Kinetic Studies of Solvolysis. X.* Transition from a van't Hoff to an Arrhenius Intermediate Caused by Steric Hindrance at the Product-Formation Step of S_N1 Reactions

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The kinetics of the two-step mechanism for the S_N1 reaction, in which an ion-pair is assumed as an intermediate, can well be treated by the steady-state approximation; the overall rate is then shown by Eq. 1:

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{(ion-pair intermediate)} \xrightarrow{k_2[Y]} RY$$

$$d[RX]/dt = k_1k_2[RX][Y]/(k_{-1}+k_2[Y]) \qquad (1)$$

In typical S_N1 reactions, the first ionization step is rate-determining, and k_2, the rate constant for the reaction of a nucleophile with the intermediate, is much larger than k_{-1}, the rate constant for the reversal of the ionization step. This intermediate formed at the rate-determining step can be classified as a van't Hoff intermediate.[1] If, on the other hand, k_{-1} is larger than k_2, a pre-equilibrium will be approximately established, followed by a rate-determining step. Here the intermediate is defined as an Arrhenius intermediate[1] and the reaction obeys second-order kinetics despite its initiation by the S_N1 ionization mechanism:

$$d[RX]/dt = k_1k_2[RX][Y]/k_{-1} \qquad (2)$$

Although the literature contains several

* Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964. Pnrt IX: K. Okamoto, K. Takeuchi and H. Shingu, This Bulletin, 37, 276 (1964).

1) a) A. Skrabal, "Homogenkinetik," T. Steinkopf, Dresden (1941), pp. 38—43; b) A. Skrabal, *Monatsh. Chem.*, 51, 93 (1929).

TABLE I. SUMMARY OF THE FIRST-ORDER RATE CONSTANTS OF THE S_N1 REACTIONS OF BENZHYDRYL CHLORIDE IN THE PRESENCE OF POTASSIUM PHENOXIDE IN ACETONITRILE

Temp. °C	Initial concn. RCl, M	Initial concn. C_6H_5OK, M	k_1[a] min^{-1}	k_2[a] $min^{-1}\,M^{-1}$
140.0			(0.6−1.4)[b]	
120.0	0.0584	0.0986	2.82×10^{-1}	(4.27)
	0.0488	0.0488	2.56×10^{-1}	(5.28)
90.0	0.0318	0.0786	7.12×10^{-2}	(0.906)
	0.0344	0.0508	7.03×10^{-2}	(1.33)
70.0	0.0445	0.0590	1.58×10^{-2}	(0.317)
	0.0234	0.0550	1.59×10^{-2}	(0.295)
	0.0241	0.0474	1.52×10^{-2}	(0.305)
	0.0200	0.0378	1.55×10^{-2}	(0.413)
	0.0197	0.0316	1.53×10^{-2}	(0.503)
	0.0198	0.0308	1.54×10^{-2}	(0.502)
	0.0214	0.0214	1.43×10^{-2}	(0.710)

a) Initial rate constants calculated by the graphical method.
b) Extrapolated from data at 70.0, 90.0 and 120.0°C.

TABLE II. SUMMARY OF THE SECOND-ORDER RATE CONSTANTS OF THE S_N1 REACTIONS OF BENZHYDRYL CHLORIDE WITH SOME HINDERED NUCLEOPHILES IN ACETONITRILE

Nucleophiles	Temp. °C	Initial concn. RCl, M	Initial concn. nucleophile M	k_2 $min^{-1}\,M^{-1}$
Potassium 2,6-di-*t*-butyl-4-methylphenoxide (I)	110.0	0.0385	0.0594	6.82×10^{-1}
	120.0	0.0368	0.0564	1.62
		0.0500	0.0500	1.62
		0.0196	0.0334	1.65
	140.0			(6.3)[a]
Tri-*n*-butylammonium phenoxide (II)	140.0	0.0840	0.1240	3.52×10^{-1}
		0.0527	0.0750	3.63×10^{-1}
		0.0500	0.0500	3.71×10^{-1}
Tri-*n*-butylamine	140.0	0.0905	0.1370	3.66×10^{-2}
Tri-*n*-butylammonium 2,6-di-*t*-butyl-4-methyl phenoxide (III)	140.0	0.0930	0.1340	2.84×10^{-2}

a) Extrapolated from data at 110 and 120°C.

references[2] to the S_N1 reaction involving Arrhenius intermediates, there have been reported to date no examples which clearly demonstrate such a transition of an carbonium-ion pair intermediate from a van't Hoff to an Arrhenius type.

We will report on an example of such a transition caused by a series of nucleophiles which have various steric requirements at the product-formation stage of the S_N1 reaction. The results of our kinetic runs and product studies[3] show that the S_N1 reactions of benzhydryl chloride with potassium 2,6-di-*t*-butyl-4-methylphenoxide (I), tri-*n*-butylamine, tri-*n*-butylammonium phenoxide (II), and tri-*n*-butylammonium 2,6-di-*t*-butyl-4-methylphenoxide (III) proceed through an Arrhenius intermediate and obey good second-order kinetics in acetonitrile, whereas the reaction with potassium phenoxide is a typical S_N1 reaction with a vant't Hoff intermediate. We will also report on the details of product studies which reveal the occurrence of a one-electron transfer reaction between the carbonium-ion intermediate and these hindered nucleophiles.

Rate Measurements and Kinetic Interpretation.—The titrimetric rate constants for the reaction of benzhydryl chloride with potassium phenoxide are given in Table I. The integrated first-order rate constants tended to show a slight decrease as the reaction progressed; therefore, the rate constant was calculated from the initial slope of a plot of the $\log(a-x)$ vs. the time, where a is the initial concentration of the chloride and x is the concentration

2) For triphenylmethyl chloride see R. F. Hudson and B. Saville, *J. Chem. Soc.*, **1955**, 4130; C. G. Swain and E. E. Pegues, *J. Am. Chem. Soc.*, **80**, 812 (1958); C. G. Swain and A. MacLachlan, ibid., **82**, 6095 (1960); L. J. Andrews and R. M. Keefer, ibid., **83**, 3708 (1961).

3) Some of the results of the product studies and kinetic runs have been published: K. Okamoto, Y. Matsui and H. Shingu, This Bulletin, **38**, 153 (1965).

of the chloride consumed. The S_N1 characteristic of the reaction was confirmed from the invariability of the first-order constants in the various initial concentrations (0.02—0.05 M). This is illustrated in Fig. 1. For purposes of comparison, the rate constants calculated for the second-order kinetics are included in Table I. In contrast to the first-order rate constants, the second-order rate constants display a clear trend toward larger rate constants in higher initial concentrations of the nucleophile.

Table II gives the second-order rate constants for the reactions of benzhydryl chloride with I, II, III and tri-*n*-butylamine in acetonitrile. The reactions were followed to about 70—80% completion; in all cases good second-order behaviors were observed. The plot of the log $a(b-x)/b(a-x)$ vs. the time, t, of a representative run is illustrated in Fig. 2, where a is the initial concentration of benzhydryl chloride and b is the initial concentration of the nucleophile. The definitely-curved plot for the first-order kinetics is also illustrated in Fig. 2.

An examination of the data in Tables I and II reveals that the S_N1 reaction of potassium phenoxide proceeds at a rate higher than any of the second-order reactions of these hindered nuclophiles. This fact evidently shows the existence of an ionized S_N1 intermediate, not only in the reaction medium where the first-order reaction of potassium phenoxide proceeded, but also in the environments in which the second-order reactions of the hindered nucleophiles were observed.

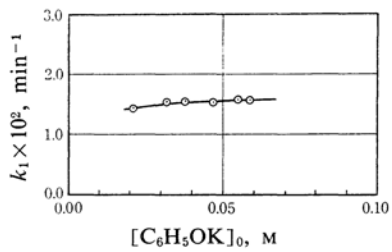


Fig. 1. First-order rate constants of the S_N1 reaction of benzhydryl chloride in acetonitrile in the presence of potassium phenoxide at 70.0°C. The initial concentrations of benzhydryl chloride, 0.02—0.04 M.

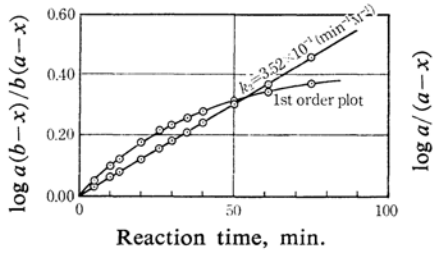


Fig. 2. Reaction rate of benzhydryl chloride in acetonitrile in the presence of tri-*n*-butylammonium phenoxide (II) at 140.0°C.
The initial concentration: the chloride, 0.0840 M; II, 0.1240 M

Thus two mechanisms for the second-order reactions of the hindered nucleophiles are possible. First, because of the large steric hindrance, the rate of a reaction between a nucleophile and the ionized intermediate became lower than the return rate of the intermediate, i.e., $k_2[Y] \ll k_{-1}$ in Eq. 1. Consequently, the reaction order changed from the first to the second, as is shown in Eq. 2, and the intermediate became an Arrhenius type. Secondly, if $k_2[Y]$ was extremely small compared with k_{-1}, the S_N1 reaction would be completely suppressed; then the S_N2 reactions between benzhydryl chloride and these hindered nucleophiles might appear, despite its sluggishness arising from the steric hindrance.

The first mechanism is more probable in view of the fact that a carbonium-ion type intermediate exists in acetonitrile in all the reactions of these nucleophiles. As has been briefly reported,[3] the results of product studies and of relevant control experiments have disclosed the formation of the compounds, which is unexplicable on the basis of the S_N2 mechanism but is conceivable as being due to a one-electron transfer reaction between the S_N1 intermediate and the nucleophile. Thus the S_N1 mechanism with an Arrhenius intermediate remains as the most probable one for the reaction with hindered nucleophiles.

Products Studies and Mechanistic Considerations.—The results of product studies, along with the reaction orders, are summarized in Table III. The products resulting from the S_N1 reaction of benzhydryl chloride and potassium phenoxide in acetonitrile at 82°C were isolated after ten half-periods; column chromatography showed that benzhydryl phenyl ether (93% yield) and *p*-benzhydrylphenol (3% yield) were formed. These are the expected products from the nucleophilic substitution of such an ambident anion.[4]

The reaction with potassium 2,6-di-*t*-butyl-4-methylphenoxide (I) was carried out in acetonitrile at 83—85°C, while the reactions with tri-*n*-butylamine and with tri-*n*-butylammouium phenoxide (III) were performed in the same solvent in a bomb at 140—160°C. The products of reactions with these hindered

4) For a general discussion of the nucleophilic substitution by an ambident anion, see N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

TABLE III. SUMMARY OF THE YIELDS OF REACTION PRODUCTS OF S_N1 REACTIONS OF BENZHYDRYL HALIDES IN ACETONITRILE

Nucleophile	Temp. °C	Conversion, %[a] (Reaction time, hr.)	Reaction products, %[b]					Reaction order[c]
			Benzhydryl phenyl ether	*p*-Benzhydrylphenol	IV[g]	*sym*-Tetraphenylethane	Diphenylmethane	
			Substrate: Benzhydryl chloride					
C_6H_5OK	82	97 (2.5)	93.2	3.1[h]	—	0.0	0.0	First
I[g]	82—85[d]	82 (18.3)	—	—	28.7	40.2	0.0	Second
II[g]	143—150[e]	95 (4.0)	83.0	11.5[h]	—	0.0	0.0	Second
$(n\text{-Bu})_3N$	146—156[e]	68 (6.5)	—	—	—	64.5	3.0	Second
III[g]	141—158[e]	82 (6.5)	—	—	0.0	22.5	0.0	Second
			Substrate: Benzhydryl bromide					
I	82[d]	97 (6.9)	—	—	24.1	3.0	0.0	—
$(n\text{-Bu})_3N$	90—93[f]	91 (18.3)	—	—	—	22.8	34.4	—

a) Conversion on the halide, calculated from determination of the halogen ion formed during the reaction.
b) Based on the halide.
c) See Tables I and II.
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, Tri-*n*-butylammonium phenoxide; III, Tri-*n*-butylammonium 2,6-di-*t*-butyl-4-methylphenoxide: IV, 1-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)-2,2-diphenylethane.
h) Contaminated with the ortho-isomer.

nucleophiles were also isolated after ten half-periods and separated by column chromatography.

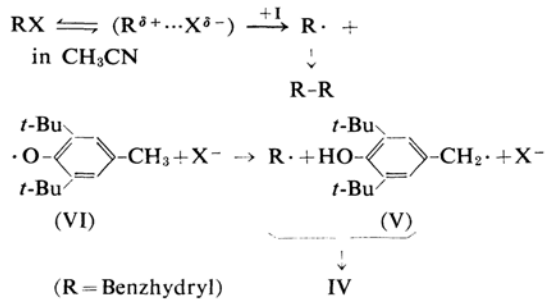
Much as with the reaction with potassium phenoxide, tri-*n*-butylammonium phenoxide and benzhydryl chloride resulted in benzhydryl phenyl ether (83% yield) and *p*-benzhydrylphenol (11.5% yield). In contrast to the reactions with these phenoxides, however, I and benzhydryl chloride yielded not the expected ether but rather *sym*-tetraphenylethane (40% yield), together with 1-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)-2,2-diphenylethane (IV) (29% yield).[5] The reactions with tri-*n*-butylamine and with III gave also *sym*-tetraphenylethane as a major product in, respectively, 65% and 23% yields; in addition, a small amount of diphenylmethane (3% yield) was obtained in the former reaction.

Although kinetic runs were not carried out for benzhydryl bromide, the reaction of this bromide with I, much as in the reaction of the chloride, gave rise to no benzhydryl 2,6-di-*t*-butyl-4-methylphenyl ether in acetonitrile. Instead, IV (24% yield) and *sym*-tetraphenylethane (3% yield) were obtained at 83°C after a 23 hr. reaction. Tri-*n*-butylamine and benzhydryl bromide in the solvent also gave *sym*-tetraphenylethane (23% yield) and diphenylmethane (34% yield) in a sealed tube after 18 hr. at 90—93°C.

Evidently, the formation of both *sym*-tetraphenylethane and diphenylmethane indicates the transient existence of a benzhydryl radical in the reaction path from the benzhydryl halide. The formation of IV is also realized as being due to coupling between a benzhydryl radical and a 3,5-di-*t*-butyl-4-hydroxybenzyl radical (V). It has been known that a benzyl radical such as V can easily be formed from a 2,6-di-*t*-butyl-4-methylphenoxy radical (VI).[6] Consequently, the formation of IV indicates that, in the reaction of the benzhydryl halide and I, a one-electron transfer reaction occurs from a 2,6-di-*t*-butyl-4-methylphenoxide anion to a benzhydryl cation or to a S_N1 intermediate containing a benzhydryl cation. This may be formulated as follows:

5) For the structural assignment, see Ref. 3.

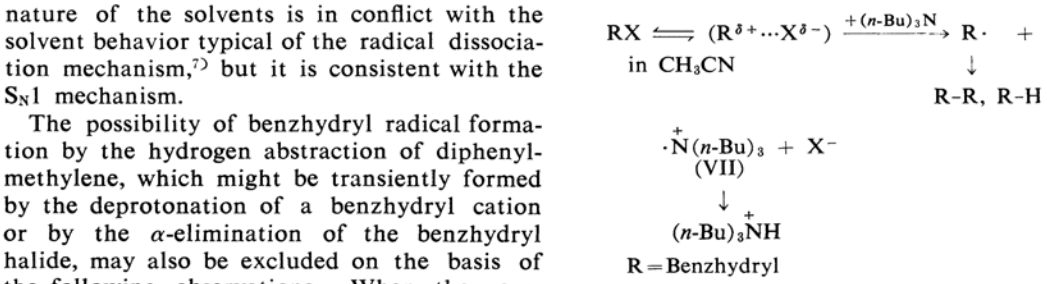
6) C. D. Cook, N. G. Nash and H. R. Flanagan, *J. Am. Chem. Soc.*, 77, 1783 (1955).



The possibility of benzhydryl radical formation by the radical dissociation of the benzhydryl halide in acetonitrile may be eliminated by a comparison of the rates in acetonitrile and in a non-polar solvent such as decalin. From the rate determination of the reaction of benzhydryl chloride and tri-*n*-butylamine in decalin at 150°C, it is estimated that only 4% or less of the starting chloride decomposes in 6.5 hr. Under identical reaction conditions, the reaction in acetonitrile proceeds to a more than 68% decomposition (Table III). Such rate sensitiveness to the nature of the solvents is in conflict with the solvent behavior typical of the radical dissociation mechanism,[7] but it is consistent with the S_N1 mechanism.

The possibility of benzhydryl radical formation by the hydrogen abstraction of diphenylmethylene, which might be transiently formed by the deprotonation of a benzhydryl cation or by the α-elimination of the benzhydryl halide, may also be excluded on the basis of the following observations. When the reaction of benzhydryl bromide and tri-*n*-butylamine was carried out in the presence of 1, 1-diphenylethylene, a powerful scavenger of diphenylmethylene,[8] no addition product of the diphenylmethylene, i.e., 1, 1, 2, 2-tetraphenylcyclopropane, was obtained. Instead, in addition to *sym*-tetraphenylethane (13% yield) and diphenylmethane (20% yield), 1, 1, 3, 3-tetraphenyl-1-propene (VIII) was obtained in a 13% yield after a 65-hr. reaction in acetonitrile at 91°C. In the absence of tri-*n*-butylamine, benzhydryl bromide and 1, 1-diphenylethylene also yielded VIII in a 82% yield under identical reaction conditions. In the latter reaction, VIII is evidently produced by the electrophilic addition of the S_N1 intermediate to 1, 1-diphenylethylene and by the succeeding dehydrobromination. Therefore, the formation of VIII in the former reaction is conceivably, realized by the same addition-elimination mechanism, and the possibility of the formation of VIII as an insertion product of diphenylmethylene to 1, 1-diphenylethylene is ruled out.

In comparison with the mechanism for the reaction of hindered phenoxides, the mechanism of benzhydryl radical formation in the presence of tri-*n*-butylamine can be explained as the reduction of an S_N1 intermediate (i.e., a benzhydryl cation or a benzhydryl ion-pair) by the tertiary amine. It has been known that a tertiary amine such as triethylamine readily yields a charge-transfer complex with tetracyanoethylene[9a] and 7, 7, 8, 8-tetracyanoquinodimethane.[9b] Furthermore, the existence of a charge transfer complex of the amine has been suggested in certain reactions of polyhalomethane and trialkylamine, in which a homolytic cleavage of carbon-halogen bond was observed.[10] Thus, for the reaction of the benzhydryl halide and tri-*n*-butylamine in acetonitrile, the reaction scheme may be shown as follows:



A part of the amminium ion radical (VII) seems to be stabilized by forming tri-*n*-butylammonium ion, which has been identified as the halide, in a yield of 50—60% in these reactions. The source of hydrogen atoms in tri-*n*-butylammonium ions and in diphenylmethane, R–H, has not yet been established.

As for the detailed mechanism of the reduction of the S_N1 intermediate by tertiary amine, there seem to be two possible pathways. One is a direct reduction of the cation by the tertiary amine. The other is the reduction through a charge-transfer complex, or a complex of Weitz's quinhydrone type,[11] between the S_N1 intermediate and the amine. In the course of these reactions, we could not observe any deep coloration due to such complex formation. However, the possibility of the formation of such a complex between the

7) For hexaphenylethane, see K. Ziegler, L. Ewald and P. Orth, *Ann.*, **479**, 277 (1930); K. Ziegler, P. Orth and K. Weber, ibid., **504**, 131 (1933); K, Ziegler, A. Seib, K. Knoevenagel, P. Herte and F. Andreas, ibid., **551**, 150 (1942).

8) For example, see R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

9) 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).

10) D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962); M. G. Reinecke, *J. Org. Chem.*, **29**, 299 (1964).

11) E. Weitz, *Angew. Chem.*, **66**, 658 (1954).

S_N1 intermediate of the carbonium-ion type and the amine can not be excluded. This will be the subject of a future paper.

Experimental[12]

Materials. — Benzhydryl chloride was prepared by the reaction of thionyl chloride with benzhydryol;[13] b. p. 131.0—133.5°C/7 mmHg. Benzhdryl bromide was prepared by the reaction of bromine with diphenylmethane;[14] b. p. 139—143°C/3 mmHg. Potassium phenoxide was prepared by refluxing a mixture of potassium with a slight excess of purified phenol in dried benzene. After the potassium had completely disappeared, the phenoxide was filtered in a nitrogen stream and dried at 50°C to a constant weight in vacuo. Potassium 2,6-di-*t*-butyl-4-methylphenoxide (I) was prepared from potassium and 2,6-di-*t*-butyl-4-methylphenol (m. p. 68.0—71.0°C), by a procedure identical with that for potassium phenoxide. 1,1-Diphenylethylene (b.p. 102.5—104.5°C/2 mmHg) was prepared by the dehydration of methyldiphenylcarbinol, which had been prepared by the reaction of phenylmagnesium bromide and ethyl acetate.[15] Tri-*n*-butylamine was fractionally distilled in vacuo; b. p. 75.0—76.0°C/5 mmHg. Acetonitrile was refluxed over phosphorus pentoxide and distilled; b. p. 81.4—82.0°C. Decalin was refluxed over sodium and distilled; b. p. 190—191.5°C. Phenol was dried over calcium chloride and distilled; b. p. 178.5°C.

Kinetic Measurements. — A sealed-ampoule technique similar to that previously described[16] was employed. The diminution of the concentrations of the nucleophiles was followed by titration with standard perchloric acid in acetic acid, using crystal violet as an indicator. Each run was followed to 70—80% completion, and the thermostat was controlled to ±0.05—0.1°C.

The Reaction of Benzhydryl Chloride and Potassium Phenoxide in Acetonitrile. — A solution of potassium phenoxide was prepared in a 500-cc. round-bottomed flask equipped with a reflux condenser and a calcium chloride tube by boiling a mixture of 3.00 g. (0.0227 mol.) of potassium phenoxide and 300 cc. of acetonitrile. Benzhydryl chloride (2.94 g., 0.0145 mol.) was then added in one portion to the warm solution, and the mixture was boiled under reflux for 2.5 hr. The reaction mixture was filtered, the filtrate was concentrated by distillation, and then ether was added to the residue. The ethereal solution was washed with water, dried over magnesium sulfate, and evaporated in vacuo to give 3.79 g. of viscous oil. The potassium chloride which precipitated during the reaction was filtered after the reaction and dissolved in water, and the chloride ion concentration was determined by the Volhard method. The yield of potassium chloride based on the starting chloride was estimated as 97%. A part (0.550 g.) of the viscous oil so obtained was chromatographed over 25 g. of basic alumina. Elution with *n*-hexane afforded 0.51 g. of benzhydryl phenyl ether; m. p. 48.3—51.1°C (lit. m. p. 54°C[17] and 55°C[18]), λ^{KBr} (infrared) 8.10 μ (C-O-C). With ethanol as the eluent, 0.04 g. of benzhydrylphenol (λ^{KBr} (infrared) 2.73 μ (monomeric OH) and 2.80 μ (polymeric OH)) was obtained. The other part (3.24 g.) of the oil precipitated some crystals after being left overnight; the recrystallization of the crystals afforded 1.76 g. of benzhydryl phenyl ether, m. p. 51.2—53.5°C, λ^{KBr} (infrared) identical with the sample mentioned above. When the mother liquors were chromatographed, 1.23 g. of additional benzhydryl phenyl ether (total 3.50 g., 93.2% of the starting chloride), m. p. 47.8—50.4°C (identical in the infrared spectrum), and 0.07 g. of benzhydrylphenol (total 0.11 g., 3.1%), m. p. 109.5—114.3°C (lit. m. p. 112°C) (*p*-benzhydrylphenol)[18] and 125°C (*o*-benzhydrylphenol)[17,18] almost identical in infrared spectrum with that of the authentic para isomer, were obtained.

The Reaction of Benzhydryl Chloride and Potassium 2,6-Di-*t*-butyl-4-methylphenoxide (I) in Acetonitrile. — A solution of 6.30 g. (0.0244 mol.) of potassium 2,6-di-*t*-butyl-4-methylphenoxide in 500 cc. of acetonitrile was prepared in a 1-l. three-necked flask with a reflux condenser, equipped with a sodalime tube, and a thermometer under a nitrogen atmosphere by refluxing the mixture. To the warm solution 4.01 g. (0.0198 mol.) of benzhydryl chloride was added; the mixture was then refluxed in a stream of nitrogen at 82—85°C for 18.3 hr. The reaction mixture was then filtered and potassium chloride was dissolved in distilled water in order to determine the chloride ion concentration by the Volhard method. The amount of the chloride ions liberated during the reaction was estimated to be 82% of the starting chloride. The filtrate was concentrated and the residue dissolved in benzene. The benzene solution was washed with water, dried with magnesium sulfate, and then concentrated in vacuo to give 7.90 g. of an oily material, which was then chromatographed over 200 g. of basic alumina. *n*-Hexane, benzene, ether and finally ethanol were used as the eluents. The first-half of the *n*-hexane fractions afforded 0.51 g. of 2,6-di-*t*-butyl-4-methylphenol, m. p. 67—70°C, identical in infrared spectrum with the authentic sample. From the second-half fractions, 2.20 g. (28.7% of the chloride) of 1-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)-2,2-diphenylethane (IV), m. p. 113—115°C (ethanol), was obtained. The structural assignment for IV has already been reported.[3] Elution with benzene afforded 1.33 g. (40.2%) of *syn*-tetraphenylethane, m. p. 207.5—208.5°C (lit. m. p. 207—208°C[19]) (identity established by m.m.p.

12) The melting points are uncorrected. The microanalyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The infrared spectra were obtained from a Shimadzu model IR-27 spectrometer.

13) H. Gilman and J. E. Kirby, *J. Am. Chem. Soc.*, **48**, 1735 (1926).

14) J. F. Norris, R. Thomas and B. M. Brown, *Ber.*, **43**, 2959 (1910).

15) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, 2nd Ed., 226 (1958).

16) K. Okamoto and H. Shingu, This Bulletin, **34**, 1131 (1961).

17) P. Schorigin, *Ber.*, **59**, 2508 (1926).

18) M. Busch and R. Knoll, ibid., **60**, 2247 (1927).

19) G. Wittig and H. Witt, ibid., **74**, 1474 (1941).

207—209°C, and the infrared spectrum). Elution with ethanol gave 1.71 g. of a brown oil, which contained a dienone, λ^{neat} (infrared) 6.00 and 6.06 μ (doublet). This oil was not identified further. No diphenylmethane was identified from the *n*-hexane fractions.

The Reaction of Benzhydryl Chloride and Tri-*n*-butylammonium Phenoxide (II) in Acetonitrile.—Phenol (1.229 g., 0.0130 mol.) 2.40 g. (0.0130 mol.) of tri-*n*-butylamine, 30 cc. of acetonitrile and finally 2.00 g. (0.00985 mol.) of benzhydryl chloride were placed in a stainless-steel bomb (50 cc.). After 4 hours of heating at 143—150°C, the mixture was distilled to remove the acetonitrile; ether was added to the residue. After the ethereal solution had been washed with cold water, the titration of a part of the combined water-washings by the Volhard method indicated that 95% of the starting chloride had reacted to give chloride ions. The evaporation of the ethereal solution under reduced pressure afforded 2.71 g. of an oil, a part (0.65 g.) of which was chromatographed over 25 g. of basic alumina. Elution with benzene afforded 0.51 g. (corresponding to 83% of the starting chloride) of benzhydryl phenyl ether, m. p. 50.1—52.3°C (identity established by m.m.p. 50.1—52.5°C and the infrared spectrum). The ether fractions gave 0.07 g. (corresponding to 11.5% of the starting chloride) of benzhydrylphenol, containing mainly of the para isomer (identity established by the infrared spectrum).

The Reaction of Benzhydryl Chloride and Tri-*n*-butylamine in Acetonitrile.—A mixture of 1.62 g. (0.0080 mol.) of benzhydryl chloride, 1.63 g. (0.00881 mol.) of tri-*n*-butylamine and 40 cc. of acetonitrile was heated in a stainless-steel bomb at 146—156°C for 6.5 hr. The reaction mixutre was then filtered to give 0.6 g. (45% yield) of *sym*-tetraphenylethane, m. p. 208—209°C (identity established by m.m.p. 207.0—208.5°C and the infrared spectrum). The filtrate was concentrated to give an additional 0.21 g. (15.8% yield) of *sym*-tetraphenylethane, m. p. 207.0—209°C) (identity established by m.m.p. 207.0—208.5°C and the infrared spectrum). The mother liquors were washed with water and concentrated to give 1.01 g. of an oily material, which was then chromatographed on basic alumina (25 g.). Elution with *n*-hexane gave 0.04 g. (3.0% yield) of diphenylmethane (identity established by the infrared spectrum) from early fractions. Succeeding fractions gave 0.05 g. (3.7% yield) of *sym*-tetraphenylethane (total yield, 64.5%), m. p. 204.5—207.0°C (identity established by the infrared spectrum). The combined water washings were then concentrated to give 1.47 g. of hygroscopic white crystals, which was found by the Volhard method to contain 64.6% of the chloride ions of the starting chloride. These crystals were dissolved in 1 N sodium hydroxide, and an oily material was extracted with ether. The etheral solution was concentrated to give 1.05 g. of the residue, which, after distillation in vacuo, gave 0.85 g. (52.2% of the starting amine) of tri-*n*-butylamine, b. p. 84.0°C/14 mmHg (identity established by the infrared spectrum).

The Reaction of Benzhydryl Chloride and Tri-*n*-butylammonium 2,6-Di-*t*-butyl-4-methylphenoxide (III) in Acetonitrile.—A mixture of 1.62 g. (0.00800 mol.) of benzhydryl chloride, 1.63 g. (0.00881 mol.) of tri-*n*-butylamine and 2.12 g. (0.00881 mol.) of 2,6-di-*t*-butyl-4-methylphenol was heated in a stainless-steel bomb (50 cc.) at 141—158°C for 6.5 hr. After the mixture had been concentrated, 0.29 g. (21.8% yield) of *sym*-tetraphenylethane, m. p. 207.5—208.5°C (identity established by m.m.p. 207.5—209.0°C and the infrared spectrum) was obtained. The filtrate and the mother liquors from the recrystallization were then combined, concentrated, taken up with *n*-hexane, washed with water, and worked up to give 3.5 g. of an oily material, which was then chromatographed over 100 g. of basic alumina. Elution with benzene afforded 0.01 g. (0.7% yield) of additional *sym*-tetraphenylethane, m. p. 198—204°C (identity established by the infrared spectrum), 0.03 g. (2.1% yield) of benzophenone (identity established by the infrared spectrum), and finally 0.05 g. of 2,6-di-*t*-butyl-4-methylphenol (identity established by the infrared spectrum). A part of the water washings was titrated by the Volhard method in order to determine the chloride ion concentration; the total amount of chloride ions was estimated to be 82% of the starting chloride. The water washings were then concentrated to give 1.33 g. of hygroscopic crystals, from which 0.76 g. (46.4% of the starting amine) of tri-*n*-butylamine, (b. p. 67—73°C/17 mmHg) (identity established by the infrared spectrum) was obtained after the usual working-up.

The Reaction of Benzhydryl Bromide and Potassium 2,6-di-*t*-butyl-4-methylphenoxide (I) in Acetonitrile.—A solution of 2.31 g. (0.00896 mol.) of I in 250 cc. of acetonitrile was prepared in a 500-cc. round-bottomed flask equipped with a reflux condenser and a sodalime tube. After the addition of 2.01 g. (0.00850 mol.) of benzhydryl bromide, the mixture was refluxed for 6.9 hr. After the filtration of the potassium bromide, a part of the filtrate (1.000 cc.) was titrated by the Volhard method in order to determine the unchanged benzhydryl bromide. The conversion of benzhydryl bromide was estimated as 97% of the starting bromide. The filtrate was then concentrated, taken up with benzene, washed with water, dried with magnesium sulfate, and finally evaporated to give 3.26 g. of an oily material, a part (0.863 g.) of which was then chromatographed over 25 g. of basic alumina. Elution with *n*-hexane afforded 0.567 g. of an oil containing a solid, which gave 0.0104 g. of *sym*-tetraphenylethane, m. p. 197—204°C (identity established by the infrared spectrum) and 0.139 g. of IV, m. p. 116—117.5°C (identity established by m.m.p. 112—116°C, and the infrared spectrum) after fractional crystallization with ethanol. Benzene-*n*-hexane (1 : 1 by volume) fractions yielded an additional 0.057 g. of IV, m. p. 112—115°C (identity established by the infrared spectrum). From these results, the yields of *sym*-tetraphenylethane and of IV were estimated to be 3.0 and 24.1% respectively.

The Reaction of Benzhydryl Bromide with Tri-*n*-butylamine in Acetonitrile.—In a 100-cc. ampoule were placed 2.98 g. (0.0121 mol.) of benzhydryl

bromide, 2.45 g. (0.0132 mol.) of tri-*n*-butylamine, and 60 cc. of acetonitrile. The free space of the ampoule was then filled with nitrogen. After being sealed, the ampoule was kept at 90—93°C for 18.3 hr. Ether (100 cc.) was added to the cooled mixture, and the ethereal solution was washed with ice water. The bromide ion concentration of the water washings was determined by the Volhard method; the conversion of the starting bromide was estimated to be 91%. The dried ethereal solution was evaporated to give 2.72 g. of an oil containing some crystals. After recrystallization from ethanol, 0.10 g. (5.0% yield) of *sym*-tetraphenylethane, m. p. 196—200°C (identity established by m.m.p. and the infrared spectrum) was obtained. The mother liquors were concentrated to give 2.59 g. of an oil, a part (0.288 g.) of which was chromatographed over 25 g. of basic alumina. Some diphenylmethane (0.0775 g.) (identity established by the infrared spectrum) was left after the evaporation of the *n*-hexane fractions. Elution with *n*-hexane - benzene (7 : 3 by volume) afforded 0.0709 g. of crystals, which were then fractionally recrystallized from ethanol to give 0.0400 g. of *sym*-tetraphenylethane, m. p. 199—203°C (identity established by the infrared spectrum) and 0.028 g. of dibenzhydryl ether, m. p. 107—110°C (lit. m. p. 110°C[20]). Benzene fractions gave 0.0055 g. of benzophenone (identity established by the infrared spectrum), while ether fractions afforded 0.0185 g. of benzhydrol (identity established by the infrared spectrum). From these results, the yields of diphenylmethane and *sym*-tetraphenylethane were estimated as 22.8 and 34.4% respectively.

The Reaction of Benzhydryl Chloride and Tri-*n*-butylamine in Decalin.—The rate of chloride ion formation was determined at 150°C, using the sealed ampoule technique. The initial concentrations of benzhydryl chloride and tri-*n*-butylamine were 0.187 and 0.207 M respectively. The conversion of the starting chloride was estimated as 4.0% after a 6.5-hr. reaction. The conversion of the chloride under same reaction conditions was 3.0% in the absence of tri-*n*-butylamine. Product analyses for these runs were not carried out.

The Reaction of Benzhydryl Bromide and Tri-*n*-butylamine in Acetonitrile in the Presence of 1, 1-Diphenylethylene.—In a 100-cc. ampoule a mixture of 2.88 g. (0.0117 mol.) of benzhydryl bromide, 2.45 g. (0.0132 mol.) of tri-*n*-butylamine, 2.16 g. (0.0120 mol.) of 1, 1-diphenylethylene, and 60 cc. of acetonitrile was placed; after being sealed, the ampoule was kept at 90—91°C for 6.5 hr. To the cooled mixture was then added 100 cc. of ether, and the ethereal solution was washed with ice water. From the determination of the bromide ion concentration by the Volhard method, the conversion of starting bromide was estimated to be 95%. After the concentration of the ethereal solution, 3.69 g. of a brown oil was obtained; this was chromatographed over 145 g. of basic alumina. From *n*-hexane fractions a mixture (1.95 g., b. p. 103—107°C/3 mmHg) of diphenylmethane and 1, 1-diphenylethylene was obtained. The composition of the mixture was estimated to be 0.388 g. (19.8% of the starting bromide) of diphenylmethane and 1.28 g. of 1, 1-diphenylethylene on the basis of the infrared spectrum of the mixture, taken in carbon disulfide. The characteristic bands used for the estimation were 13.5 μ for diphenylmethane and 11.1 μ for 1, 1-diphenylethylene. The first half of the benzene-*n*-hexane (1 : 9 by volume) fractions afforded 0.395 g. of a solid, which was then recrystallized from ethanol-benzene (5 : 1 by volume) to give 0.187 g. (4.5% of the starting bromide) of 1, 1, 3, 3-tetraphenylpropene, m. p. 122—127°C (lit. m. p. 127—127.5°C[21]) (identity established by the infrared spectrum). From the second-half fractions 0.741 g. of an oil was obtained with a solid, which was then recrystallized from ethanol-benzene (5 : 1 by volume) to afford 0.212 g. (12.7% yield) of *sym*-tetraphenylethane, m. p. 203—205.5°C (identity established by the infrared spectrum). After the concentration of the mother liquors and recrystallization from ethanol-benzene (5 : 1 by volume), 0.341 g. (8.2% yield) of additional 1, 1, 3, 3-tetraphenylpropene, m. p. 127—128°C (identity established by m.m.p. 125—126°C and the infrared spectrum) was obtained. Elution with *n*-hexane - benzene (3 : 1 by volume) gave 0.12 g. of crystals of a hydrocarbon containing a benzene nucleus (confirmed by the infrared spectrum), m. p. 165—167°C (Found: C, 93.27; H, 6.69%). The crystals showed a mixed melting point of 139—169°C on admixture with 1, 1, 2, 2-tetraphenylcyclopropane (m. p. 164.5—166°C). Further identification for these crystals has not been carried out. From fractions eluted with ether 0.066 g. (3.1% yield) of benzophenone (identity established by the infrared spectrum) was obtained. The water washings were extracted with ether after the addition of sodium hydroxide, and the extracts were worked up to give 2.00 g. of tri-*n*-butylamine, b. p. 75—76°C/5 mmHg (identity established by the infrared spectrum).

The Reaction of Benzhydryl Bromide and 1, 1-Diphenylethylene in Acetonitrile.—In a 100-cc. ampoule were placed 2.98 g. (0.0121 mol.) of benzhydryl bromide, 2.16 g. (0.0120 mol.) of 1, 1-diphenylethylene and 60 cc. of acetonitrile; after it had been sealed, the ampoule was kept at 90—91°C for 63.9 hr. The white crystals (ca. 0.3 g.) which deposited on the glass wall in the upper part of the free space of the ampoule were examined in order to determine their bromide ion content by the Volhard method; Calcd. for $CH_3CN(HBr)_2$: Br, 78.8. Found: Br, 75.8%. The crystals, which precipitated in the acetonitrile solution, were filtered and washed with ether to give 2.66 g. (63.5% yield) of 1, 1, 3, 3-tetraphenylpropene, m. p. 127—128°C (identity established by the infrared spectrum). A part of the filtrate (1.000 cc.) was added to 10 cc. of ether and washed with ice water, and the ethereal solution was titrated in order to estimate the unchanged benzhydryl bromide by the Volhard method. The conversion of the starting bromide was estimated as 97%. The mother liquors were concentrated and the residue was taken up with benzene, washed with water, dried

20) J. U. Nef, *Ann.*, **298**, 232 (1897).

21) J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4189 (1962).

with magnesium sulfate and concentrated to give 1.56 g. of a solid, which in turn afforded 0.80 g. (19.2% yield) of 1,1,3,3-tetraphenylpropene, m. p. 124—126°C, (identity established by the infrared spectum) after recrystallization with benzene. The filtrate was concentrated to give 0.50 g. of an oil, which was chromatographed over 25 g. of basic alumina. Elution with *n*-hexane gave a mixture of 1,1-diphenylethylene (0.097 g.) and diphenylmethane (0.130 g., 6.4% yield). The composition was estimated by the infrared analysis mentioned above. The last fractions eluted with benzene gave 0.114 g. (5.2% yield) of benzophenone (identity established by the infrared spectrum), while those eluted with ethanol afforded 0.013 g. of benzhydrol (identity established by the infrared spectrum).

Summary

1. The S_N1 reactions of benzhydryl halides and hindered nucleophiles, i. e., potassium 2, 6-di-*t*-butyl-4-methylphenoxide (I), tri-*n*-butylammonium 2, 6-di-*t*-butyl-4-methylphenoxide (III), tri-*n*-butylamine and tri-*n*-butylammonium phenoxide (II), proceed through an Arrhenius intermediate[1] and obey good second-order kinetics in acetonitrile at 110—140°C, whereas in the same solvent the reaction with potassium phenoxide is a typical S_N1 reaction with a van't Hoff intermediate[1] at 70—120°C. This transition of the characteristics of the intermediates from a van't Hoff to an Arrhenius type has been explained as being due to steric hindrance at the product-formation step of the S_N1 reactions.

2. The reactions of benzhydryl halides and some hindered nucleophiles, i. e., tri-*n*-butylamine, I and III, afford not products anticipated for the nucleophilic substitution in acetonitrile, but rather products derived from benzhydyl radicals, i. e., *sym*-tetraphenylethane, diphenylmethane and 1-(3′, 5′-di-*t*-butyl-4′-hydroxyphenyl)-2, 2-diphenylethane, whereas potassium phenoxide and II give rise to substitution products typical of the nucleophilic reactions, i. e., benzhydryl phenyl ether and *p*-benzhydrylphenol. A one-electron transfer mechanism between these hindered nucleophiles, such as tri-*n*-butylamine, I and III, and the S_N1 intermediate has been suggested for the formation of benzhydryl radicals.

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