Summary

1. Aliphatic sulfides react with sodium in liquid ammonia chiefly according to the equation

$$R_2S + 2Na + NH_3 = RSNa + NaNH_2 + RH$$

2. Under the same conditions, aliphatic disulfides are reduced quantitatively to the corresponding mercaptides

$$R_2S_2 + 2Na = 2RSNa$$

3. Aliphatic mercaptans react as follows

$$RSH + NH_3 = RSNH_4$$
$$RSNH_4 + Na = RSNa + NH_3 + {}^1/_2H_2$$

4. No sodium sulfide is produced in any of these reactions; the reaction stops with the formation of mercaptide.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF "TRI-ISOBUTYLENE" BY OZONE

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The preparation of the so-called tri-isobutylene was first described in detail by Butlerow,[1] who dissolved isobutylene in a cold mixture of five parts of sulfuric acid to one part of water. The resulting oil boiled at 177.5–179° (749 mm.) and had a specific gravity of 0.774 at 0°. Dichromate oxidation yielded carbon dioxide, trimethylacetic acid, acetic acid, an acid $C_{11}H_{22}O_2$, acetone, and a neutral oil. The acid $C_{11}H_{22}O_2$ distilled at 266° and melted at 66–70°. The neutral oil had a boiling range of 100–220°, reacted with phosphorus trichloride and sodium, but did not reduce Tollens' reagent. In order to explain the formation of the solid acid Butlerow assumed the structure of the hydrocarbon to be $[(CH_3)_3C]_2{=}C(CH_3)_2$. He stated that the oxidation might first involve a pinacolone rearrangement with the formation of $[(CH_3)_3C]_2C(CH_3)COCH_3$. Further oxidation of this compound would result in the production of $[(CH_3)_3C]_2C(CH_3)COOH$, which would account for a solid acid having the formula $C_{11}H_{22}O_2$.

In a recent communication[2] the author described the preparation of di-isobutylene, the method of treating it with ozone, and the products resulting from the hydrolysis of the ozonide. In the work with tri-isobutylene a very similar procedure was followed.

Preparation of Tri-isobutylene.—Seven hundred fifty ml. of sulfuric acid and 250 ml. of water were mixed and cooled to about 5°. Then one liter of tertiary butyl

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[1] Butlerow, *Ber.*, 12, 1482 (1879).

[2] McCubbin and Adkins, THIS JOURNAL, 52, 2547 (1930).

alcohol was slowly added with constant shaking, care being taken to keep the temperature between 20 and 25°. The mixture was allowed to stand for about twelve hours and the oil layer removed. It was washed with dilute sodium hydroxide solution, dried over calcium chloride and fractionated twice over sodium, using a Widmer column. The yield of olefin, b. p. 175.5–179° (740 mm.), was 60–65%.

Formation and Hydrolysis of Ozonide.—Eighty-four grams (0.5 mole) of tri-isobutylene was placed in each reaction flask, using 100 ml. of glacial acetic acid containing 1.5–2.0% acetic anhydride as a solvent. The ozonization was carried out at 10°, the oxygen rate being 0.9–1.0 cu. ft. per hour. Under these conditions fifteen to eighteen hours sufficed for complete oxidation of 0.5 mole. The ozonide obtained from 1.5 or 2.0 moles of olefin was placed (with the acetic acid used as a solvent) in a 2-liter, three-necked flask equipped with a stirrer, a thermometer and an efficient reflux condenser. Stirring was commenced and about 5 ml. of water and 5 g. of zinc dust were added. Considerable heat was evolved and the flask had to be cooled. About 80 ml. of water and 60–70 g. of zinc were added over a two-hour period. The contents of the flask were allowed to warm up gradually to 50–60°, and when most of the zinc had reacted the flask was warmed until gentle refluxing took place. This was continued for at least an hour. Then enough water was added to dissolve most of the zinc acetate sludge and the oil layer was removed and dried over anhydrous magnesium sulfate.

After drying, the oil was fractionated up to 130°. The remainder was washed free of acids with a solution of sodium bicarbonate. The water solution containing the sodium salts was saved and evaporated to dryness. The oil remaining was again dried and fractionated. The sodium salts just mentioned were distilled with phosphoric acid. Trimethylacetic acid was the only organic acid isolated, and it had resulted from the secondary oxidation of trimethylacetaldehyde, which was one of the principal scission products obtained from tri-isobutylene ozonide.

Hydrolysis Products.—In Table I are listed the principal fractions obtained from the hydrolysis of tri-isobutylene ozonide.

TABLE I

HYDROLYSIS PRODUCTS OF TRI-ISOBUTYLENE OZONIDE

Fraction	B. p., °C.	Formula	Yield, moles	Average yield
A	60–80	$(CH_3)_3CCHO$ (74°)	0.30–0.44	0.38
B	120–130	$(CH_3)_3CCH_2COCH_3$ (124°)	.20– .50	.40
C	180–190	$[(CH_3)_3CCH_2]_2C{=}O$ (182–185°)	.16– .23	.18
D	158–162 (23 mm.)	$[(CH_3)_3C]_2C(CH_3)COCH_3$	.1– .3	.16

Fraction A, trimethylacetaldehyde, was identified by means of the semicarbazone, m. p. 191°. Fraction B was characterized as dimethyl-4,4-pentanone-2. Its semicarbazone melted at 176°.[2] Fraction C could not be obtained in a sufficient degree of purity to give consistent and conclusive analyses, but upon oxidation with dichromate two acids boiling at 164–165 and 177–182° were obtained. These acids were proved to be trimethylacetic and tertiary butylacetic by means of the amides, m. p. 153.5 and 131°, respectively. These facts indicate that this portion should have the structure assigned to it, although no ketonic derivatives could be obtained.

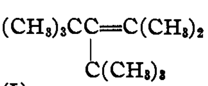
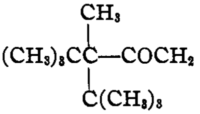
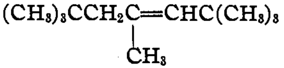
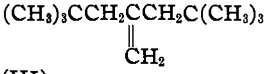
Fraction D also yielded no ketonic derivatives, but by further oxidation (dichromate) a solid acid (neut. eq. 186, b. p. 258–262°, m. p. 69–71°) was obtained. This corresponds to the acid obtained by Butlerow,[1] which he designated as methyldi-*tert.*-butylacetic acid.

In this table the amount of trimethylacetic acid obtained was calculated as trimethylacetaldehyde and it may be seen that the amounts of Fractions A and B are almost identical, indicating that these hydrolysis products are obtained from the same parent hydrocarbon.

In Table II are shown the hydrocarbons which would give rise to the above hydrolysis products of their ozonides.

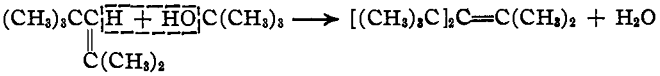
TABLE II

STRUCTURE OF ISOMERIC TRI-ISOBUTYLENES

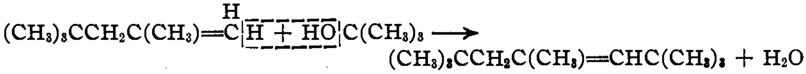
Hydrocarbon	Hydrolysis products
 $(CH_3)_3C\underset{\displaystyle C(CH_3)_3}{\underset{\vert}{C}}{=}C(CH_3)_2$ (I)	 $(CH_3)_3C\overset{\displaystyle CH_3}{\underset{\displaystyle C(CH_3)_3}{\overset{\vert}{\underset{\vert}{C}}}}{-}COCH_2$
 $(CH_3)_3CCH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}{=}CHC(CH_3)_3$ (II)	$(CH_3)_3CCH_2COCH_3$ and $(CH_3)_3CCHO$
 $(CH_3)_3CCH_2\underset{\displaystyle CH_2}{\underset{\Vert}{C}}CH_2C(CH_3)_3$ (III)	$[(CH_3)_3CCH_2]_2CO$ and $HCHO \longrightarrow CO_2 + H_2O$

In order to obtain the ketone indicated from hydrocarbon number I it is necessary to assume that the pinacolone rearrangement suggested by Butlerow[1] has taken place during ozonolysis. Otherwise, acetone and hexamethylacetone, $[(CH_3)_3C]_2CO$, would be formed and no such products were obtained from this reaction.

In view of these facts, it is possible to assume that the formation of tri-isobutylene is actually a condensation involving the hydroxyl group of tertiary butyl alcohol and an hydrogen atom of di-isobutylene. Since the latter hydrocarbon exists in two isomeric forms, this mode of formation accounts for two forms of tri-isobutylene as follows

(I) 

$$(CH_3)_3C\underset{\displaystyle C(CH_3)_2}{\underset{\Vert}{C}}\boxed{H + HO}C(CH_3)_3 \longrightarrow [(CH_3)_3C]_2C{=}C(CH_3)_2 + H_2O$$

(II) 

$$(CH_3)_3CCH_2C(CH_3){=}\overset{H}{C}\boxed{H + HO}C(CH_3)_3 \longrightarrow (CH_3)_3CCH_2C(CH_3){=}CHC(CH_3)_3 + H_2O$$

Then a shifting of the double bond in the second hydrocarbon would produce a third isomer, *e. g.*

(III) $(CH_3)_3CCH_2C(CH_3){=}CHC(CH_3)_3 \longrightarrow [(CH_3)_3CCH_2]_2C{=}CH_2$

This theory is in accordance with the work of Lermontoff,[3] who synthesized di- and tri-isobutylene by saturating tertiary butyl iodide with isobutylene and heating this solution in a sealed tube with calcium oxide.

However, the above mechanism does not seem adequate to explain the formation of polymers when isobutylene is dissolved in cold concentrated sulfuric acid. The following formulas indicate a mode of formation which

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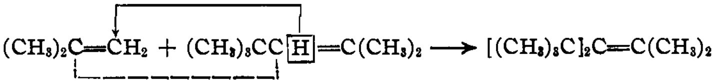
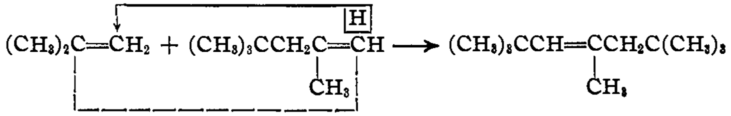
[3] Lermontoff, *Ann.*, **196**, 116–122 (1879).

would produce the above olefins without requiring the presence of an alcohol or other derivative.

(IA) 

$(CH_3)_2C{=}CH_2 + (CH_3)_3CC\boxed{H}{=}C(CH_3)_2 \longrightarrow [(CH_3)_3C]_2C{=}C(CH_3)_2$

(IIA) 

$(CH_3)_2C{=}CH_2 + (CH_3)_3CCH_2\underset{CH_3}{C}{=}\overset{\boxed{H}}{C}H \longrightarrow (CH_3)_3CCH{=}\underset{CH_3}{C}CH_2C(CH_3)_3$

(IIIA) Same as III

Conclusions

From the data thus obtained, it appears that the hydrocarbon, known as tri-isobutylene, prepared by the action of sulfuric acid on tertiary butyl alcohol exists in at least three isomeric forms. These olefins are present in an approximate ratio of two moles of pentamethyl-2,2,4,6,6-heptene-3,4 (formula II) and one mole each of trimethyl-2,4,4-*tert.*-butyl-3-pentene-2,3 (formula I) and dimethyl-4,4-neopentyl-2-pentene-1,2 (formula III). It also seems apparent that during hydrolysis of the ozonide the hydrocarbon of formula I undergoes a pinacolone rearrangement instead of breaking down into two simple ketones.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. IV. THE DEGRADATION OF CHLOROPHYLL AND ALLOMERIZED CHLOROPHYLL TO SIMPLE CHLORINS

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The thermal decomposition of chlorin *e* was described in the first paper of this series; the chief product of the reaction is pyrochlorin *e*, a monobasic acid whose spectrum resembles that of the parent compound. We have now studied this relatively simple chlorin in more detail and found that it is very closely related to phylloporphyrin. The ester of pyrochlorin *e* appears to be isomeric with the ester of phylloporphyrin, although the pyrochlorin *e* itself contains an additional molecule of water (a similar relationship between the hydrated free acid and the ester is found with chlorin *e*). By catalytic hydrogenation or reduction with hydrogen iodide by Fischer's method[1] and reoxidation, phylloporphyrin is formed in good yields. In the light of Fischer's recent syntheses,[2] phylloporphyrin appears to have one more carbon atom than was formerly supposed. This explains

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[1] Fischer and Bäumler, *Ann.*, **474**, 65 (1929).

[2] Fischer and Helberger, *ibid.*, **480**, 235 (1930).