

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

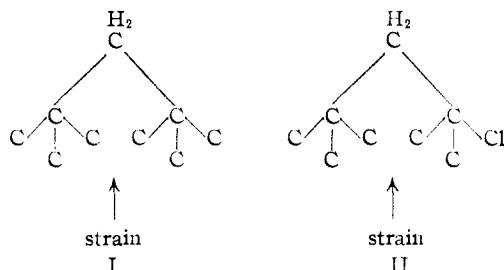
Steric Strains as a Factor in the Solvolytic Reactions of Neopentylidimethyl and Dineopentylmethylcarbonyl Chlorides<sup>1,2</sup>BY HERBERT C. BROWN<sup>3</sup> AND HANS L. BERNEIS<sup>4</sup>

RECEIVED FEBRUARY 28, 1952

Rate data were obtained for the solvolysis of neopentylidimethyl- and dineopentylmethylcarbonyl chlorides in a number of solvents at several temperatures. The solvolysis (in 80% ethanol at 25°) of neopentylidimethylcarbonyl chloride proceeds at a rate of 21 times that of *t*-butyl chloride, while dineopentylmethylcarbonyl chloride solvolyzes at a rate 580 that of *t*-butyl chloride. The energies of activation for the two highly branched chlorides are 0.5 and 3.7 kcal. lower than for *t*-butyl chloride. Dineopentylmethylcarbonyl chloride is stable only at low temperatures—at 25° it dissociates into olefin and hydrogen chloride with a half-time of 39 hours. Hydrolysis of neopentylidimethylcarbonyl chloride under neutral conditions gives 80% neopentylidimethylcarbinol. Under the same conditions dineopentylmethylcarbonyl chloride yields 100% olefin. Rates of solvolysis and olefin formation support the existence of large steric strains in these compounds. The predominant formation of the 1-olefin (Hofmann rule) in the E1 reactions of neopentylidimethylcarbonyl chloride suggests that steric strain must be an important factor in controlling the direction of eliminations. It is suggested that the Saytzeff rule represents control by the electromeric factor; the Hofmann rule, control by the steric factor.

## Introduction

It has been proposed that the solvolysis of tertiary halides with large bulky groups is assisted by the relief of steric strain accompanying the formation of a planar carbonium ion.<sup>5,6</sup> The heat of dissociation of *t*-butylamine-trimethylboron points to a strain in this molecule of 5.4 kcal.<sup>7</sup> From the similarity in atomic dimensions, strains of this magnitude should also be present in di-*t*-butylmethane (I) and neopentylidimethylcarbonyl chloride (II).



A study of the solvolysis and elimination reactions of this tertiary chloride appeared desirable to test further the B-strain hypothesis<sup>5,6</sup> and to examine the utility of the concept of strained homomorphs.<sup>8</sup> In this connection the chemistry of dineopentylmethylcarbonyl chloride was also of interest and a study of its preparation and reactions was therefore undertaken. A comparison of the reactions and properties of this substance with those of simpler tertiary halides, such as diethylmethylcarbonyl chloride, offers strong support to the B-strain concept.

## Results and Discussion

Neopentylidimethylcarbonyl chloride is reported to be readily synthesized by addition of hydrogen

chloride to diisobutylene.<sup>9</sup> However, we observed that a sample of diisobutylene, purified by distillation through a column of 100 theoretical plates, did not add hydrogen chloride over a period of hours. Addition of a drop of water, or, even more effectively, a minute crystal of ferric chloride caused the addition to occur at a satisfactory rate. A commercial sample of diisobutylene added hydrogen chloride rapidly, even when thoroughly dried. Moreover, tests for iron were negative. Thus the precise nature of the catalyst is unknown, but the facts indicate that the addition of hydrogen chloride to olefins at an appreciable rate requires a catalyst, even in the case of highly reactive tertiary olefins.<sup>10</sup>

Another interesting phenomenon was encountered in the preparation of dineopentylmethylcarbonyl chloride by the addition of hydrogen chloride to 1,1-dineopentylethylene.<sup>11</sup> The absorption of dry hydrogen chloride by the olefin occurred extremely slowly at 0° and somewhat more rapidly at -20°. In order to obtain quantitative absorption of hydrogen chloride at a satisfactory rate, it was necessary to lower the temperature to -40° as the reaction

TABLE I  
RATES OF SOLVOLYSIS OF NEOPENTYLDIMETHYL- AND DINEOPENTYLMETHYLCARBONYL CHLORIDES IN "80% ETHANOL"

Compound, chloride	First-order rate constants, $k_1$ (hr. <sup>-1</sup> )				$E_{act}$ , kcal.	log A
	0°	15°	25°	45°		
<i>t</i> -Butyl <sup>9,10</sup>	0.000877		0.0326	0.373	23.3	15.58
Neopentylidimethylcarbonyl <sup>9</sup>	.0200	0.181	.680		22.8	16.57
Dineopentylmethylcarbonyl <sup>b</sup>	.005	5.80	18.9		19.6	15.63

<sup>a</sup> Density of solvent,  $d^{25}_4$  0.8492. <sup>b</sup>  $d^{25}_4$  0.8497; *t*-butyl chloride,  $k_1$  0.0347 at 25°. To be strictly comparable with the remaining data, the values of dineopentylmethylcarbonyl chloride should be decreased by approximately 6% (0.0347/0.0326). However, this correction is insignificant compared to the ratios in rates under discussion and will, therefore, be ignored. <sup>c</sup> E. D. Hughes [*J. Chem. Soc.*, 256 (1935)] reports  $k_1$  0.0329 at 25°,  $E_{act}$  23.1 kcal.

(1) Chemical Effects of Steric Strains. VI. Strained Homomorphs. III.

(2) Based upon a thesis submitted by Hans L. Berneis to the Faculty of Wayne University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Department of Chemistry, Purdue University.

(4) Standard Oil Co. (Indiana) Fellow at Wayne University (1946-1948).

(5) H. C. Brown, *Science*, **103**, 385 (1946).

(6) H. C. Brown and R. S. Fletcher, *THIS JOURNAL*, **71**, 1845 (1949).

(7) H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953).

(8) H. C. Brown, *et al.*, *ibid.*, **75**, 1 (1953).

(9) (a) F. C. Whitmore and H. A. Southgate, *ibid.*, **60**, 2572 (1938);

(b) F. C. Whitmore, C. D. Wilson, J. V. Capinjala, C. O. Tongberg,

G. H. Fleming, R. V. McGrew and J. N. Cosby, *ibid.*, **63**, 2041 (1941).

(10) F. R. Mayo and J. J. Katz, *ibid.*, **69**, 1339 (1947).

(11) P. D. Bartlett, G. L. Fraser and R. B. Woodward, *ibid.*, **63**, 495 (1941).

proceeded, operating just above the freezing point of the solution. The tertiary chloride is unstable at room temperature, giving off hydrogen chloride and reforming olefin. At 25° a sample of the chloride loses half of the available hydrogen chloride in 39 hours. This loss of hydrogen chloride from aliphatic tertiary chloride at room temperature is itself quite unusual and points to a high degree of steric strain in this chloride.

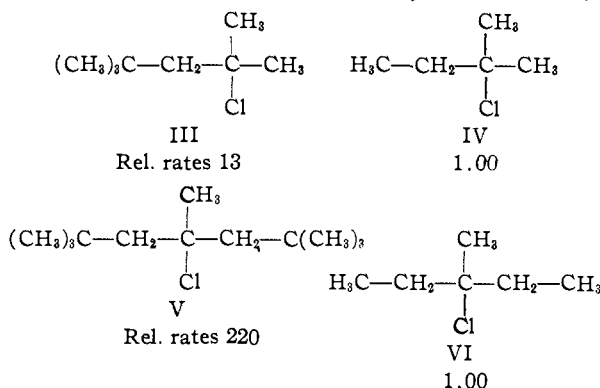
The rates of solvolysis were studied in "80% ethanol." The rate constants and derived data are listed in Table I. The temperature dependence of the rate constants is shown in Fig. 1.

The relative rates of solvolysis for these tertiary chlorides are compared with those for related simpler tertiary halides<sup>6</sup> in Table II.

TABLE II  
RELATIVE RATES OF SOLVOLYSIS FOR RELATED TERTIARY HALIDES IN "80% ETHANOL" AT 25°

Compound, chloride	Rate constant, $k_1$ (hr. <sup>-1</sup> )	Relative rate
Trimethylcarbinyl	0.0326	1.00
Neopentyl dimethylcarbinyl	0.680	21
Dineopentyl methylcarbinyl	18.9	580
Ethyl dimethylcarbinyl	0.055	1.7
<i>n</i> -Butyl dimethylcarbinyl	.047	1.4
Diethyl methylcarbinyl	.086	2.6

It is particularly instructive to compare neopentyl dimethylcarbinyl chloride (III) with *t*-amyl chloride (IV) and dineopentyl methylcarbinyl chloride (V) with diethyl methylcarbinyl chloride (VI).



The similarity in rates of *n*-butyl- and ethyl dimethylcarbinyl chlorides (Table II) suggests that the inductive effect is not very important beyond the second carbon atom. Therefore the inductive effect of the neopentyl group,  $(\text{CH}_3)_3\text{CCH}_2-$ , should not differ significantly from that of the ethyl group,  $\text{H}_3\text{CCH}_2-$ . Moreover, since both groups have two secondary hydrogen atoms at the  $\alpha$ -position, there should not be any important difference in their hyperconjugative contributions. It follows that the factors of 13 in the case of neopentyl dimethylcarbinyl chloride and of 220 in the case of dineopentylcarbinyl chloride do not appear explicable in terms of the differing electrical properties of neopentyl and ethyl groups. The steric strain postulated for homomorphs of di-*t*-butylmethane<sup>8</sup> (I) offers a reasonable explanation for the increased rates.

However, attention should be called to a peculi-

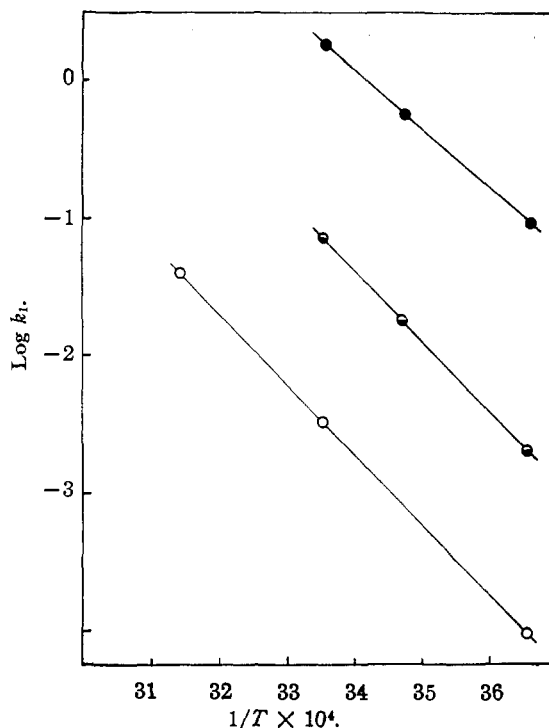
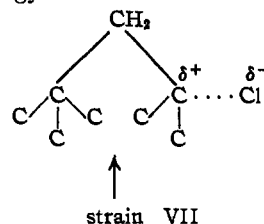


Fig. 1.—Activation energies for the solvolysis of *t*-butyl chloride (●), neopentyl dimethylcarbinyl chloride (◐) and dineopentyl methylcarbinyl chloride (○) in 80% ethanol.

arity in the data. The strain postulated in homomorphs of di-*t*-butylmethane is 5.4 kcal.<sup>8</sup> This strain is presumably largely relieved in the transition state of the tertiary chloride. An appreciable decrease in the activation energy for the solvolysis would therefore be anticipated. However, the decrease is only 0.5 kcal. for neopentyl dimethyl- and 3.7 kcal. for neopentyl dimethylcarbinyl chloride. It is probable that the difficulty of solvating simultaneously both the incipient chloride ion and the incipient carbonium ion in the transition state (VIII) decreases its stability and reduces the apparent effect of the decrease in steric strain on the observed activation energy.



We have also postulated that steric effects are of importance in the elimination reaction.<sup>12</sup> According to this interpretation, the carbonium ion from a highly strained tertiary chloride will have relatively little tendency to react with water to reform the original highly strained system. Instead, the carbonium ion will tend to react by loss of a proton to the solvent to form the olefin.

Solvolysis of dineopentyl methylcarbinyl chloride in "80% ethanol" could not be followed by the usual bromometric procedure,<sup>12</sup> since dineopentyl-

(12) H. C. Brown and R. S. Fletcher, *THIS JOURNAL*, **72**, 1223 (1950).

ethylene does not add bromine.<sup>11</sup> Consequently we sought another procedure to compare the two olefins. It was decided to solvolyse the tertiary chlorides with a large excess of water under neutral conditions and to compare, by actual isolation, the relative quantities of olefin and alcohol formed. Under these conditions neopentylidimethylcarbinyl chloride underwent hydrolysis to give an 80% yield of the tertiary alcohol with 20% of mixed diisobutylenes (75% 2,4,4-trimethyl-1-pentene and 25% 2,4,4-trimethyl-2-pentene), whereas dineopentylmethylcarbinyl chloride yielded 100% olefin. Failure to obtain any alcohol in the latter instance under conditions which provide 80% alcohol in the case of neopentylidimethylcarbinyl chloride, again supports the postulated large strains in the dineopentyl derivative. The dependence of olefin formation in the solvolysis upon the postulated strains in the tertiary chloride is evident from the data in Table III.

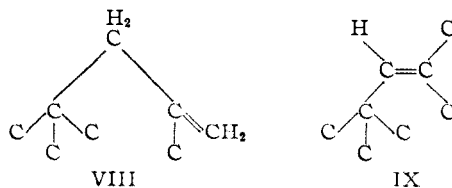
TABLE III  
OLEFIN FORMATION IN THE SOLVOLYSIS OF TERTIARY ALKYL CHLORIDES (25°, 80% ETHANOL)

Alkyl chloride	$k_E/(k_E + k_B)$
Trimethylcarbinyl	0.16
Ethylidimethylcarbinyl	.34 <sup>a</sup>
Diethylmethylcarbinyl	.41 <sup>a</sup>
Neopentylidimethylcarbinyl	.64
Dineopentylmethylcarbinyl	1.00 <sup>b</sup>

<sup>a</sup> Ref. 12. <sup>b</sup> Estimated from the results in water.

Previously, neopentylidimethylcarbinol has been available only by the action of silver oxide on the tertiary iodide,<sup>13</sup> and by the reaction of methylmagnesium halide with neopentylmethyl ketone.<sup>9b,14</sup> The present synthesis is far superior and makes this and other related tertiary alcohols readily available from the corresponding olefins and chlorides.

Finally it is important to note that the solvolysis of neopentylidimethylcarbinyl chloride yields the 1-olefin in major amount. This, then, represents an instance of the Hofmann rule controlling the direction of elimination in a reaction of the E1 type. Hughes, Ingold and co-workers have postulated that only electromeric effects control the direction of elimination from alkyl halides and that such eliminations follow the contrary Saytzeff rule.<sup>15</sup> In the present instance it appears that steric effects must control the direction of elimination. One cannot account for the preferred formation of the 1-olefin (VIII) in terms of the electromeric effect. However, it is apparent that the lower stability of the 2-olefin (IX) must be due to steric strain arising



(13) A. Butlerow, *Ann.*, **189**, 53 (1877).

(14) R. C. Huston, R. L. Guile, J. J. Sculati and W. N. Wasson, *J. Org. Chem.*, **6**, 252 (1941).

(15) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

from conflicting steric requirements of the *cis*-methyl and *t*-butyl groups.

Schramm has recently pointed out that the control of the direction of elimination in the E-2 reactions of quaternary ammonium ions (Hofmann rule) may also be the result of steric effects.<sup>16</sup> It follows that eliminations of all types may proceed according to the Hofmann rule if steric effects are of dominant importance, whereas eliminations may follow the Saytzeff rule in instances where electromeric effects are controlling. This possibility is under investigation.<sup>17</sup>

Rate data were obtained for the solvolysis of neopentylidimethyl- and dineopentylmethylcarbinyl chlorides in 70, 80, 90 and 100% ethanol and in 80% (by volume) methyl, ethyl, isopropyl and *t*-butyl alcohols. These are summarized in the Experimental section.

### Experimental Part

**Dineopentylmethylcarbinyl Chloride.**—Triisobutylene (Eastman Kodak Co.) was distilled through a 15-plate column and the fraction distilling between 176–178° at 745–750 mm. was collected. This product was oxidized with alkaline potassium permanganate in molar quantities to obtain 1,1-dineopentylethylene (51%), b.p. 85–86° at 40 mm.,  $n_D^{25}$  1.4270, m.p. –25°.

In a tube (50 mm.) equipped with stirrer, gas inlet and outlet, were placed 46.9 g. of 1,1-dineopentylethylene. The tube was cooled to –20° and hydrogen chloride passed in as the reaction mixture was stirred. The temperature was slowly lowered to –40°, always maintaining it above the solidification temperature of the mixture. After five hours no further increase in weight was observed and the crude product was subjected to rapid distillation at low pressures from a Claisen flask fitted with a very wide side arm. The product distilled at 44–48° at 0.3–0.6 mm.,  $n_D^{25}$  1.4473–1.4477. A total of 47.7 g. of tertiary chloride was isolated; in the cold trap were 9.1 g. of olefin with a small quantity of the chloride.

A sample of the tertiary chloride was analyzed for hydrogen chloride produced on solvolysis. A 0.2857-g. sample yielded 0.05063 g. HCl versus 0.05088 g. HCl calculated. The purity is thereby indicated to be at least 99.5%. The compound was stored as a solid at –80°.

**Neopentylidimethylcarbinyl Chloride.**—Hydrogen chloride was passed into 504 g. (4.5 moles) of commercial diisobutylene<sup>9</sup> for 15–20 hours at 0 to –10°. A 98.5% yield was obtained, b.p. 38.5–39.0° at 12 mm.,  $n_D^{25}$  1.4307.

**Kinetic Studies.**—The rate determinations were made by the procedure previously described.<sup>9</sup> Since the rate of solvolysis of dineopentylmethylcarbinyl chloride is appreciable even in absolute alcohol at 0°, acetone was used to stop the reaction in the case of this compound. Typical data are shown in Fig. 2.

**Hydrolysis of Neopentylidimethylcarbinyl Chloride under Neutral Conditions.**—One mole of neopentylidimethylcarbinyl chloride (148.5 g.), 1.5 l. of water, and 2 moles of sodium bicarbonate (168 g.) were placed in a 3-neck, 3-l. flask equipped with a thermometer, a motor driven stirrer and a reflux condenser. The reaction mixture was stirred until tests indicated the absence of tertiary chloride in the upper layer. The reaction required 30 hours at room temperature, 10 hours at 50–55° and 3 hours at 80°. After hydrolysis was complete, the upper layer was separated and the aque-

(16) C. H. Schramm, *Science*, **112**, 367 (1950).

(17) Work in progress with Dr. I. Moritani.

(18) The course of the reaction was followed by removing a sample from the upper layer with a 0.1-ml. pipet. This sample was added to 50% aqueous ethanol and titrated with standard alkali after an hour. The following data for a run at 50–55° are typical (0.0367 *N* sodium hydroxide):

Time, hr.	0	0.5	1.0	2	3	4	5	8	10
Base, ml.	14.9	14.0	12.4	8.3	4.5	2.3	1.0	0.1	0.0

From the data the rate apparently increases after the first hour. It is probable that the tertiary alcohol first formed increases the solubility of the tertiary chloride in the aqueous phase.

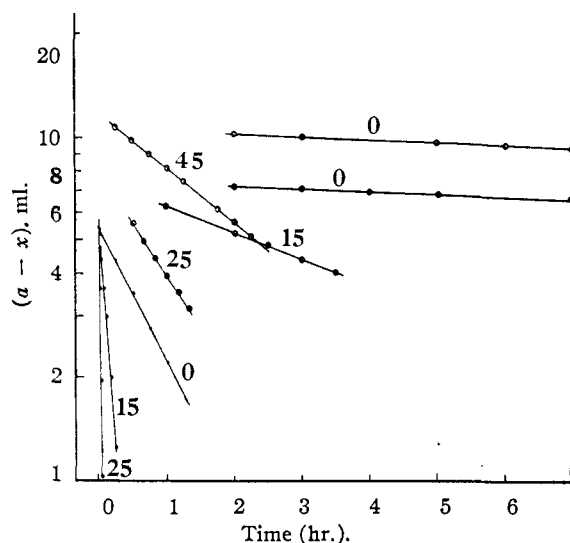


Fig. 2.—The rates of solvolysis of *t*-butyl chloride (O), neopentyldimethylcarbinyl chloride (⊖) and dineopentylmethylcarbinyl chloride (●) in 80% ethanol.

ous layer was twice extracted with 200 ml. of ether. The combined organic fractions were dried over potassium carbonate and then distilled through a helices-packed, 20-plate column. The olefin fraction, b.p. 99–105°, was collected for determination of the isomeric composition of the diisobutylenes. Neopentyldimethylcarbinol was collected at 146–146.5° at 750 mm.,  $n_D^{25}$  1.4256, as a colorless oil with a pleasant camphoraceous odor. The yields were 74–80%.

The olefin fraction was distilled through a 5-plate micro column. From its refractive index,  $n_D^{20}$  1.4104–1.4105, it is estimated to contain 25–26% 2-olefin. Several experiments were carried out with synthetic mixtures of the two isomeric olefins. In each case recovery and analysis by the procedure described gave the composition of each component to within  $\pm 3\%$ .

The results obtained in a number of such hydrolysis experiments at several temperatures are summarized in Table IV.

TABLE IV

NEUTRAL HYDROLYSIS OF NEOPENTYLDIMETHYLCARBINYL CHLORIDE

Temp., °C.	Time, hr.	Yield of carbinol, %	Yield of olefin, %	2-Olefin, %
25	72	79	21	26
25	72	80	20	26
25	25	73	27	25
50–55	10	80	20	25
80	3	74	26	25

**Solvolysis of Neopentyldimethylcarbinyl Chloride in Aqueous Methyl, Ethyl, Isopropyl and *t*-Butyl Alcohols.**—It was of interest to examine the effect of the alcohol used in the solvent on the rate of hydrolysis. The solvents were made up by adding sufficient alcohol to 200 ml. of water to make 1 l. of solution. The rate data are presented in Table V.

TABLE V

RATE CONSTANTS FOR THE SOLVOLYSIS OF NEOPENTYLDIMETHYLCARBINYL CHLORIDE IN "80%" AQUEOUS ALCOHOLS

Solvent	Rate constant, $k_1$ (hr. <sup>-1</sup> )
"80%" aqueous methyl alcohol	2.88
"80%" aqueous ethyl alcohol	0.688
"80%" aqueous isopropyl alcohol	.285
"80%" aqueous <i>t</i> -butyl alcohol	.158

The data show a marked decrease in rate in the sequence MeOH < EtOH < *i*-PrOH < *t*-BuOH, with a 20-fold dif-

TABLE VI  
RATE DATA FOR SOLVOLYSIS IN AQUEOUS ETHANOL SOLVENTS

Compound, chloride	Solvent, % ethanol	Temp., °C.	Rate constant, $k_1$ (hr. <sup>-1</sup> )	Eact., kcal.	log <i>A</i>
<i>t</i> -Butyl	70.00	25.0	0.128		
	79.56	25.0	.0347		
	90.11	25.0	.00586		
Neopentyldimethylcarbinyl	70.00	0.1	.0698	22.8	17.07
		14.9	.615		
		25.0	2.33		
	79.56	0.1	.0219	22.9	16.65
		14.9	.193		
		25.0	.753		
	90.11	14.9	.0412	23.0	16.06
		25.0	.164		
		35.0	.556		
Dineopentylmethylcarbinyl	79.56	0.1	.905	19.6	15.63
		14.9	5.80		
		25.0	18.9		
	90.11	0.1	.246	20.2	15.54
		14.9	1.65		
		25.0	5.47		
	95.15	0.1	.0944	21.0	15.76
		14.9	.701		
		25.0	2.39		
100.0	14.9	.228	21.6	15.73	
	25.0	.806			
	35.0	2.66			

\* Composition of the solvent established by density measurements.

ference between methyl alcohol and *t*-butyl alcohol. Presumably the decrease observed in going to the tertiary alco-

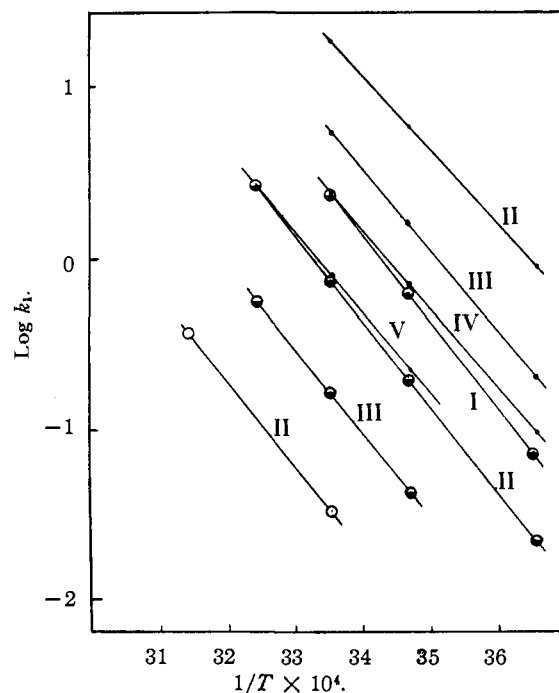


Fig. 3.—Activation energies for the solvolysis of *t*-butyl chloride (O), neopentyldimethylcarbinyl chloride (⊖), and dineopentylmethylcarbinyl chloride (●) in 70% (I), 79.56% (II), 90.11% (III), 95.15% (IV) and 100% (V) ethanol.

hol is due to a combination of three factors: decreased ability of *t*-butyl alcohol to serve as a nucleophilic solvating agent for the incipient carbonium ion, decreased ability of the tertiary hydroxyl group to solvate the incipient chloride ion, and reduced dielectric constant of the solvent. However, considerable additional work would be required to establish the relative importance of each of these factors.

**The Influence of the Water Content of Aqueous Ethanol on the Solvolysis Rates.**—The solvolysis of neopentyltrimethyl- and dineopentylmethylcarbinyl chlorides in 70, 80, 90 and 100% ethanol was observed. The data are reported in Table VI and Fig. 3.

Using these data and the expression  $\log k = mY + \log k_0$

proposed by Grunwald and Winstein<sup>19</sup> it is possible to calculate the values of the parameter  $m$  for the two highly branched chlorides under investigation. The following data for  $m$  are of interest: *t*-butyl chloride, 1.000; *t*-amyl chloride, 0.873; neopentyltrimethylcarbinyl chloride, 0.858; dineopentylmethylcarbinyl chloride, 0.698. It appears that  $m$  may measure the relative importance of the contribution by the solvent, with a low value of  $m$  indicating that the halide under consideration requires a relatively small contribution from the solvent in the ionization stage.

(19) E. Grunwald and S. Winstein, *THIS JOURNAL*, **70**, 846 (1948).  
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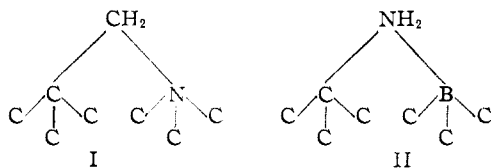
## Neopentyltrimethylammonium Ion as a Strained Homomorph; the Rates of Reaction of Neopentyltrimethylammonium Ion with Alkyl Iodides<sup>1,2</sup>

By HERBERT C. BROWN AND W. HALLAM BONNER<sup>3</sup>

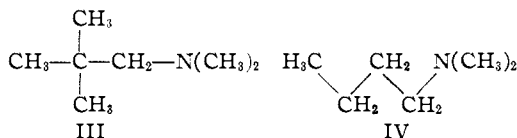
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Neopentyltrimethylammonium ion is a homomorph of the strained molecules, *t*-butylamine-trimethylboron and di-*t*-butylmethane. The predicted slow rate of reaction of neopentyltrimethylamine with methyl and ethyl iodides is observed—the rate constants are less than  $1/100$  those of the corresponding reactions of *n*-butyltrimethylamine and the energies of activation are 2.2–2.7 kcal. greater. The increase in steric strain in the reaction neopentyltrimethylamine → neopentyltrimethylammonium ion was estimated from heats of formation data for homomorphous hydrocarbons. The result, 2.0–2.5 kcal., is considered to be in satisfactory agreement with the observed increase in activation energy.

Neopentyltrimethylammonium ion (I) is a homomorph of the strained molecules, *t*-butylamine-trimethylboron (II) and di-*t*-butylmethane. The



addition compound, *t*-butylamine-trimethylboron, is some 5.4 kcal. less stable than estimated.<sup>4</sup> It is proposed that such strains, measured by the stability of molecular addition compounds, exist in homomorphs of the parent molecule and should markedly affect their properties. It follows that neopentyltrimethylamine (III) should behave as a



highly hindered amine in its reaction with methyl iodide and other alkyl halides, as contrasted with the behavior of an aliphatic amine without the unusual features of the neopentyl derivative.

In neopentyltrimethylamine the branch is two atoms from the reaction center. Classically, this is not a molecule which would be expected to exhibit steric hindrance in a great degree. Actually, neopentyltrimethylammonium iodide was prepared some time ago by Ingold and Patel<sup>5</sup> by the reaction

(1) Chemical Effects of Steric Strains. VII. Strained Homomorphs. IV.

(2) Based upon a thesis submitted by W. Hallam Bonner to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Purdue Research Foundation Fellow (1949–1951).

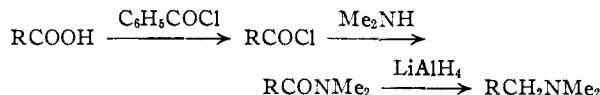
(4) H. C. Brown and G. K. Barbaras, *THIS JOURNAL*, **75**, 6 (1953).

(5) C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 67 (1933).

of neopentyltrimethylamine and methyl iodide in the absence of a solvent. However, they did not report that the reaction displayed any unusual characteristics.

It appeared desirable, therefore, to examine the rate of reaction of neopentyltrimethylamine with methyl and ethyl iodides and to compare these rates with those for a related amine without the unique structural features of the neopentyl derivative. *n*-Butyltrimethylamine (IV) was selected for comparison.

The two tertiary amines were made by the sequence of reactions



The reactions with methyl and ethyl iodides were studied in nitrobenzene solution. The rate data are summarized in Table I and Fig. 1.

At 40° the reaction of methyl iodide with *n*-butyltrimethylamine proceeds at a rate 120 times greater than that of the corresponding reaction with neopentyltrimethylamine. Similarly, in the reaction with ethyl iodide there is a factor of 132 in the relative rates. This is certainly a very large difference which cannot be accounted for in terms of the minor differences in the polar effects of the neopentyl and *n*-butyl groups.

The differences in the energies of activation of the two amines with methyl iodide is 2.7 kcal. In the case of ethyl iodide, the difference is 2.2 kcal. Because of the lower precision of the kinetic data for the reaction of *n*-butyltrimethylamine with methyl iodide, the smaller value is considered to be the better estimate of the difference in strains in the transition states for the neopentyl and *n*-butyl derivatives.

According to the concepts discussed in this series