Reaction of Potassium Cyanide with the Ditosylate of 2-Methylpropanediol.—This reaction was also carried out in the same fashion as that described for the ditosylate of 2,2-dimethyl-1,3-propanediol. A solution of 83.6 g. (0.22 mole) of the ditosylate of 2-methylpropanediol and 43.0 g. (0.66 mole) of potassium cyanide in 600 ml. of ethylene glycol was heated. There was no distillate below the boiling point of ethylene glycol. Extraction of the 175 ml. of distillate with *n*-pentane, and evaporation of the pentane, yielded no product.
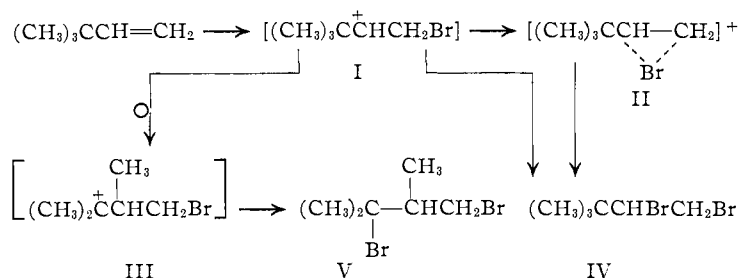

The Reaction of *t*-Butylethylene and 1-Hexene with Bromine in Methanol[1a]

BY W. H. PUTERBAUGH[1b] AND MELVIN S. NEWMAN

The addition of bromine in methanol to *t*-butylethylene produces 1,2-dibromo-3,3-dimethylbutane (IV) and 2-bromo-1-methoxy-3,3-dimethylbutane (VI) in roughly equal amounts. The addition of bromine in methanol to 1-hexene produces about 31% of 1,2-dibromohexane and 59% of a mixture of 1-bromo-2-methoxyhexane and 2-bromo-1-methoxyhexane in the ratio four-to-one, respectively. The mechanism of these reactions is discussed.

The work herein described was undertaken to obtain qualitative evidence about the mechanism of addition of bromine to *t*-butylethylene in particular and to olefins in general. The interest in this work was aroused by the report that the rate of bromination of *t*-butylethylene was only slightly less than that of *n*-butylethylene[2] (0.70 to 1.05).

The rate-determining step undoubtedly involves the formation of a positively-charged bromine-containing intermediate since the rates are first order with respect to olefin and bromine.[2] If the first-formed intermediate is the carbonium ion I, the further reaction of I with the reaction medium might involve attachment of bromine directly to the internal carbon of I. Alternatively, compound I might rearrange to the cyclic bromonium ion II or to skeletally rearranged III. Both I and II would yield the dibromide IV, whereas III would yield the 1,3-dibromide V.

In our analysis of this problem we believed that if Compound I were formed directly, it would rearrange rapidly to II which would then be expected to react further at the terminal less hindered carbon to yield IV.[4] The noteworthy feature of this over-all reaction path is that *both bromine atoms enter the final molecule by attack at the terminal carbon.*[5,6]

In order to test this hypothesis, we have studied the reaction of *t*-butylethylene and of *n*-butylethylene with solutions of bromine in methanol, a reagent which adds bromo and methoxy groups to an olefin.[7]

The addition of a solution of bromine in methanol to *t*-butylethylene yielded about 45% of 1,2-dibromo-3,3-dimethylbutane (IV) and 44% of 2-bromo-1-methoxy-3,3-dimethylbutane (VI). The structure of IV was proved by debromination with zinc to yield *t*-butylethylene. The structure of VI was proved by dehydrobromination with sodium amide in liquid ammonia to an unsaturated ether VII, which on treatment with 2,4-dinitrophenylhydrazine reagent afforded the 2,4-dinitrophenylhydrazone of *t*-butylacetaldehyde in high yield. This result supports the hypothesis that both addenda enter the molecule by attack at the terminal carbon, although the first-formed species may be either I or II.

Although the accuracy of our experimental work does not exclude the possibility that small amounts of skeletally rearranged substances were formed, certainly the quantities were very small, if any. This finding is of interest in light of the fact that addition of hydro-
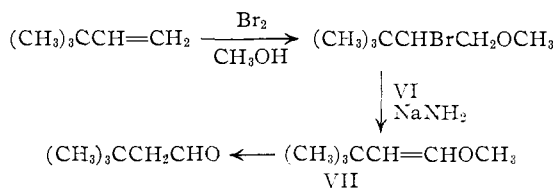

$(CH_3)_3CCH{=}CH_2 \longrightarrow [(CH_3)_3C\overset{+}{C}HCH_2Br] \longrightarrow [(CH_3)_3CCH{-}CH_2]^+$
I
Br
II

$\left[(CH_3)_2\overset{+}{C}CHCH_2Br\right] \longrightarrow (CH_3)_2C{-}CHCH_2Br \quad (CH_3)_3CCHBrCH_2Br$
III   V   IV

with Br below the central carbon of V; CH₃ groups shown above III and V.

Although the British authors recognized that the further reaction of I would be expected to be slow[3] because of the neopentyl character of the intermediate, they did not go into any further discussion of how I forms final product nor did they prove the structure of the dibromide formed.

(1a) This work was supported by a grant from the National Science Foundation. (b) Thiel College, Greenville, Pennsylvania.

(2) P. W. Robertson, J. K. Heyes and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952). In this paper steric factors are ruled out on what seems to us inadequate grounds.

(3) However, if the formation of the bromine-containing intermediate I is the rate-determining step, the rate of further reaction of I would not affect the over-all rate.

(4) The stereochemistry of addition of bromine to *cis*- and *trans*-olefins demands an intermediate of type II. However, with *t*-butyl-ethylene it is conceivable that an intermediate of type I could form first and then go into a type II intermediate.

(5) See M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 243.

(6) See also S. Winstein and L. Goodman, THIS JOURNAL, **76**, 4373 (1954), for an example of non-Markownikow addition of the elements of bromine and methoxyl to α,α-dimethylallyl alcohol.
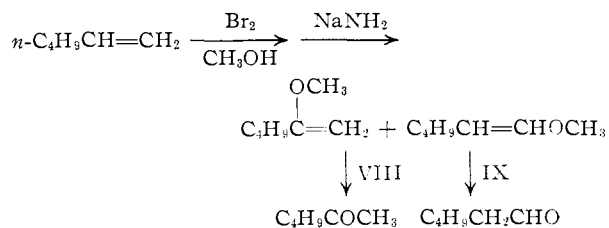
(7) P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).

gen chloride to *t*-butylethylene gives from 60 to 65% of rearranged chloride, 2-chloro-2,3-dimethyl-

$$(CH_3)_3CCH=CH_2 \xrightarrow[CH_3OH]{Br_2} (CH_3)_3CCHBrCH_2OCH_3$$

$$\Bigg\downarrow \begin{array}{c} VI \\ NaNH_2 \end{array}$$

$$(CH_3)_3CCH_2CHO \longleftarrow (CH_3)_3CCH=CHOCH_3$$
$$VII$$

butane.[8] Furthermore, when neopentyl-type carbonium ions are formed from neopentyl halides and alcohols by bond cleavage, rearrangement almost always occurs to a large extent.

For comparison we added bromine in methanol to 1-hexene and obtained about 31% of dibromide and 59% of methoxybromide.[9] The latter was shown to consist of about 4–5 parts of 1-bromo-2-methoxyhexane to 1 part of 2-bromo-1-methoxyhexane by dehydrobromination to a mixture of enol ethers VIII and IX. The composition of this mixture was estimated by crude separation of the 2,4-dinitrophenylhydrazones obtained therefrom and by hydrolysis to a mixture of 2-hexanone and hexanal which was analyzed by oxidation and titration of the hexanoic acid produced, as described in the Experimental part. Further work in this field is being carried out.

$$n\text{-}C_4H_9CH=CH_2 \xrightarrow[CH_3OH]{Br_2} \xrightarrow{NaNH_2}$$

$$\begin{array}{c} OCH_3 \\ | \\ C_4H_9C=CH_2 \ + \ C_4H_9CH=CHOCH_3 \end{array}$$

$$\Bigg\downarrow VIII \qquad \Bigg\downarrow IX$$

$$C_4H_9COCH_3 \qquad C_4H_9CH_2CHO$$

Experimental[10]

t-Butylethylene.—To a stirred mixture of 12.6 g. (0.33 mole) of lithium aluminum hydride and 350 ml. of ether was added dropwise over 3.25 hr., 100 g. (1.00 mole) of pinacolone[11] in 125 ml. of ether. After stirring and refluxing for 45 minutes the mixture was cooled to room temperature and 163 g. (1.60 moles) of acetic anhydride added dropwise over 1.5 hr. The mixture was refluxed for 4 hr. and 84 g. (1.40 moles) of glacial acetic acid then added rapidly. After stirring overnight (12 hr.) at room temperature the reaction mixture was decomposed by adding a solution of 120 ml. of concentrated hydrochloric acid in 240 ml. of ice-water. The crude acetate was pyrolyzed by dropwise addition over 3 hr. to a pyrolysis tube heated to 510° under a constant stream of nitrogen as described previously.[12] The pyrolysate was taken up in toluene, washed with several portions of saturated sodium bicarbonate solution, once with saturated sodium chloride solution and dried over calcium sulfate. Distillation at atmospheric pressure afforded 57 g. (68%) of *t*-butylethylene, b.p. 40–42°.

Bromomethoxylation of *t*-Butylethylene.—To a stirred ice-cooled solution of 31 g. of *t*-butylethylene in 1 l. of absolute methanol protected from light was added dropwise over

(8) G. G. Ecke, N. C. Cook and F. C. Whitmore, THIS JOURNAL, 72, 1511 (1950).

(9) This proportion was obtained when potassium acetate was present. When no potassium acetate was present, a lower proportion of methoxybromide was obtained, but qualitatively the rate of bromine addition (decolorization) seemed about the same.

(10) Analyses by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points uncorrected except where noted.

(11) M. S. Newman and A. S. Smith, J. Org. Chem., 13, 592 (1948).

(12) W. J. Bailey and H. R. Golden, THIS JOURNAL, 75, 4780 (1953); W. J. Bailey, J. Rosenberg and L. J. Young, ibid., 76, 2251 (1954); W. J. Bailey and C. King, ibid., 77, 75 (1955).

3.5 hr. a solution of 60 g. of bromine in 300 ml. of methanol. After stirring for an additional 0.5 hr., the mixture was poured into 2 l. of ice-water containing 20.2 g. of sodium bicarbonate. The mixture was extracted with petroleum ether, b.p. 35–40° (Skellysolve F). Rectification of the washed and dried reaction products through a small packed column afforded 32 g. (44%) of methoxybromide IV, b.p. 81–82° at 30 mm., and 41 g. (45%) of dibromide III, b.p. 100–101° at 30 mm.

The methoxybromide fraction was redistilled to obtain an analytical sample of 1-methoxy-2-bromo-3,3-dimethylbutane (IV), b.p. 81° at 30 mm., $n^{20}D$ 1.4588, d^{27} 1.214.

Anal. Calcd. for $C_7H_{15}OBr$: C, 43.1; H, 7.8; Br, 41.0. Found: C, 43.0; H, 7.6; Br, 41.1.

The dibromide fraction also was redistilled to obtain an analytical sample of III,[13] b.p. 85° at 12 mm., $n^{20}D$ 1.5055, d^{27} 1.620.

Anal. Calcd. for $C_6H_{12}Br_2$: C, 29.5; H, 5.0; Br, 65.5. Found: C, 29.7; H, 5.1; Br, 65.3.

Debromination of III.—A solution of 40 g. of III in 40 ml. of alcohol was added dropwise with stirring to a mixture of 33 g. of zinc dust and 80 ml. of alcohol. After the exothermic reaction moderated, the mixture was heated and stirred for 90 minutes. There was isolated 6.6 g. (48%) of pure *t*-butylethylene, identical in physical properties and infrared spectrum to authentic *t*-butylethylene. No other olefin was found in appreciable amount.

Dehydrobromination of *t*-Butylethylene Methoxybromide (IV).—To a stirred suspension of sodium amide prepared from 5.2 g. (0.226 mole) of sodium and 450 ml. of liquid ammonia was added over 0.5 hr. 40 g. (0.205 mole) of IV in 100 ml. of ether. The mixture was stirred for 1.5 hr. in liquid ammonia until the ammonia evaporated, then refluxed for 0.5 hr. in ether. To the cooled mixture was added 100 ml. of ether followed by 75 ml. of water. The washed and dried reaction products on rectification yielded 12.7 g. (54%) of the enol ether, b.p. 100–106° at 750 mm., and 11.4 g. (28%) of recovered IV, b.p. 75–80° at 30 mm. The enol ether was redistilled to yield 11.5 g. (49%) of 1-methoxy-3,3-dimethyl-1-butene (VII), b.p. 103–106°. After stirring with saturated sodium bisulfite solution, the enol ether was redistilled to give the analytical sample, b.p. 106° at 750 mm., $n^{20}D$ 1.4092.

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 73.7; H, 12.6.

Proof of Structure of VII.—To the reagent prepared from 1.7 g. of 2,4-dinitrophenylhydrazine, 3.5 ml. of concentrated hydrochloric acid and 35 ml. of 95% ethanol was added 1.0 g. of VII obtained as described above. An immediate precipitate formed which on cooling was filtered to yield 2.21 g. (92%) of *t*-butylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 142–146°. One recrystallization of a portion from 95% ethanol gave product, m.p. 147.5–148.0°, in 90% recovery. The reported[14] m.p. for *t*-butylacetaldehyde 2,4-dinitrophenylhydrazone is 146–147°. The reported[15] melting point for pinacolone 2,4-dinitrophenylhydrazone is 125°.

Treatment of the enol ether with dimedon reagent gave the dimedon derivative of *t*-butylacetaldehyde, m.p. 163.0–163.5° (reported[15] m.p. 162–163°), after one recrystallization from petroleum ether (b.p. 90–100°, Skellysolve C).

Bromo-methoxylation of *n*-Butylethylene.—Hexene-1 (Phillips Petroleum Co.) was bromo-methoxylated essentially as described for *t*-butylethylene with the exception that potassium acetate was added to the reaction mixture to absorb the hydrogen bromide formed. From the addition during 2 hr. of 119 g. (0.72 mole) of bromine in 450 ml. of methanol to 60 g. (0.714 mole) of hexene-1 and 74 g. (0.72 mole) of potassium acetate dissolved in 1300 ml. of methanol, there was obtained on distillation at 15 mm., 73 g. of methoxybromide, b.p. 75–78°; 20 g. of intermediate fraction, b.p. 78–88°, and 44 g. of dibromide, b.p. 88–90°. Assuming the intermediate fraction to consist of equal amounts of methoxybromide and dibromide, the yield of methoxybromide was 59% and of dibromide 31%.

Redistillation of the methoxybromide fraction gave an analytical sample, b.p. 68° at 10 mm., $n^{23}D$ 1.4495.

(13) This compound has been reported previously (M. F. Claessens Bull. soc. chim., [4] 5, 113 (1909)), but the structure was not proved.

(14) L. Schmerling, U. S. Patent 2,481,157, Sept. 6, 1949.

(15) C. F. H. Allen, THIS JOURNAL, 52, 2955 (1930).

Anal. Calcd. for $C_7H_{15}OBr$: C, 43.1; H, 7.8; Br, 41.0. Found: C, 43.0; H, 7.9; Br, 41.2.

Dehydrobromination of *n*-Butylethylene Methoxybromide.—Treatment of 50 g. (0.256 mole) of the methoxybromide obtained from *n*-butylethylene with sodium amide prepared from 6.9 g. (0.3 mole) of sodium essentially as described above for *t*-butylethylene methoxybromide gave on distillation, 11.2 g. (38%) of enol ether, b.p. 120–126° (760 mm.), and 14.1 g. (28%) of recovered methoxybromide, b.p. 75–80° (20 mm.). There was also obtained 4.9 g. (23%) of hexyne-1, b.p. 60–64°. The enol ether fraction was redistilled to obtain an analytical sample, b.p. 122° at 750 mm.

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 73.5; H, 12.4.

Structure of Enol Ether Obtained from *n*-Butylethylene Methoxybromide.—To the 2,4-dinitrophenylhydrazine reagent prepared from 1.7 g. of 2,4-dinitrophenylhydrazine, 3.5 ml. of concentrated hydrochloric acid and 40 ml. of 95% ethanol was added 1 g. of the enol ether fraction, b.p. 120–126°, obtained as described above. The precipitate was filtered to yield 2.1 g. (89%) of a mixture of methyl *n*-butyl ketone and *n*-hexaldehyde 2,4-dinitrophenylhydrazones, m.p. 80–102°. Recrystallization of a 1.33-g. portion from 60 ml. of 95% ethanol gave as first crop, 0.88 g. (66%) of short orange crystals, m.p. 103.5–107°. The mixed m.p. with authentic methyl *n*-butyl ketone 2,4-dinitrophenylhydrazone (m.p. 107.5-108.5°) was 106–108°. Partial evaporation and freezing of the filtrate yielded 0.4 g. of yellow-orange crystals, m.p. 82–95°. From the latter it was possible to separate by hand a few long yellow needles, m.p. 105.5–107.5°, mixed m.p. with authentic *n*-hexaldehyde 2,4-dinitrophenylhydrazone (m.p. 105.5–107.5°) 106.0–107.5°. However, attempts to further separate the second crop quantitatively by recrystallization and chromatography were unsuccessful.

The amount of terminal enol ether in the enol ether mixture, which was shown above to be less than 34%, was estimated by conversion to a mixture of aldehyde and ketone, oxidation of the mixture with silver oxide and titration of the acid formed from oxidation of the aldehyde, as described below.

A mixture of 8.5 g. of enol ether, 2 ml. of concentrated hydrochloric acid, 6 ml. of water and 10 ml. of ethanol was refluxed 5 minutes. The mixture was diluted with water, taken up in ether, dried and distilled to yield 5 g. (67%), b.p. 124–125°, of a mixture of methyl *n*-butyl ketone and *n*-hexaldehyde. To a silver oxide reagent prepared from 3.40 g. of silver nitrate in 10 ml. of water and 2.40 g. of sodium hydroxide in 10 ml. of water was added 2.50 g. of the ketone–aldehyde mixture. After stirring for 30 minutes, the mixture was filtered with suction and extracted with ether. Then the aqueous layer was then carefully acidified, salted out and extracted with four 20-ml. portions of ether. The ether extracts were washed with saturated sodium chloride solution and dried. Removal of the solvent left an acidic residue, which on titration with standard base was shown to contain 4.7 mmoles (19%) of acid calculated as caproic acid. The acid isolated from this titration was refluxed with excess aniline for 2 hr. One recrystallization of the crude anilide from 95% ethanol gave *n*-caproanilide, m.p. 95.0–95.5° (reported[16] m.p. 96°). A duplicate run gave an acid yield of 15%. A check on the method with a mixture of 0.02 mole of methyl ethyl ketone and 0.005 mole of *n*-heptaldehyde gave on titration 0.0049 mole (98% of theory) of acid formed.

The enol ether formed from dehydrobromination of the methoxybromide obtained from *n*-butylethylene was thus shown by these methods to consist of approximately 80–85% of 2-methoxyhexene-1 and 15–20% of 1-methoxyhexene-1.

(16) A. Ludwig and S. Tache, *Bull. chim. soc. Romane chim.*, **39**, 87 (1937).

COLUMBUS 10, OHIO

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aci-Nitroalkanes. IV. The Mechanism of the Hydrolysis of 1-Chloronitroethane

BY M. FREDERICK HAWTHORNE AND R. DONALD STRAHM

In water at 35.0° and in independent first-order rate determinations, 1-chloronitroethane has been found to release chloride ion approximately one-third as rapidly as it absorbs bromine. 1-Deutero-1-chloronitroethane when examined in an identical manner showed approximately a twofold diminution in both measured rate constants. These facts prove that the hydrolytic release of chloride ion from 1-chloronitroethane is preceded by a tautomerization to the reactive *aci*-isomer and that return of the *aci*-isomer to reactant is kinetically important relative to the hydrolysis of the *aci*-isomer. The products of hydrolysis of 1-chloronitroethane have been found to be equivalent amounts of hydrogen chloride, acetic acid and a colorless gas which is probably nitrous oxide. Conductometric examination of the rate of hydrolysis of 1-chloronitroethane affords an instance in which the approach of a reaction system to a steady state situation may be observed.

It was recently reported by Pearson and Dillon[1] that 1-chloronitroethane hydrolyzed in aqueous solution at 34.9° to yield chloride ion at a rate equal to approximately one-half the rate at which the same nitroalkane ionized (absorbed bromine) under the same conditions. In view of the recent finding that the displacement of chloride ion from 1-chloronitroethane by nitrite ion is preceded by the tautomerization of the nitro compound to its *aci*-nitroisomer, it was proposed[2] that the hydrolysis of 1-chloronitroethane and the kinetic observations of Pearson and Dillon[1] could be explained on a similar basis if the rate of return of *aci*-1-chloronitroethane to its hydrolytically stable isomer were comparable to the rate of displacement of chloride ion from the reactive *aci*-isomeride by solvent water ($k_{-1} \sim k_2$).
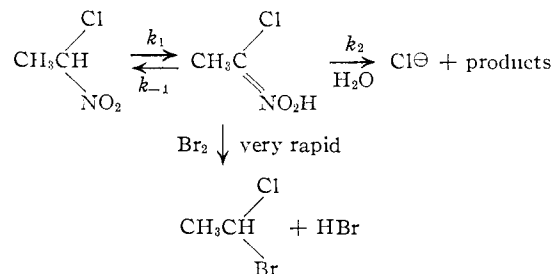
Therefore

$$\frac{d[Cl^\ominus]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [CH_3ClNO_2] \text{ and}$$

$$\frac{-d[Br_2]}{dt} = k_1[CH_3ClNO_2] \quad (1)$$

(1) R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).
(2) M. F. Hawthorne, *ibid.*, **78**, 4980 (1956).