

worked up in the usual manner. A value of 1.98 mfaraday/mmol was obtained (six determinations). Vpc analysis of the ether extracts showed them to contain 2,2'-diiodobiphenyl, biphenyl (in substantially larger amounts than after electrolysis on wave I), and a trace amount of a third component that was trapped at the exit port of the gas chromatograph. The retention time of this material as well as a mass spectroscopic comparison with authentic material showed it to be biphenylene. Trace amounts of the white solid (mp 160–162°) were also sometimes present after electrolysis, especially in those runs where n was less than 2.0.

Electrolysis of 4,5-Phenanthryleneiodonium Bisulfate (3).

Wave I.—Electrolyses were carried out on 0.150 mM solutions in the usual manner at -0.4 to -0.6 V. A value of 1.97 mfaraday/mmol was obtained (six determinations). Work-up in the usual manner afforded a brown solid from the ether extracts as well as phenanthrene (vpc). The brown solid was washed with ether and dried under vacuum. It exhibited the following properties: mp $\sim 366^\circ$ dec; ir (KBr) 3040 (w), 1440 (w), 1395 (w), 1290 (w), 1180 (vw), 1140 (vw), 990 (vw), 820 (s), 730 and 710 cm^{-1} ; mass spectrum (50 eV) m/e 556,* 506,* 456,* and 329.*

Anal. Found: C, 42.98; H, 2.37; Hg, 45.02; I, 9.36.

The chemical (see below) as well as the spectroscopic evidence accumulated strongly suggest a mixture of di-4-phenanthrylmercury and 4-phenanthrylmercuric iodide as the chemical composition of this material.

When decomposition of this solid was effected in a capillary tube, the lower portion of which was immersed in an oil bath, a yellow solid was deposited on the upper (cooler) portion of the tube. A mass spectrum (80 eV) of this material (90°) was identical with that of phenanthrene except for a characteristic mercury cluster between m/e 198 and 204. At 160° the spectrum became more complicated with the highest m/e observed being at 456 (mercury containing). A comparison of this spectrum with that of authentic mercuric iodide (above m/e 202) showed them to be virtually identical.

Electrolysis of 4,5-Phenanthryleneiodonium Bisulfate (3).

Wave II.—Electrolysis of the bisulfate was carried out in the usual manner between -1.20 and -1.30 V. Work-up afforded phenanthrene as the major product. Only trace amounts of the brown mercury-containing solid were obtained. A value of 3.13 mfaraday/mmol was obtained (five determinations) by coulometry.

Reactions of the Electrolysis Product of 3 at Wave I. Reaction with Hydrochloric Acid.—The brown solid was suspended in about 1 ml of THF. To this suspension was added approximately an equal volume of concentrated HCl. An immediate exothermic

reaction occurred along with a color change from clear to yellow. Extraction of the mixture with ether followed by drying (MgSO_4) afforded phenanthrene (vpc) as the organic product.

Reaction with Aqueous Halide/Halogen.—The brown solid was suspended in about 1 ml of an aqueous potassium bromide (or iodide) solution. Addition of several drops (milligrams) of bromine (or iodine) was followed by heating on a steam bath for about 1 hr. Extraction with ether, drying (MgSO_4), and vpc analysis subsequently revealed the 4-halophenanthrene as the product (determined by mixed injection with 4-iodo- and 4-bromophenanthrenes).

Reaction with Glacial Acetic Acid/THF.—The brown solid was suspended in about 3 ml of THF. To the suspension was added approximately 6 ml of glacial acetic acid. The suspension was heated for 3 hr on a steam bath. At the end of this period some of the solid remained undissolved while some appeared to have gone into solution. After the solution had cooled, the undissolved material was filtered and washed with water and ether. After drying (under vacuum) the solid melted at $\sim 240^\circ$. This material is apparently not a pure compound.

Anal. Calcd for 4-phenanthrylmercuric iodide ($\text{C}_{14}\text{H}_9\text{HgI}$): C, 33.38; H, 1.60; I, 25.19. Found: C, 28.62; H, 1.54; I, 27.58.

A second solid was obtained from the solution by addition of water to the solution. After similar treatment this material melted at 210° .

Anal. Calcd for 4-phenanthrylmercuric acetate ($\text{C}_{16}\text{H}_{12}\text{HgO}_2$): C, 43.99; H, 2.77. Found: C, 40.95; H, 2.36; I, 4.20.

This solid also showed a strong carbonyl stretching band at 1580 cm^{-1} identical with that shown by phenylmercuric acetate.

Neutralization of the acidic solution with sodium carbonate, followed by extraction with ether and drying, afforded phenanthrene (vpc).

Although treatment of the electrolysis product with acetic acid apparently did result in the formation of 4-phenanthrylmercuric acetate while leaving the 4-phenanthrylmercuric iodide unreacted, separation of these materials into analytically pure samples was not accomplished.

Registry No.—1, 10182-84-0; 1 tosylate, 6293-66-9; 2, 244-54-2; 2 tetrafluoroborate, 18116-06-8; 3, 25504-50-1; 3 bisulfate, 34737-75-2; bis-2-(2'-iodobiphenyl)mercury, 34737-76-3; di-4-phenanthrylmercury, 34737-77-4; 4-phenanthrylmercuric iodide, 34737-78-5; 4-phenanthrylmercuric acetate, 34737-79-6.

Substituent Effects upon the Reductive Fission of Aryl Alcohols

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Reductive fission of substituted 1-phenyl-1-ethanols by potassium metal in *tert*-butyl alcohol occurs most readily when strongly electron-withdrawing substituents are present. In competitive reductions, the relative reactivity increases for electron-withdrawing substituents ($-I$), but decreases for several $+I$ substituents as the amount of added potassium is increased. The former behavior is believed to be associated with the importance of a dianion pathway and the latter, a radical-anion pathway. Halide substituents (except *p*-F) are anomalous, with the initial reaction being the loss of halogen. Reactivity is diminished by increasing side chain substitution.

Reductive cleavages of allyl and benzyl alcohols to propene and toluene were first studied by Chablay over 60 years ago.¹ Similar cleavages of alkyl-aryl ethers with sodium and liquid ammonia were investigated by Freudenberg and coworkers,² and later also investi-

gated by Birch, who determined the order of activating influence of aromatic substituent: $o\text{-OCH}_3 > m\text{-OCH}_3 > \text{H} > o\text{-CH}_3 > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OCH}_3$.³ Sowa and coworkers found similar substituent effects upon the mode of cleavage of certain diaryl ethers.⁴ Two mechanisms have been advanced for these active metal reductions, a radical-anion pathway and a dianion

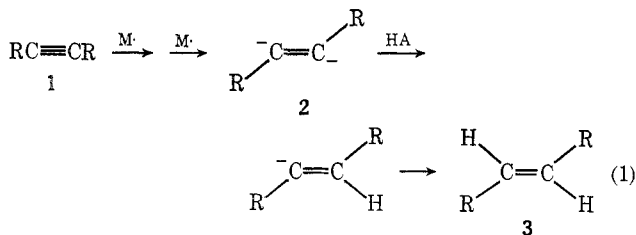
(1) (a) E. Chablay, *C. R. Acad. Sci.*, **140**, 1343 (1905); (b) *ibid.*, **143**, 829 (1906); (c) *ibid.*, **143**, 173 (1906); (d) see also L. Bouveault and G. Blanc, *ibid.*, **136**, 1676 (1903).

(2) (a) K. Freudenberg, K. Engler, F. Klink, E. Flickinger, and A. Sobek, *Chem. Ber.*, **71**, 1810 (1938); (b) K. Freudenberg, F. Klink, E. Flickinger, and A. Sobek, *ibid.*, **72**, 217 (1939).

(3) (a) A. J. Birch, *J. Chem. Soc.*, 102 (1947); (b) A. J. Birch, A. Fogiel, and G. J. Harvey, *Aust. J. Chem.*, **7**, 261 (1954).

(4) F. C. Weber and F. J. Sowa, *J. Amer. Chem. Soc.*, **60**, 94 (1938).

pathway.^{5,6} Older work was generally interpreted in terms of the dianion pathway, *e.g.*, the reduction of alkynes to trans alkenes (eq 1).^{7,8} More recently, Dauben and Wolf postulated a dianion intermediate for the reductive cleavage of certain cyclopropyl ketones.⁹



The advent of electron spin resonance^{10,11} has permitted the observation of a plethora of radical anions. Radical anions were shown to be present in the sodium and liquid ammonia solutions of aromatics.⁵ In recent years radical-anion reduction mechanisms have gained popularity, and indeed Krapcho and Bothner-By found kinetic evidence for these intermediates in the reduction of aromatics.¹² More recently the MIT group of workers presented strong evidence for a radical-anion pathway in the reduction of alkyl-substituted unsaturated ketones.¹³

Notable among the radical-anion mechanisms was Zimmermann's interpretation¹⁴ of Birch's observation¹⁵ that *o*- and *m*-methoxybenzyl alcohols were reduced to methoxytoluenes, whereas *p*-methoxybenzyl alcohol suffered ring reduction. LCAO-MO calculations were used to show that the ring position of the radical anion adjacent to the $-\text{CH}_2\text{OH}$ function was comparatively electron rich in the ortho and meta isomers. It was suggested that this factor promoted facile expulsion of the hydroxyl function.

In contrast to the case with radical anions, a relatively small number of dianions are known in which both charges reside in the same π system.^{16,17} Usually

(5) Several reviews have appeared: (a) H. Smith, "Chemistry in Non-aqueous Ionizing Solvents," Vol. 1, Interscience, New York, N. Y., 1963, p 212; (b) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (c) A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958); (d) M. Schlosser, *Angew. Chem.*, **76**, 124 (1964); (e) N. L. Holy and J. D. Marcum, *ibid.*, **10**, 115 (1971).

(6) (a) K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 216 (1941); (b) *ibid.*, **63**, 2683 (1941); (c) K. W. Greenlee and W. C. Fernelius, *ibid.*, **64**, 2505 (1942); (d) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 71, presents a more modern mechanism.

(7) D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).

(8) (a) G. Stork and J. Tsuji, *J. Amer. Chem. Soc.*, **83**, 2783 (1961); (b) G. Stork and S. D. Darling, *ibid.*, **82**, 1512 (1960); (c) *ibid.*, **86**, 1761 (1964).

(9) W. G. Dauben and R. F. Wolf, *J. Org. Chem.*, **35**, 374 (1970).

(10) L. A. Blynmenfel'd, V. V. Voerodskii, and S. P. Solodornik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 158 (1964).

(11) D. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956), in later papers.

(12) (a) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959); see also J. F. Eastham and D. R. Larkin, *ibid.*, **81**, 3652 (1959); (c) J. F. Eastham, C. W. Keenan, and H. V. Secor, *ibid.*, **81**, 6523 (1959); (d) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **82**, 751 (1960).

(13) (a) K. W. Bowers, R. Giese, J. Grinshaw, H. O. House, N. Kolodny, K. Kronberger, and D. Roe, *ibid.*, **92**, 2783 (1970); (b) H. O. House, R. Giese, K. Kronberger, J. Kaplan, and J. F. Simeine, *ibid.*, **92**, 2800 (1970).

(14) H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

(15) A. J. Birch, *J. Chem. Soc.*, 809 (1945).

(16) (a) C. Mao, C. R. Hauser, and M. L. Miles, *J. Amer. Chem. Soc.*, **89**, 5303 (1967); (b) R. L. Gay and C. R. Hauser, *ibid.*, **89**, 1647 (1967); (c) F. E. Henoch, K. Hampton, and C. R. Hauser, *ibid.*, **89**, 463 (1967).

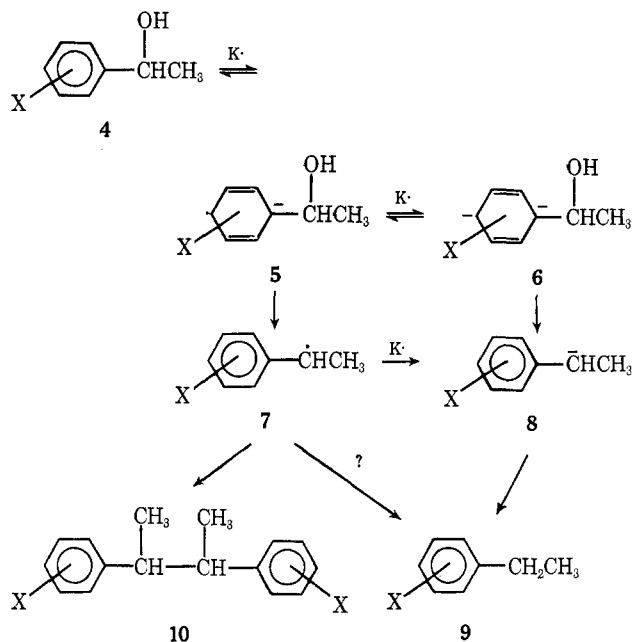
(17) (a) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1967), and references cited therein; (b) G. J. Hoijtink and P. H. van der Meij, *Z. Phys. Chem. (Leipzig)*, **20**, 1 (1959); (c) P. Balk, G. J. Hoijtink, and J. Schreurs, *Recl. Trav. Chim. Pays-Bas*, **76**, 813 (1957); (d) E. de Boer and S. I. Weissman, *ibid.*, **76**, 813 (1957); (e) A. Czerhegyi, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 1892 (1969), found the equilibrium between two radical anions and a dianion plus a neutral molecule to be markedly solvent sensitive.

these dianions are derived from polynuclear hydrocarbons in which resonance structures can be drawn with the charges well separated. Other dianions are stabilized by quantum mechanical factors associated with the Huckel $4n + 2$ rule.¹⁸

Although organic dianions are rare and obviously destabilized by charge repulsion, dianions may serve as transient intermediates in some of the reductions cited above. The most attractive mechanism to us was that advanced by Birch, which considered the possibility of both radical-anion and dianion pathways. Recent work upon the solvent effect on the reduction of certain indoles was interpreted in terms of a duality of mechanism.^{19,20} Recently Levin and Szwarc have shown that, although the radical anions of methyl phenyl acetylene are the most common species resulting from electron transfer, the disproportionation reaction of methyl phenyl acetylene takes place through a dianion intermediate.²¹ In other cases, preservation of some optical activity in the reductive fission of aryl carbinols seems best explained in terms of proton capture by a short-lived carbanion intermediate, although some sort of surface reaction cannot be excluded.²²

The present study is concerned with the competitive reduction of substituted 1-aryl-1-ethanols with potassium in *tert*-butyl alcohol. As a working hypothesis, an adaptation of Birch's mechanism⁵ will be used (Scheme I).

SCHEME I



The importance of unsaturation in the compound to be reduced was appreciated by the early workers¹ and this observation is corroborated here. The saturated analog of **4**, 1-cyclohexyl-1-ethanol (**11**), was unreactive

(18) (a) T. J. Katz and J. Schulman, *J. Amer. Chem. Soc.*, **86**, 3169 (1964); (b) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964); (c) T. J. Katz, *ibid.*, **82**, 3784 (1960); (d) D. R. Dimmel and S. B. Gharpure, *ibid.*, **93**, 3991 (1971).

(19) (a) W. A. Remers, G. Gibs, C. Pidaaks, and M. J. Weiss, *J. Amer. Chem. Soc.*, **89**, 5513 (1967).

(20) H. Walborsky, F. P. Johnson, and J. Pierce, *ibid.*, **90**, 5222 (1968).

(21) G. Levin and M. Szwarc, *Chem. Commun.*, 1029 (1971).

(22) D. J. Cram, C. A. Kingsbury, and A. Langemann, *ibid.*, **81**, 5785 (1959); (b) R. Wepster, *Recl. Trav. Chim. Pays-Bas*, **83**, 1149 (1964).

under the conditions that the aromatic alcohol reacted smoothly. From this and other work,¹⁻⁴ the initial step involving the addition of electrons to the π system seems very probable. The unsaturated center need not be adjacent to the leaving group, as shown by the reduction of β -aryl mesylates.²³

Although the radical intermediate **7** could dimerize to form **10**, comparison of the vpc traces of several of the reaction products with the vpc traces of authentic *meso*- and *dl*-**10** showed these products to be less than ca. 1% of theoretical yield.

The reductions with potassium in *tert*-butyl alcohol were, of course, surface reactions. The reaction of potassium and solvent also formed hydrogen gas and potassium *tert*-butoxide. In these reductions the "nascent hydrogen" mechanism of von Baeyer²⁴ cannot be specifically excluded, although it was considered unlikely in the liquid ammonia work.¹² The reduction of **4** to form **9** by potassium remarkably efficient compared to the reaction of potassium with solvent.

Although the metal-solvent system used in this study was heterogeneous and otherwise quite different from the liquid ammonia work cited above, the reduction seem quite similar in certain cases. For example, the reduction of 1-(4-anisyl)-1-ethanol gave a complex mixture of products which have resisted separation. However, it is quite clear from the nmr spectra that ring reduction has extensively occurred. The ortho and meta isomers underwent simple hydroxide displacement.

Table I lists the results for competitive reduction of

TABLE I
RELATIVE REACTIVITY FOR COMPETITIVE REDUCTION^c OF
X-SUBSTITUTED 1-PHENYL-1-ETHANOLS VS. THE
STANDARD COMPOUND (X = H)

Compd	X	Rel reactivity		
		0.3 g K ^b	0.6 g K ^b	1.2 g K ^b
4a	<i>o</i> -CH ₃	0.85	0.89	0.93
4b^d	<i>m</i> -CH ₃	0.71	0.72	0.76
4c	<i>p</i> -CH ₃	1.04	0.90	0.77
4d	2,4-di-CH ₃ ^a	0.44	0.44	0.39
4e	2,4,6-tri-CH ₃	0.15	0.16	0.16
4f	<i>p-t</i> -C ₄ H ₉	0.22	0.18	0.17
4g	<i>o</i> -OCH ₃ ^a	1.13	1.17	1.30
4h	<i>m</i> -OCH ₃		1.37	1.40
4i	<i>m</i> -CF ₃ ^a	1.14		1.47
4j	<i>p</i> -CF ₃ ^a	1.08	1.36	2.61
4k	<i>p</i> -F ^a	0.78	0.81	0.86
4l	<i>m</i> -Cl ^a	0.62	0.76	0.82
4m	<i>p</i> -Cl ^a	0.92	0.78	0.78
4n	H	(1.00)	(1.00)	(1.00)

^a To avoid superposition of vpc peaks, the *m*-methyl compound **4b** was used as standard, and the data were corrected to represent the reactivity vs. X = H. ^b These reactions used a standard quantity of solvent, 35 \pm 2 ml. ^c Reproducibility was checked in seven cases and found to be within 5% of the quoted value. ^d With **4b**, 20, 48, and 71% of starting material was consumed using 0.3, 0.6, and 0.9 g of potassium, respectively.

13 substituted 1-aryl-1-ethanols relative to the unsubstituted compound taken as standard. The ethylbenzene reduction products (**9**) were observed in the vpc analyses in approximately the correct ratios with respect to the amounts of reactants destroyed. However, owing to the necessity for an evaporative work-up,

the ratios of these fairly volatile products are not considered reliable. Following the treatment of Krapcho and Bothner-By, the reaction mixtures were analyzed for unreacted starting materials, and the data were converted to relative rate constants as shown in eq 2,

$$\frac{d(S_X)/dt}{d(S_H)/dt} = \frac{k_X S_X K}{k_H S_H K} \quad (2)$$

$$\frac{k_X}{k_H} = \frac{\ln(S_X/S_X^0)}{\ln(S_H/S_H^0)}$$

where S_X = final substrate concentration, S_X^0 = initial substrate concentration, S_H^0 = initial standard concentration, and K = effective surface area of potassium metal. This treatment was considered to give true relative rate constants, k_X/k_H only if the order of reaction was the same for the substituted compounds and the standard.¹² As the data in Table I show, substantial variations in $\ln(S_X/S_X^0)/\ln(S_H/S_H^0)$ were observed as the amount of potassium metal was varied (keeping solvent volume constant). This variation is taken as indicative of the incursion of a higher order term in the effective surface area of potassium for certain compounds. The expression $\ln(S_X/S_X^0)/\ln(S_H/S_H^0)$ will be termed "relative reactivity" hereafter.

Compounds with strongly electron withdrawing groups, *i.e.*, **4i** and **4j** (X = CF₃), were observed to be much more reactive than the standard. These compounds also show increasing relative reactivity with increasing levels of potassium. If either **5** \rightarrow **6** or **6** \rightarrow **8** were rate determining, the reaction would be second order in the effective surface of the potassium metal for that part of the reaction which proceeded by the **4** \rightarrow **5** \rightarrow **6** \rightarrow **8** pathway. The strong sensitivity of **4i** and **4j** to the amount of added metal is suggestive that the dianion route, **4** \rightarrow **5** \rightarrow **6** \rightarrow **8**, is more important for these substrates than for the standard. The **5** \rightarrow **8** conversion may be more or less concerted. The extensive charge repulsion in **6** would then be diminished by the partial separation of the hydroxide anion. The high reactivity of **4i** and **4j** occurs despite the fact that *tert*-butoxide, which develops as the reaction progresses, converts the free alcohols in part to their less reactive alkoxide forms.

As Table I shows, compounds with alkyl substituents are generally less reactive than the standard. The order of reactivity is H > *p*-CH₃ > *o*-CH₃ > *m*-CH₃ > 2,4-di-CH₃ > *p-t*-C₄H₉ > 2,4,6-tri-CH₃ (using 0.6 g of potassium). The steric effect of large groups is apparent upon comparing the *p*-CH₃ and *p-t*-C₄H₉ compounds (**4c** and **4f**). Large para substituents impede approach of the aromatic ring to the metal surface, but these substituents are remote from the leaving group. This steric effect adds emphasis to the fact that electrons are added to the ring from the metal and the benzylic carbon becomes involved at a later stage of the reaction. In other work, steric hindrance to solvation of the intermediate(s) was considered to be important.¹² The electron-donating character of these alkyl groups would also hinder electron addition to the ring.

Certain of the alkyl-substituted compounds show slightly increasing relative reactivities, whereas others show diminishing values with increasing levels of potassium. It is noteworthy that all compounds which show diminishing values have para substituents. The radical-anion pathway, **4** \rightarrow **5** \rightarrow **7** \rightarrow **8**, may be some-

(23) D. J. Cram and C. Dalton, *J. Amer. Chem. Soc.*, **85**, 1268 (1963).

(24) A. von Baeyer, *Justus Liebig's Ann. Chem.*, **269**, 145 (1892).

what more important for these compounds than for the standard.²⁵

The possibility of medium effects upon the relative reactivities was briefly investigated (Table II). In

TABLE II
EFFECT OF 0.5 M POTASSIUM *tert*-BUTOXIDE
ON RELATIVE REACTIVITY^a

Compd	X	Rel reactivity		
		0.3 g K	0.6 g K	1.2 g K
4a	<i>o</i> -CH ₃	0.87	0.89	0.91
4b	<i>m</i> -CH ₃	0.75	0.78	0.78
4k	<i>p</i> -F	0.76	0.80	0.86
4b OCH ₃ ^c	<i>m</i> -CH ₃	0.88	0.88	0.90
		(0.90) ^b	(0.90) ^b	(0.93) ^b

^a These data are the average of duplicate runs. Reproducibility is $\pm 5\%$. ^b The data in parentheses refer to reactions run in the absence of added 0.5 M potassium *tert*-butoxides prior to addition of potassium. ^c Methyl ether of alcohol 4b. The standard used was the methyl ether of 4n.

runs using 1.2 g of potassium, the metal reacts mainly with solvent, forming *ca.* 0.5 M potassium *tert*-butoxide. This reaction becomes markedly slower as the level of *tert*-butoxide increases. Table II shows the effect on relative reactivities of an initial added quantity of *tert*-butoxide. Within experimental error, added *tert*-butoxide has no effect on the magnitude or the trends of the reactivities.

Table II also shows the effect of changing to the leaving group to methoxide. The relative reactivity of the methyl ether of 4b was significantly different from that of the alcohol and this relative reactivity was not affected by *tert*-butoxide (Table II). The methyl ether of 4b (*m*-CH₃) was 8% more reactive than 4b itself. However, the methyl ether of 4c (*p*-CH₃) was ~60% less reactive than 4c itself. The steps of the reaction that directly involve the leaving group are 5 \rightarrow 7 and 6 \rightarrow 8. The fact that a leaving group effect is noted suggests that these step(s) may be kinetically and energetically significant. However, the complexity of the leaving group effect also suggests that Scheme I may be an oversimplification.

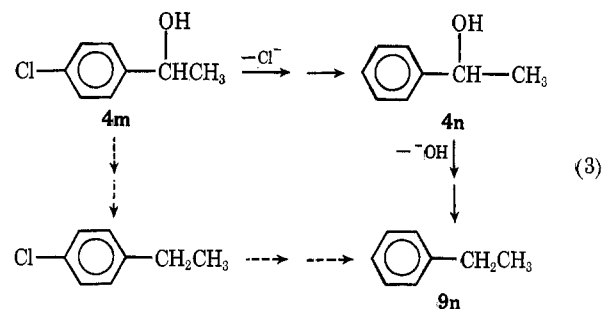
The halogen-containing compounds were surprisingly unreactive. Inspection of the reaction products revealed that the halogen had been lost in the course of the reduction for the chloro and bromo, but not lost for the fluoro compound.²⁶ When the reaction was carried out to a small conversion to product (Table III), 1-phenyl-1-ethanol (4n) and ethylbenzene (9n) were observed, but *p*-chloroethylbenzene was not observed. The reaction course very likely involves initial reduc-

TABLE III
REDUCTIVE FISSION OF 1-(4-CHLOROPHENYL)-1-ETHANOL (4m)
AND 1-(4-BROMOPHENYL)-1-ETHANOL (4o) WITH POTASSIUM IN
tert-BUTYL ALCOHOL^a

Compd	<i>p</i> -Cl (4m), %	<i>p</i> -Br (4o), %
Unreacted carbinol	90.6	88.5
1-Phenyl-1-ethanol (4n)	2.6	4.0
Ethylbenzene (9n)	6.8	7.5

^a The standard, 4n, was omitted.

tive cleavage of the halogen-ring bond, then cleavage of the side chain hydroxyl bond (eq 3). It is conceiv-



able that the addition of an electron occurs to the d orbitals of chloride or bromide. However, this does not account for the lack of reactivity of the *p*-F compound toward hydroxide displacement.

In other experiments, the effect of side chain substitution was investigated. The relative order of reactivity (Scheme II) parallels the order of carbanion (8)

SCHEME II

	OH PhCH ₂	OH Ph ₂ CH	OH PhCHCH ₃	OH PhCCH ₃ CH ₃	OH PhCC ₂ H ₅ C ₂ H ₅
	12	13	4n	14	15
rel reactivity (0.4 g K)	1.59	1.14	(1.00)	0.55	0.27

stability and not the order of radical (7) stability (with the possible exception of 13). However, steric hindrance is again important, as shown by the relative reactivities of 14 and 15. Since steps 5 \rightarrow 7 and/or 6 \rightarrow 8 are kinetically significant, the substituent stabilization of the developing carbanion or radical should also affect the energetics of the reaction. The parallel to the order of carbanion stability (with a reservation because of steric effects) reinforces the earlier judgment that a carbanion route does exist. With increasing amounts of potassium, 12 showed a strong increase in relative reactivity: 1.59 (using 0.4 g of K), 2.34 (0.8), and 2.4 (1.2). Surprisingly, 14 also showed increasing relative reactivities: 0.55 (0.4 g of K), 0.82 (0.8), and 0.83 (1.2). The one heterocycle tested, 1-(2-thienyl)-1-ethanol, proved to be the most reactive compound of all, relative reactivity 1.89 (0.4 g of K).

(25) The reason for the greater importance of the radical-anion route for para substituents which are electron donating may be related to the fact that the node of the antibonding orbital passes through the para groups: T. R. Tuttle, Jr., and S. Weissman, *J. Amer. Chem. Soc.*, **80**, 5342 (1958). In a dianion route, a second electron would probably be added to this orbital which ineffectively leads to loss of hydroxide since charge density is not increased at the ring carbon bearing the leaving group function (see ref 14). For -I substituents, the nodes of the antibonding orbital are quite different: S. K. Bowers, "Radical-Anions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1960, p 211.

(26) (a) J. J. van Daalen, A. Kraak, and J. Arens, *Recl. Trav. Chim. Pays-Bas*, **80**, 810 (1961); (b) P. Bruck, *Tetrahedron Lett.*, 449 (1962); (c) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); (d) see, however, G. D. Sargent, *J. Amer. Chem. Soc.*, **93**, 5269 (1971); (e) J. F. Garst and J. T. Barbas, *ibid.*, **91**, 3385 (1969).

Experimental Section

Preparation of 1-Phenyl-1-ethanol (4n).—This material was prepared essentially by the method of Vogel,²⁷ by adding phenylmagnesium bromide (0.35 mol) to acetaldehyde (13.2 g, 0.3 mol). The crude product was vacuum distilled. The fraction boiling at 60° (0.5 mm) was collected (25 g, 72%): 60 MHz nmr δ 1.30 (d, 3, CH₃CH), 3.76 (s, 1, OH), 4.65 (q, 1, CH₃CH), and 7.2 (s, 5, C₆H₅).

Preparation of 1-(2-Methylphenyl)-1-ethanol (4a).—The same procedure as for the preparation of 4n was used. From 54.5 g (0.319 mol) of *o*-bromotoluene, 7.76 g (0.319 g-atom) of magnesium, and 14.1 g (0.36 mol) of acetaldehyde, product 4a (27.7 g, 63.8%) was obtained: bp 70° (0.7 mm); nmr δ 1.30 (d, 3, CH₃CH), 2.28 (s, 3, CH₃Ar), 3.85 (s, 1, OH), 5.03 (q, 1, CH₃CH), and 7.50 (m, 4, C₆H₄).

Preparation of 1-(3-Methylphenyl)-1-ethanol (4b).—This material was prepared by lithium aluminum hydride (12) (3.8 g, 0.10 mol) reduction of 1-acetyl-3-methylbenzene (25.0 g, 0.186 mol) by the procedure of Vogel. The crude product was distilled under vacuum, with the fraction boiling at 61° (0.7 mm) being collected (18 g, 71%): nmr δ 1.28 (d, 3, CH₃CH), 2.28 (s, 3, CH₃Ar), 3.73 (s, 1, OH), 4.57 (q, 1, CHCH₃), and 7.0 (s, 4, C₆H₄).

Preparation of 1-(4-Methylphenyl)-1-ethanol (4c).—The procedure for the preparation of 4n was used. Vacuum distillation of the crude product afforded 13 g (60%): bp 68° (0.55 mm); nmr δ 1.30 (d, 3, CH₃CH), 2.30 (s, 3, CH₃Ar), 3.75 (s, 1, OH), 4.65 (q, 1, CH₃CH), and 7.10 (s, 4, C₆H₄).

Preparation of 1-(2,4-Dimethylphenyl)-1-ethanol (4d).—From 34.6 (0.26 mol) of aluminum chloride, 26.5 g (0.25 mol) of *m*-xylene, and 21.2 g (0.27 mol) of acetyl chloride, 2,4-dimethylacetophenone (30 g, 80%) was prepared following the procedure of Vogel: bp 70–72° (0.5 mm); nmr δ 2.30 (s, 3, CH₃CO), 2.45 [s, 6, (CH₃)₂Ar], 7.25 (m, 3, C₆H₃). Upon reduction of 14.8 g (0.1 mol) of this ketone by 17 (1.9 g, 0.05 mol) by the procedure used for 4b, the product 4d (11 g, 76%) was obtained: bp 75–78° (1 mm); nmr δ 1.23 (d, 3, CH₃CH), 2.14 (s, 3, CH₃Ar), 2.21 (s, 3, CH₃Ar), 3.56 (s, 1, OH), 4.77 (q, 1, CH₃CH), 7.01 (m, 3, C₆H₃).

Preparation of 1-(2,4,6-Trimethylphenyl)-1-ethanol (4e).—The Grignard preparation, as with 4n, was successful, using 25.0 g (0.125 mol) of bromomesitylene, 3.04 g (0.125 g-atom) of magnesium, and 5.5 g (0.125 mol) of acetaldehyde. Very careful acidification during work was necessary. Ammonium chloride solution was added dropwise until the reaction mixture became clear, pH *ca.* 7. The organic layer was separated and dried (MgSO₄). The ether was evaporated and hexane was added. The chilled solution crystallized, mp 68–70°, yielding 8.3 g (45%) of 4e: nmr δ 1.33 (d, 3, CH₃CH), 2.20 (s, 3, *p*-CH₃Ar), 2.31 [s, 6, *o*-(CH₃)₂Ar], 2.71 (s, 1, OH), 5.21 (q, 1, CH₃CH), 6.77 (s, 2, C₆H₂).

Preparation of 1-[4-(1,1-Dimethylethyl)phenyl]-1-ethanol (4f).—Reduction of *p*-*tert*-butylacetophenone (17.6 g, 0.1 mol) with 17 (1.9 g, 0.05 mol) formed 4f, which crystallized from ether (16.0 g, 90%): mp 58–60°; nmr δ 1.30 (s, 9, *t*-C₄H₉), 1.30 (s, 3, CH₃CH), 3.47 (s, 1, OH), 4.60 (q, 1, CH₃CH), and 7.18 (s, 4, C₆H₄).

Preparation of 1-(2-Methoxyphenyl)-1-ethanol (4g).—The Grignard preparation was used. Beginning with 43.5 g (0.32 mol) of freshly distilled *o*-methoxybenzaldehyde, 8.5 g (0.35 g-atom) of magnesium, and 49.9 g (0.35 mol) of methyl iodide, the product 4g was obtained by vacuum distillation: bp 97° (1.8 mm) (38.6 g, 79.3%); nmr δ 51.36 (d, 3, CH₃CH), 2.69 (s, 1, OH), 3.80 (s, 3, CH₃O), 5.04 (q, 1, CH₃CH), and 7.06 (m, 4, C₆H₄).

Preparation of 1-(3-Methoxyphenyl)-1-ethanol (4h).—The Grignard preparation was used. From *m*-bromoanisole (12.5 g, 0.067 mol), magnesium (1.63 g, 0.067 g-atom), and acetaldehyde (3.1 g, 0.07 mol), the product 4h was obtained (5.0 g, 49%): bp 120° (8 mm); nmr δ 1.30 (d, 3, CH₃CH), 3.61 (s, 3, CH₃O), 3.71 (s, 1, OH), 4.56 (q, 1, CH₃CH), and 6.80 (m, 4, C₆H₄).

Preparation of 1-(3-Trifluoromethylphenyl)-1-ethanol (4i).—From *m*-bromotrifluoromethylbenzene (32.5 g, 0.144 mol), magnesium (3.5 g, 0.144 g-atom), and acetaldehyde (5.3 g,

0.12 mol), the product 4i was obtained (15.4 g, 56%): bp 100–102° (17 mm); nmr δ 1.30 (d, 3, CH₃CH), 4.13 (s, 1, OH), 4.64 (q, 1, CH₃CH), and 7.34 (m, 4, C₆H₄).

Preparation of 1-(4-Trifluoromethylphenyl)-1-ethanol (4j).—From *p*-bromotrifluoromethylbenzene (11.3 g, 0.05 mol), magnesium (1.22 g, 0.05 g-atom), and acetaldehyde (2.64 g, 0.06 mol), the product 4j was obtained (5.0 g, 53%): mp 64° (0.05 mm); nmr δ 1.33 (d, 3, CH₃CH), 4.00 (s, 1, OH), 4.70 (q, 1, CH₃CH), and 7.34 (m, 4, C₆H₄).

Preparation of 1-(4-Fluorophenyl)-1-ethanol (4k).—The hydride reduction was used. From *p*-fluoroacetophenone (13.8 g, 0.10 mol) and 17 (19 g, 0.05 mol), the product 4k (12.5 g, 89.5%) was obtained: bp 49.5° (0.4 mm); nmr δ 1.25 (d, 3, CH₃CH), 3.90 (s, 1, OH), 4.53 (q, 1, CH₃CH), and 6.90 (m, 4, C₆H₄).

Preparation of 1-(3-Chlorophenyl)-1-ethanol (4l).—From *m*-chlorobromobenzene (24.0 g, 0.125 mol), magnesium (3.04 g, 0.125 g-atom), and acetaldehyde (6.2 g, 0.14 mol), the product 4l (14.0 g, 71%) was obtained: bp 98–100° (4 mm); nmr δ 1.33 (d, 3, CH₃CH), 4.03 (s, 1, OH), 4.68 (q, 1, CH₃CH), and 7.25 (m, 4, C₆H₄).

Preparation of 1-(4-Chlorophenyl)-1-ethanol (4m).—From methyl iodide (49.9 g, 0.35 mol), magnesium (8.5 g, 0.35 g-atom), and *p*-chlorobenzaldehyde (42.15 g, 0.3 mol), the product 4m (30.0 g, 65%) was obtained: bp 80° (0.5 mm); nmr δ 1.30 (d, 3, CH₃CH), 4.17 (s, 1, OH), 4.60 (q, 1, CH₃CH), and 7.15 (s, 4, C₆H₄).

Preparation of 1-(4-Bromophenyl)-1-ethanol (4o).—From *p*-bromoacetophenone (39.8 g, 0.2 mol) and 17 (3.8 g, 0.1 mol), the product 4o was obtained: bp 76° (0.4 mm); nmr δ 1.25 (d, 3, CH₃CH), 3.81 (s, 1, OH), 4.43 (q, 1, CH₃CH), and 6.97 (m, 4, C₆H₄).

Preparation of 1-Cyclohexyl-1-ethanol (11).—From bromocyclohexane (24.8 g, 0.15 mol), magnesium (3.9 g, 0.16 g-atom), and acetaldehyde (6.1 g, 0.15 mol), the above product was obtained (15 g, 64%): bp 43° (0.4 mm); nmr δ 1.04 (d, 3, CH₂CH) *ca.* 1.42 (m, 11, C₆H₁₁), 3.28 (q, 1, CH₃CH), and 3.40 (s, 1, OH).

Preparation of 2-Phenyl-2-propanol (14).—From methyl iodide (49.9 g, 0.35 mol), magnesium (8.5 g, 0.35 g-atom), and acetophenone (36.0 g, 0.30 mol), the product 14 (25.0 g, 62.5%) was obtained: bp 62–64° (2 mm); nmr δ 1.43 [s, 6, (CH₃)₂], 3.54 (s, 1, OH), and 7.30 (m, 5, C₆H₅).

Preparation of 3-Phenyl-3-pentanol (15).—From bromobenzene (15.79 g, 0.10 mol), magnesium (2.4 g, 0.10 g-atom), and 3-pentanone (8.6 g, 0.1 mol), the product 15 (12.0 g, 73%) was obtained: bp 80° (2 mm); nmr δ 0.8 (t, 6, CH₃CH₂), and 7.23 (m, 5, C₆H₅).

Preparation of 1-Thienyl-1-ethanol (16).—From 2-bromothiophene (25.0 g, 0.143 mol), magnesium (3.72 g, 0.153 g-atom), and acetaldehyde (6.6 g, 0.15 mol), the product 16 (13.0 g, 67%) was obtained: bp 72° (3 mm); nmr δ 1.44 (d, 3, CH₃CHO), 3.89 (s, 1, OH), 4.90 (q, 1, CH₃CH), and *ca.* 6.97 (m, C₄H₃S).

Procedure for the Reductive Cleavages.—To a 500-ml, three-necked flask, fitted with condenser, stirrer, and addition funnel, which had been dried and placed under nitrogen, 35.0 ml of *tert*-butyl alcohol (previously distilled from sodium) was added. About 4 mmol of accurately weighed samples of the two alcohols (1:1 molar ratio) was added, using *tert*-butyl alcohol to wash the sample into the flask. Freshly cut potassium was added and the flask was stirred until all the potassium had disappeared (30–50 min). Necessarily the weight of the potassium was rather rough (\pm 0.1 g) since quickness was necessary. Isopropyl alcohol was added to the final reaction mixture to react with any remaining bits of potassium. After stirring for 5 min, 200 ml of H₂O was added (*careful—fire danger*). The resulting solution was extracted twice with two 100-ml portions of pentane–ether (1:1). The combined organic layer was extracted with three 100-ml portions of water, dried (MgSO₄), and evaporated through a 25-cm Vigreux column until 3–5 ml of solution remained. This solution was analyzed by vapor phase chromatography on a Varian Aerograph A90-P-3 instrument using a 5-ft 3% SE-30 column (on Var-A-Fort 30 support). The result from at least three vpc traces were averaged. In most cases 4n was used as the standard substrate, but owing to superposition of vpc peaks, the *m*-methyl compound 4b was necessary in some cases. The relative reactivity of 4n and 4b was carefully determined at a range of potassium levels. The vpc molar response ratios of the various substrates were determined by running vpc traces of accurately measured quantities of substrate in question *vs.* 4b or 4n. Again at least three integrations were averaged.

(27) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, pp 812, 885.

Registry No.—**4a**, 7287-82-3; **4b**, 7287-81-2; **4b** methyl ether, 34386-38-4; **4c**, 536-50-5; **4d**, 5379-19-1; **4e**, 31108-34-6; **4f**, 34386-42-0; **4g**, 13513-82-1; **4h**, 23308-82-9; **4i**, 454-91-1; **4j**, 1737-26-4; **4k**, 403-41-8; **4l**, 6939-95-3; **4m**, 3391-10-4; **4n**, 98-85-1;

4n methyl ether, 4013-34-7; **4o**, 5391-88-8; **11**, 1193-81-3; **14**, 617-94-7; **15**, 1565-71-5; **16**, 2309-47-9; potassium *tert*-butoxide, 865-47-4.

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Semipinacolic Deamination of 2-Amino-1-(2-methoxyphenyl)-1-phenylethanol¹

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To elucidate the behavior of the *o*-methoxyphenyl group in cationic rearrangements, 2-amino-1-(2-methoxyphenyl)-1-phenylethanol (**1**) has been deaminated with sodium nitrite in 50% aqueous acetic acid. This reaction produced 2-methoxydeoxybenzoin (**2**), 2'-methoxydeoxybenzoin (**3**), and 3-phenylbenzofuran (**4**), respectively, in proportions 47:12:27 at 0° and 43:13:19 at 30°. Ketones **2** and **3** were not produced in equal proportions as has previously been reported. Production of **4** demonstrates for the first time methoxy oxygen (*o*-MeO-5) involvement in deaminative rearrangements and shows that use of the ratio of **3** to **2** to determine "migratory aptitude" of *o*-methoxyphenyl is improper. A mechanism is presented to account for the observed products.

Considerable attention has been given to migratory abilities of various aryl groups in pinacol and related rearrangements. Bachmann and coworkers,² in their studies of rearrangements of symmetrical tetraaryl glycols, assigned migratory aptitudes to a series of substituted aryl groups relative to phenyl; a few examples are *p*-methoxyphenyl (500), *p*-tolyl (15.7), phenyl (1.0), and *o*-methoxyphenyl (0.3).³ With the exception of ortho-substituted phenyl groups, these relative migratory aptitudes follow the order expected from consideration of relative rates of electrophilic aromatic substitution. The low migratory abilities for the ortho-substituted phenyl groups have been ascribed to steric hindrance⁴ or "ortho effect."⁵ Matsumoto and coworkers^{5b,6,7} reinvestigated the pinacolic rearrangement of the symmetrical di-*o*-methoxyphenyldiphenyl glycol, as suggested by Pocker.^{3a} Their results, though varying with the diastereomer investigated, demonstrated a migratory aptitude of *o*-methoxyphenyl roughly in agreement with the above value. Matsumoto⁷ concluded that Pocker's suggestion^{3a} of *o*-anisyl oxygen involvement⁸ with the developing carbonium ion was not in accord with his thermodynamic data.

A number of deaminations of substituted aminoethanols (semipinacols) of the type ArPhC(OH)CH₂(NH₂)R are known in which the predicted (on the basis of relative migratory aptitudes) aryl group does not migrate to provide the majority of rearranged prod-

uct.⁹ Curtin, *et al.*,⁹ explained these results by means of a transition-state "cis effect," whereas Collins, *et al.*,¹⁰ ascribe such behavior to ground-state conformational control. In cases in which the migration terminus is primary, the migratory aptitudes of aryl groups during deamination follow the expected order, but the values are much reduced compared to the symmetrical tetraaryl glycol cases. For example, in 2-amino-1-aryl-1-phenylethanol the migratory aptitudes (phenyl = 1.0) are *p*-methoxyphenyl (1.5), *p*-tolyl (1.3), and *p*-chlorophenyl (0.9).^{9f} Rather similar results are obtained in systems lacking the hydroxyl group.¹¹

Our desire to elucidate the behavior of the *o*-methoxyphenyl group in cationic rearrangements led us to inquire into the semipinacolic deamination of 2-amino-1-(2-methoxyphenyl)-1-phenylethanol (**1**), a case in which steric hindrance in the transition state should not play an important role. Here the apparently anomalous migratory aptitude of the *o*-methoxyphenyl group, as in the symmetrical tetraaryl glycol rearrangement, should not obtain if that behavior arises from steric effects in the transition state. Indeed, Kharasch, *et al.*,¹² demonstrated that treatment of *o*-anisylidiphenylcarbinol with *tert*-butyl hydroperoxide and perchloric acid in glacial acetic acid yields mostly guaiacol and benzophenone, which arise from predominant *o*-anisyl (rather than phenyl) migration to oxygen in the ion resulting from heterolytic scission of the first-formed peroxide. Further, there should be a likely possibility of *o*-anisyl oxygen involvement with the developing ionic center (the so-called *o*-MeO-5 participation⁸) during deamination of **1**, with the resulting

(1) Taken in part from the M.S. Thesis of C. E. S., San Fernando Valley State College, 1972.

(2) W. E. Bachmann and J. W. Ferguson, *J. Amer. Chem. Soc.*, **56**, 2081 (1934); W. E. Bachmann and H. R. Sternberger, *ibid.*, **56**, 170 (1934); W. E. Bachmann, *ibid.*, **54**, 2112 (1932); W. E. Bachmann and F. H. Mosher, *ibid.*, **54**, 1124 (1932).

(3) For compilations of these and other results, see (a) Y. Pocker in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 1; (b) C. J. Collins, *Quart. Rev. Chem. Soc.*, **14**, 357 (1960).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 478.

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(6) R. Goto, K. Matsumoto, and A. Sera, *ibid.*, **87**, 93 (1966).

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(10) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **63**, 3654 (1961).

(11) L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952); P. S. Bailey and J. G. Burr, Jr., *ibid.*, **75**, 2951 (1953); B. M. Benjamin and C. J. Collins, *ibid.*, **78**, 4952 (1956). See also V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958), for comparison of solvolytic rearrangement of glycols and aldehydes with deamination of primary amines.

(12) M. S. Kharasch, A. Fono, W. Nudenberg, and A. C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).