

yl-2-hexene, 3,4,5,5-tetramethyl-2-hexene, 3,5,5-trimethyl-2-heptene and 2,2,3,5,5-pentamethyl-3-heptene.

4. The mechanism for the formation of these products is discussed.

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Some Reactions of *t*-Butylethylene¹

BY GEORGE G. ECKE,^{2a} NEWELL C. COOK^{2b} AND F. C. WHITMORE³

Several reactions of *t*-butylethylene have been investigated to throw further light on the behavior of compounds containing the neopentyl system.

Addition of chlorine was found to produce principally unrearranged dichlorides which yielded on dehydrochlorination both the 1- and 2-chloro-3,3-dimethylbutenes. Contrary to expectations gained from a study of pinacolyl alcohol, hydrogen chloride added to *t*-butylethylene to give considerable amounts of pinacolyl chloride. The presence of benzoyl peroxide caused an increase in the yield of pinacolyl chloride, and produced a peroxide effect in those reactions which contained low ratios of hydrogen chloride to olefin, giving 1-chloro-3,3-dimethylbutane. Hydrogen iodide added to *t*-butylethylene almost completely without rearrangement, giving 90% pinacolyl iodide.

Experimental

Distillations were made through columns of the adiabatic, total reflux, variable take-off type, packed with (A) $\frac{3}{32}$ " glass helices, packed section 1.5×70 cm., 30 theoretical plates, (B) $\frac{3}{32}$ " glass helices, 1.4×40 cm., 20 theoretical plates, (C) $\frac{1}{16}$ " glass helices, 0.8×28 cm., 30 theoretical plates, (D) $\frac{1}{16}$ " glass helices, 1.5×145 cm., 80 theoretical plates.

Reaction of Chlorine with *t*-Butylethylene.—The olefin mixtures from the dehydration of 3,3-dimethyl-2-butanol with alumina as described by Cramer and Glasebrook⁴ were fractionated through Column D to produce a *t*-butylethylene fraction with constant boiling point and refractive index, b. p. 41° , n_D^{20} 1.3760. For the hydrogen chloride addition reactions the olefin was given a subsequent distillation under nitrogen and kept in sealed ampules until needed.

Chlorine was bubbled into a 2-mole (168-g.) portion of *t*-butylethylene and a 111 g. (78% theoretical) gain in weight noted over an eight-hour period. The mixture was stirred, protected from light, and maintained at $0-5^\circ$ during the reaction. Preliminary distillation under reduced pressure through column B gave an olefin fraction, a dichloride fraction, and a higher chloride fraction. Fractionation of these products by parts through column C gave 31 g. (16%) recovered *t*-butylethylene, b. p. 41° , n_D^{20} 1.3758-1.3761, 20 g. (6%) of dichloride, b. p. $46-52$ (11 mm.), n_D^{20} 1.4553-1.4622 (believed to be mainly unsaturated dichlorides), 163 g. (53%) 1,2-dichloro-3,3-dimethylbutane (I), b. p. 52° (11 mm.), n_D^{20} 1.4553, and 42 g. of a mixture of higher chlorides, b. p. $55-100^\circ$ (10 mm.), n_D^{20} 1.4644-1.5024.

Reaction of *t*-Butylethylene with Sulfuryl Chloride.—A solution of 7 moles (588 g.) of *t*-butylethylene and 3 g.

of dibenzoyl peroxide was heated to reflux and 6.8 moles (920 g.) of sulfuryl chloride added over a four-hour period. Heating was continued an additional four hours, the pot temperature finally reaching 98° . The 905 g. of product was given a preliminary fractionation through Column A to yield 640 g. (61%) crude (I) and 210 g. of higher chlorides. Fractionation of the crude (I) through column A gave 575 g. of the pure dichloride, b. p. 52° (11 mm.), n_D^{20} 1.4551, d_4^{20} 1.071.

Dehydrochlorination of 1,2-Dichloro-3,3-dimethylbutane.—To 3.76 moles (584 g.) of (I) was added 1040 ml. of 3.97 *N* ethanolic potassium hydroxide representing a 10% excess for the removal of one hydrogen chloride per molecule. The mixture was stirred and heated to reflux for three hours. After cooling 2500 ml. of water was added. The organic layer was removed, washed with water, and steam distilled. Titration of the water layer from the reaction indicated 87% dehydrochlorination for the removal of one hydrogen chloride per molecule of dichloride. Fractionation of the organic layer from the steam distillation gave an unsaturated monochloride fraction, 378 g. (85% conversion) and a recovered dichloride fraction, 53 g. (94% material balance). The monochloride fraction was refractionated through column D to yield 2-chloro-3,3-dimethyl-1-butene (II), b. p. 95.5° (730 mm.), n_D^{20} 1.4247, d_4^{20} 0.8888 and 1-chloro-3,3-dimethyl-1-butene (III), b. p. 105° (730 mm.), n_D^{20} 1.4276, d_4^{20} 0.8835 in a ratio of 1.7:1. No evidence of the *cis-trans* pair of (III) was found.

Ozonolysis of the Unsaturated Monochlorides.—A 10-ml. portion of (II) was dissolved in 150 ml. of pentane and ozonized at ice temperature over an eleven-hour period. Ozone absorption was definitely sluggish. Decomposition of the ozonide with boiling water and zinc dust gave a steam distillate, the water layer of which yielded the 2,4-dinitrophenylhydrazone of formaldehyde, m. p. and a mixed m. p. $161-162^\circ$. The pentane layer yielded a low melting solid which was purified through conversion to and regeneration from the potassium salt. It melted at about 28° and was not depressed by an authentic sample of pivalic acid. These results indicate the low boiling isomer to be 2-chloro-3,3-dimethyl-1-butene and establish the unrearranged structure of the parent dichloride.

A 10-ml. sample of the high boiling flat was ozonized in a similar manner except that ozone absorption was rapid. Decomposition of the ozonide yielded the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. $210-211^\circ$. The cold trap from the ozonolysis exhaust gases gave a copious quantity of hydrogen chloride upon warming as evidenced by their reaction with moist litmus and silver nitrate solution. These facts indicate the high boiling isomer to be 1-chloro-3,3-dimethyl-1-butene and affirm the structure of (I).

Reactivities of the Unsaturated Monochlorides.—A series of sealed glass tubes were prepared each containing 5 ml. of 1.276 *N* ethanolic potassium hydroxide along with 2 ml. of the desired halide. The tubes were placed in a steam-bath and one tube of each isomer removed at appropriate times. Whereas (III) was less than 5% reacted at the end of forty-six hours, (II) showed greater than 95% reaction.

Both ozone and permanganate in acetone reacted more rapidly with (III) than with (II). Attempts to form

(1) Presented before the Organic Division of the American Chemical Society, Atlantic City, September, 1949.

(2) (a) Present address: Ethyl Gas Corporation, Detroit, Michigan; (b) General Electric Company, Schenectady, New York;

(3) Deceased.

(4) Cramer and Glasebrook, *THIS JOURNAL*, **61**, 230 (1939).

Grignard reagents with either of these compounds were unsuccessful.

Addition of Hydrogen Chloride to *t*-Butylethylene.—The reaction was carried out in a closed glass system to preclude the presence of oxygen and moisture. The *t*-butylethylene was distilled in an evacuated system into a Dry Ice Carius reaction tube which contained benzoyl peroxide when so desired. During this process the olefin vapor passed over 14–20 mesh activated alumina which had been previously dried by heating to 400°. After transfer of the olefin to the reaction tube, the drying and distribution part of the system was sealed off with a torch from the reaction tube.

The Carius tube was attached to a cylinder of Harshaw anhydrous hydrogen chloride by means of Tygon tubing which had been clamped off until this time. Also between the reaction tube and the cylinder was a side arm connected to an exit bubbler so that the pressure would not rise above one atmosphere when the tank was opened. The bubbler system was filled with nitrogen, the tank opened and the nitrogen displaced with hydrogen chloride, and finally the clamps opened and the hydrogen chloride admitted to the evacuated reaction tube. The olefin in the reaction tube was maintained at Dry-Ice temperature and gently shaken to hasten the solution of hydrogen chloride. After the liquid level had risen to the desired height, the reaction tube was clamped off and the reaction tube sealed off with the torch at a constricted section. The reaction tube was placed in a steel pipe, one end of which had been welded shut, and shaken by inverting until all the peroxide had dissolved. While all runs were shaken to ensure homogeneity, an error was made in the case of Run 2 in that shaking was not continued long enough to dissolve the peroxide. The reaction tube was let stand one week in the dark at room temperature.

After slowly cooling to Dry-Ice temperature, the tube was opened. The unreacted hydrogen chloride boiled off while warming to room temperature. Distillation through column C separated the unreacted olefin from the chloride fraction. Care was taken during this distillation to keep the pressure sufficiently low that the distillation pot did not rise above 60° at any time, and in the case of the peroxide runs a preliminary rapid distillation was performed at very low pressure to avoid having benzoyl peroxide in the still pot during the fractionation.

The chloride fraction (b. p. 50–51° (95 mm.)) was analyzed by means of infrared (Perkin & Elmer) spectra, the following standards being used: 1-chloro-3,3-dimethylbutane (IV) (b. p.) 116.0–116.5° (735 mm.), n_D^{20} 1.4160; 2-chloro-3,3-dimethylbutane (V) (b. p.) 111.0° (760 mm.), n_D^{20} 1.4182; 2-chloro-2,3-dimethylbutane (VI) (b. p.) 111.9–112.1° (760 mm.), n_D^{20} 1.4192. The first two of

these standards were supplied through the courtesy of Mr. Ivan S. Kolarik who prepared them by the chlorination of 2,2-dimethylbutane with sulfuryl chloride. The latter compound was prepared by the action of aqueous hydrochloric acid upon tetramethylethylene. Data from the analyses are presented in Table I; (accuracy $\pm 5\%$ of value shown).

Preparation of Anilides.—Anilides were prepared from each of the spectroscopic standards by conversion to the Grignard reagent and reaction with phenyl isocyanate. The melting points of the anilides were from (VI) 78°; from (V) 116°; from (IV) 140°. The first two anilides have not been reported before in the literature.

Two peroxide-catalyzed runs were carried out in the usual manner using a 0.28:1 ratio of hydrogen chloride to *t*-butylethylene. The products were combined and after a rapid distillation to separate the chloride fraction from the olefin and peroxide, the chlorides were carefully fractionated through column C. The first four fractions consisted largely of (VI) and (V) b. p. 49.0–49.9° (90 mm.), n_D^{20} 1.4186–1.4188. The last fraction was largely (IV) and was obtained by flashing over the material in the pot and on the packing through pressure reduction, n_D^{20} 1.4178. The anilide prepared from this last fraction melted at 140° and gave no melting point depression when mixed with an authentic sample of that from (IV). This derivative confirms the presence of (IV) as shown in the infrared analyses.

Addition of Hydrogen Iodide to *t*-Butylethylene.—The preparation of anhydrous hydrogen iodide was carried out by adding 1.0 mole (150 g.) of sodium iodide to a solution of 2.0 moles (226 g.) of 85% phosphoric acid and 0.35 mole of phosphorus pentoxide in a 500-ml. round-bottom flask. This flask was connected to a series of cold traps, the first maintained at 0°, the second at –40°, and the third at –80°. Upon heating the flask with a bunsen burner, hydrogen iodide was collected in the latter two traps. Some care was necessary to avoid plugging the train with solid hydrogen iodide. A 50% yield of hydrogen iodide was usually obtained. When the generation of the hydrogen iodide appeared complete, the system was closed off between the first two traps, and upon warming to room temperature the material in the –40° trap distilled into the –80° trap. The latter trap entrance was then closed off and the exit connected to a tube extending just above the surface of a 1-mole portion of *t*-butylethylene cooled to –80°. The trap was allowed to come to room temperature and the hydrogen iodide absorbed by the cold *t*-butylethylene. Upon completion of the transfer the colorless reaction mixture was partially closed off by a glass wool plug. It was kept in the dark during the reaction time at the end of which it had usually acquired a red color.

After standing the desired time the product was distilled through column C to separate the olefin from the iodides. No attempt was made to fractionate the iodides, and they were rapidly flashed over under low pressures to avoid decomposition.

Analysis of the iodide mixture was effected through dehydrohalogenation to *t*-butylethylene and tetramethylethylene. In a typical run 225 ml. of *n*-propyl alcohol was added to 1.0 mole of potassium hydroxide and then after cooling 0.393 mole (83.3 g.) of crude iodides. The mixture was placed under column A and crude olefin distilled off as formed. The distillate was washed and analyzed by fractionation through column C. The results are presented in Table II.

TABLE I

Run	Molar ratio HCl:olefin	Conversion (HCl basis), %	Percentage composition of chloride fraction		
			VI	V	IV
9 ^a	0.23	19	53	42	2
1 ^a	.37	59	67	26	4
3 ^a	.87	84	61	38	0.3
4 ^b	.66	56	65	33	0.4
5 ^c	.87	94	72	27	0.5
2 ^{d,e}	.29	52	25	55	11
8 ^{d,f}	.29	52	27	58	11
7 ^d	.34	112	5	71	24
6 ^d	.87	66	57	41	0
10 ^d	.89	74	56	43	0

^a No catalyst present. ^b 0.68 mole % water added. ^c Reaction run in iron pipe with probable trace of moisture. ^d Reaction run in presence of 1.3 mole % benzoyl peroxide (relative to olefin). ^e Peroxide not appreciably dissolved at start of run due to insufficient shaking. ^f Same product as Run 2 submitted as control on analyses.

TABLE II

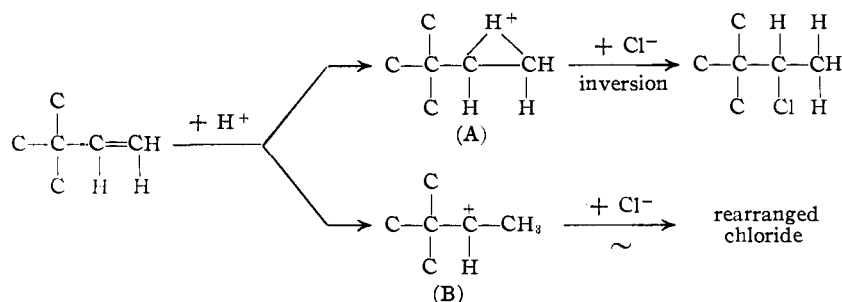
Run	A	B
Ratio HI:olefin	0.50	0.54
% Conversion to iodides on HI basis	84	96
% Unrearranged iodide (based on <i>t</i> -butylethylene)	80	90
% Rearranged iodide (based on tetramethylethylene)	20	10
Reaction time, days	15	7

The unrearranged iodide is believed to be largely or entirely 2-iodo-3,3-dimethylbutane on basis of the fact that only the anilide of that structure could be obtained, m. p. and mixed m. p. 116°.

Discussion

Regarding the addition of hydrogen chloride to *t*-butylethylene the following facts have been taken from the data presented in Table I. (1) In the absence of catalysts the principal product is the rearranged chloride (VI). (2) Traces of water have little effect on the amount or nature of the compounds produced in the absence of peroxide. (3) The presence of peroxide at low hydrogen chloride ratios leads to the formation of abnormal addition product (IV) and also causes the normal (V) to predominate over the rearranged (VI) addition product. (4) The peroxide effect is either prevented or obscured at high hydrogen chloride ratios.

The characteristic rearrangement of the neopentyl group, indicative of a carbonium ion mechanism, was found to be the dominant reaction in the normal addition of hydrogen chloride to



t-butylethylene. A weaker electrolyte might favor the formation of stabilized addition products.⁶ The decrease in the percentage of rearranged product in the peroxide runs at low hydrogen chloride-olefin ratios might be due to the peroxide acting as a base to produce a conjugate acid with hydrogen chloride. Such an acid may favor the formation of a stabilized intermediate (as represented by A) and make it possible for the chloride ion to attack the neopentyl carbon by a Walden mechanism. This effect would be expected to disappear, and did, at high hydrogen chloride-olefin ratios.

The high yield (90%) of unrearranged iodide from *t*-butylethylene represents the extreme extension of the stabilized transition mechanism. Although it might be argued that the iodide ion has a faster rate of addition than the chloride ion, thus leaving less time for (B) to rearrange, it seems more likely that an explanation lies in a transition product more stable than that formed from hydrogen chloride, which reacts by inversion with an iodide ion.

The disappearance of the peroxide effect at high hydrogen chloride-olefin ratios is attributed to the kinetics of the two mechanisms. It would be

suspected that the peroxide-free hydrogen chloride addition rate is a function of the concentrations of the hydrogen chloride and olefin. On the other hand the peroxide-catalyzed runs may be largely dependent upon the free radical concentration. Thus at high hydrogen chloride ratios, the peroxide catalyzed addition is obscured by the rapid carbonium ion reaction, whereas at low ratios the ionic reaction is slow in contrast to the relatively unaltered rate of the peroxide reaction. Mayo and Katz⁶ in a study of the kinetics of the reaction of hydrogen chloride with isobutylene found that the rate is third order in respect to hydrogen chloride, and first order in respect to olefin concentrations.

The peroxide effect in hydrogen chloride-olefin reactions has been observed by Raley, Rust and Vaughan⁷ in their study of the reaction of hydrogen chloride with ethylene and propylene. Similarly the production of straight-chain primary chlorides at elevated temperatures through the reaction of hydrogen chloride with ethylene in the presence of a free radical source by Ford and Harmon⁸ further supports the existence of a peroxide effect. This is the first time that a peroxide effect has been observed for hydrogen chloride under conditions which were previously found to influence only hydrogen bromide additions. The presence of traces of abnormal addition product in the products of runs 1 and 9 is believed to be due to difficulties in obtaining olefin completely free of peroxides.

Summary

1. Hydrogen chloride reacts with *t*-butylethylene to give 35-40% rearranged chloride and 60-65% unrearranged (pinacolyl) chloride.
2. In the presence of benzoyl peroxide and at low hydrogen chloride-olefin ratios the products are 20-25% rearranged chloride, 55-60% unrearranged chloride and 10-25% primary chloride (from abnormal addition).
3. At high hydrogen chloride-olefin ratios, benzoyl peroxide had no effect on the reaction.
4. Hydrogen iodide reacts with *t*-butylethylene to give 10% rearranged iodide and 90% unrearranged (pinacolyl) iodide.
5. *t*-Butylethylene dichloride is dehydrohalogenated by base to 70% 2-chloro-3,3-dimethyl-1-butene and 30% 1-chloro-3,3-dimethyl-1-butene, believed to be the *trans*-isomer.
6. Possible mechanisms of the above reactions have been discussed.

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(6) Mayo and Katz, *THIS JOURNAL*, **69**, 1339 (1947).

(7) Raley, Rust and Vaughan, *ibid.*, **70**, 2767 (1948).

(8) Ford and Harmon, Paper 57, Organic Section, American Chemical Society, Chicago Meeting, April 1948.

(5) Price, "Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 35-44.