[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Highly Branched Molecules. II. The Chlorides from Tri-*t*-butylcarbinol and its Lower Homologs[1a]

BY PAUL D. BARTLETT AND MARGUERITE S. SWAIN[1b]

RECEIVED SEPTEMBER 20, 1954

A series of highly branched alcohols, culminating in tri-*t*-butylcarbinol, have been converted into chlorides by the action of gaseous hydrogen chloride at 0°. The highly branched chlorides are in each case minor products accompanying major amounts of olefin. Kinetic analysis of the chlorides shows that they consist of mixtures of highly reactive components with reaction rate constants in 90% acetone as much as 50,000 times that of *t*-butyl chloride calculated for the same conditions by the Grunwald–Winstein equation. The products are olefinic. The rate constants of the components of the several chloride mixtures do not form smooth series and indicate that the alcohols do not yield chlorides of corresponding structures under these conditions. The results strengthen the evidence that steric factors can be of great importance in ionization processes.

Introduction.—One of the first points of interest about diisopropyl-*t*-butylcarbinol, isopropyldi-*t*-butylcarbinol and tri-*t*-butylcarbinol[1a] was the question of what their behavior would be in replacement of the hydroxyl by negative groups and how these replacement products would behave under conditions of solvolysis. Among conditions that might be conducive to the ready formation of carbonium ions, these highly branched molecules lack the possibilities of hydrogen hyperconjugation such as might be written for the *t*-butyl cation and they might be expected also to show some hindrance to solvation in an ionizing solvent. On the other hand, the mutual interference of the three bulky groups at tetrahedral angles might well produce a driving force for coplanarity and this would be favorable to the formation of a carbonium ion.[2] Brown and Fletcher found that the solvolysis rates of a series of tertiary chlorides took a sharp upturn as soon as one of the groups attached to the central carbon atom was as bulky as a *t*-butyl or neopentyl. In a preliminary report[3] it was noted that this trend continues and reaches spectacular proportions in the chlorides derived from the alcohols now under discussion. In the present paper the experimental work leading to this conclusion will be described and the results interpreted in the light of the more recent findings to be reported in parts III and IV of this series.[4]

The Highly Branched Chlorides.—The less highly branched tertiary chlorides can be prepared pure and in good yield from the corresponding alcohols. Several of these chlorides were prepared and their rates of solvolysis studied in enough solvents so that we could establish a standard basis of conversion of the rates from one solvent medium into another. This was necessary because the high reactivity of the highly branched chlorides necessitated working in 90% acetone solution where the simpler tertiary chlorides are solvolyzed at rates too low for convenient measurement. The more highly branched alcohols, including the triisopropylcarbinol, diisopropyl-*t*-butylcarbinol, methyldi-*t*-butylcarbinol, isopropyldi-*t*-butylcarbinol and tri-*t*-butylcarbinol, were difficult to convert into chlorides. All methods gave increased percentages of olefin with increasing branching of the initial alcohol, and the yield of chloride became very low with the more highly branched alcohols. The method adopted consisted of treatment with hydrogen chloride without a solvent at 0°. The yields of chloride were as low as 6%, the rest being olefin. The chlorides were mostly liquid mixtures, very sensitive to moisture and heat. The chlorides could not be hydrolyzed back to the original alcohol, nor could the accompanying olefins be rehydrated. The olefins did not form dibromides and the chlorides did not yield Grignard reagents.

Under these circumstances the most that could be accomplished was to characterize each mixture of chlorides kinetically by its rate of liberation of acid in aqueous acetone. To avoid decomposition each chloride mixture was isolated by evaporation and dissolved directly in the aqueous acetone, the liberation of acid being followed by the method of Peters and Walker.[5] Under these conditions the simpler tertiary chlorides showed clean first-order kinetics, while some of the more branched ones

TABLE I

REACTION RATES OF CHLORIDE IN 90% AQUEOUS ACETONE AT 25°, μ = 0.15

Alcohol from which prepared	Component	k_1 in sec.$^{-1}$ $\times 10^7$	k_1 relative to *t*-BuCl[f]	Component in mixed chlorides, %
t-BuOH		2.58[a]	(1.0)	
Me_2-*i*-PrCOH		4.55[b]	1.8	
Me_2-*t*-BuCOH		6.41[c]	2.5	
Me(*t*-Bu)$_2$COH	A	71,900[d]	27,900	21
	B	61[e]	24	79
(*i*-Pr)$_3$COH	A	650	252	6
	B	13	5	94
(*i*-Pr)$_2$*t*-BuCOH		3,300	1,280	94
i-Pr(*t*-Bu)$_2$COH	A	130,000	50,400	40
	B	11,700	450	26
	C	500	194	22
(*t*-Bu)$_3$COH	A	7,000	2,700	63
	B	350	136	25

[a] Calcd. from k_1 = 0.0054 in 25% acetone. [b] Calcd. from k_1 = 0.0095 in 25% acetone. [c] Calcd. from k_1 = 0.0134 in 25% acetone. [d] Calcd. from k_1 = 0.065 in 80% acetone. [e] Calcd. from k_1 = 0.000055 in 80% acetone. [f] The relative rate constants given here differ from those reported in ref. 3, chiefly through modifications in the procedure for correcting from one solvent to another.

---

(1) (a) Part I of this series, P. D. Bartlett and A. Schneider, THIS JOURNAL, **67**, 141 (1945). (b) Part of the doctoral thesis of Marguerite S. Swain at Radcliffe College, 1948.

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

(3) P. D. Bartlett, *Bull. soc. chim. France*, [5] **18**, C100 (1951).

(4) THIS JOURNAL, **77**, 2804, 2806 (1955).

(5) R. A. Peters and E. Walker, *Biochem. J.*, **17**, 260 (1923).

showed rates which could be resolved into the contributions of two and in one case three components, each reacting in a first-order manner. Table I shows the results of this resolution.

By means of the Grunwald–Winstein[6] equation, it is possible to estimate values of the solvolysis rate constants of the simpler tertiary chlorides in 90% acetone (by volume) at 25° and 0.15 ionic strength, adopted as the standard conditions for the fast reacting members of the series. We can thus express the rate constants of the various components of the chloride mixtures as multiples of the rate constant for *t*-butyl chloride as has been done in Table I.

In the course of this work we have determined Y values of 2.77 for 25% acetone and 1.30 for 50% acetone, by measuring the hydrolysis of *t*-butyl chloride in these media. The fast and slow components of the chloride mixture from triisopropylcarbinol have values of $m = 1.02$ and 1.04, respectively, compared to $m = 1.00$ by definition for *t*-butyl chloride.

The Problem of Interpreting the Rates.—The fact that mixtures of chlorides are obtained shows that molecular rearrangement is not only possible but favored in the replacement of the hydroxyl of these highly branched alcohol molecules. Nothing but olefins has been found among the solvolysis products and in no case has it been possible to convert one of these chlorides or olefins back into a recognizable alcohol. This means that it has not been possible to assign structures to the chlorides in our mixtures. There is of course no evidence that any of the chlorides from the three most highly branched alcohols has a structure corresponding to that of the alcohol from which it was prepared. Although the number of reasonable rearrangement products is limited, this number exceeds the number of components in one of the chloride mixtures and hence there are not enough data at hand to assign the rate constants of the components to structures. It will be noted also that no set of components in the chlorides from the increasingly branched alcohols forms the kind of smooth series of reaction rate that might be anticipated for the chlorides with unrearranged structures. It is not at all unlikely therefore that the unrearranged chloride is completely missing from the reaction product in some or all of the cases. It will be shown in Part IV that the product of solvolysis of the *p*-nitrobenzoate of tri-*t*-butylcarbinol consists principally of a twice rearranged olefin, although an olefin from a single rearrangement would appear to have been possible.

The conclusion that can be drawn from these results is that a high degree of branching in a tertiary alcohol or chloride results in a strong driving force toward ionization and this tells us that steric strain in the highly branched molecule is more important than a combination of hydrogen hyperconjugation possibilities and access of solvent to the center of charge in an ion. The present results do not indicate whether the release of steric strain in ionization is accomplished through the formation of a coplanar classical carbonium ion with bond angles of 120° which then immediately undergoes rearrangement[7] or whether the steric requirement of the bulky groups may be relieved instead through the formation of a bridged ion by participation of a neighboring methyl group in the ionization process.[3] Since methyl groups have not been observed to form bridged ions in systems previously investigated, such a phenomenon, if it exists here, would be a consequence of all atomic centers being at appreciably closer quarters than is ever the case in an unbranched acyclic compound.

Experimental[8]

Dimethyl-*t*-butylcarbinol was prepared according to the method of Henri.[9] Crystals of the hydrate were obtained, f.p. 15°.

Methyldi-*t*-butylcarbinol was prepared according to Whitmore and Laughlin[10]; m.p. 42–43°.

Triisopropylcarbinol was prepared by the procedure of Young and Roberts[11]; b.p. 90–92.5° (27 mm.), nD 1.4454, yield 59–69%.

Diisopropyl-*t*-butylcarbinol was prepared from trimethylacetyl chloride and isopropyl lithium in *n*-pentane under nitrogen. In working up the product, it was necessary to heat the material under reflux with the alkaline solution resulting from the addition of water to the completed reaction for an hour in order to complete the hydrolysis of the excess trimethylacetyl chloride and prevent it from having a dehydrating action upon the alcohol. The product, b.p. 47–59° (0.6–1.0 mm.), $n^{20.4}$D 1.4550, was obtained in 62.5% yield, based on the trimethylacetyl chloride.

Isopropyldi-*t*-butylcarbinol was prepared in similar fashion from isopropyl lithium and hexamethylacetone made by the method of Bartlett and Schneider.[1] The carbinol, b.p. 62–64° (0.75 mm.), n^{25}D 1.4632, was obtained in a yield of 70% based on ketone.

Tri-*t*-butylcarbinol was prepared by the method of Bartlett and Schneider[1] using sodium, *t*-butyl chloride and hexamethylacetone or methyl pivalate. The yields were very poor over a wide range of variation in conditions. In view of the greatly improved preparation of tri-*t*-butylcarbinol to be reported in Part III, it will no longer be necessary to use this unsatisfactory procedure. The best tri-*t*-butylcarbinol obtained melted at 112–113° but material melting as low as 94–95° gave an identical infrared spectrum. The hydroxyl stretching frequency for tri-*t*-butylcarbinol occurs at 2.75 μ, indicating a lack of hydrogen bonding as would be expected for this highly hindered hydroxyl group. The OH band of pivaloin at 2.82 mμ suggests the internal hydrogen bonding which would be expected of an acyloin. Tetra-*t*-butylethylene glycol possesses peaks at both places, since only internal hydrogen bonding is possible in this compound, and only one of the two hydrogens can be so bonded.

Residues of Hexamethylacetone Preparation from the Bureau of Standards.—Through the kindness of Dr. F. L. Howard of the National Bureau of Standards, we had the opportunity to work over the residues of a large-scale preparation of hexamethylacetone which they had made according to the method of Bartlett and Schneider.[12] It was hoped that some tri-*t*-butylcarbinol might be found in these residues. Instead, there were found pivaloin, tetra-*t*-butylethylene glycol and a compound crystallizing in small white needles of m.p. 135.5°. A Rast molecular weight determination yielded the value 290. This compound was prepared synthetically by the addition of benzylmagnesium

---

(6) E. Grunwald and S. Winstein, This Journal, **70**, 846 (1948).

(7) H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4510 (1954).

(8) The infrared spectra referred to in this paper have been deposited as Document number 4428 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

(9) L. Henri, *Rec. trav. chim.*, **26**, 106 (1907).

(10) F. C. Whitmore and K. C. Laughlin, This Journal, **55**, 3736 (1933).

(11) W. G. Young and J. D. Roberts, *ibid.*, **66**, 1444 (1944).

(12) F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 385 (1947).

chloride to the α-diketone pivalil. The synthetic product melted at 135–135.5° alone and when mixed with the isolated product.

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.80; H, 9.98. Found: C, 77.69; H, 10.03.

A Zerewitinoff determination indicated one active hydrogen and no carbonyl group. It is not surprising that this carbonyl group, which is even more hindered than the one in hexamethylacetone, fails to react with the methyl Grignard reagent. This product evidently owes its origin to toluene used in preparing the sodium sand which became involved in the reaction through metalation by intermediate organosodium compounds.[13]

Preparation of Chlorides. Dimethylisopropylcarbinyl chloride, b.p. 67–68° (170 mm.), was prepared by hydrogen-halogen exchange between *t*-butyl chloride and 2,3-dimethylbutane in the presence of aluminum chloride.[14]

Dimethyl-*t*-butylcarbinyl chloride, m.p. 130–132° (sealed tube), was prepared by treating the carbinol with excess acetyl chloride.[15]

Chlorides from Methyldi-*t*-butylcarbinol.—Fourteen grams (0.089 mole) of methyldi-*t*-butylcarbinol, m.p. 42–43°, was dissolved in 5 cc. of dry ether and cooled to 0° in an ice-bath; some solid precipitated. Dry hydrogen chloride gas was bubbled through the slurry for one hour by which time all the solid had disappeared. An orange layer of hydrogen chloride etherate was removed by pipet and 20 cc. of cold petroleum ether (reagent grade, 30–60°) was added. While the solution was kept cold, anhydrous potassium carbonate was added in small amounts until the excess hydrogen chloride was decomposed. The solution was kept over fresh anhydrous potassium carbonate for a half hour longer. The solvent was removed at 20 mm. pressure and also a few tenths of a cc. of liquid having $n^{25}\mathrm{D}$ 1.4388. The semi-solid remaining was recrystallized twice from *n*-pentane. Beautiful white camphor-like crystals, m.p. 68–70° dec., were used immediately for kinetic experiments.

A similar procedure served for the preparation of chlorides from the more highly branched alcohols. In the cases of alcohols which were liquid, the solvent ether could be omitted. In the case of di-isopropyl-*t*-butylcarbinol a white solid separated during the first ten minutes of passage of hydrogen chloride gas, and disappeared after a further ten minutes.

The solvolysis products were identified as olefins by their infrared spectra in carbon tetrachloride, which showed strong bands at 5.85 and 6.2 μ, and no O–H stretching frequency at 2.7–2.8 μ.

Kinetic Measurements.—The rate measurements were made by an adaptation of the titration method of Peters and Walker.[6,16] The total volume of solution taken for a run was 100 cc. In the runs containing 50% or more of acetone, the concentration of the titrating reagent was made high enough so that only one cc. of it was added during a run, to avoid significantly altering the composition of the medium. "Infinite" or total hydrolysis was taken as the volume of base required after ten times the longest half-life represented among the components of the chloride mixture being solvolyzed. The runs were made in a thermostat at 25.0°.

Determination of the Rate Constants in Mixtures.—For each kinetic run the logarithm of the organic chloride concentration was plotted against the time, yielding straight lines in the cases of the chlorides from *t*-butyl alcohol, dimethyl-*t*-butyl, dimethylisopropyl and diisopropyl-*t*-butylcarbinols. The method of resolution of the reaction rates of the others is illustrated by the case of the chlorides from isopropyldi-*t*-butylcarbinol, the only one with three distinguishable components. In each case the logarithmic plot approached linearity toward the end, permitting the assignment of a rate constant to the slowest component of the mixture and the calculation of its presumed concentration at earlier times during the run. The concentration of reacting chloride minus this component was then plotted similarly on a logarithmic graph, which was now found to end in a new substantially linear portion. When in turn the slope of this line was determined and the concentration of the slower component calculated, the so estimated concentrations of the remaining component could be plotted and were seen to follow the first-order rate law. Though subject to the suspicion which rightly falls on any three-constant fit, this assignment represents the experimental findings well. Because of the considerable separation of the successive rate constants, the assignment is not subject to very much variation (the rate constants of the three components stand in the ratio 260:23:1). Table II shows the observed hydrolysis rate for this chloride mixture, together with the results calculated using the rate constants shown in Table I.

TABLE II

RATE OF REACTION OF THE CHLORIDE MIXTURE FROM ISOPROPYLDI-*t*-BUTYLCARBINOL IN 90% ACETONE (BY VOLUME) AT 25°, AT IONIC STRENGTH 0.15

Run 62, concentration of chloride = 0.0163 *M*

	Calcd. % of total titer remaining as			Total % remaining		
Minutes	A	B	C	Calcd.	Obsd.	Dev.
0.053	38.1	26.3	22.0	86.3	86.8	−0.5
.32	31.0	25.7	22.0	78.7	80.3	−1.6
.59	25.0	25.2	22.0	72.2	73.7	−1.5
.87	20.1	24.8	21.9	66.8	67.1	−0.3
1.38	13.5	23.9	21.9	59.3	60.6	−1.3
1.94	8.7	23.0	21.9	53.6	53.9	−0.3
2.96	3.9	21.4	21.8	47.1	47.4	−0.3
4.75	1.0	18.9	21.7	41.6	40.8	+0.8
10.25	0.0	12.9	21.3	34.2	34.2	0
19.58		6.7	20.7	27.4	27.6	−0.2
46.66		1.0	19.1	20.1	21.1	−1.0
90		0	16.8	16.8	17.2	−0.4
171			13.2	13.2	13.2	0
320			8.4	8.4	8.5	−0.1
inf.			0	0	0.1	−0.1

The mean deviation between the calculated and observed titers throughout the run is 0.55%, or 0.7% of the total change in the titer during the run.

It is of interest that no components of the chloride mixture are observed having rate constants in the neighborhood of those of *t*-butyl or *t*-amyl chloride or of 2-chloro-2,3-dimethylbutane. Such components, if present, would be expected to disturb the fit of the kinetic equations to the late parts of the runs. If molecular fission occurred in the preparation of our chlorides,[17] any *t*-butyl and *t*-amyl chlorides evidently were removed in the course of the low-temperature evaporation used in the isolation of the product. Hence the rate constants observed must belong to rearrangement products rather than cleavage products of the branched alcohols.

CAMBRIDGE, MASS.

---

[13] E. H. Rodd and F. W. Linch, *J. Chem. Soc.*, 2179 (1927).

[14] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1537 (1944).

[15] L. Henri, *Rec. trav. chim.*, **26**, 93 (1907).

[16] For a description see P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1409 (1949).

[17] F. Brown, T. D. Davies, J. Dostrovsky, O. J. Evans and E. D. Hughes, *Nature*, **167**, 987 (1951).