ence between the stabilities of the phenyl, *o*-tolyl and *p*-tolyl cyclopropyl ketimines to rearrangement.

According to some work of Cervini,[11] the N-bromomagnesium derivative of a cyclopropyl ketimine (VI) will also undergo rearrangement on heating to give the pyrroline derivative (XI). The presence of these cyclopropyl derivatives (VI or VII) constitutes an additional reason for the pyrolysis process[2,4] in the preparation of pyrrolines by the action of Grignard reagents on γ-chlorobutyronitrile or its derivatives, unless this brings about undesirable secondary reactions.

Rearrangement of Ketimmonium Chlorides.—The ketimmonium chlorides (VII·HCl) are still more sensitive to thermal rearrangement than are the corresponding bases. For example, *o*-tolyl ketimmonium chloride was found to melt at 106–107°, to resolidify on account of its rearrangement to the higher melting pyrrolinium chloride (XII·HCl) and to remelt at 148°, which is only a few degrees lower than that of the pyrrolinium salt (156°, Table I). Other data will be found in Table II.

A Low Melting Pyrrolinium Chloride.—The residue from the pyrolysis of 1 g. of *p*-tolyl cyclopropyl ketimine was dissolved in ether, the solution filtered and treated with hydrogen chloride in ether. The gummy precipitate was dissolved in alcohol and reprecipitated by the addition of ether, m. p. 57–58.5°.

Anal. Calcd. for $C_{11}H_{14}NCl$: Cl, 18.14. Found: Cl, 18.02.

This low melting hydrochloride gave a picrate of m. p. 178–179° and a chloroplatinate of m. p. 181.5–183.5.

IV. Rates of Reaction of Cyclopropyl Ketimmonium Chlorides with Water at 0°.—Cyclopropyl ketimmonium chlorides, $\underline{CH_2CH_2CH}{-}C({=}NH_2Cl)R$ (VII·HCl), react with water in accordance with the monomolecular law to give the corresponding ketone (II) and ammonium chloride.[5]

In Table III for the *o*-tolyl salt, line 2 gives the cc. of 0.1 *N* sodium hydroxide which was neutralized by the ketimine salt in 10-cc. portions of solution, containing 0.5380 g. per 55 cc., at the end of times t_1, t_2, etc. The constant k is calculated from the expression $k = 2.303/(t_2 - t_1) \log (V_1/V_2)$, where V_1, V_2 represent the cc. of sodium hydroxide. Since the graphical representation shows that the first point is definitely out of line, the second point has been employed in the calculations.

TABLE III

Time from start, min.	4	185	1340	2760	4740
0.1 *N* Sodium hydroxide, cc.	4.34	4.19	3.72	3.20	2.65
k, min.$^{-1}$ at 0°	..	(0.0_31901)	0.0_31030	0.0_31047	0.0_31006
k (average)					0.0_31028

Table IV presents a summary of the constants, k, min.$^{-1}$, for the reaction of several of our compounds with water at 0°. In general, the values are averages of only two or three runs on small samples of ketimmonium salt. It will be noted that with the exception of the *o*-tolyl and α-naphthyl radicals, which are interchanged, the order of reactivity of the radicals corresponds to the order of radicals given by Kharasch[12] and his associates.

TABLE IV

Cyclopropyl ketimmonium chloride	Molarity	k, min^{-1}, at 0°
o-Tolyl	0.05	0.0001
α-Naphthyl	.005	.0002
p-Tolyl	.05	.0089
m-Tolyl	.05	.0183
Phenyl[5]	.05	.0249
Ethyl[5]	.05	.0363

Summary

1. The 2-*o*, *m* and *p*-tolylpyrrolines may be obtained by the hydrolysis or ammonolysis of the products obtained by the action of the tolylmagnesium bromides on γ-chlorobutyronitrile.
2. The tolyl cyclopropyl ketimines and the corresponding ketimmonium salts rearrange on heating to give respectively the isomeric pyrrolines or the pyrrolinium salts.
3. The reaction rates of several aryl and alkyl cyclopropyl ketimmonium chlorides with water at 0° increase in the order *o*-tolyl, α-naphthyl, *p*-tolyl, *m*-tolyl, phenyl and ethyl, which order corresponds closely with that of the same radicals in the Kharasch series.

TROY, N. Y. RECEIVED JUNE 8, 1945

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[11] J. J. Cervini, "Thesis," R. P. I., June, 1932.

[12] *E. g.*, Kharasch and Reinmuth, *J. Chem. Ed.*, **5**, 408 (1928).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Polymerization of Olefins. VIII.[1] The Depolymerization of Olefins in Relation to Intramolecular Rearrangements. II[2]

BY FRANK C. WHITMORE AND ELDON E. STAHLY[3,4]

The dehydration of di-*t*-butylcarbinol at 200° with a sulfonic acid catalyst to give trimethylethylene, isobutylene and their polymers was thought to be a new alcohol reaction until a search of the literature showed that Slawjanow[5] had obtained acetone and tetramethylethylene when hexamethyl-1,3-propanediol was treated with acid reagents. This apparently peculiar change agrees with the current working hypothesis of rearrangements.[4,6] The first step is the addition of a proton to form an oxonium ion with one of the hydroxyl groups followed by the loss of water leaving the carbonium ion A with its open sextet of electrons, indicated by an asterisk

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[1] Whitmore and Surmatis, THIS JOURNAL, **63**, 2200 (1941).

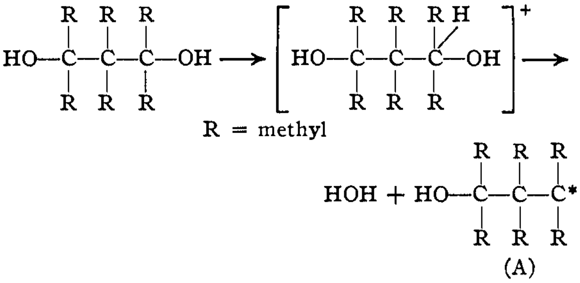
[2] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

[3] Present address, Mellon Institute, Pittsburgh, Pa.

[4] Full particulars are available in the Ph.D. thesis of Eldon E. Stahly (1934) in The Pennsylvania State College Library, Willard P. Lewis, Librarian. After the present work was completed, several similar reactions were published by Nazarov; see *Ber.*, **70B**, 606, 617 (1937), for leading references.

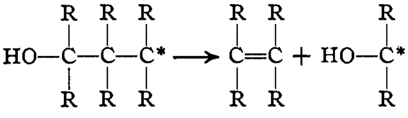
[5] Slawjanow, *Chem. Zentr.*, **78**, II, 135 (1907).

[6] Whitmore, THIS JOURNAL, **54**, 3274 (1932).



(A)

This fragment is unstable and will change in such a way as to convert the sextet to an octet. This might be accomplished by one of the following: (1) Union with a negative ion from the solution. Apparently this does not take place as Slawjanow failed to find any trace of the corresponding bromide which was the objective of his research; (2) by the attraction of an electron pair from within one of the methyl groups attached directly to the electronically deficient atom thereby liberating a proton and forming a double bond. Apparently even the mildest acid reagents cause the reversal of this process; (3) by the attraction of an electron pair *with* its methyl group from the central carbon atom. This change would give a *t*-butyl group. No such product was found; (4) by the attraction of an electron pair with the attached group, $HO(CH_3)_2C$:. This would give a fragment identical with A; (5) or by attracting the last indicated electron pair *without its attached group*. This would give tetramethylethylene, one of the observed products



(A)

and a new carbonium ion which would be readily stabilized by the loss of a proton with the formation of acetone, the other observed product. It will thus be seen that this process follows the same course as the splitting of di-*t*-butylcarbinol.[2] The extraordinary ease with which Slawjanow's compound was split, namely, by dilute acids as compared with sulfonic acids at 200°, encouraged a study of other carbinols containing the critical grouping $R_3C—C—C—OH$. The results indicate that little or no splitting occurs if the middle carbon has two hydrogen atoms as in neopentylcarbinol, $(CH_3)_3CCH_2CH_2OH$, and methylneopentylcarbinol, $(CH_3)_3CCH_2CHOHCH_3$. With one alkyl group on the middle carbon, splitting is possible at 200° with sulfonic acid catalyst; with two alkyl groups on the middle carbon, splitting is still easier.

The splitting of the carbinols by this reaction presumably involves the same intermediates as the splitting or depolymerization of certain types of olefins. Therefore, the present study has been extended to include the related olefins as well. The depolymerization consists in the elimination of a "positive" tertiary alkyl group to leave a smaller olefin molecule. Thus it is the exact reverse of certain polymerizations which consist in the addition of a positive tertiary carbonium ion to an olefin followed by proton elimination.[7] The two

TABLE I

ATTEMPTED CLEAVAGE OF CARBINOLS AND OLEFINS WITH 1,4-CHLORONAPHTHALENESULFONIC ACID AT ABOUT 200°

	Products, %		
Carbinol or olefin	Iso-C_4H_8	Higher Polymers	Other products
Neopentylcarbinol	0	0	90 unchanged
Methylneopentylcarbinol	1	0	80 C_7H_{14}
2,2,5-Trimethyl-3-hexene	1	0	1 C_3H_6, 82 C_7H_{14}
2,4-Dimethyl-2-pentene	0	60	32 C_7H_{14}
Isopropyl-*t*-butylcarbinol	9	64	9 C_9H_{18}
2,3,4-Trimethyl-1-pentene and 2-isomer	0	50	20 Unchanged 20 Diisobutylenes
Olefins from Methylisopropylneopentylcarbinol			
A. Low boiling	2.2	0	62 $C_{10}H_{20}$ 10 $C_{12}H_{24}$
B. Intermediate fractions	1	13	28 C_6H_{12} 18 Diisobutylenes 37 $C_{18}H_{20}$
C. High boiling	8	58	6 C_6H_{12} 26 Diisobutylenes
3,4,4-Trimethyl-2-pentene	1	0	91 C_8H_{16}
Methylbutylneopentylcarbinol	5	11	19 C_7H_{14} 3 Diisobutylenes 59 $C_{11}H_{22}$
Olefins from dibutylneopentylcarbinol	1	91	6 $C_{10}H_{20}$
Diethylneopentylcarbinol	2	13	5 C_6H_{12} 2 Diisobutylenes 75 $C_{10}H_{20}$
Olefins from methylethylneopentylcarbinol	2	27	17 C_5H_{10} 9 Diisobutylenes 18 C_8H_{18}
t-Butylneopentylcarbinol	8	16	11 C_6H_{12} 7 Diisobutylenes 53 $C_{10}H_{20}$
Methyl-*t*-butylneopentylcarbinol	7	15	62 C_7H_{14} 19 Diisobutylenes
Di-*t*-butylcarbinol	4	46	41 C_5H_{10}
Nonenes from di-*t*-butylcarbinol	18	40	40 C_5H_{10}
t-Butyl-*t*-amylcarbinol (165–200°)	1	1	68 C_5H_{10} 11 C_6H_{12} 3 Diisobutylenes 3 C_9H_{18} 10 $C_{10}H_{20}$
t-Butyl-*t*-amylcarbinol (150–170°)	1	18	40 C_5H_{10} 15 C_6H_{12} 3 Diisobutylenes 2 C_9H_{18} 14 $C_{10}H_{20}$
Methyl-*t*-butyl-*t*-amylcarbinol	1	9	24 C_5H_{10} 24 C_6H_{12} 21 C_7H_{14} 8 Diisobutylenes
2,2,6,6-Tetramethyl-3-heptene	1	75	
Diisobutylenes	44	37	8 Unchanged 7 Triisobutylene
Triisobutylene			
A. Low boiling	44	13	18 Diisobutylenes 20 Triisobutylenes
B. High boiling	20	11	50 Diisobutylenes 19 Triisobutylenes

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[7] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

TABLE II

CLEAVAGE OF DI-*t*-BUTYLCARBINOL WITH ACIDIC REAGENTS

Product, %	1,4-Chloronaphthalenesulfonic acid	β-Naphthalenesulfonic acid	*p*-Toluenesulfonic acid	Fuming sulfuric (d. 1.88)	Oxalic acid	Phosphorus pentoxide	Zinc chloride	Hydriodic acid
Isobutylenes	2	6	15	3	8	20	3	0
Amylenes	42	40	55	15	9	52	14	0
Diisobutylenes	5	16	11	6	0	15	3	0
Nonenes	10	29	0	50	78	5	70	92
Polymers	25	10	18	17	0	4	10	0

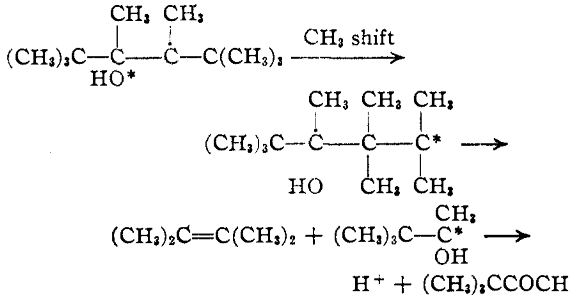
processes may be illustrated by

$$2(CH_3)_2C::CH_2 + H^+ \rightleftarrows$$
$$(CH_3)_2C::CH_2 + (CH_3)_3C^* \rightleftarrows$$
$$(CH_3)_2C^*CH_2C(CH_3)_3 \rightleftarrows$$
$$H^+ + (CH_3)_2C::CHC(CH_3)_3, \text{ etc.}$$

As shown in Table II, various acid reagents other than the 1,4-chloronaphthalenesulfonic acid originally studied cause the splitting.

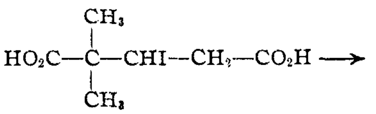
Lebedew[8] polymerized olefins by means of floridin at low temperatures while at higher temperatures the same catalyst depolymerized diamylene and polyisobutylenes.

Another cleavage similar to that of the present investigation is the splitting of *sym*-dimethyldi-*t*-butylethylene glycol to give pinacolone and tetramethylethylene.[9] This change involves the steps

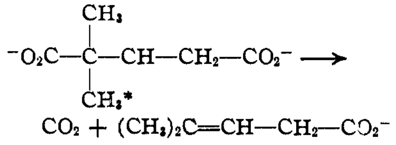


$$\underset{\text{HO}^*}{(CH_3)_3C{-}\overset{CH_3}{C}{-}\overset{CH_3}{C}{-}C(CH_3)_3} \xrightarrow{\text{CH}_3\text{ shift}}$$
$$(CH_3)_3C{-}\underset{HO}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C^*}} \longrightarrow$$
$$(CH_3)_2C{=}C(CH_3)_2 + (CH_3)_3C{-}\underset{OH}{\overset{CH_3}{C^*}} \longrightarrow$$
$$H^+ + (CH_3)_3CCOCH_3$$

This type of change is probably not limited to reactions with acids. The formation of the critical fragment, $R_3C{-}C{-}C^*$, or its equivalent by any means, should result in a similar cleavage of the molecule. Thus 2,2-dimethyl-3-iodoglutaric acid with sodium carbonate solution gives 3-isohexenoic acid



$$HO_2C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CHI{-}CH_2{-}CO_2H \longrightarrow$$



$$^-O_2C{-}\underset{CH_3^*}{\overset{CH_3}{C}}{-}CH{-}CH_2{-}CO_2^- \longrightarrow$$
$$CO_2 + (CH_3)_2C{=}CH{-}CH_2{-}CO_2^-$$

Similar changes undoubtedly are involved in the conversion of dibromocinnamic acid to ω-bromostyrene and similar processes. In such changes the carboxyl group serves as the easily eliminated tertiary group in the critical fragment. The electronically deficient atom in the beta position is stabilized by taking the electron pair which holds the carboxyl group thus liberating the latter as carbon dioxide.

In the present study twenty-two alcohols or related olefin mixtures have been heated with a sulfonic acid at 200° under conditions to allow the escape and collection of depolymerization products from the reaction mixture. The results appear in Table I while the details of the analytical distillations can be found in the thesis.[4] The results obtained with di-*t*-butylcarbinol and various acidic agents are contained in Table II.

The authors thank Dr. W. A. Mosher of the University of Delaware for his assistance.

Summary

1. The previously reported cleavage of di-*t*-butylcarbinol by acidic agents to trimethylethylene and isobutylene and its polymers has been confirmed and extended to more than twenty compounds, including alcohols and olefins.

2. Cleavage is shown most readily with compounds capable of forming a carbonium ion including $R_3{-}C{-}C{-}C^*$.

3. The reaction studied, in addition to the analogous cleavage of hexamethyl-1,3-propanediol to acetone and tetramethylethylene discovered by Slawjanow in 1907 and similar changes, are interpreted on the basis of the current theory of molecular rearrangements.

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[8] Lebedew, *Chem. Zentr.*, **99**, II, 1199 (1928); *Ber.*, **63B**, 1432 (1930).

[9] Couturier, *Ann. chim.*, [6] **86**, 497 (1892); Delacre, *Bull. soc. chim.*, [4] **1**, 539 (1907).