

TABLE I  
 BENZYL BENZOATE ANALOGS

Benzoate formed	Molar ratio of sodium benzoate to chloride <sup>a</sup>	Boiling point		Yield, g.	$n_D^{20}$	$d_4^{25}$	Formula	Carbon, %		Hydrogen, %	
		°C.	Mm.					Calcd.	Found	Calcd.	Found
<i>p</i> -Chlorobenzyl	2.5	153	1/2-1	43.0 <sup>b</sup>	....	...	C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> Cl <sup>f</sup>	68.16	68.5-68.9	4.49	4.73-4.53
Benzyl <i>p</i> -chloro	2.0	155-160	1/2-1	42.8 <sup>c</sup>	1.5792	...	C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> Cl <sup>g</sup>	68.16	68.0-68.2	4.49	4.58-4.60
<i>o</i> -Methylbenzyl	2.0	155	1/2-1	67.9	1.5680	1.102	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.4-79.6	6.24	6.42-6.56
<i>m</i> -Methylbenzyl	4.0	159-160	2	35.2	1.5632	1.092	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.4-79.7	6.24	6.31-6.33
<i>p</i> -Methylbenzyl	4.0	133-135	1/4-1/2	25.8	1.5618	1.085	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.7-79.9	6.24	6.57-6.65
Benzyl <i>o</i> -methyl	2.0	128	1/4-1/2	65.4	1.5662	1.102	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.6-79.7	6.24	6.40
Benzyl <i>m</i> -methyl	2.0	125-127	1/2	79.0	1.5652	1.096	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.60	6.24	6.21-6.35
Benzyl <i>p</i> -methyl	2.0	124-126	1/4-1/2	80.9 <sup>d</sup>	....	...	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub>	79.62	79.6-79.7	6.24	6.23-6.31
2,5-Dimethylbenzyl	2.0	160-161	1/2-1	60.1	1.5618	1.087	C <sub>14</sub> H <sub>16</sub> O <sub>2</sub>	79.92	79.7-79.9	6.71	6.90-7.00
<i>p</i> -Chlorobenzyl- <i>p</i> -chloro	2.7	165-166	1/2-1	56.6 <sup>e</sup>	....	...	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>2</sub> <sup>h</sup>	59.81	59.8-60.0	3.59	3.71-3.75

<sup>a</sup> One mole of sodium benzoate was used throughout, except in the preparation of benzyl *p*-chlorobenzoate, where 0.72 mole of sodium *p*-chlorobenzoate was used. <sup>b</sup> M. p. 58.0-58.5°. <sup>c</sup> M. p. 26-27°. <sup>d</sup> M. p. 45-47°. <sup>e</sup> M. p. 71.5-72.0°. <sup>f</sup> %Cl calcd. 14.37; found 14.43. <sup>g</sup> %Cl calcd. 14.37; found 13.98. <sup>h</sup> %Cl calcd. 25.22; found 25.08.

the reflux condenser. The reaction mixture was allowed to stir at reflux temperature (about 110°) for approximately four hours.

At the end of the reaction period, the product was transferred to a separatory funnel and the aqueous layer removed. The organic layer was washed with several portions of 5% aqueous sodium hydroxide. Usually, for runs where 1 mole of acid was used, three washings of 200 ml. each sufficed to extract the unused organic acid from the reaction product. The basic washes were followed by two water washes of about 200 ml. each. The initial water layer, the aqueous caustic extracts and the water washings were combined and extracted once with 50 ml. of carbon tetrachloride. The carbon tetrachloride extract was added to the washed organic product layer. Addition of concentrated hydrochloric acid to the combined aqueous extracts resulted in the recovery of unused benzoic acid.

The organic products were stripped free of carbon tetrachloride at about 200 mm. pressure, after which the pressure was reduced rapidly to about 0.25 to 1.0 mm. There was always encountered a small fraction of a benzyl alcohol (obtained through hydrolysis of the chloride) just prior to the distillation of the ester. All distillations of the products were carried out in a still having approximately a six-inch unpacked column of one inch diameter.

**Acknowledgment.**—The authors are grateful to Mr. Eugene L. Rose and Lt. Russell H. Maas of this Laboratory for having performed the necessary analyses.

### Summary

The following benzoates have been prepared by refluxing aqueous sodium benzoate, or a nuclearly substituted derivative thereof, with benzyl chloride or some of its nuclear substitution analogs: *p*-chlorobenzyl, benzyl *p*-chloro-, *p*-chlorobenzyl *p*-chloro-, *o*-methylbenzyl-, *m*-methylbenzyl-, *p*-methylbenzyl-, benzyl *o*-methyl-, benzyl *m*-methyl-, benzyl *p*-methyl- and 2,5-dimethylbenzyl.

The substituted benzyl chlorides necessary for the syntheses of the esters were prepared by the action of sulfonyl chloride on the corresponding methylbenzenes in the presence of benzoyl peroxide as catalyst.

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RECEIVED SEPTEMBER 1, 1945

[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

## 2-Tolylpyrrolines and the Rearrangement and Hydrolysis of Aryl Cyclopropyl Ketimines

By JOHN B. CLOKE, LOUIS H. BAER,<sup>1</sup> JAMES M. ROBBINS<sup>2</sup> AND GUSTAVUS E. SMITH<sup>3</sup>

The present paper is an extension of earlier work on (1) the synthesis of pyrrolines by the  $\gamma$ -chlorobutyronitrile-Grignard reaction,<sup>4</sup> (2) the preparation of aryl cyclopropyl ketimines (VII) and their hydrochlorides (VII·HCl), (3) the rearrangement of (VII) and (VII·HCl) to the isomeric pyrrolines (XII) and pyrrolinium chlorides (XII·HCl) and (4) the rates of reaction of (VII·HCl) with water.<sup>5</sup>

(1) Most of the data on the ortho and meta compounds have been taken from a manuscript written by L. H. Baer in 1927-1928. Present address: U. S. Patent Office.

(2) From a thesis for the degree of Chemical Engineer, R. P. I. (1928). Present address: The B. F. Goodrich Co., Akron, Ohio.

(3) From a thesis for the degree of Ch.E. in 1931. Present address: U. S. Navy.

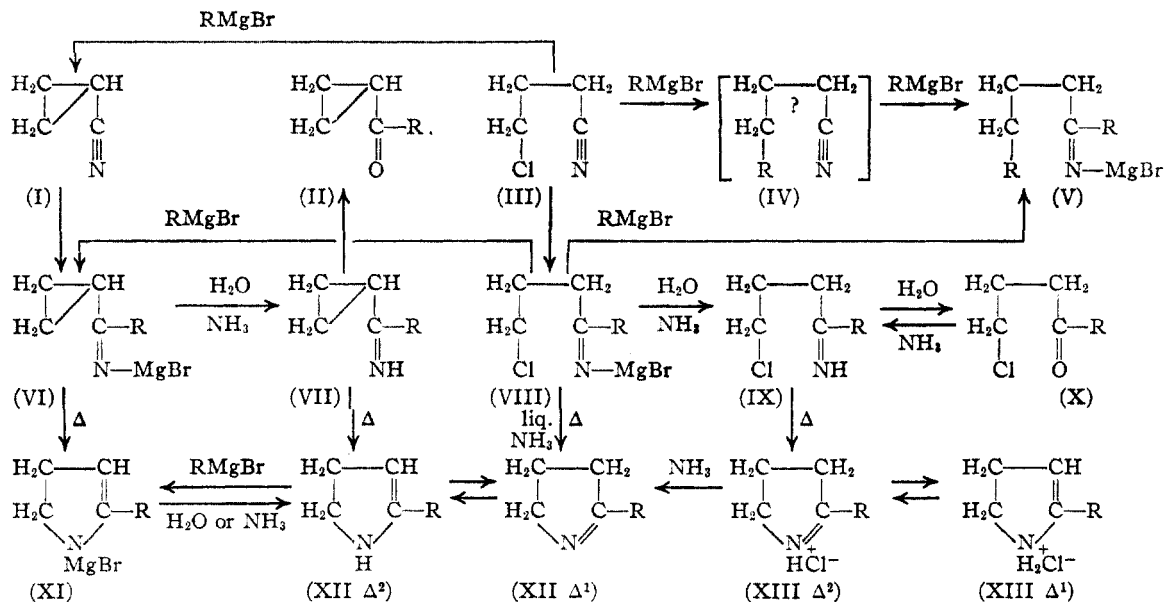
(4) Cloke, *THIS JOURNAL*, **51**, 1174 (1929).

(5) Cloke, *ibid.*, **62**, 117 (1940).

### Experimental

**I. The  $\gamma$ -Chlorobutyronitrile-Grignard Reaction.**—The initial reaction of a Grignard reagent with  $\gamma$ -chlorobutyronitrile (III) follows two main paths as shown in the flow sheet. Of primary importance is the formation of the halogenomagnesium derivative of a  $\gamma$ -chloropropyl ketimine (VIII),<sup>4</sup> which may give a pyrroline (XII) by three paths. (1) The hydrolysis of (VIII) gives the unstable ketimine<sup>4</sup> (IX), which by rapid extraction, to avoid further saponification to the ketone (X), and gentle warming gives the pyrrolinium salt (XIII) and thence the pyrroline (XII) which compounds may be tautomeric. The hydrolysis procedure may give some of the ketone related to (V). (2) The pyrolysis of (VIII) gives (XII) directly,<sup>2,6</sup> and therefore (VIII) and (XII) may be found together following the interaction of RMgX and (III). (3) The am-

(6) Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).



monolysis of (VIII) gives (XII) by two possible paths, directly or *via* (IX) and (XIII), although the stability of (IX) in liquid ammonia at  $-33^\circ$  has not been studied. The 2-*o*- and 2-*p*-tolylpyrrolines were prepared by the old hydrolysis method (1) and the *m*-compound by ammonolysis (3).

A variable amount of a cyclopropyl ketimine (VII) may also accompany the pyrroline (XII) obtained by the hydrolysis and ammonolysis methods. Although (VII) is usually regarded as being formed from (III) through cyclopropanecarbonitrile (I),<sup>7</sup> it may possibly originate in part by the action of RMgX on (VIII) to give (VI) and then (VII). A consideration of the rearrangement of (VII) to (XII) follows in section (III).

**2-*o*-Tolylpyrroline from (III).**—A weight of 15.5 g. of  $\gamma$ -chlorobutyronitrile (III) in ether was added to a solution of *o*-tolylmagnesium bromide, prepared from 34.9 g. of Eastman *o*-bromotoluene and 4.8 g. of magnesium in ether and the mixture boiled for ten hours. The mixture was decomposed with shaved ice and ammonium chloride, the dried ether extract evaporated, the residue dissolved in chloroform, treated with ammonia and the filtered solution distilled. The colorless oily fraction of b. p.  $115-115.5^\circ$  at 7 mm. weighed 12.6 g.;  $d^{20}_4$  1.0256;  $n^{20}_D$  1.56667;  $MR_D$  50.66.

*Anal.* Calcd. for  $C_{11}H_{13}N$ : N, 8.80. Found: N, 8.72, 8.51.

The calculated  $MR_D$  for the  $\Delta^2$ -formula, assuming the atomic refractivity of 2.502 for the nitrogen, is 50.332. The  $MR_D$  for the  $\Delta^1$ -structure, assuming the value of 3.776 for the N, is 49.873. Although the experimental molecular refractivity points to the  $\Delta^1$ -structure, the behavior of the compound with methylmagnesium iodide in isoamyl ether indicates the  $\Delta^1$  formula, at least to the extent of 95%.

**2-*m*-Tolylpyrroline.**—Thirteen grams of  $\gamma$ -chlorobutyronitrile was added slowly to *m*-tolylmagnesium bromide, prepared from 4.8 g. of magnesium and 34.9 g. of *m*-bromotoluene.<sup>8</sup> The solution was boiled, a portion of the ether removed by evaporation and the residue treated with about 200 cc. of liquid ammonia in a Dewar flask for twenty-four hours. The residue was extracted with ether and the extract evaporated and heated to  $150^\circ$ , giving 17.8 g. of crude pyrroline, which was precipitated as the

hydrochloride by the addition of dry hydrogen chloride to an ethereal solution. The chloride was washed with ether, dissolved in chloroform, the solution saturated with dry ammonia and the filtered solution distilled. The yield of colorless 2-*m*-tolylpyrroline was 9.8 g.; b. p.  $137-138^\circ$  at 15 mm.;  $d^{20}_4$  1.0189;  $n^{20}_D$  1.56377;  $MR_D$  50.82.<sup>9</sup>

**2-*p*-Tolylpyrroline.**—The base was prepared from 7.05 g. of magnesium, 51.3 g. of *p*-bromotoluene, 200 cc. of ether and 15 g. of  $\gamma$ -chlorobutyronitrile by the hydrolysis method. A yield of 6.3 g. of white solid, which soon turned yellow, was obtained; b. p.  $123-124^\circ$  at 7 mm.; freezing point,  $55.3^\circ$  by method of cooling curve.<sup>10</sup> The free base gave no ethane with ethylmagnesium bromide, which points to the  $\Delta^1$ -structure.

*Anal.* Calcd. for  $C_{11}H_{13}N$ : N, 8.80. Found: N, 8.72.

**Pyrrolinium Salts.**—The pyrrolinium chlorides were precipitated by the addition of dry hydrogen chloride to an ethereal solution of the base. They may be recrystallized from alcohol and ether. The chloroplatinates were prepared by the addition of chloroplatinic acid to an alcoholic solution of the chlorides.

**II. Preparation of Cyclopropyl Ketimines.**—The aryl ketimmonium chlorides were prepared from the free bases (VII), which were obtained by the hydrolysis or ammonolysis<sup>4,5</sup> of the bromomagnesium derivatives (VI). These, in turn, were synthesized by the action of the appropriate Grignard reagent on cyclopropanecarbonitrile (I).

***o*-Tolyl Cyclopropyl Ketimine.**—To a Grignard reagent, prepared from 4.8 g. of magnesium and 32 g. of *o*-bromotoluene, was added 15 g. of cyclopropanecarbonitrile,<sup>4</sup> which had been distilled eight times over sodium hydroxide and aluminum oxide in order to remove sensitizing chlorine compound. The addition product (VI) was decomposed with shaved ice and ammonium chloride and extracted with ether. The evaporation of the dried ether extract under diminished pressure at room temperature gave the somewhat impure oily ketimine. No further attempt was made to purify the ketimine in view of its sensitivity to rearrangement:  $d^{20}_4$  0.9967;  $n^{20}_D$  1.54542;  $MR_D$  50.62.

*Anal.* Calcd. for  $C_{11}H_{13}N$ : N, 8.80. Found: N, 8.50, 8.28.

(7) Bruylants, *Bull. sci. acad. roy. Belg.*, **12**, 1082 (1908); de Booseré, *Bull. soc. chim. Belg.*, **32**, 26 (1923).

(8) Bigelow, Johnson and Sandborn, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., p. 128.

(9) J. Lachmann, Thesis, R. P. I., 1931, prepared the following 2-substituted pyrrolines by the ammonolysis method: methyl (10-23%), ethyl (38-40%), *n*-propyl (51%), *n*-butyl (66%) and benzyl (45-67%).

(10) Starr, Bulbrook and Hixon, ref. 6, report m. p.  $60-61^\circ$ .

TABLE I  
TOLYLPYRROLINIUM SALTS

	Chlorides		Chloroplatinates			Picrates M. p., °C.
	Calcd. for $C_{11}H_{13}NCl$ : M. p., °C.	Cl, 18.14 found	Calcd. for $C_{11}H_{13}NCl_2Pt$ : M. p., °C.	Pt, 26.81 found, %		
<i>o</i> -Tolyl	155.5–156.5	18.32	176.5–177.5	26.86 26.94		160–161
<i>m</i> -Tolyl	186–187	18.19	196–197	28.7		153–154
<i>p</i> -Tolyl	197.5–198	18.10	185–186 dec.	26.90 26.85		182–183

***p*-Tolyl Cyclopropyl Ketimine.**—A Grignard solution, prepared from 4.8 g. of magnesium, 34.9 g. of *p*-bromotoluene and 115 cc. of ether, was heated for three hours with 9.75 g. of cyclopropanecarbonitrile and the mixture added to liquid ammonia in a Dewar flask. The mixture was allowed to stand overnight and extracted with ether. The evaporation of the filtered ethereal solution gave 11.7 g. of residue.

*Anal.* Calcd. for  $C_{11}H_{13}N$ : N, 8.80. Found: N, 9.22, 9.11.

**Cyclopropyl Ketimmonium Chlorides (VII·HCl).**—For the preparation of the *m*-tolyl salt 5 g. of cyclopropanecarbonitrile was boiled for several hours with a Grignard solution made from 43 g. of *m*-bromotoluene, 4.8 g. of magnesium and ether. The product was allowed to react with 500 cc. of liquid ammonia for twelve hours. The ketimine was extracted with dry ether, the solution filtered, the ammonia removed and dry hydrogen chloride added. The precipitated salt was dissolved in dry chloroform, reprecipitated by the addition of dry ether and dried under diminished pressure at 50° for several hours in order to remove chloroform of crystallization. The *o*- and *p*-tolyl ketimmonium chlorides were prepared from the bases already described.

TABLE II  
TOLYL CYCLOPROPYL KETIMMONIUM CHLORIDES

Salt	M. p., °C.	Second m. p., °C.	Chloride ion, %	
			Calcd. for $C_{11}H_{13}NCl$	Found
<i>o</i> -Tolyl	106–107	148	18.14	17.68
<i>m</i> -Tolyl	118–119	187–188		18.10
<i>p</i> -Tolyl	104–105	159–163		18.19

A poor yield of  $\alpha$ -naphthyl cyclopropyl ketimmonium chloride was obtained from 52 g. of  $\alpha$ -naphthyl bromide, 4.8 g. of magnesium and 5 g. of cyclopropanecarbonitrile. The salt was difficult to purify, retaining a dark color after two crystallizations from chloroform.

*Anal.* Calcd. for  $C_{11}H_{13}NCl \cdot CHCl_3$ : Cl ion, 10.11. Found: Cl ion, 10.13. The chloroform was removed by warming the salt at 50° under diminished pressure. *Anal.* Calcd. for  $C_{11}H_{13}NCl$ : Cl, 15.32. Found: Cl, 15.25.

**III. The Cyclopropyl Ketimine–Pyrroline Rearrangement.**—An aryl cyclopropyl ketimine (VII), when heated, rearranges to give the isomeric 2-arylpyrroline (XII), whereby the unstable triatomic ring is opened and a new stable five atom ring is closed.

**Rearrangement of Bases.**—In order to ascertain the comparative ease of thermal isomerization of the ketimine bases, one leg of a differential chromel–constantan thermocouple was immersed in a sample of base (VII) and the other in an equal amount of liquid petrolatum. Both substances, contained in small test-tubes, were then heated uniformly in a well stirred bath, and simultaneous readings were taken on a potentiometer, which was connected to the thermocouple and on a thermometer which was immersed in the bath.

The behavior of the *o*-tolyl cyclopropyl ketimine on heating is shown by the curves of Fig. 1. Curve A for the fresh ketimine would indicate that the rearrangement begins around 120° and rises to a first maximum around 170° when the temperature drops and then rises to a new high at around 207°, when it falls abruptly. Curve B for an older sample of ketimine shows the same comparative behavior but at lower temperatures. That the isomeric

pyrroline was formed in each case was established by the isolation of the pyrrolinium chloride (XII·HCl) from the residue. The two maxima shown in Fig. 1 are more strik-

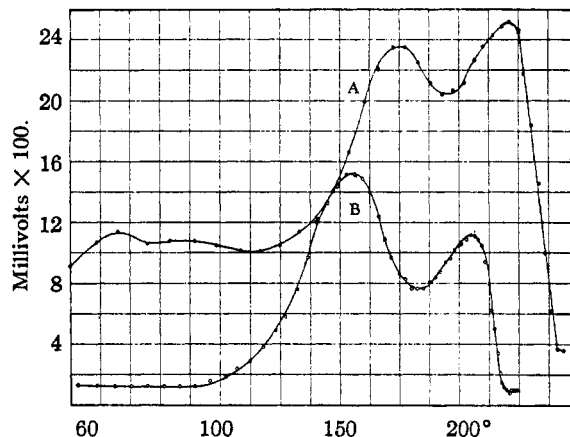


Fig. 1.—Curve A represents the effect of heating on 0.3099 g. of undistilled *o*-tolyl cyclopropyl ketimine. Curve B shows the behavior of 0.3854 g. of the ketimine thirty-five days later.

ing than those for phenyl cyclopropyl ketimine<sup>4</sup> and for *p*-tolyl cyclopropyl ketimine (Curve C of Fig. 2). A rather obvious interpretation of the two maxima is that the rearrangement occurs in two stages, possibly from ketimine to  $\Delta^2$ -pyrroline (XII- $\Delta^2$ ) and then to  $\Delta^1$ -pyrroline (XII- $\Delta^1$ ), but there are other explanations which will be considered in the future.

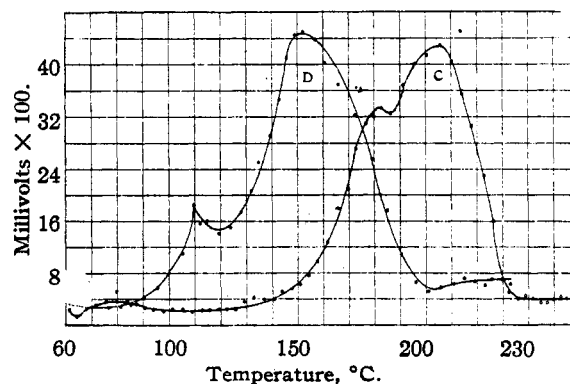


Fig. 2.—Curve C depicts the behavior of a gram of *p*-tolyl cyclopropyl ketimine on heating. Curve D shows the effect of 5% of *p*-tolylpyrrolinium chloride on a half gram of the ketimine base.

The rearrangement of *p*-tolyl cyclopropyl ketimine is shown in Curve C of Fig. 2. That the rearrangement is catalyzed by the addition of pyrrolinium salt is indicated by curve D of Fig. 2. In the light of the foregoing and previous<sup>4</sup> data there appears to be little significant differ-

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

According to some work of Cervini,<sup>11</sup> 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<sup>2,4</sup> in the preparation of pyrrolines by the action of Grignard reagents on  $\gamma$ -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<sub>11</sub>H<sub>14</sub>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,  $\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{NH}_2\text{Cl})\text{R}$  (VII·HCl), react

with water in accordance with the monomolecular law to give the corresponding ketone (II) and ammonium chloride.<sup>5</sup>

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

TABLE III

Time from start, min.	4	185	1340	2760	4740
0.1 <i>N</i> Sodium hydroxide, cc.	4.34	4.19	3.72	3.20	2.65
<i>k</i> , min. <sup>-1</sup> at 0°	..	(0.031901)	0.031030	0.031047	0.031006
<i>k</i> (average)					0.031028

(11) J. J. Cervini, "Thesis," R. P. I., June, 1932.

salt in 10-cc. portions of solution, containing 0.5380 g. per 55 cc., at the end of times *t*<sub>1</sub>, *t*<sub>2</sub>, etc. The constant *k* is calculated from the expression  $k = 2.303/(t_2 - t_1) \log (V_1/V_2)$ , where *V*<sub>1</sub>, *V*<sub>2</sub> 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 IV presents a summary of the constants, *k*, min.<sup>-1</sup>, 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  $\alpha$ -naphthyl radicals, which are interchanged, the order of reactivity of the radicals corresponds to the order of radicals given by Kharasch<sup>12</sup> and his associates.

TABLE IV

Cyclopropyl ketimmonium chloride	Molarity	<i>k</i> , min. <sup>-1</sup> , at 0°
<i>o</i> -Tolyl	0.05	0.0001
$\alpha$ -Naphthyl	.005	.0002
<i>p</i> -Tolyl	.05	.0089
<i>m</i> -Tolyl	.05	.0183
Phenyl <sup>6</sup>	.05	.0249
Ethyl <sup>6</sup>	.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  $\gamma$ -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,  $\alpha$ -naphthyl, *p*-tolyl, *m*-tolyl, phenyl and ethyl, which order corresponds closely with that of the same radicals in the Kharasch series.

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

TROY, N. Y.

RECEIVED JUNE 8, 1945

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

## The Polymerization of Olefins. VIII.<sup>1</sup> The Depolymerization of Olefins in Relation to Intramolecular Rearrangements. II<sup>2</sup>

BY FRANK C. WHITMORE AND ELDON E. STAHLY<sup>3,4</sup>

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 Slaw-

janow<sup>5</sup> 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.<sup>4,6</sup> 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

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

(2) Whitmore and Stahl, *ibid.*, **55**, 4153 (1933).

(3) Present address, Mellon Institute, Pittsburgh, Pa.

(4) Full particulars are available in the Ph.D. thesis of Eldon E. Stahl (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).