[Contribution from the Chemical Laboratory of McGill University]

# The Mechanism of Elimination Reactions. I. The Decomposition of Quaternary Ammonium Bases and of Xanthate Esters[1]

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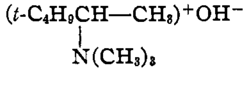
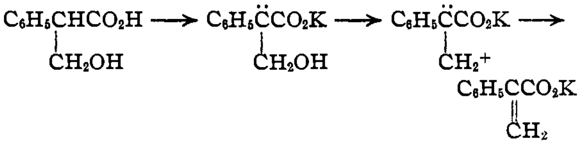
## I. Quaternary Ammonium Bases

In contrast to many other elimination reactions, a molecular rearrangement seldom if ever occurs in the decomposition of quaternary ammonium bases. Ingold and co-workers[4] have proposed that the decomposition starts with the loss of a proton, usually in the $\beta$ position. If scission of the nitrogen from carbon is envisioned as leaving an open sextet, the free pair of electrons then available in the $\beta$ position allows the reaction to be completed with no electron capture involving a rearrangement.[5,6]

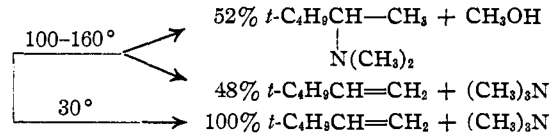


$$(t\text{-}C_4H_9\underset{\overset{|}{N(CH_3)_3}}{CH}—CH_3)^+OH^-$$



$$C_6H_5\underset{\overset{|}{CH_2OH}}{CH}CO_2H \longrightarrow C_6H_5\underset{\overset{|}{CH_2OH}}{\ddot{C}}CO_2K \longrightarrow C_6H_5\underset{\overset{|}{CH_2^+}}{\ddot{C}}CO_2K \longrightarrow C_6H_5\underset{\overset{\|}{CH_2}}{C}CO_2K$$

Although a great number of quaternary bases have been investigated,[7] little work has been done to test this theory adequately. We have, therefore, studied the decomposition of pinacolyltrimethylammonium hydroxide, since this system is peculiarly prone to rearrangement, though free from the special stereochemical influences often found with the bicyclic compounds usually employed in these studies, and because the possible, well-known products are readily separated. We find that the decomposition of the above base, both at 30° and at elevated temperatures, yields only one hydrocarbon, the expected $t$-butylethylene, b. p. 41°, which was shown to be pure by careful and efficient fractional distillation. At 30°, the olefin and trimethylamine were produced exclusively, and at 100–160°, methanol and the mixed tertiary amine appeared as the only other products.



Inasmuch as a free radical mechanism involving the pinacolyl radical[8] would require by disproportionation substantial amounts of neohexane, b. p. 49–50°, and trimethylcyclopropane, b. p. 56–57°, as well as a higher boiling coupling product, free radical formation can be excluded completely. The absence of any rearranged olefins likewise rules out any scission between nitrogen and carbon before elimination of the $\beta$ hydrogen. The mechanism must then involve the elimination of a proton first, as outlined by Ingold and co-workers, that is E2[9]; and this mechanism of elimination can be applied to all quaternary bases.

Instead of simple proton elimination, we consider that a hydrogen bond is first formed *intermolecularly* between the $\beta$ hydrogen[10] and the anion, and that the proton is then removed completely. While there is no proof of this hydrogen bonding, such a preliminary reaction phase is consistent with the behavior of these bases, both in the presence of potassium hydroxide, and of glycerol, and furthermore gives a reasonable explanation for the decomposition of the quaternary salts.[11]

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[4] Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927); Hughes, Ingold and Patel, *ibid.*, 526 (1933).

[5] Compare Hauser, This Journal, **62**, 933 (1940).

[6] A similar case of elimination by strong bases of a proton first [compare Hauser and Breslow, *ibid.*, **62**, 3344 (1940)] is the dehydration of tropic acid by concentrated potassium hydroxide (Baker and Eccles, *J. Chem. Soc.*, 2129 (1927)).

[7] For a comprehensive review of these substances, see J. H. Richmond, Dissertation, McGill University, Montreal, 1940.

[8] Compare Whitmore, Popkin, Bernstein and Wilkins, This Journal, **63**, 124 (1941); Whitmore and Carney, *ibid.*, **63**, 2633 (1941).

[9] Hughes, Ingold and Scott, *J. Chem. Soc.*, 1273 (1937).

[10] According to Hückel, Tapp and Legutke [*Ann.*, **543**, 191 (1940)], the *trans*-hydrogen will be the favored one for elimination, due to steric shielding of the *cis*-hydrogen by the $—N(CH_3)_3$ group.

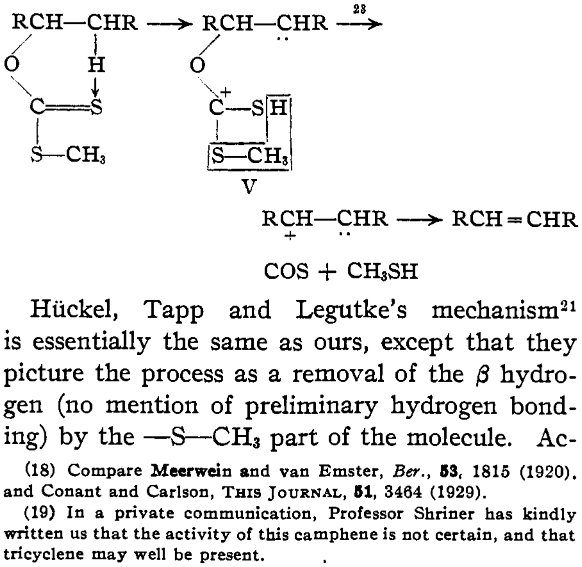
[11] The addition of potassium hydroxide may favor $\beta$ elimination because of the increase in hydroxyl ion concentration, hence in the opportunity for $\beta$ bonding and elimination, while addition of glycerol, with its reactive hydrogen atoms for bonding, blocks the anion from attacking the $\beta$ hydrogen, and so favors alcohol formation [von Braun and Buchman, *Ber.*, **64**, 2610 (1931)]. Water can react likewise, and this explains why most ammonium bases do not begin to decompose until all or most of the water has been removed, for not until then are the hydroxyl ions unblocked from their hydrated or bonded water molecules, and so become free to bond and attack hydrogen atoms attached to carbon. Ammonium salts may decompose differently from the bases because the halide ion has such a small

Very likely this intermolecular hydrogen bonding can occur in the $\alpha$,[12] $\gamma$,[13] or even $\delta$[14] position, but, according to Ingold and co-workers, in most cases the $\beta$ hydrogen is the most loosely held, and this, coupled with the greater ease of olefin formation by a loss of $\beta$ hydrogen, accounts for the usual elimination. But if $\beta$ bonding is impossible, or if some other hydrogen is more loosely held, then elimination may follow the lines resulting from other bondings, as in the formation of ethylene oxides from those quaternary bases derived from ephedrine.[15] Both $\beta$ and $\gamma$ elimination occur here, the $\beta$ leading to propiophenone via the enol[16]; but the $\gamma$ type predominates because the $\gamma$ hydrogen (attached to oxygen) is obviously more easily removed as a proton.

Those few bases which yield rearrangement products are not exceptions to this mechanism. Either the normal product suffers subsequent rearrangement, or the dipoles formed after proton elimination and nitrogen–carbon scission, cannot form olefins or ring structures, and so undergo the rearrangements expected from the presence of an open sextet or its equivalent. For example the formation of *d*-camphene[17] from bornyltrimethylammonium hydroxide can be due to a Wagner rearrangement of the 1,3 dipole formed by $\gamma$ ($\omega$ position) elimination; *dl*-camphene would result from the formation and subsequent rearrangement of tricyclene[18] due to $\gamma$ (6 position) elimination and ring closure; and *l*-camphene would result from $\delta$ ($\pi$ position) elimination with Wagner and pinacolyl rearrangements. In the case of the bornyl base, we should expect the reaction to go mainly via tricyclene.[19] The determining factors in every case will be the proton elimination tendency, the steric relations and the energy changes. The important point is that if a rearrangement occurs, it does so *after* a proton has been expelled, and not before.

## II. Xanthate Esters

**a. Aliphatic.**—Another elimination reaction not generally involving rearrangement is the Chugaev xanthate decomposition.[20] Few attempts[7,21,22] have been made to elucidate the reaction, but it can now be simply explained by extending the mechanism proposed for the quaternary ammonium bases to include a possible *intramolecular* hydrogen bonding prior to the proton elimination. Study of atomic models shows that six-membered, also seven- and eight-membered, rings with a hydrogen bond can be easily formed, and decomposition could then proceed as follows:



Hückel, Tapp and Legutke's mechanism[21] is essentially the same as ours, except that they picture the process as a removal of the $\beta$ hydrogen (no mention of preliminary hydrogen bonding) by the —S—$CH_3$ part of the molecule. Ac-

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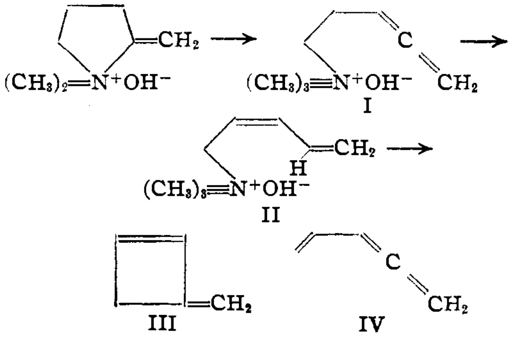
tendency to form hydrogen bonds (compared to the hydroxyl ion), that before $\beta$ bonding can become effective to promote $\beta$ elimination, an alkyl halide is formed instead.

[12] Ingold and Jessup, *J. Chem. Soc.*, 2357 (1929).

[13] Ingold and Rogers, *ibid.*, 722 (1935); Tiffeneau, *Compt. rend.*, **158**, 1580 (1914).

[14] The formation of pirylene, assuming it to be methylenecyclobutene III, from what von Braun and Teuffert [*Ber.*, **61**, 1092 (1928)] claim to be an allene quaternary base I, is puzzling to say the least, for not only is there no hydrogen in the $\delta$ position, but the $\beta$ hydrogen is already activated by the adjacent double linkage. The above authors suggested that the expected ethylenic allene IV rearranged to pirylene. This does not seem likely to us. A more plausible scheme, rearrangement of I to a conjugated diene II, would make $\delta$ hydrogen available for bonding, and elimination would then give III.



[15] Rabe and Hallensleben, *Ber.*, **43**, 2622 (1910).

[16] Schmidt, *Arch. der Pharm.*, **249**, 309 (1911).

[17] Shriner and Sutherland, THIS JOURNAL, **60**, 1314 (1938).

[18] Compare Meerwein and van Emster, *Ber.*, **53**, 1815 (1920), and Conant and Carlson, THIS JOURNAL, **51**, 3464 (1929).

[19] In a private communication, Professor Shriner has kindly written us that the activity of this camphene is not certain, and that tricyclene may well be present.

[20] Chugaev, *Ber.*, **32**, 332 (1899).

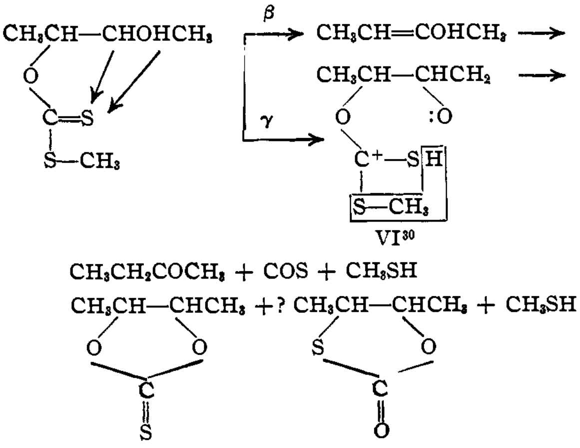
[21] Hückel, Tapp and Legutke (*loc. cit.*), whose paper was not available to us until after this work was completed, have advanced a mechanism similar to ours here.

[22] Laakso [*C. A.*, **34**, 5059 (1940)] reports that during decomposition, xanthates may rearrange to isoxanthates (dithiolcarbonates) R—S—CO—S—$CH_3$, but that these, while more stable, give the same products as the xanthates. In our discussion we shall assume that this is so, and shall consider the xanthates only.

[23] Closure of V to a four-membered ring is highly unlikely.

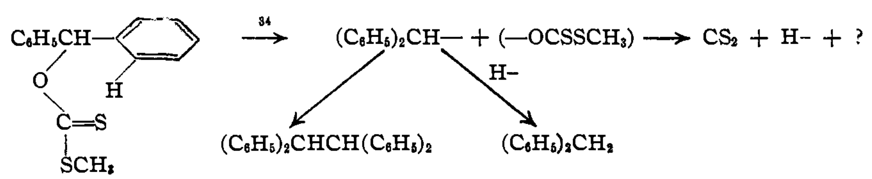
cording to our scheme, this would correspond to hydrogen bonding to the thio-ether sulfur atom, but we prefer bonding with the doubly-bound sulfur because of the great activity of the thiocarbonyl group, and also because the isoxanthates (dithiolcarbonates) are more stable than the xanthates.[22] If it were the thio-ether sulfur which bonded, the isoxanthates should be less stable than the xanthates, since from bond distances and energies,[24] the R—S link (the other factor influencing stability) should be weaker than the corresponding R—O link of the xanthates. The pyrolysis of other esters such as acetates,[25] benzoates,[26] phthalates,[27] and oxalates[28] may well proceed in like fashion, since little or no rearranged olefins are formed.

The close analogy between the decomposition of xanthates and quaternary bases is shown by the decomposition of 2,3-butylene glycol monoxanthate.[29] As predicted from the behavior of hydroxy bases, the products were mainly the thiocarbonate VII (possibly mixed with the thiolcarbonate VIII), and a little methyl ethyl ketone ($\beta$ bonding and elimination via the enol).



VII VIII

**b. Aromatic.**—A study of the decomposition of benzhydryl xanthate was undertaken to see whether $\alpha$ elimination could occur, when no $\beta$ hydrogen was available, and the $\gamma$ hydrogens were inactive. Since intramolecular hydrogen bonding would require the formation of a five-membered ring (not usually considered as sterically possible), $\alpha$ bonding and elimination must proceed intermolecularly, and indeed the products then expected, tetraphenylethylene, carbonoxysulfide and methyl mercaptan have already been reported by Kursanov[31] from the decomposition of this xanthate. Unlike Kursanov, however, we failed to get tetraphenylethylene, but obtained instead tetraphenylethane and diphenylmethane in 30 and 58% yields, respectively, together with carbon disulfide, and very little carbonoxysulfide or methyl mercaptan. These results force us to conclude that intermolecular $\alpha$ elimination, even though possible, does not occur,[32] and the appearance of the two saturated hydrocarbons shows that decomposition may take an entirely different course,[33] very likely via the free radicals diphenylmethyl. To be sure, the appearance of diphenylmethane without its disproportionation partner, tetraphenylethylene, is odd if we accept the free radical mechanism, but it may be that the other products of the reaction (as suggested by the appearance of carbon disulfide) furnish the necessary hydrogen to form diphenylmethane. No thio-lactone corresponding to $\gamma$ elimination was found.



## Conclusions

The pyrolysis of most xanthates can be explained by intramolecular bonding, loss of a proton[35] to the doubly-bound sulfur, and then a carbon–oxygen scission, resulting in elimination without rearrangement, or in ring formation.

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[24] Bond distances: C—O, 1.41 Å.; C—S, 1.82 Å. [Brockway and Jenkins, THIS JOURNAL, **58**, 2036 (1936)]. Bond energies: C—O, 3.55 v. e.; C—S, 3.20 v. e. [predicted by Pauling, *ibid.*, **54**, 3570 (1932)].

[25] Cramer and Mulligan, *ibid.*, **58**, 373 (1936).

[26] Windaus, Lettré and Schenck, *Ann.*, **520**, 98 (1935).

[27] Komppa and Nyman, *ibid.*, **535**, 252 (1938).

[28] Nybergh, Dissertation, Helsingfors, 101 (1921).

[29] Compare Fomin, *J. Gen. Chem.* (U. S. S. R.), **5**, 1192 (1935).

[30] In contrast to V, dipole VI is not hindered from ring formation; and ring formation here is good evidence that the xanthate decomposition runs stepwise as indicated above, with the breaking of the R—O link not necessarily being simultaneous with the removal of the proton.

[31] Kursanov, *J. Russ. Phys.-Chem. Soc.*, **60**, 921 (1928).

[32] By analogy, decomposition of simple xanthates does not occur intermolecularly.

[33] Compare Bergmann and Bergmann, THIS JOURNAL, **59**, 1443 (1937), for a similar case.

[34] Rearrangement to an isoxanthate during pyrolysis should not interfere with a free radical interpretation.

[35] If several $\beta$ hydrogen atoms are available, according to Hückel, Tapp and Legutke (*loc. cit.*), it is the *cis*-hydrogen which is mainly eliminated.

The decomposition of xanthates is more complex than that of the quaternary bases (as shown by side reactions, the formation of isoxanthates, etc.) but we believe that fundamentally the two classes of compounds undergo elimination by the same type of mechanism. Xanthates with aryl groups, however, may decompose via free radicals.

The formation of rearrangement products from bicyclic xanthates can be explained in the same way as those from the analogous quaternary bases. We consider that the same factors control the situation, *i. e.*, the relative proton elimination tendency, steric factors, and energy changes, and that the abnormal products are due to subsequent rearrangement of the primary products, or to rearrangement of the dipoles formed, in case no olefin or ring structure can be formed directly.[36]

At present there are no simple cases of $\gamma$ elimination, other than those of the glycols, or the bicyclic terpenols, where steric factors influence the course of reaction, and the products are difficult to separate. To avoid these complications, and to gain a clearer picture of this type of $\gamma$ elimination, a study of the decomposition of phenyl-*t*-butylcarbinyl xanthate is now being made.

## Experimental Part

**Pinacolylamine.**—This amine is best prepared by the reduction of pinacolone with ammonium formate.[37] 42 g. of ammonium formate was placed in a 500-ml. three-necked flask, fitted with a thermometer extending to the bottom, a dropping funnel, and a Soxhlet extractor with a reflux condenser. The Soxhlet was modified by having the siphon removed, and replaced with a short piece of rubber tubing with a pinchcock; 21 g. of pinacolone was added slowly to the ammonium formate preheated to 125°. By means of the rubber tube and pinchcock, the distillate was separated, the water removed, and the pinacolone returned from time to time. The heating was continued until no more ketone distilled, and the temperature reached 175°. The flask was now cooled, 25 ml. of concentrated hydrochloric acid added, the mixture refluxed for not less than five hours and then extracted with benzene to remove any unchanged organic material. The water layer was separated, and evaporated until the salt began to precipitate. An excess of 30% aqueous caustic was added, the free amine separated, dried over solid caustic and distilled, b. p. 103–104° (755 mm.), yield 66%. In addition to this amine, there appeared small amounts (5–10%) of a more volatile amine, b. p. 86° (760 mm.), $n^{25}\text{D}$ 1.4142, picrate m. p. 180°, phenylurea m. p. 175°. Attempts to determine its structure were unsuccessful, but it was not a secondary amine, as it gave no nitroso derivative with nitrous acid, nor was it *s*-isoamylamine,[38] whose phenylurea melted at 130°.

**Methylation.**—Methylation with methyl iodide in the presence of sodium hydroxide led to the tertiary amine hydriodide, m. p. 260–261°, which with bases liberated the free amine, b. p. 129–130° (759 mm.), $n^{25}\text{D}$ 1.4160, $d^{25}_4$ 0.7627, picrate, m. p. 214° (*Anal.* Calcd. for $C_{14}H_{22}O_7N_4$: N, 15.6. Found: N, 15.7). Further treatment of this base with methyl iodide in benzene solution yielded the quaternary iodide, m. p. 260° from alcohol. *Anal.* Calcd. for $C_9H_{22}NI$: I, 46.8. Found: I, 46.7.

**Pinacolyltrimethylammonium Hydroxide.**—The free base was prepared by treating the quaternary iodide, 84 g., with excess silver oxide in water solution, which, after filtration, was distilled in a current of purified nitrogen at the ordinary pressure. After considerable water had been removed, the base began to decompose, and the temperature of the reaction mixture rose gradually to 160°. The tertiary amines were collected in 6 *N* hydrochloric acid cooled to −10°; and the olefin in a trap at −78°. The acid solution on distillation yielded appreciable amounts of methyl alcohol, identified as the 3,5-dinitrobenzoate, m. p. 107°. No hexyl alcohol was observed. The remaining salts were treated with strong caustic, and the free bases fractionally distilled. The trimethylamine, 7 g., was thus removed and identified as the picrate, m. p. 216°. The less volatile amine, 17 g., was dried over sodium hydroxide, and identified as dimethylpinacolylamine through the picrate, mixed m. p. 214°. The hydrocarbon, 8 g., was dried over anhydrous potassium carbonate.

The above decomposition was repeated *in vacuo* at 25–30°. Water was first removed at 15–20 mm. until a white solid began to precipitate. Then the pressure was reduced to 0.01–0.005 mm., collecting the products in traps at −78° and at liquid air temperature. The decomposition proceeded slowly, but after three and one-half weeks 86.5% of the base had decomposed. Weighing of the condensate showed that only 2.5 g. of material had been lost, out of an expected 46 g. The condensate was treated with water, and the hydrocarbon layer was separated, washed thrice with 3% hydrochloric acid, twice with 2% aqueous potassium carbonate, and dried over powdered sodium hydroxide. Thirteen grams of olefin was thus obtained, and this was fractionated through an efficient three-foot reflux column packed with glass helices. In Table I are the data on this fractionation, together with those on the first distillation from the decomposition at 100–160°.

The amine fraction from the decomposition at 25–30°, redistilled in a current of dry nitrogen, volatilized com-

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(36) A case illustrating this point is that of camphenilyl xanthate. Pyrolysis yields mainly apocyclene with a little apobornylene [Komppa and Roschier, *Ann.*, **429**, 175 (1922)]. The former is readily explained by $\gamma$ (six position) elimination and ring closure. The latter could arise by thermal rearrangement of apocyclene, or could be formed via $\beta$ bonding and elimination from the 1,2 dipole (which cannot form an olefin due to Bredt's rule), followed by a Wagner rearrangement. But it is highly improbable that apobornylene is formed by a Wagner rearrangement *before* proton elimination. Such an elimination reaction would produce first an open sextet, or its equivalent, and then the product would be santene, the principal acid dehydration product [Komppa and Hintikka, *Bull. soc. chim.*, [4] **21**, 14 (1917)]. The decomposition of fenchyl, bornyl, and isobornyl xanthates [Shavrygin, *C. A.*, **35**, 2491 (1941)] can be treated in much the same way.

(37) Ingersoll, *Org. Syn.*, **17**, 76 (1937).

(38) Authentic *s*-isoamylamine was prepared by the above method from isopropyl methyl ketone and ammonium formate, b. p. 86° (760 mm.), $n^{25}\text{D}$ 1.4021.

TABLE I

| Decomposition temp., °C. | Fraction | B. p., cor., °C. | Mm. | $n^{20}D$ | Remarks |
|---|---|---|---|---|---|
| 100–160 | | | | 1.3772 | Before distn. |
| | 1 | 40.3 | 760 | 1.3769 | Packed column |
| | 2 | 40.6 | 760 | 1.3769 | Packed column |
| | 3 | 40.6 | 760 | 1.3767 | Packed column |
| | Residue | | | 1.3790 | |
| 25–30 | 1 | 41.1[39] | 761 | 1.3762 | Packed column |
| | 2 | 41.1 | 761 | 1.3762 | Packed column |
| | 3 | 41.1 | 761 | 1.3763 | Packed column |
| | 4 | 41.1 | 761 | 1.3762 | Packed column |
| | 5 | 41.1 | 761 | 1.3763 | Packed column |
| | 6 (2 ml.) | 41.3–41.6 | 761 | 1.3762 | Ordinary distg. flask |
| | Residue (0.1 ml.) | | | 1.3822 | |

pletely at room temperature, dissolved completely in water and therefore contained little or no pinacolyldimethylamine.

**Monoxanthate of 2,3-Butylene Glycol.**—A mixture of 50 g. of the glycol, b. p. 86° (10 mm.) dissolved in 150 ml. of toluene, and 12.8 g. of sodium was refluxed until the sodium disappeared. After cooling, 40 ml. of carbon disulfide was added and the mixture refluxed again for several hours. Forty ml. of methyl iodide was added, the mixture allowed to stand overnight, the clear solution decanted from the sticky inorganic precipitate, and the toluene removed by distillation. The residual liquid was taken up in ether, washed with water, dried over anhydrous potassium carbonate, and the ether distilled. The residue, the monoxanthate, weighed 73 g. This was now heated to boiling (bath 200°) for about sixty hours, and the volatile products were collected in a trap at −78°. The condensate was redistilled, but there was no evidence of any carbonoxysulfide, only methyl mercaptan. A small amount of higher boiling material was identified as methyl ethyl ketone through the 2,4-dinitrophenylhydrazone, m. p. 110°.

The red-orange thiocarbonate, 25 ml., from the pyrolysis was twice distilled *in vacuo*, taking the fraction b. p. 87° (8 mm.), $n^{25}D$ 1.6082, $d^{25}_4$ 1.216. In spite of repeated analyses, the sulfur content was somewhat low: calcd. for $C_5H_8O_2S$: S, 24.2. Found: S, 22.5. The calculated molecular refractivity, using 10.64[40] for the atomic factor for thio-keto sulfur, and +0.04 for the ring factor, was 34.85, found 37.57, Me: +2.72.

Hydrolysis of the thiocarbonate with hot aqueous alcoholic caustic gave salts which with acids liberated hydrogen sulfide. The salts were filtered off, and the aqueous-alcoholic filtrate was distilled, yielding as a residue a small amount of a high boiling liquid, b. p. 180° (Siwolobov's micro method).[41] The expected glycol likewise boiled at 180°. The aqueous-alcoholic distillate was treated with bromine, and then with ferric chloride. Addition of hydroxylamine and nickel chloride in the usual way gave a red precipitate of nickel dimethylglyoxime,[42] thus proving the presence of the glycol.

**Benzhydryl Xanthate.**—Forty grams of benzhydrol, dissolved in 75 ml. of toluene, was treated with 5 g. of sodium. After boiling for eight hours, then cooling, 20 ml. of carbon disulfide was added, the mixture refluxed for several hours, 25 ml. of methyl iodide added and the product allowed to stand overnight. The inorganic salts were filtered off, the filtrate was washed with water, dried over anhydrous sodium sulfate and the toluene removed *in vacuo*. The xanthate weighed 48 g., and was pyrolyzed in the usual way, the bath temperature being about 330°. The distillate, collected in a trap at −78°, consisted mainly of carbon disulfide, with a little methyl mercaptan and carbonoxysulfide. The residue was distilled *in vacuo*, yielding 19.5 g. of a yellowish oil, b. p. 135–140° (15 mm.). More of this oil was obtained by steam distillation of the residue. It was identified as diphenylmethane by recrystallization from aqueous alcohol, m. p. 24–25°, yield 58.8%.

The residue was boiled with alkali, filtered, and the filtrate acidified. There was only a small amount of a tarry acid, soluble in sodium carbonate. The insoluble portion, 11 g., was recrystallized from benzene, m. p. 208-209°, and showed no depression when mixed with an authentic sample of tetraphenylethane, m. p. 209°.[43]

## Summary

1. The decomposition of pinacolyltrimethylammonium hydroxide at 100–160° yields 52% mixed amine and methyl alcohol, and 48% *t*-butylethylene and trimethylamine. At 30°, the products are 100% *t*-butylethylene and trimethyl amine.

2. 2,3-Butylene glycol monoxanthate yields on decomposition a cyclic thiocarbonate, methyl ethyl ketone and methyl mercaptan.

3. Benzhydryl xanthate yields diphenylmethane, tetraphenylethane and carbon disulfide.

4. The various mechanisms of these elimination reactions have been discussed.

MONTREAL, CANADA RECEIVED JULY 16, 1941

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[39] Dolliver, Gresham, Kistiakowsky and Vaughan, THIS JOURNAL, **59**, 831 (1937), reported b. p. 41.18° (760 mm.), $n^{20}D$ 1.3765.

[40] Price and Twiss, *J. Chem. Soc.*, 1259 (1912).

[41] Siwolobov, *Ber.*, **19**, 795 (1886).

[42] Moureu and Dode, *C. A.*, **28**, 6239 (1934).

[43] Prepared by the method of Norris, Thomas and Brown, *Ber.*, **43**, 2940 (1910).