[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CITY COLLEGE OF NEW YORK]

Aluminum Chloride-Catalyzed Formation of 2,5-Dichloro-2,5-dimethylhexane from *tert*-Butyl Chloride

F. E. CONDON

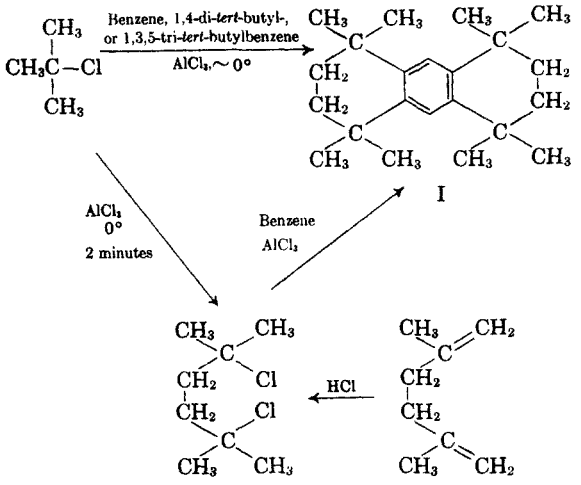
Received February 27, 1956

tert-Butyl chloride produces about 1% of 2,5-dichloro-2,5-dimethylhexane when contacted briefly with aluminum chloride near 0°. The significance of this result to the mechanisms of some alkylation and isomerization reactions is discussed.

In work described in 1953, Schlubach and Franzen[1] obtained 2,5-dichloro-2,5-dimethylhexane, a crystalline solid melting about 64°, as a by-product of the reaction of *tert*-butyl chloride and acetylene in the presence of aluminum chloride and made an unsuccessful attempt to isolate it from a room temperature reaction of aluminum chloride with *tert*-butyl chloride alone.

Several years ago, during a study of the aluminum halide-catalyzed exchange of halogen and hydrogen between alkyl halides and saturated hydrocarbons,[2] a small amount of a solid having the composition and properties of 2,5-dichloro-2,5-dimethylhexane was obtained from a reaction of aluminum chloride with *tert*-butyl chloride near 0°.[3] This early work has now been repeated and the solid has been identified as 2,5-dichloro-2,5-dimethylhexane by means of a mixture melting point. The yield was about 1% of the *tert*-butyl chloride converted. This dichloride is also produced, along with 10–17% of *tert*-butyl chloride, from *tert*-amyl chloride in the presence of hydrofluoric acid.[4]

The formation of even so little as 1% of 2,5-dichloro-2,5-dimethylhexane from *tert*-butyl chloride and aluminum chloride gains significance from recent work of Barclay and Betts,[5] who showed that a high-melting hydrocarbon obtained in quantity from the aluminum chloride-catalyzed alkylation of benzene,[6] 1,4-di-*tert*-butylbenzene,[6,7] or 1,3,5-tri-*tert*-butylbenzene[5] with *tert*-butyl chloride is identical with 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (I) prepared by the aluminum chloride-catalyzed alkylation of benzene with 2,5-dichloro-2,5-dimethylhexane.[5,8] The relationships among these phenomena are shown by the chart.



Furthermore, 2,5-dimethylhexane and other dimethylhexanes are found among the products of the acid-catalyzed alkylation of isobutane[9] or aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane,[10] for example, reactions in which, like those involved here, a *tert*-butyl positive ion is a postulated intermediate. Whatever may be the mechanism of formation of 2,5-dichloro-2,5-dimethylhexane or of the hydrocarbon I from *tert*-butyl chloride may therefore also be the mechanism of formation of dimethylhexanes in these other acid-catalyzed reactions, especially since hydrocarbon isomerization by shift of a methyl along a chain of fixed length is well known to be facile and rapid in the presence of acidic catalysts.[11]

(1) H. H. Schlubach and V. Franzen, *Ann.*, **583**, 93–99 (1953).

(2) P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531–1539 (1944).

(3) F. E. Condon, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1944, p. 83.

(4) J. H. Simons, G. H. Fleming, F. C. Whitmore, and W. E. Bissinger, *J. Am. Chem. Soc.*, **60**, 2267–2269 (1938). Private communication from Dr. W. E. Bissinger.

(5) L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735–5737 (1955).

(6) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672–678 (1955).

(7) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349–2353 (1954).

(8) H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36–39 (1940).

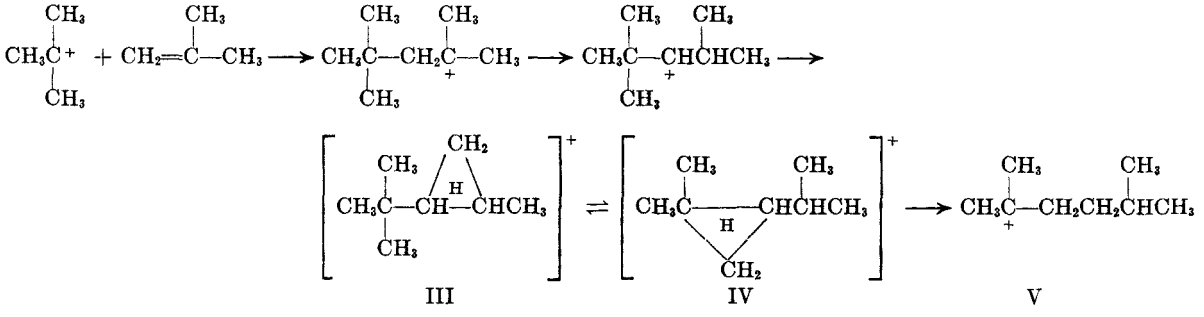
(9) (a) G. M. Webb and W. S. Galloway, *Pet. Processing*, **2**, 444–448 (1947); (b) A. Schneider and R. M. Kennedy, *J. Am. Chem. Soc.*, **73**, 5013–5029 (1951).

(10) F. E. Condon, *J. Am. Chem. Soc.*, **73**, 3938–3947 (1951).

(11) (a) A. K. Roebuck and B. L. Evering, *J. Am. Chem. Soc.*, **75**, 1631–1635 (1953); (b) B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **45**, 582–589 (1953); (c) L. G. Maury, R. L. Burwell, and R. H. Tuxworth, *J. Am. Chem. Soc.*, **76**, 5831–5835 (1954).

In order to explain the formation of the hydrocarbon I from *tert*-butyl chloride and *p*-di-*tert*-butylbenzene, Barclay and Betts proposed a route with 1,3,5-tri-*tert*-butylbenzene as an intermediate.[5] The results presented here suggest as an alternative route the direct formation of the 2,5-dimethylhexyl carbon skeleton from *tert*-butyl chloride followed by displacement of *tert*-butyl by 2,5-dimethyl-2-hexyl on the aromatic nucleus. Cyclization may then occur through formation of a positive center at the remaining tertiary carbon on the 2,5-dimethyl-2-hexyl side chain.

The large amount of hydrocarbon I obtainable[12] indicates that the *tert*-butyl system is a potential reservoir for the 2,5-dimethylhexyl system and that a poly-*tert*-butylbenzene is a particularly efficient trap for the 2,5-dimethylhexyl system. In the absence of such an effective trap, presumably a small steady-state concentration of the 2,5-dimethylhexyl system is built up and appears as 2,5-dichloro-2,5-dimethylhexane in the product of reaction of aluminum chloride with *tert*-butyl chloride alone and as isomeric dimethylhexanes in products of the acid-catalyzed alkylation of isobutane and the aluminum bromide-catalyzed isomerization of 2,2,4-trimethylpentane.



III IV V

As to the mode of formation of the 2,5-dimethylhexyl system from the *tert*-butyl system, the most simple but least attractive mechanism involves rearrangement of the *tert*-butyl positive ion to the isobutyl positive ion by hydride shift, followed by attachment of the isobutyl positive ion to isobutylene. A proposed route involving rearrangement of the 2,3,4-trimethyl-1-pentyl positive ion to the 2,3-dimethyl-4-hexyl positive ion[13] is also unattractive because of its length and because of its use of high energy primary carbonium ions. An alternative mechanism, attractive because it avoids use of a high energy primary carbonium ion, involves a nonclassical "protonated cyclopropane" structure for an intermediate carbonium ion.[14]

Stability may be ascribed to the protonated cyclopropane system III $\rightleftharpoons$ IV because of the numerous structures that may be written for it.[14] Structure IV has options of opening to the 2,5-dimethylhexyl, 2,2,4-trimethylpentyl, or 2,3,4-trimethylpentyl structures, all of which are found in products of acid-catalyzed alkylation and isomerization reactions.[9,10]

Under the conditions of the experiment described here, the 2,5-dimethyl-2-hexyl ion (V) would be expected to acquire a chloride ion to form 2-chloro-2,5-dimethylhexane, which then would be expected to undergo the well-known rapid exchange of tertiary hydrogen for halogen with *tert*-butyl chloride,[2] leading to 2,5-dichloro-2,5-dimethylhexane.

Acknowledgment. The author is indebted to Miss Eve Ehrenfeld for a sample of 2,5-dimethyl-1,5-hexadiene.

EXPERIMENTAL

2,5-Dichloro-2,5-dimethylhexane from tert-butyl chloride. (*i*). Details of an early experiment may be found in Reference (3) in which the solid dichloride was isolated by careful fractionation of a product of contacting *tert*-butyl chloride with aluminum chloride near 0°.

(*ii*). Powdered anhydrous aluminum chloride (7.0 g., 0.053 mole) was placed in a 1-l. three-necked flask fitted with a Hershberg stirrer,[15] a dropping-funnel, and a thermometer held in a cork notched for the escape of gaseous products. The flask was surrounded with an ice-bath and 100 g. (1.08 mole) of cold *tert*-butyl chloride was added from the dropping-funnel with stirring in the course of 23 seconds. Hydrogen chloride was evolved. The thermometer registered 2°. Two minutes from the start of addition of the *tert*-butyl chloride, 45 ml. of cold water was added rapidly from

(12) Published data are insufficient to determine the maximum yield of compound I obtainable from *tert*-butyl chloride. Barclay and Betts[5] obtained 20 g. (0.067 mole) of slightly impure I from an experiment using 0.25 mole of *p*-di-*tert*-butylbenzene (II) and 2.7 moles of *tert*-butyl chloride. According to the stoichiometry of the reaction, four moles of *tert*-butyl chloride are consumed for each mole of I produced (two moles of isobutane being produced also). In the experiment mentioned, therefore, 0.268 mole, or about 10%, of the *tert*-butyl chloride charged was consumed in the reaction:

$$4\ tert\text{-}C_4H_9Cl + C_{14}H_{22} \longrightarrow 2\ i\text{-}C_4H_{10} + C_{22}H_{31} + 4\ HCl$$
$$\text{II} \qquad\qquad \text{I}$$

(13) Reference 9(b), p. 5029.

(14) Cf. D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *J. Am. Chem. Soc.*, **74**, 3276 (1952); see J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, **76**, 4506 (1954) for an atomic orbital representation of a "protonated cyclopropane."

(15) E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

the dropping-funnel. The temperature rose to 36°. Stirring was continued until the temperature dropped to 20°. The organic layer was separated, washed with two small portions of ice-water, and dried with 3 g. of potassium carbonate.

The product (88 g.) was distilled from a 125-ml. Claisen flask. The following fractions were obtained:

No.	B.p. range, °C.	Wt., g.
1	40–70	67
2	70–96	5
	Residue	15
	Continued at 25 mm.	
3	30–75	6
4	75–110	3
	Residue	2

Fraction 4 was left in a refrigerator overnight, but failed to crystallize. Consequently, fraction 3 was redistilled at 25 mm. and yielded 4.5 g. boiling at 30–70° and a small residue to which fraction 4 was added; and distillation was continued at 20 mm. There were obtained 2 g. boiling at 70–96° and a 1-g. residue. The last volatile fraction deposited white crystals on being cooled in an ice-bath. It was filtered with suction and the solid was spread on filter paper and dried in the air for several minutes. Yield: 283 mg., m.p. 50–63°. Recrystallization from petroleum ether yielded 214 mg., melting at 63–67°.

Identification by mixture melting point. 2,5-Dichloro-2,5-dimethylhexane was prepared by addition of HCl to a 50% alcoholic solution of 2,5-dimethyl-1,5-hexadiene.[5] The crude product was crystallized from petroleum ether, m.p. 63–66.5°. Mixed with the solid obtained in experiment (*ii*) above, the melting point was 63–66.5°. The two substances were identical in crystalline form, odor, and melting behavior.

NEW YORK 31, NEW YORK