

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

**An Acetylenic Analog of Neopentyl Bromide; Evidence that the Hindrance to Displacement Reactions in Neopentyl Halides is Steric in Nature**

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The extreme lack of reactivity of neopentyl alcohol and halides<sup>1</sup> in comparison to the isomeric *n*-amyl compounds is limited to reactions in which the functional group undergoes replacement by another atom or radical of similar (negative) ionic type. This is the class of reaction, variously called "bimolecular negative substitution" or "bimolecular nucleophilic substitution" ( $S_N2$ ), which at an optically active center is generally attended by Walden inversion, and which is accordingly believed to proceed by concerted attachment of the new substituent on one face of the carbon atom and release of the old one from the opposite face.

Figure 1 shows a Stuart<sup>2</sup> model of neopentyl chloride. Examined with bimolecular inversion in mind, this model shows a peculiarity of the neopentyl system which is not shared by its less branched homologs such as isobutyl chloride. There is no possible orientation of the  $CH_2Cl$  group by rotation about the bond joining it to the *t*-butyl group which will permit unhindered access of a substituting reagent by the "inversion" mechanism. Unlike the planar formula, the space model leads to the prediction of definite steric hindrance to bimolecular negative substitutions in neopentyl compounds. This would appear to offer a satisfactory explanation of the "neopentyl effect."

Since inferences of steric hindrance from models have often been misleading, it has seemed desirable to put the hindrance in the present case to a new kind of test. If the hindrance to displacement reactions in the neopentyl halides is not steric, then it can only be "chemical" in nature, which means that the normal polarization at the C-Cl bond attending reaction is opposed by some electronic effect of the *t*-butyl group, not present in an *n*-butyl group similarly situated. All chemical effects of this sort are partially transmitted through unsaturated linkages when these are in-

(1) (a) Whitmore and Rothrock, *THIS JOURNAL*, **54**, 3431 (1932); (b) Whitmore and Fleming, *ibid.*, **55**, 4161 (1933); (c) Whitmore, Wittle and Harriman, *ibid.*, **61**, 1585 (1939); (d) Whitmore, Wittle and Popkin, *ibid.*, **61**, 1586 (1939); (e) Ingold and Patel, *J. Chem. Soc.*, 67-68 (1933); (f) Whitmore and Rohrmann, *THIS JOURNAL*, **61**, 1591 (1939); (g) see also Whitmore and Homeyer, *ibid.*, **54**, 3435 (1932).

(2) H. A. Stuart, *Z. physik. Chem.*, **27B**, 354 (1934).

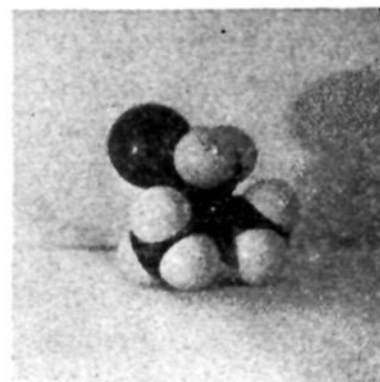
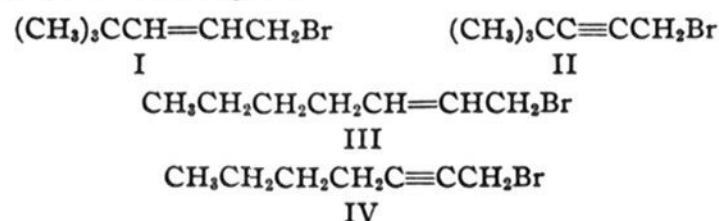


Fig. 1.

terposed between the affecting and the affected group.<sup>3</sup> Thus, the chemical effects of a series of *p*-substituents on the rate of hydrolysis of ethyl benzoate are reflected when the same substituents are introduced into ethyl cinnamate.<sup>4</sup> The nitro group, for example, in the para position increases the velocity constant of hydrolysis for ethyl benzoate 100-fold, and that for ethyl cinnamate 10-fold.<sup>5</sup> If the *t*-butyl group in neopentyl bromide is exerting a chemical effect, then this effect should appear in some degree in the vinyllog I and in the acetylenic analog II.



These, compared with III and with IV, respectively, should show some reflection of the reluctance to enter into displacement reactions which marks neopentyl compared to *n*-amyl bromide. On the other hand, if the hindrance where present is purely steric, then II and the *trans*-isomer of I should show no trace of the effect.

Because of the necessity of comparing only similar geometrical isomers of I and III, this part of the work has encountered difficulties and will not be reported until its completion. The comparison of II and IV, being free from this complication, gives an unequivocal answer to our question. Both compounds, along with some related

(3) Fuson, *Chem. Rev.*, **16**, 2 (1935).

(4) Kindler, *Ann.*, **464**, 278 (1928).

(5) The effect of the phenyl group is felt in the high reactivity of cinnamyl and  $\gamma$ -phenylpropargyl chlorides toward potassium iodide in acetone [Murray, *THIS JOURNAL*, **60**, 2662 (1938)].

saturated bromides, have been treated under identical conditions with potassium iodide in acetone and the bimolecular velocity constants for the displacement of bromine by iodine have been measured. Not only is there no hindrance in II compared to IV, but the former isomer actually reacts slightly faster than the latter, as shown by the data in Table I. We conclude that the hindrance to displacement reactions in neopentyl halides cannot be chemical in nature, and must be steric.

In such work as this, allylic rearrangements during the conversion of the alcohols to bromides are a potential source of difficulty. Fortunately, with the acetylenic compounds here investigated such rearrangements would result in the formation of substituted bromo-allenes. These would be so inert as to be easily distinguished from the desired propargyl bromides. The reactivity of our acetylenic bromides is evidence that they are of the propargyl type, while the good velocity constants obtained constitute evidence that they are not contaminated to any important extent with rearrangement products.

TABLE I

BIMOLECULAR VELOCITY CONSTANTS FOR THE REACTION BETWEEN ORGANIC BROMIDES AND POTASSIUM IODIDE IN ACETONE AT 25°

R	$k \times 10^3$ (time in minutes)	Relative $k$ (Neopentyl = 1)
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	109	474
	107	465
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	131	570
	125	543
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	0.23	1
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub>	6.6	29
(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub>	4.3	19
	4.5	20
(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	108	470
CH <sub>2</sub> =CHCH <sub>2</sub>	7630	33,200
	6970	30,300
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C≡CCH <sub>2</sub>	4220	18,300
	4080	17,700
(CH <sub>3</sub> ) <sub>2</sub> CC≡CCH <sub>2</sub>	5350	23,300
	5130	22,300

The reactivity of the series formed by the addition of successive CH<sub>2</sub>-groups to the neopentyl chain is also in accord with the conclusion that we are dealing with steric effects; the addition of the first methylene group multiplies the velocity constant by twenty, and the second methylene group raises it, by a further factor of a little over twenty,

to the value characteristic of the normal alkyl bromides.

Cyclohexyl bromide is even slower than neopentyl bromide, and is too slow to measure at 25°. At 60° we obtained a rate constant of  $1.44 \times 10^{-3}$ , but the reaction was not free from side-reactions. Elimination of hydrogen iodide from the product occurred during the reaction. The resistance of cyclohexyl halides to bimolecular displacement reactions might<sup>6</sup> be accounted for on steric grounds, as involving shielding by the unreacting portion of the strainless ring, but some example should be found which can be studied in terms of energy and entropy of activation.<sup>7</sup>

### Experimental

**Preparation of 2,2-Dichloro-3,3-dimethylbutane.**—This compound was prepared by a modification of the procedure of Ivitzky<sup>8</sup> and de Graef.<sup>9</sup> To 250 g. (1.2 moles) of finely powdered phosphorus pentachloride was added, with mechanical stirring, 120 g. (1.2 moles) of pinacolone, the reaction being maintained at 0–5°. The time of addition was three hours, after which stirring was continued for nine hours. The mixture was poured on 700 g. of ice. The solid was removed by filtration, washed with water, and air-dried. This amounted to 90 g. of crude dichloride. There was also a liquid organic product which was taken up in ether, washed with water, 10% bicarbonate solution, and water, and dried over anhydrous sodium sulfate. Removal of the ether yielded 63 g. of crude 2-chloro-3,3-dimethylbutene-1 (combined crude yield 91.4%). The pure dichloride, obtained by sublimation, melted at 151–152° and the pure unsaturated monochloride, isolated by fractionation through a 90-cm. Podbielniak column, boiled at 97–99°.

**3,3-Dimethylbutyne-1** was prepared according to the directions of Ivitzky and de Graef. The yields of products were quite dependent upon the intimate mixing of the dichloride with the powdered anhydrous potassium hydroxide. In this preparation, the acetylenic product was accompanied by unsaturated monochloride and this, together with that produced from pinacolone in the previous reaction, was converted into 3,3-dimethylbutyne-1 by the following procedure: a mixture of 60 g. of 2-chloro-3,3-dimethylbutene-1 with 20 cc. of absolute ethanol was poured on 200 g. of dry powdered potassium hydroxide. This mixture was heated gradually to a bath temperature of 160–165° over a period of five hours, after which the temperature was raised to 200°. The combined distillates, b. p. 40–60°, were washed with water, dried, and fractionated, yielding 33 g. (80.5% yield) of *t*-butylacetylene, b. p. 36.4–37.8° at 788.3 mm.

**4,4-Dimethylpentyn-2-ol-1.**—One mole (82 g.) of *t*-butylacetylene, in its own volume of ether, was added to a solution of ethylmagnesium bromide prepared from 24 g. of magnesium, 109.4 g. of dry ethyl bromide, and 600 cc. of

(6) Cf. Conant and Hussey, *THIS JOURNAL*, **47**, 476 (1925).

(7) Cf. Hammett and Price, *ibid.*, **68**, 2387 (1941).

(8) Ivitzky, *Bull. soc. chim.*, **35**, 357 (1924).

(9) De Graef, *Bull. Soc. Chim. Belg.*, **34**, 428 (1925).

dry ether. After an addition period of five hours the stirring was continued overnight (fifteen hours) when ethane was no longer evolved and there was a heavy white precipitate of the acetylenic Grignard reagent filling the flask. This suspension was stirred vigorously while gaseous formaldehyde, generated by heating dry trioxymethylene, was passed in, causing the precipitate to redissolve. When tests for the presence of the Grignard reagent were negative, the reaction mixture was worked up in the usual way. Vacuum distillation yielded 79 g. (70.5%) of the desired alcohol, b. p. (18 mm.) 71.6°. The material was further purified by two more vacuum fractionations, then showing the following constants; b. p. (767.6 mm.) 162.4–163.4°;  $n_D^{21.5}$  1.4427;  $d_4^{23}$  0.8565;  $MR$  calcd. 34.06; found 34.72. *Anal.*<sup>10</sup> Calcd. for  $C_7H_{12}O$ : C, 75.00; H, 10.70. Found: C, 75.16; H, 10.87.

A solution of 0.7 g. of the alcohol in absolute ethanol when hydrogenated with 75 mg. of Adams catalyst absorbed the calculated amount of hydrogen in thirty minutes. The product was identified as 4,4-dimethylpentanol-1 by its  $\alpha$ -naphthylurethan, m. p. 80–81°, undepressed by mixture with a sample prepared according to Whitmore and Homeyer.<sup>11</sup>

The following derivatives of 4,4-dimethylpentyn-2-ol-1 were prepared: *p*-bromobenzoate, m. p. 63–64.5°; m. w., calcd. for  $C_{14}H_{18}O_2Br$ , 295; found, 287. 3,5-Dinitrobenzoate, m. p. 101.5–102°. *Anal.* Calcd. for  $C_{14}H_{14}O_6N_2$ : N, 9.15. Found: N, 9.16.  $\alpha$ -Naphthylurethan, m. p. 163–164°. *Anal.* Calcd. for  $C_{18}H_{18}O_2N$ : N, 4.98. Found: N, 4.98. Phenylurethan, m. p. 81.5–82.5°. *Anal.* Calcd. for  $C_{14}H_{17}O_2N$ : N, 6.06. Found: N, 6.03. The nitrogen analyses were performed by the Kjeldahl method.

**Preparation of 1-Bromo-4,4-dimethylpentyn-2-ol-1.**—Phosphorus tribromide (40 g., 0.15 mole) was added dropwise to a solution of 35 g. (0.31 mole) of 4,4-dimethylpentyn-2-ol-1 and 10 g. of dry pyridine in 100 cc. of dry ether. During the addition period of two hours the flask was kept in an ice-bath and the reaction mixture was stirred vigorously. After the addition the reaction mixture was brought to room temperature and then kept for two hours at 40–50°; it was then poured into 500 cc. of ice-cold water. After several extractions, and drying, distillation yielded 22 g. (41%) of the bromide boiling at 50–52.5° (18–20 mm.). This product had the following constants:  $n_D^{20}$  1.4751;  $d_4^{24}$  1.180;  $MR$  calcd., 40.30; found, 41.70. *Anal.* Calcd. for  $C_7H_{11}Br$ : Br, 45.68. Found: Br, 45.34.

**4,4-Dimethylpentanol-1**, prepared by the hydrogenation of 4,4-dimethylpentyn-2-ol-1 with Adams catalyst, boiled at 74° (22 mm.). It yielded an  $\alpha$ -naphthylurethan, m. p. 80–81°,<sup>12</sup> phenylurethan, m. p. 51–52°. (*Anal.* Calcd. for  $C_{14}H_{21}O_2N$ : N, 5.95. Found: N, 5.72) and 3,5-dinitrobenzoate, m. p. 66–67° (*Anal.* Calcd. for  $C_{14}H_{18}O_6N_2$ : N, 9.03. Found: N, 8.85).

**1-Bromo-4,4-dimethylpentane.**—This was prepared in a manner similar to the preparation of the unsaturated bromide, but without the use of pyridine. The product boiled at 61.5–62.0° (31 mm.), and had a  $n_D^{20.4}$  1.4482 constant in agreement with Whitmore and Homeyer.

(10) This analysis was performed by Dr. Carl Tiedcke of New York.

(11) Whitmore and Homeyer, *THIS JOURNAL*, **55**, 4655 (1933).

**Hexyne-1** was prepared according to Nieuwland and co-workers.<sup>13</sup> It boiled at 71–72° (760 mm.).

**Heptyn-2-ol-1** was prepared as reported by Toussaint and Wenzke.<sup>14</sup> Its boiling point (22 mm.) was 93.6°, and it had  $n_D^{20.5}$  1.4552.

**Preparation of 1-Bromoheptyne-2.**<sup>14,15</sup>—This bromide was prepared in similar fashion to the 1-bromo-4,4-dimethylpentyn-2. The product was purified by vacuum fractionation, boiling at 88.6° (27 mm.),  $n_D^{20.5}$  1.4898.

*n*-Heptyl bromide, obtained from the Eastman Kodak Co., was fractionally distilled several times. The fraction boiling from 177 to 178°, having  $n_D^{20}$  1.4488, was used.

Allyl bromide was obtained from the Eastman Kodak Co. Two distillations yielded the fraction, b. p. 70–71°,  $n_D^{20}$  1.4656, which was used in the kinetic studies.

*n*-Butyl bromide was washed successively with water, concentrated sulfuric acid, water, 10% sodium bicarbonate solution, and water. It was dried over anhydrous calcium chloride and fractionated three times. The fraction used had b. p. 100–101° (765 mm.),  $n_D^{20}$  1.4400.

**1-Bromo-2-methylbutane,**<sup>16,17</sup> **1-bromo-3,3-dimethylbutane,**<sup>18</sup> and **neopentyl bromide**<sup>19</sup> were prepared by methods in the literature. The fractions used had the following properties: 1-bromo-2-methylbutane, b. p. 119–120°,  $n_D^{21}$  1.4448; 1-bromo-3,3-dimethylbutane, b. p. (40 mm.) 50.5°,  $n_D^{22}$  1.4445; neopentyl bromide, b. p. 105–107°,  $n_D^{21}$  1.4370,  $d_4^{22.7}$  1.196.

**Kinetic Measurements.**—The reaction of the alkyl bromides with potassium iodide in purified acetone was followed by the titration method of Andrews<sup>20</sup> and also of Juvala.<sup>21</sup> In the cases of the saturated bromides the iodide was at an initial concentration of 0.02 *M* while the organic bromide was at an initial concentration of 0.06 *M*. In the cases of the more rapidly reacting acetylenic bromides, these initial concentrations became 0.01 *M* and 0.015 *M*, respectively, in order to obtain rates which were not too fast to measure. With the saturated bromides sampling was made by a pipet, while the samples in the reactions of the unsaturated bromides were put up separately to facilitate more rapid analyses. All the reactions were carried out in a thermostat at 25.00  $\pm$  0.05°. The data were plotted according to the form of the equation for a bimolecular reaction

$$kt = \frac{2.303}{(M-1)b} \log_{10} \frac{M-z}{M(1-z)}$$

where *M* is the initial molecular proportion of or-

(12) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 5 (1937).

(13) Toussaint and Wenzke, *THIS JOURNAL*, **57**, 668 (1935).

(14) Toussaint and Wenzke, *loc. cit.*

(15) Tschao Yin Lai, *Bull. soc. chim.*, **53**, 682 (1933).

(16) Jones, *J. Chem. Soc.*, **87**, 138 (1905).

(17) Levene, Rothen and Marker, *J. Chem. Phys.*, **4**, 442 (1936).

(18) Strating and Backer, *Rec. Trav. Chim.*, **55**, 910 (1936).

(19) Whitmore, Wittle and Popkin, *THIS JOURNAL*, **61**, 1585 (1939).

(20) Andrews, *ibid.*, **25**, 756 (1903).

(21) Juvala, *Ber.*, **63B**, 1995 (1930).

ganic bromide to inorganic iodide,  $b$  is the initial concentration of iodide, and  $z$  is the fraction of the iodide which has reacted in the time  $t$ . From the linear plot of this equation the best value of the velocity constant  $k$  can be chosen. All the bromides yielded satisfactory straight lines, and successive runs on the same compound yielded constants within 5% of the mean. Most of the runs were carried to more than 75% of completion.

The table gives the data for a sample run in

TABLE II

RATE OF REACTION BETWEEN 1-BROMO-4,4-DIMETHYLPENTYNE-2 AND POTASSIUM IODIDE IN ACETONE SOLUTION AT 25°

Initial molarity of potassium iodide, 0.01044; of 1-bromo-4,4-dimethylpentyne-1, 0.01530; initial titer of potassium iodide (determined on blank) 34.80 cc.;  $M = 1.466$ .

Time in minutes	Titer	$z$	$\log \frac{M-z}{M(1-z)}$
2.52	22.80	0.345	0.0673
4.26	18.60	.466	.1065
6.00	16.35	.530	.1331
9.00	14.40	.586	.1613
10.02	13.50	.612	.1766
17.52	9.85	.717	.2566
25.02	8.90	.744	.2841

which the rate of reaction of 1-bromo-4,4-dimethylpentyne-2 with potassium iodide was measured. The first and last points on the plot of the logarithmic quantity against time are below the straight line determined by the other points. This is not typical of the runs. The slope of the straight line yields the value  $k = 5.35$  for the bimolecular velocity constant of the reaction.

### Summary

The rates of reaction between potassium iodide in acetone and some organic bromides have been measured in order to gain an insight into the nature of the hindrance to displacement reactions in neopentyl halides. From the fact that 1-bromo-4,4-dimethylpentyne-2 is not hindered in comparison to 1-bromo-heptyne-2 it is concluded that the "neopentyl effect" is not capable of transmission through an unsaturated linkage and is hence not a chemical but a steric effect. A consideration of the mechanism of displacement reactions in terms of models and the reactivities of the compounds studied are in agreement with this conclusion.

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## Vapor Pressures and Critical Constants of Isobutene

BY JAMES A. BEATTIE, HENRY G. INGERSOLL AND WALTER H. STOCKMAYER

In previous publications<sup>1</sup> determinations of vapor pressures and critical constants of ethane, propane, *n*-butane, and *n*-heptane have been given. The apparatus and method have been published elsewhere.<sup>2</sup> In the present paper data on isobutene are presented. The compressibility bomb with a glass liner<sup>2</sup> was used.

The isobutene was obtained from the M. W. Kellogg Company through the courtesy of Dr. Manson Benedict. It was prepared by the dehydration of isobutyl alcohol over activated alumina followed by fractionation. We distilled the sample several times to remove permanent gases.

### Vapor Pressures

The vapor pressure of isobutene has been measured from  $-79$  to  $+22^\circ$  by Coffin and Maass,<sup>3</sup>

(1) For the last report on this work see J. A. Beattie, G. J. Su, and G. L. Simard, *This Journal*, **61**, 924-925 (1939).

(2) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389-405 (1934).

(3) C. C. Coffin and O. Maass, *Trans. Roy. Soc. Canada*, [3] III, **21**, 33-40 (1927).

from  $36^\circ$  to the critical point by Scheeline and Gilliland,<sup>4</sup> and from  $-57$  to  $0^\circ$  by Lamb and Roper.<sup>5</sup>

In Table I are given the results of our measurements made in the compressibility apparatus. The variation of vapor pressure with vapor volume affords a test of the purity of the sample. The small increase of vapor pressure with decrease of vapor volume indicates that the amount of permanent gas present was entirely negligible and that the effect of the condensable impurity present was slightly greater than the reproducibility of the measurements.

In Table II is given the comparison of the observed vapor pressures with those computed from a two-constant equation. The equation yields a value at  $0^\circ$  (an extrapolation of  $25^\circ$ ) in excellent

(4) H. W. Scheeline and E. R. Gilliland, *Ind. Chem. Eng.*, **31**, 1050-1057 (1939).

(5) A. B. Lamb and E. E. Roper, *This Journal*, **62**, 806-814 (1940).