

lowing, in general, the cell temperatures to rise during the electrolysis to 25–35° and in some cases even to 40° (in the runs with XIV and XV).

The electrofluorination runs gave, with the exception of the run with dipiperidylmethane, the fully fluorinated analogs and in all cases fluorinated cleavage products of the organic starting materials. The electrochemical fluorination of pyridine (XII) yielded, as expected, perfluoropentane (X), nitrogen trifluoride contaminated with about 5% of carbon tetrafluoride and as the main product perfluoropiperidine (II). The formation of perfluoro-1,1'-dipiperidyl (III) from XII is noteworthy. Condensations of this type occur possibly in all electrofluorinations but, in general, the resulting products are not formed in small runs in amounts sufficient for isolation and identification.

The electrofluorination of 4-*n*-propylpyridine (XIV) yielded some of the fully fluorinated analog V which according to its NMR spectrum appeared to be free of isomers. The NMR analysis of the perfluoro-3-ethylhexane (VI) fraction which had been formed in this run by rupture of the two carbon-to-nitrogen bonds indicated the absence of isomers but showed contamination with a small amount of other impurities.

The isomeric 4-isopropylpyridine (XV) gave in an analogous manner perfluoro-4-isopropylpiperidine (VII) which, however, appeared to contain V as a contaminant. The NMR analysis of the cleavage product C<sub>8</sub>F<sub>18</sub> from this run indicated the major component to be VI with some perfluoro-2-methyl-3-ethylpentane, (CF<sub>3</sub>)<sub>2</sub>CF(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>, present as an impurity. A similar conversion of a branched carbon skeleton to a straight chain has been observed in the electrochemical fluorination of *t*-butyl disulfide<sup>1</sup> which yielded as one of the cleavage products a perfluorobutane fraction consisting of approximately 85–90% of perfluoro-*n*-butane and 15–10% of perfluoroisobutane.

The only material which failed to give the perfluorinated analog was dipiperidylmethane (XIII). Only the cleavage products II, IV and X were obtained. It is interesting to note that in this run as well as in the electrofluorination of XIV, where the electrode pack consisted of alternating iron cathodes and nickel anodes, none, or at best only a relatively small yield, of the fully fluorinated analogs was formed. The amount of tarry materials obtained in the cells during these runs was correspondingly large. The electrochemical fluorination of XV employing an all-nickel electrode pack gave a larger yield of perfluorinated analog than the run with XIV using alternating iron and nickel electrodes (260 g. as compared to 85.7 g.). This observation was rather surprising since one might expect the more branched carbon skeleton of XV to be more susceptible to degradation than that of XIV.

The electrofluorination of morpholine (XVI) resulted in a relatively good yield of perfluoromorpholine (VIII) and a considerable amount of perfluoro-diethyl oxide (XI) indicating extensive cleavage of the C–N bonds of the starting material. Similar results were obtained with 1-methylmorpholine (XVII) which yielded, as expected, the fully fluorinated analog IX and the cleavage product XI.

A detailed discussion of the NMR and infrared spectra of the various compounds obtained in this study will be published by members of the Spectroscopy Group, Physical Measurements Branch, of these laboratories in a forthcoming paper.

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ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## Neighboring Carbon and Hydrogen. XXIX. $\rho$ - $\sigma$ Analysis of Acetolysis of Substituted Neophyl Arylsulfonates

BY R. HECK AND S. WINSTEIN

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In acetolysis of neophyl *p*-bromobenzenesulfonate, ionization is exclusively anchimerically assisted, only neighboring phenyl participating. Rates of aryl-assisted ionization of a series of substituted neophyl *p*-bromobenzenesulfonates have been measured and correlated with the aid of the Hammett  $\rho$ - $\sigma$  relation. Omitting the *p*-MeO group,  $\log k$  of acetolysis is approximately linear in  $\sigma$  with a slope  $\rho$  of  $-3.65$ . The value of  $\log k$  for the *p*-MeO substituent falls substantially above the line through the other points. By using  $\sigma^+$ -values of Brown and Okamoto which reflect a blend of inductive and resonance influences of the substituents more appropriate for an electron-demanding reaction, the *p*-MeO group may be treated along with the other substituents. The slope of the  $\log k$  vs.  $\sigma^+$  line is  $-2.96$ .

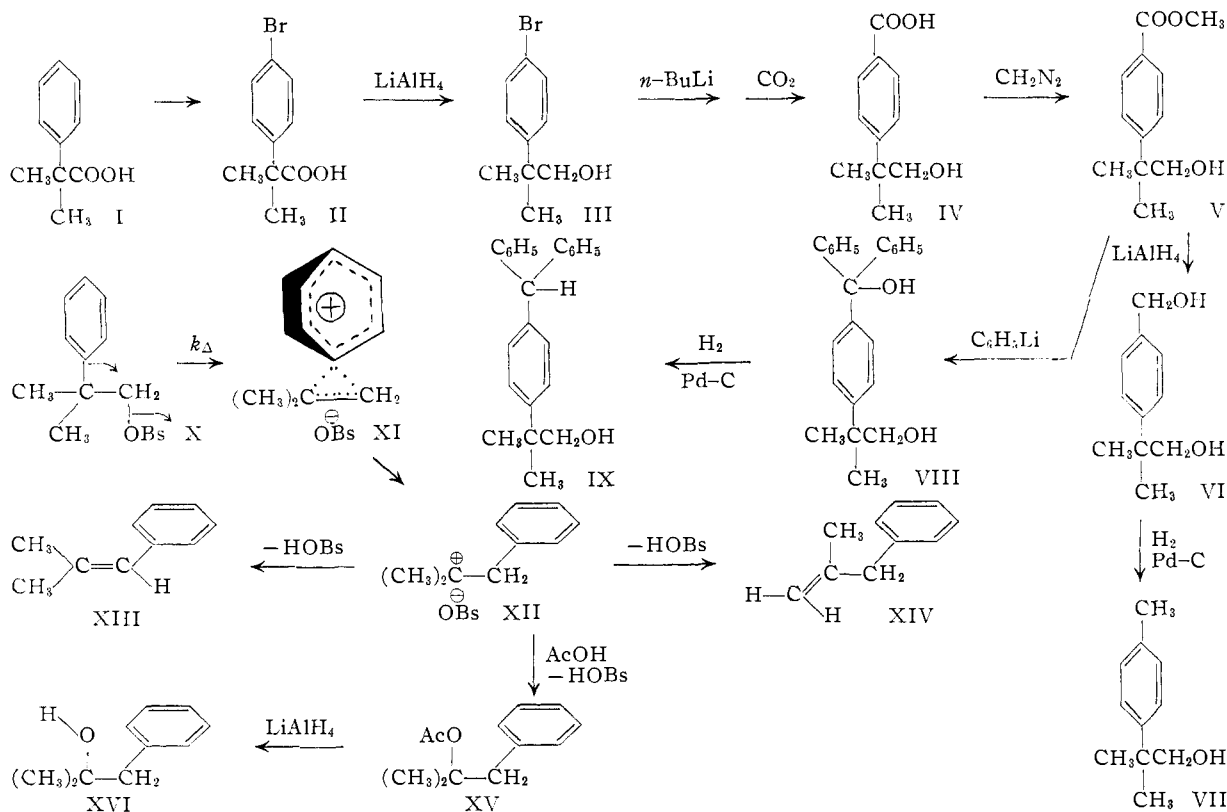
In connection with another investigation,<sup>1</sup> it became necessary to prepare *p*-benzhydrylneophyl alcohol (IX). The synthetic route employed involved preparation of the *p*-bromo- and *p*-carbomethoxyneophyl alcohols (III) and (V). Since these were available and the *p*-carbomethoxyneophyl alcohol was converted easily to the *p*-

methyl analog, we were prompted to extend the previous study<sup>2</sup> of the effect of substituents on solvolysis rate of neophyl arylsulfonates. The results obtained and their analysis with the aid of Hammett's  $\rho$ - $\sigma$ -relation<sup>3</sup> are given in the present article

(2) S. Winstein and R. Heck, *THIS JOURNAL*, **78**, 4801 (1956).

(3) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VI; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(1) P. Magee, R. Heck and S. Winstein, unpublished work.



**Substituted Neophyl Bromobenzenesulfonates.**—All of the *p*-bromobenzenesulfonates required in the present study were prepared by the usual method from the corresponding alcohols. The preparation of several of the required alcohols began with the bromination of  $\alpha,\alpha$ -dimethylphenylacetic acid (I) which was available from the nitrile obtained by the alkylation of benzyl cyanide with sodamide and methyl iodide. From the bromination was obtained the  $\alpha,\alpha$ -dimethyl-*p*-bromophenylacetic acid (II). Lithium aluminum hydride reduction of the latter yielded *p*-bromoneophyl alcohol (III).

To confirm the *p*-position of the bromine atom in the brominated acid II and alcohol III, oxidation to *p*-bromobenzoic acid was carried out. Oxidation of the bromophenylisobutyric acid II with boiling alkaline potassium permanganate proceeded very slowly and yielded only a trace of pure *p*-bromobenzoic acid. However, much more satisfactory results were obtained by treatment of the bromoneophyl alcohol III with thionyl chloride and oxidizing the product with alkaline permanganate. Evidently, the reaction of the alcohol III with thionyl chloride proceeds with Wagner-Meerwein rearrangement, the aryl group migrating so that tertiary chloride and related olefins are produced. Oxidation of the whole crude reaction mixture gave a substantial yield of pure *p*-bromobenzoic acid.

*p*-Bromoneophyl alcohol (III) was converted to the aryllithium derivative, though in poor yield, by reaction with two equivalents of *n*-butyllithium in ether solution. Carbonation yielded *p*-carboxyneophyl alcohol (IV) which was con-

verted to *p*-carbomethoxyneophyl alcohol (V) with diazomethane. Reduction of this ester with lithium aluminum hydride yielded *p*-hydroxymethylneophyl alcohol (VI). Hydrogenolysis of the latter over palladium-on-charcoal led to *p*-methylneophyl alcohol (VII).

The reaction of 3 equivalents of phenyllithium with *p*-carbomethoxyneophyl alcohol (V) gave *p*-diphenylhydroxymethylneophyl alcohol (VIII), hydrogenolysis of the latter leading to *p*-benzhydri-*p*-neophyl alcohol (IX).

The remaining new alcohol, *m*-methylneophyl alcohol, was prepared by the lithium aluminum hydride reduction of the corresponding acid. This acid,  $\alpha,\alpha$ -dimethyl-*m*-tolylacetic acid, was prepared by the hydrolysis of the nitrile which, in turn, was obtained by alkylating *m*-methylbenzyl cyanide with sodamide and methyl iodide.

**Acetolysis.**—All of the bromobenzenesulfonates investigated in the present work obeyed good first-order kinetics in acetolysis, the measured first-order rate constants being summarized in Table I, which also includes a comparison of the rates with those of three neophyl derivatives previously investigated.<sup>3,4</sup>

In order to verify<sup>4,5</sup> the course of acetolysis of the reference compound, neophyl *p*-bromobenzenesulfonate (X), the products of solvolysis of 0.05 *M* material in acetic acid, 0.06 *M* in lithium or sodium acetate, were investigated. Treatment of the reaction product with lithium aluminum hydride and

(4) A. H. Fainberg and S. Winstein, *THIS JOURNAL*, **78**, 2763 (1956).

(5) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

TABLE I  
 RATES OF ACETOLYSIS OF SOME SUBSTITUTED NEOPHYL *p*-BROMOBENZENESULFONATES

Substituent	Concn., 10 <sup>2</sup> <i>M</i>	Temp., °C.	Rate constant, sec. <sup>-1</sup>	Rel. rate 75.0°	Δ <i>H</i> * <sub>s</sub>	Δ <i>S</i> * <sub>s</sub>
<i>p</i> -OMe	..	75.0	6.05 × 10 <sup>-3a</sup>	88.5	23.2 <sup>b</sup>	-4.4 <sup>b</sup>
<i>p</i> -Me	3.02	50.0	(2.91 ± 0.04) × 10 <sup>-5</sup>			
	2.96	75.0	(4.97 ± 0.05) × 10 <sup>-4</sup>	7.27	24.7	-3.1
<i>p</i> -(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH	2.16	50.0	(1.01 ± 0.01) × 10 <sup>-5</sup>			
	2.66	75.0	(1.83 ± 0.03) × 10 <sup>-4</sup>	2.68	25.2	-3.5
<i>m</i> -Me	3.32	75.0	(1.318 ± 0.005) × 10 <sup>-4</sup>	1.93	25.8	-2.4
	3.45	100.0	(1.72 ± 0.03) × 10 <sup>-3</sup>			
H <sup>4</sup>	2.14	75.0	(6.84 ± 0.03) × 10 <sup>-5</sup>	1.00	25.5	-4.6
					26.0 <sup>b</sup>	-5.7 <sup>b</sup>
<i>m</i> -MeO	3.42	75.0	4.75 × 10 <sup>-5a</sup>	0.69	25.4 <sup>b</sup>	-8.1 <sup>b</sup>
<i>p</i> -Br	2.84	75.0	(1.09 ± 0.01) × 10 <sup>-5</sup>	0.16	26.5	-5.4
	3.16	100.0	(1.52 ± 0.02) × 10 <sup>-4</sup>			
<i>p</i> -CH <sub>2</sub> OCO	3.13	75.0	(1.32 ± 0.01) × 10 <sup>-6</sup>	0.019	28.1	-5.1
	2.82	100.0	(2.14 ± 0.02) × 10 <sup>-5</sup>			

<sup>a</sup> Rate constant for *p*-toluenesulfonate<sup>2</sup> multiplied by 3.42, the factor between toluenesulfonate and *p*-bromobenzenesulfonate.<sup>4</sup> <sup>b</sup> Values for the *p*-toluenesulfonate.

 TABLE II  
 SUMMARY OF PRODUCTS FROM NEOPHYL *p*-BROMOBENZENESULFONATE IN ACETIC ACID AT 75°

Run (ROBs), <i>M</i>	1 0.0508 <sup>a</sup>	2 0.0508	Average	
Salt	0.0625 <i>M</i> LiOAc	0.0625 <i>M</i> NaOAc		
Time, hours	28	28		
Total % recov.	90.7	91.8	91.3	
Product alcohol	% yield	31.1	30.3	
	<i>n</i> <sup>25</sup> <sub>D</sub>	1.5128	1.5120	
	m.p., °C.	25-26	24.5-25.5	
	b.p., °C. (mm.)	65-68 (1.5)	65-68 (2)	
% neophyl	ca. 0.5-0.75	ca. 1	ca. 0.8	
Product olefin	% yield	59.6	61.5	
	<i>n</i> <sup>25</sup> <sub>D</sub>	1.5207	1.5200	
	ε at λ = 244 mμ	6912	6880	
	% conjug. (XIII)	49, <sup>b</sup> 52 <sup>c</sup>	52 <sup>c</sup>	51
	% unconjug. (XIV)	51, <sup>b</sup> 48 <sup>c</sup>	48 <sup>c</sup>	49
Total product compn.	% olefin	65.7	66.9	
	% rearr. alc.	34.1	32.8	
	% neophyl alc.	0.2	0.3	

<sup>a</sup> Three times recrystallized bromobenzenesulfonate was employed. <sup>b</sup> From the *n*<sup>25</sup><sub>D</sub>, using *n*<sup>25</sup><sub>D</sub> 1.5364 for XIII and 1.5037 for XIV.<sup>6</sup> <sup>c</sup> From ultraviolet absorption, using ε 14,000 for XIII and 77 for XIV in isoöctane.<sup>6</sup>

subsequent chromatography gave rise to olefin and alcohol fractions.

In quantitative hydrogenation, a sample of the olefin product consumed the correct quantity of hydrogen calculated for a mixture of β,β-dimethylstyrene (XIII) and 1-phenyl-2-methyl-2-propene (XIV). Also, the hydrogenation product proved to be pure isobutylbenzene, the infrared spectrum being identical with that of a pure standard. The analysis of the olefin product for conjugated and unconjugated components, XIII and XIV, respectively, could be based on either ultraviolet absorption spectrum or refractive index, both methods agreeing well. As summarized in Table II, the olefin proved to be 51% conjugated (XIII) and 49% unconjugated (XIV).

The alcohol product, m.p. 25-26°, was essentially pure rearranged tertiary alcohol XVI, the authentic synthetic material having m.p. 25.5-26.5°. There was some indication from the infrared spectrum of a trace of unrearranged material in the al-

cohol product. The alcohol product displayed an infrared spectrum nearly identical with that of authentic benzyl-dimethylcarbinol (XVI), except for the presence of slightly high absorption at 1000-1075 cm.<sup>-1</sup> and slightly low absorption at 1125-1250 cm.<sup>-1</sup>. Since neophyl alcohol has a very strong band at 1030 cm.<sup>-1</sup> and is relatively transparent at 1125-1250 cm.<sup>-1</sup>, it seems probable that a small amount of neophyl alcohol is present in the acetolysis product. By preparing a synthetic mixture containing 1.6% neophyl alcohol in the tertiary alcohol and comparing its spectrum with that of the solvolysis product, it was possible to estimate that the product alcohol contained 0.5-0.75% neophyl alcohol.

While the indications are that the over-all solvolysis product contains ca. 0.2% neophyl alcohol, it is not clear what its mode of formation is. Some of it may arise during lithium aluminum hydride treatment of the reaction product, since the latter would contain 0.1% of unreacted neophyl bromobenzenesulfonate after ten solvolysis half-lives

(6) S. J. Lapporte, unpublished work.

(28 hr.). Some of the unrearranged neophyl product may arise from second-order reaction of neophyl bromobenzenesulfonate with acetate ion. For these reasons, it is not possible, without more controls, to associate the neophyl alcohol with any definite competing reaction path such as anchimerically unassisted solvolysis of neophyl bromobenzenesulfonate.

The present observations on the nature of the products further strengthens the previous conclusion,<sup>2,5</sup> based on rate and  $\Delta S^\ddagger$ , that neophyl bromobenzenesulfonate solvolyzes essentially exclusively with anchimerically assisted ionization. It seems likely that anchimerically unassisted solvolysis would lead to a product containing at least a substantial proportion of unrearranged material. The virtual absence of such a material indicates the proportion of solvolysis by an anchimerically unassisted route must be extremely small.

**$\rho$ - $\sigma$  Correlation.**—As is brought out in Table I, the relative solvolysis rates at 75° of the neophyl bromobenzenesulfonates studied in the present and previous<sup>2</sup> work cover a range of 4500. The *p*-methoxyl substituent enhances rate by a factor of 88.5 and the *p*-carbomethoxy group depresses rate by a factor of 52. Even in the latter case, aryl-assisted ionization can be assumed to dominate the acetolysis; with anchimerically assisted ionization depressed by a factor of only *ca.* 50, one would not yet expect other processes, so negligible in solvolysis of neophyl bromobenzenesulfonate, to be too serious. On this basis, one can expect sufficient uniformity of mechanism of solvolysis of the series of neophyl bromobenzenesulfonates to warrant application of the Hammett relation<sup>3</sup> (1) to the rate data.

As is clear from Fig. 1, the plot of  $\log k$  vs.  $\sigma$  is roughly linear, with the point for *p*-OCH<sub>3</sub> lying

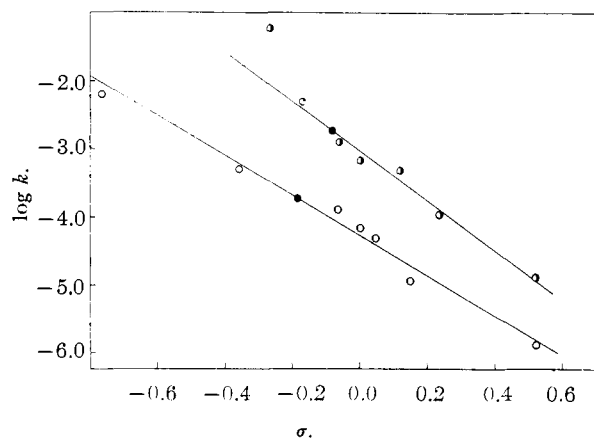


Fig. 1.—Plot of  $\log k$  for acetolysis of neophyl *p*-bromobenzenesulfonates at 75° vs.  $\sigma$ :  $\bullet$ ,  $1 + \log k$  vs.  $\sigma$ ;  $\circ$ ,  $\log k$  vs.  $\sigma^+$ ;  $\bullet$ , *p*-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH group.

substantially above the line outlined by the other points. As summarized in Table III, after omitting the *p*-OCH<sub>3</sub> group, the remaining points fit the Hammett linear relation (1) with a slope  $\rho$  equal to  $-3.65$ , the probable error of the fit being  $0.085$  in  $\log k$ . In line with the nature<sup>5</sup> of the an-

$$\log k = \log k^0 + \rho\sigma \quad (1)$$

chimerically assisted rate-determining ionization step,  $\rho$  is negative and relatively large in magnitude. This is expected for an electron-demanding reaction.

TABLE III

SUMMARY OF LEAST SQUARES FITS OF  $\log k$  OF ACETOLYSIS OF NEOPHYL *p*-BROMOBENZENESULFONATES TO THE HAMMETT  $\rho$ - $\sigma$  RELATION AT 75°

Substit. constant <sup>a,b</sup>	$\log k^0$	$\rho$	$r^c$
$\sigma^{db}$	-4.037	-3.650	0.085 <sup>d</sup>
$\sigma^+$	-4.281	-2.959	.125

<sup>a</sup> For *p*-COOCH<sub>3</sub>,  $\sigma$  and  $\sigma^+$  equal to  $+0.522$  employed;  $\sigma^+$  values of Brown and Okamoto were used: *p*-OCH<sub>3</sub>,  $-0.764$ ; *p*-CH<sub>3</sub>,  $-0.306$ ; *m*-CH<sub>3</sub>,  $-0.0652$ ; *m*-OCH<sub>3</sub>,  $-0.0465$ ; *p*-Br,  $0.148$ . <sup>b</sup> The least squares lines yield  $\sigma = -0.082$  and  $\sigma^+ = -0.184$  for the *p*-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH group. <sup>c</sup> Probable error in  $\log k$ . <sup>d</sup> Omitting the *p*-OCH<sub>3</sub> group from the least-squares line.

The upward curvature of the  $\log k$  vs.  $\sigma$  plot for the point corresponding to the *p*-methoxyl group is to be expected, since one cannot expect the blend<sup>7-10</sup> of inductive and resonance influences reflected by  $\sigma$  to be appropriate for a strongly electron-demanding reaction. Such failure of the Hammett  $\rho$ - $\sigma$ -relation is common, for example, in solvolysis of benzhydryl halides<sup>11</sup> or brominolysis of benzeneboronic acids.<sup>12</sup> It is common also in connection with other rearrangement reactions similar to the present example. A few such rearrangements are listed in Table IV for comparison with the present work.

Table IV includes examples of aryl migration to carbon or oxygen, as well as a number of cases of migration to nitrogen. The latter include the Beckmann, Lossen, Hofmann and Stieglitz rearrangements, as well as Schmidt reactions of benzoic acids and 1,1-diarylethenes. Some of the applications of the Hammett relation are to rate data. When the substituent is in the migrating phenyl group, the Hammett relation is supposed to account for the modification of the inductive and anchimeric effects<sup>5</sup> of the phenyl group by the substituent. When the substituent is on a non-participating phenyl, the Hammett relation is supposed to account for the modification of the inductive and any conjugative effects<sup>5</sup> of the phenyl group.

Some of the applications of the Hammett relation in Table IV are to relative migration aptitudes. If we take anchimerically assisted ionization of 2,2-diphenylethyl<sup>5,13</sup> toluenesulfonates XV and XVI for illustration, the meaning of the plot of  $\log$  of relative migration aptitude vs.  $\sigma$  may be clarified

(7) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(8) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(9) H. C. Brown and Y. Okamoto, Page 59-O of Abstracts, American Chemical Society meeting, Atlantic City, N. J., September 16-21, 1956.

(10) G. S. Hammond and F. T. Fang, Page 87-O of Abstracts, American Chemical Society meeting, Atlantic City, N. J., September 16-21, 1956.

(11) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 144.

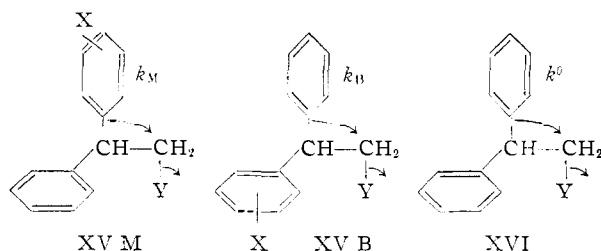
(12) (a) H. G. Kuivila and A. R. Hendrikson, *THIS JOURNAL*, **74**, 5068 (1952); (b) ref. 11, p. 353.

(13) J. G. Burr, Jr., *THIS JOURNAL*, **75**, 5008 (1953); *Chemistry & Industry*, 850 (1954).

TABLE IV  
SUMMARY OF APPLICATION OF HAMMETT'S RELATION TO  
CERTAIN REARRANGEMENTS

Reaction series	Ref.	$-\rho_M$	$-(\rho_M - \rho_B)$	$-\rho_B$
$\text{XC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{CH}_2\text{OBs}$ , AcOH, 75.0°		3.7		
$\text{XC}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{OTs}$ , AcOH, 99.5°	13	4.2		2.0
$\text{XC}_6\text{H}_4\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{OH}$ , $\text{P}_2\text{O}_5$ , xylene	14		2.3	
$\text{XC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{OOCOC}_6\text{H}_4\text{NO}_2$ , AcOH, 25.0°	15	5.1		
$(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NOC}_6\text{H}_4(\text{NO}_2)_2$ , $\text{CCl}_4$ , 90.8°	16	4.3		1.9
$\text{XC}_6\text{H}_4\text{CONHOCOC}_6\text{H}_5$ , aq. $\text{NH}_3$ , 30°	17	2.6		
$\text{XC}_6\text{H}_4\text{CONHBr}$ , aq. $\text{NaOH}$ , 30°	18	2.5		
$\text{XC}_6\text{H}_4\text{COOH}$ , $\text{HN}_3$ , $\text{H}_2\text{SO}_4$ , $\text{Cl}_2\text{C}=\text{CHCl}$ , 40°	19a	2.0		
$\text{XC}_6\text{H}_4\text{CN}(\text{C}_6\text{H}_5)(\text{CH}_3)$ , $\text{H}_2\text{SO}_4$ , $\text{C}_6\text{H}_6$	20		2.8	
$(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{CH}_2$ , $\text{HN}_3$ , $\text{H}_2\text{SO}_4$	19b		2.1	
$(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNHOH}$ , $\text{PCl}_5$ , $\text{C}_6\text{H}_6$	21		1	

in the following way. To the extent that the Hammett relation will account successfully for the rates of the anchimerically assisted rate-determining ionizations, we may write relation (2) for  $k_M$ , where the substituent is in the migrating phenyl (XVM), and relation (3) for  $k_B$ , where the substituent is in the phenyl group which remains



behind (XVB). In these relations,  $k^0$  is half the rate constant of ionization of 2,2-diphenylethyl toluenesulfonate (XVI).

$$\log k_M = \log k^0 + \rho_M \sigma \quad (2)$$

$$\log k_B = \log k^0 + \rho_B \sigma \quad (3)$$

$$\log (k_M/k_B) = (\rho_M - \rho_B) \sigma \quad (4)$$

The relative migration aptitude of the substituted phenyl group, defined equal to the ratio  $k_M/k_B$ , is then given by relation 4. The latter is a linear relation between log of relative migration aptitude and  $\sigma$ , the proportionality constant being  $(\rho_M - \rho_B)$ . The situation is similar for cases where aryl does not participate in the rate-determining step but migrates at a later stage of the reaction. For such cases,  $k_M$ ,  $k_B$  and  $k^0$  are rate constants for the reaction steps involving aryl shift.

In most of the applications of the Hammett relation in Table IV, considerable tendency for curvature in the  $\log k$  or  $\log (k_M/k_B)$  vs.  $\sigma$  plot is evident. In such cases, the values of  $\rho$  listed are either for elec-

(14) J. G. Burr, Jr., and L. S. Ciereszko, *THIS JOURNAL*, **74**, 5426 (1952).

(15) K. Nelson, unpublished work.

(16) A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936). We are indebted to A. H. Fainberg for calculation of the data to a single temperature.

(17) (a) W. B. Renfrow, Jr., and C. R. Hauser, *THIS JOURNAL*, **59**, 2308 (1937); (b) ref. 3a, p. 191.

(18) C. R. Hauser and W. B. Renfrow, Jr., *THIS JOURNAL*, **59**, 121 (1937).

(19) (a) L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943); (b) W. E. McEwen and N. B. Mehta, *THIS JOURNAL*, **74**, 526 (1952).

(20) S. N. Ege and K. W. Sher, *ibid.*, **75**, 354 (1953).

(21) M. S. Newman and P. M. Hay, *ibid.*, **75**, 2322 (1953).

tron-withdrawing substituents or for a range of substituents including none more electron-supplying than  $p\text{-CH}_3$ . Within a factor of ca. 2, the various  $\rho_M$  values, some of them quite rough, are similar for all the rearrangements listed.

By choosing new  $\sigma$  values<sup>7,9,10</sup> which do reflect a blend of inductive and resonance influences more appropriate to electron-demanding reactions, one can hope to treat the present reactivity data more satisfactorily with relation 1. The set of  $\sigma$  values, labeled  $\sigma^+$  values, which we have employed for this purpose is one derived by Brown and Okamoto<sup>9,22</sup> from rates of hydrolysis of substituted phenyldimethylcarbinyl chlorides in aqueous acetone. The plot of  $\log k$  of acetolysis of the neophyl bromobenzenesulfonates vs.  $\sigma^+$  is shown in Fig. 1, from which it is evident that the point for  $p\text{-OCH}_3$  comes closer to fitting on the same line with the other substituents. The  $\sigma^+$  value employed for  $p\text{-OCH}_3$  somewhat over-corrects the present situation, since the  $p\text{-OCH}_3$  point now falls below the line. The least-squares fit of the data to relation 1, including the  $p\text{-OCH}_3$  point, is summarized in Table III. By using  $\sigma^+$  values, the fit of the data including the  $p\text{-OCH}_3$  point is comparable to that obtained using  $\sigma$  values but omitting  $p\text{-OCH}_3$ .

In principle, the fit of the other rearrangements in Table IV by the Hammett relation might be improved by the use of  $\sigma^+$  instead of  $\sigma$ -values. However, the available data are too scanty in most cases to make a thorough recalculation worthwhile. In general, the  $\sigma^+$  values seem to correct too far to account well for the  $p\text{-OCH}_3$  group. If sufficient data were available, it would probably be desirable, in accounting for relative migration aptitudes, to use different  $\sigma$  values in equations 2 and 3, since it is unlikely that the same blend of inductive and resonance influences of the substituent group is appropriate in both the migrating and non-migrating phenyl groups.

For lack of  $\sigma$  or  $\sigma^+$  values for the benzhydryl group, the point for this group was not included in the least-squares fit of the data to relation 1. Instead,  $\sigma$  and  $\sigma^+$  values for the  $p\text{-(C}_6\text{H}_5)_2\text{CH}$  group were calculated from relation 1, and these are listed in a footnote to Table III. From the  $\sigma^+$  value, it is evident that, in the present electron-demanding reaction,  $p\text{-(C}_6\text{H}_5)_2\text{CH}$  is electron-supplying, less so than  $p\text{-CH}_3$  but considerably more so than  $m\text{-CH}_3$ .

### Experimental Part

**$\beta$ -*p*-Bromophenylisobutyric Acid.**—A mixture of 133 g. of  $\beta$ -phenylisobutyric acid, 135 g. of bromine and 0.2 g. of iron wire in 150 cc. of carbon tetrachloride was refluxed overnight. After being cooled, the solution was washed with cold dilute acid and then water. Finally, the product was extracted with a solution of 50 g. of sodium hydroxide in 500 cc. of water. Acidification of the basic extract and cooling gave rise to the crude acid. Four crystallizations from aqueous methanol yielded 118 g. of acid, m.p. 124–125.5°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ : C, 49.40; H, 4.56. Found: C, 49.42; H, 4.79.

The oxidation of  $\beta$ -*p*-bromophenylisobutyric acid with boiling basic potassium permanganate solution proceeded very slowly, and only a trace of pure *p*-bromobenzoic acid was obtained.

(22) We are indebted to Professor H. C. Brown, who kindly made the set of  $\sigma^+$  values available to us prior to publication.

***p*-Bromoneophyl Alcohol.**—A 46-g. quantity of the above acid in 200 cc. of ether was added slowly with stirring to 7.5 g. of lithium aluminum hydride in 500 cc. of ether. After the addition, the solution was refluxed for 1 hr., cooled and treated with cold dilute hydrochloric acid. The ether solution was washed with water and aqueous sodium bicarbonate. Then it was dried and concentrated. Distillation yielded 36.5 g. of crude alcohol, b.p. 120–123° (2.0 mm.),  $n_D^{25}$  1.5598. Recrystallization from pentane yielded 33.3 g. of material, m.p. 44–47°, m.p. 46–47.5° after a second crystallization.

*Anal.* Calcd. for  $C_{10}H_{18}OBr$ : C, 52.42; H, 5.72. Found: C, 52.46; H, 5.94.

A 1.0-g. quantity of the alcohol was refluxed 1 hr. with 10 cc. of thionyl chloride. The excess thionyl chloride was removed under vacuum, and the remaining oil was refluxed overnight with a solution of 4 g. of potassium permanganate and 2 cc. of 5% sodium hydroxide in 80 cc. of water. Cold dilute sulfuric acid was added and boiling was continued for 10 minutes. After the mixture was cooled to 0°, an excess of aqueous sodium bisulfite was added and the solid was filtered off. Recrystallization from benzene gave 0.30 g. (34%) of *p*-bromobenzoic acid, m.p. 248–250°, mixed m.p. 248–250°.

***p*-Carboxyneophyl Alcohol.**—*n*-Butyllithium was prepared from 10.5 g. of lithium ribbon and 90 g. of butyl bromide in 300 cc. of ether at –10° as described by Gilman.<sup>23</sup> To this solution, cooled to 0°, was added a solution of 48 g. of *p*-bromoneophyl alcohol in 150 cc. of ether with stirring during *ca.* 10 min. The mixture was then stirred for 30 minutes at room temperature and poured onto an excess of Dry Ice. When the Dry Ice had disappeared and the solution had come to room temperature, cold dilute hydrochloric acid was added. The ether phase was separated and the aqueous solution was extracted with ether. The combined extracts were washed with water and the product was extracted with a solution of 30 g. of sodium bicarbonate in water. Acidification gave the crude acid. Two crystallizations from aqueous methanol yielded 5.8 g. of material, m.p. 155–157°. Another crystallization raised the m.p. to 158–159°.

*Anal.* Calcd. for  $C_{11}H_{14}O_3$ : C, 68.02; H, 7.26. Found: C, 67.80; H, 7.23.

***p*-Carbomethoxyneophyl alcohol** was prepared from 7.0 g. of the above acid and an excess of ethereal diazomethane. The product, b.p. 135–140° (1.5 mm.), obtained by distillation, was recrystallized twice from ether–pentane to yield 5.0 g. of material, m.p. 42–43.5°.

*Anal.* Calcd. for  $C_{12}H_{16}O_3$ : C, 69.21; H, 7.75. Found: C, 69.25; H, 7.80.

***p*-Diphenylhydroxymethylneophyl Alcohol.**—Phenyllithium was prepared from 1.4 g. of lithium ribbon and 15 g. of bromobenzene in 200 cc. of ether. To this stirred solution was added dropwise 5.0 g. of *p*-carbomethoxyneophyl alcohol in 50 cc. of ether. After the addition, the solution was refluxed for 2 hr. Then cold water was added with cooling. The aqueous phase was separated and extracted twice with ether. The combined ether solutions were washed with water, dried and concentrated. The residual oil crystallized on standing overnight. Two crystallizations from ligroin–benzene gave 6.0 g. of the glycol, m.p. 114–116.5°.

*Anal.* Calcd. for  $C_{23}H_{24}O_2$ : C, 83.10; H, 7.28. Found: C, 83.10; H, 7.25.

***p*-Benzhydrylneophyl Alcohol.**—A solution of 6.0 g. of *p*-diphenylhydroxymethylneophyl alcohol in 50 cc. of pure methanol was shaken with 0.2 g. of 10% palladium-on-charcoal and 3 drops of 2 *N* hydrochloric acid under 35 p.s.i. of hydrogen for *ca.* 24 hr. The solution was filtered through Celite and poured into dilute aqueous sodium bicarbonate. The product was extracted with two portions of ether. The extracts were washed with water, dried and concentrated. The oil obtained was crystallized twice from ether–pentane. This gave 3.0 g. of alcohol, m.p. 75.5–77°.

*Anal.* Calcd. for  $C_{23}H_{24}O$ : C, 87.30; H, 7.64. Found: C, 87.17; H, 7.44.

***p*-Hydroxymethylneophyl Alcohol.**—A solution of 4.5 g. of *p*-carbomethoxyneophyl alcohol in 50 cc. of ether was added cautiously to 3 g. of lithium aluminum hydride in 100 cc. of ether. A precipitate formed immediately. It was

necessary to reflux the solution for 20 hr. in order to complete the reduction. Cold dilute sulfuric acid was added cautiously and the aqueous phase was separated and extracted with ether. The combined extracts were washed with water and aqueous sodium bicarbonate. The solution was dried and the ether was evaporated. The residue was recrystallized three times from ether–pentane. The product, 2.1 g., formed long colorless needles, m.p. 58–59°.

*Anal.* Calcd. for  $C_{11}H_{16}O_2$ : C, 73.30; H, 8.95. Found: C, 73.39; H, 9.02.

***p*-Methylneophyl Alcohol.**—The above glycol, 2.0 g., was dissolved in 25 cc. of pure methanol and hydrogenated at 35 p.s.i. using 0.2 g. of 10% palladium-on-charcoal as catalyst. The hydrogenation was complete in 3 hr. The resulting solution was filtered through Celite, and the filtrate was evaporated on a steam-bath. Vacuum distillation yielded 1.5 g. of alcohol, b.p. 87–88° (1.5 mm.),  $n_D^{25}$  1.5193.

*Anal.* Calcd. for  $C_{11}H_{16}O$ : C, 80.44; H, 9.82. Found: C, 80.25; H, 9.84.

**$\alpha,\alpha$ -Dimethyl-*m*-methylbenzyl Cyanide.**—Sodamide was prepared in 500 cc. of liquid ammonia from 20 g. of sodium, ferric chloride being used as catalyst. The 500 cc. of dry benzene was added while the ammonia was evaporated. The benzene finally was boiled in order to expel the last traces of ammonia. To the warm solution, 48 g. of *m*-methylbenzyl cyanide<sup>24</sup> was added with stirring and slight cooling. A vacuum was applied to the warm solution to remove the ammonia formed. Then 130 g. of methyl iodide was added as rapidly as possible to the still warm, stirred solution, slight cooling being necessary to keep the reaction mixture from boiling too vigorously. The hot solution was stirred 10 minutes more and cooled. A little methanol was added to destroy any remaining sodamide and then ice-water. The benzene layer was separated, washed with water, cold dilute hydrochloric acid, water and finally with aqueous sodium bicarbonate. The solution was dried and concentrated. The dark brown product was fractionated under vacuum through a center-rod column (*ca.* 20 plates). The pure nitrile, 32 g., boiled at 119–120° (15 mm.).

*Anal.* Calcd. for  $C_{11}H_{13}N$ : C, 82.97; H, 8.23. Found: C, 82.81; H, 8.20.

**$\alpha,\alpha$ -Dimethyl-*m*-tolylacetic Acid.**—The above nitrile, 15 g., was refluxed for 2 hr. with 12 g. of potassium hydroxide in 50 cc. of ethylene glycol. After being cooled, the solution was poured onto ice and hydrochloric acid. The oil which separated could be induced to crystallize, three crystallizations from pentane yielding 10.4 g. of material, m.p. 70.5–73°. Another crystallization raised the m.p. to 73–74°.

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 74.13; H, 7.92. Found: C, 73.86; H, 7.85.

***m*-Methylneophyl Alcohol.**—The reduction of 8.0 g. of  $\alpha,\alpha$ -dimethyl-*m*-tolylacetic acid with 2.0 g. of lithium aluminum hydride in ether proceeded readily. The usual isolation yielded 7.0 g. of the pure alcohol, b.p. 91–94° (2.5 mm.),  $n_D^{25}$  1.5210.

*Anal.* Calcd. for  $C_{11}H_{16}O$ : C, 80.44; H, 9.82. Found: C, 80.45; H, 9.56.

**Bromobenzenesulfonates.**—The *p*-bromobenzenesulfonates were prepared from the corresponding alcohols by the usual pyridine method. Most of the esters were recrystallized from benzene–ligroin. Table V summarizes the melting points and analyses of the five new *p*-bromobenzenesulfonates employed in the present work. The equivalent weights observed in acetolysis were close to the theoretical values except in the *p*-benzhydryl case, for which acetolysis indicated a purity of only 85%.

**1,1-Dimethyl-2-phenylethanol.**—This alcohol was prepared by the reaction between ethyl phenylacetate and methylmagnesium iodide. The crude alcohol was chromatographed carefully on alumina and recrystallized 4 times from pentane at –80°. The pure alcohol has the properties: m.p. 25.5–26.5°,  $n_D^{25}$  1.5128, b.p. 59–60° (1.5 mm.).

**Acetolysis of Neophyl *p*-Bromobenzenesulfonate.**—A solution of 50.0 cc. of 1.00 *M* lithium acetate and 750 cc. of dry acetic acid was heated to 75.0°, and 15.0 g. of the pure *p*-bromobenzenesulfonate,<sup>4</sup> m.p. 80.5–81.5°, three times recrystallized from ligroin, was added. The solvolysis solution was kept at 75.0° for 28 hr., and then it was

(23) H. Gilman, *et al.*, THIS JOURNAL, 71, 1499 (1949).

(24) A. F. Titeley, *J. Chem. Soc.*, 514 (1926).

TABLE V  
 PROPERTIES AND ANALYSES OF SUBSTITUTED NEOPHYL *p*-BROMOBENZENESULFONATES

Substituent	M.p., °C.	Formula	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
<i>p</i> -Br	116-117	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> SBr <sub>2</sub>	42.87	43.05	3.60	3.87
<i>p</i> -COOCH <sub>3</sub>	117-118	C <sub>18</sub> H <sub>18</sub> O <sub>5</sub> SBr	50.59	50.70	4.48	4.59
<i>p</i> -(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH	112 dec.	C <sub>25</sub> H <sub>27</sub> O <sub>3</sub> SBr	65.04	65.17	5.08	5.07
<i>p</i> -CH <sub>3</sub>	91-92 dec.	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub> SBr	53.27	53.29	5.00	5.18
<i>m</i> -CH <sub>3</sub>	89-90 <sup>a</sup>	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub> SBr	53.27	53.15	5.00	4.89

<sup>a</sup> Mixed m.p. with *p*-isomer, 74-90°.

cooled and poured into water. The products were extracted with 5 portions of pentane, and the extracts were washed with water and aqueous sodium bicarbonate. The extract was dried and the solvent was distilled off carefully through a Vigreux column. The crude products were reduced with 1.5 g. of lithium aluminum hydride in ether. The products were isolated by adding water to the solution and decanting the ether solution from the insoluble salts. The solids were extracted several times with ether and the extracts were washed with water, dried and concentrated. Chromatography on 200 g. of alumina separated the products into olefin and alcohol. The olefins, 3.2 g. (59.6%),  $n_D^{25}$  1.5207, were eluted with pentane and the alcohols, 1.90 g. (31.1%),  $n_D^{25}$  1.5128, b.p. 65-68° (1.5 mm.), were eluted with ether.

The olefin fraction in isoctane displayed an  $\epsilon$  6912 at  $\lambda$  244 m $\mu$  in ultraviolet absorption. A 0.8843-g. sample of the olefin product was hydrogenated in acetic acid at 27.5° and 752 mm., using 10% palladium-on-charcoal as catalyst. A total of 169 cc. of hydrogen (99%) was absorbed in 90 minutes. The hydrogenated product was isolated by pouring the acetic acid solution into water and extracting with pentane. The pentane extracts were washed with aqueous sodium bicarbonate and dried. The solvent was evaporated, and the residue was refluxed with sodium metal until the metal remained bright. A final distillation gave 0.45 g. of product, b.p. 172°,  $n_D^{25}$  1.4837. The infrared spectrum of this material was identical with that of isobutylbenzene,<sup>5</sup>  $n_D^{25}$  1.4841.

The alcohol fraction from the chromatography of the solvolysis product had m.p. 25-26°, mixed m.p. with 1,1-dimethyl-2-phenylethanol, 25-26°. The infrared spectrum indicated the presence of 0.5-0.75% of neophyl alcohol in

the tertiary alcohol. Definite absorption was observed at 1000-1075 cm.<sup>-1</sup> where neophyl alcohol absorbs strongly, and slightly low absorption was observed at 1125-1150 cm.<sup>-1</sup> where neophyl alcohol is relatively transparent. The infrared spectrum of the solvolysis product was intermediate between a synthetic mixture containing 1.6% neophyl alcohol in the tertiary alcohol and the pure tertiary alcohol.

In a second solvolysis carried out as above with slightly less pure *p*-bromobenzenesulfonate, a 61.5% yield of olefin was obtained and a 30.3% yield of alcohol. The olefin fraction,  $n_D^{25}$  1.5200, displayed  $\epsilon$  6880 at  $\lambda$  244 m $\mu$  in ultraviolet absorption. The alcohol, m.p. and mixed m.p. 24.5-25.5°, b.p. 65-68° (2 mm.),  $n_D^{25}$  1.5120, had an infrared spectrum consistent with the presence of more than 99% tertiary alcohol and ca. 1% neophyl alcohol.

In a control experiment, a solution of 1.5 g. of the tertiary alcohol, 1 cc. of acetic anhydride, 1 cc. of 1.00 *M* lithium acetate in dry acetic acid and 100 cc. of dry acetic acid was heated to 75.0° for 30 hr. The reaction mixture was worked up in the usual way, and the recovered product was reduced with 0.5 g. of lithium aluminum hydride in ether. The excess hydride decomposed with water, and the ether solution was decanted from the salts. The salts were extracted several times with fresh ether. The combined extracts were washed with water, dried and concentrated. Distillation gave 1.3 g. of product, b.p. 65° (1.5 mm.),  $n_D^{25}$  1.5130, m.p. 24-25.5°. A comparison of the -OH band at 3350 cm.<sup>-1</sup> of the product with that of pure tertiary alcohol showed the product to contain a small amount of non-hydroxylic material, probably olefin. Otherwise, the infrared spectra of the two materials were very similar.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

## Mechanisms of Elimination Reactions. XVIII. Reactivities of Some 2,3-Norbornane Derivatives<sup>1,2</sup>

BY STANLEY J. CRISTOL AND ERHARD F. HOEGGER

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Rate constants have been determined for the second-order reaction of sodium 1-pentoxide in 1-pentanol with *endo-cis*- and *trans*-2,3-dichloronorbornane at 101.3 and 116.2°, and with *exo-2-p*-toluenesulfonyl-*endo*-3-chloronorbornane at 0 and at 12°. The relative reactivities toward elimination of the elements of hydrogen chloride from these boat-form cyclohexane rings have been interpreted on the basis of an elimination process involving a carbanion intermediate.

Elimination of the elements of hydrogen chloride from 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene with alkali has been shown<sup>3</sup> to be very sluggish and to be relatively non-stereospecific, *cis* elimination being preferred over *trans* by a factor of about 8, in contrast to the generally observed large preference of *trans* over *cis* elimination.<sup>4</sup> The

striking lack of stereospecificity was rationalized<sup>8</sup> by the assumption that normal *trans* elimination (in acyclic systems or in cyclic systems without severe hindrance to rotation or ring conversion) utilizes a concerted *trans* coplanar transition state<sup>4,5</sup>; this transition state is forbidden to *cis* groups in ordinary small rings or to either *cis* or *trans* groups in bicyclo[2,2,2]octane derivatives without excessive torsional strain. Norbornane, or bicyclo[2,2,1]-heptane is locked by the 1,4-methano bridge in a boat-form cyclohexane ring in the same way as the 1,4-ethano bridge affects the cyclohexane ring in

(1) Previous paper in series: S. J. Cristol, F. R. Stermitz and P. S. Ramey, *THIS JOURNAL*, **78**, 4939 (1956).

(2) This work was reported at the 14th National Organic Chemistry Symposium at Lafayette, Indiana, June 13, 1955.

(3) S. J. Cristol and N. L. Hause, *THIS JOURNAL*, **74**, 2193 (1952).

(4) See, for example: (a) S. J. Cristol, *ibid.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954).

(5) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).