 k_2}{k_{-1}}[RX][Y].$$

Therefore, we propose a bimolecular one-electron transfer mechanism for the transient formation of benzhydryl radicals in the reaction of the S_N1 intermediate and hindered nucleophiles. This is illustrated in the following scheme:

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[1] R. C. Kerber, G. W. Urry and N. Kornblum, *J. Am. Chem. Soc.*, **86**, 3904 (1964).

[2] E. Weitz, *Angew. Chem.*, **66**, 658 (1954).

[3] K. Okamoto, Y. Matsui and H. Shingu, Abstracts of the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964, p. 128.

[4] We are indebted to Professor Kenichi Fukui and Mr. Isao Morishima for their assistance with the measurement of the NMR spectrum. The spectrum was taken with tetramethylsilane as an internal standard on a Varian Associates Model A-60 spectrometer.

TABLE I. PRODUCTS AND RATES IN THE REACTION OF BENZHYDRYL HALIDES AND NUCLEOPHILES IN ACETONITRILE

Nucleophile	Temp. °C	Conversion %[a] (Reaction time, hr.)	Reaction products, %[b]					Rates[c] k_1 (min^{-1}) or k_2 (min^{-1} M^{-1})
			sym-Tetraphenylethane	Diphenylmethane	II[g]	Benzhydrylphenyl ether	*p*-Benzhydrylphenol	
			Substrate: Benzhydryl chloride					
I[g]	82—85[d]	82 (18.3)	40.2	0.0	28.7	—	—	k_2 (110.0°C) 6.82×10^{-1}
$(n\text{-Bu})_3N$	146—156[e]	68 (6.5)	64.5	3.0	—	—	—	k_2 (140.0°C) 3.66×10^{-2}
Potassium phenoxide	82[d]	97 (2.5)	0.0	0.0	—	93.2	3.1[h]	k_1 (70.0°C) 1.58×10^{-2}
			Substrate: Benzhdryl bromide					
I	82[d]	97 (6.9)	3.0	0.0	24.1	—	—	—
$(n\text{-Bu})_3N$	90—93[f]	91 (18.3)	22.8	34.4	—	—	—	—

a) Conversion of the halide, calculated from determination of the halide ions formed during the reaction.

b) Based on the halide.

c) Determined by sealed ampoule technique. Initial concentrations of the substrate and nucleophiles were 0.05—0.13 M.

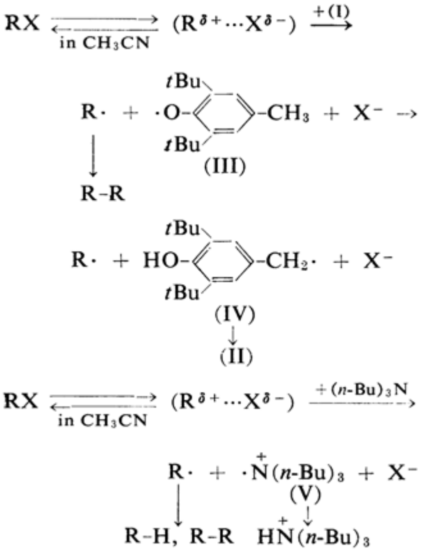
d) Reflux temperature.

e) Reaction in a stainless-steel bomb.

f) Reaction in a sealed tube.

g) I; Potassium 2,6-di-*t*-butyl-4-methylphenoxide; II; 1-(3′,5′-Di-*t*-butyl-4′-hydroxyphenyl)-2,2-diphenylethane.

h) Contaminated with the ortho-isomer.



(R=Benzhydryl)

It is known[5] that I easily undergoes oxidation to give the 2,6-di-*t*-butyl-4-methylphenoxy radical (III) and that III isomerizes rapidly to the 3,5-di-*t*-butyl-4-hydroxybenzyl radical (IV). In our experiments, a coupling product II between a benzhydryl radical and a radical IV has been isolated. It is also known that aliphatic tertiary amines, e.g., triethylamine, lose one electron to yield a charge-transfer complex with tetracyanoethylene[6a] and 7,7,8,8-tetracyanoquinodimethane.[6b] A part of the amminium ion radical (V) seems to be stabilized by forming tri-*n*-butylammonium ions, which have been isolated in our experiments as the halide with a yield of 50—60%. The source of the hydrogen atoms has not been established.

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[5] C. D. Cook, N. G. Nash and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

[6] a) O. W. Webster, W. Mahler and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962); b) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, ibid., **84**, 3374 (1962).