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

Rearrangement of Ketones in Acid Media[1]

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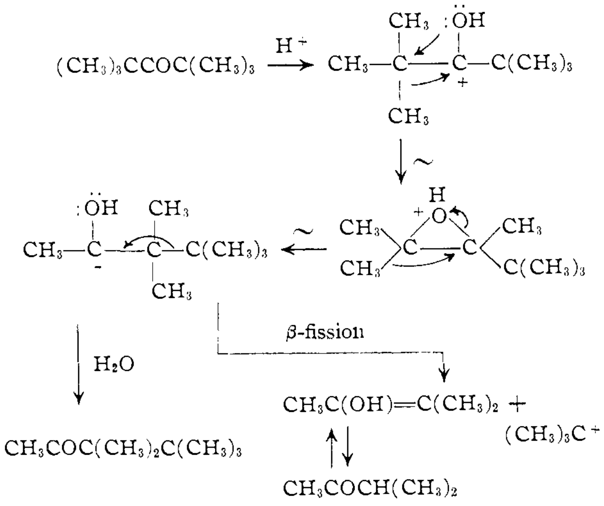
Ketones with two alkyl or two phenyl groups in the α-position rearrange to isomeric ketones in 83–97% sulfuric acid. A single product or an equilibrium mixture of a single product and the original ketone is obtained. The positions of the equilibria are qualitatively in accord with resonance and hyperconjugation theories. Methyl pentamethylethyl ketone, the initial product from the rearrangement of hexamethylacetone, undergoes β-fission to methyl isopropyl ketone. The rearrangements and cleavage have been studied kinetically.

In connection with a study of the Schmidt reaction, it was shown that ethyl *t*-butyl ketone undergoes molecular rearrangement to methyl *t*-amyl ketone in concentrated sulfuric acid.[2] The rearrangement is analogous to that reported previously for hexamethylacetone.[3] This paper describes the behavior of nine ketones in 83–97% sulfuric acid.

The rearrangement of hexamethylacetone is most interesting. When equal weights of this ketone and 97% sulfuric acid were heated for six hours at 75°, approximately half of the ketone was converted to methyl pentamethylethyl ketone. However, methyl isopropyl ketone also was identified as a product of the reaction. Similar results were obtained at 30°, where the rate of rearrangement was found to increase as the ratio of sulfuric acid to ketone was increased. Finally, eight experiments were carried out at 30.0° with 0.14 *M* solutions of hexamethylacetone in several concentrations of aqueous sulfuric acid. Aliquots were quenched in ice and extracted with carbon tetrachloride. The three ketones were determined quantitatively by infrared analysis.

The disappearance of hexamethylacetone followed a first-order rate law with a half-life varying from 40 min. in 96% sulfuric acid to 176 min. in 83.6% acid (Fig. 1). Methyl isopropyl ketone was formed at the expense of the rearranged product, methyl pentamethylethyl ketone, by a consecutive first-order reaction, the half-life of which was four to eight times greater than that for the initial rearrangement.



The over-all process of rearrangement and cleavage is most simply represented by two concerted nucleophilic substitutions involving the protonated ketone and protonated oxide followed by a β-fission of protonated methyl pentamethylethyl ketone.

Rearrangement of the *t*-butyl group rather than a methyl group in the protonated oxide would give the same product.

TABLE I

REARRANGEMENT AND FISSION OF KETONES RCOR'

R	R'	H_2SO_4, %	A_0[a]	k[b]	k'[c]
$(CH_3)_3C-$	$(CH_3)_3C-$	96.1	0.13	28.8	
		95.7	.145	27.5	
		95.4	.145	27.5	
		93.7	.14	27.3	6.5[d]
		93.2	.13	26.6	6.0[d]
		87.2	.13	15.8	1.9[d]
		86.8	.135	15.5	
		83.6	.13	6.6	0.8[d]
$(CH_3)_3C-$	$(CH_3)_2CH-$	95.5	.15	2.2	
		94.2	.15	1.8	
		91.8	.15	1.7	
$(CH_3)_3C-$	CH_3CH_2-	93.0	.17	1.6	
$(CH_3)_3CC(CH_3)_2$	CH_3-	93.2	.064		6.0
		93.2	.046		5.8
		87.2	.058		2.1
		83.6	.058		0.7
$(CH_3)_2CHC(CH_3)_2-$	CH_3-	94.2		0.3[e]	
$C_2H_5C(CH_3)_2$	CH_3-	93.2	.16	0.3	
$(C_6H_5)_3C-$	CH_3-	96.7	.0073	>700	
$(CH_3)_2CH-$	$(CH_3)_2CH-$	95.5		0.00	
$(C_6H_5)_2CCH_3$	C_6H_5-	95.5	.0075	0.00	

[a] Initial concentration of ketone in moles/liter. [b] First order rate constant for rearrangement at 30.0° in sec.$^{-1}$ × 10^5. [c] First-order rate constant for cleavage at 30.0° in sec.$^{-1}$ × 10^5. [d] Cleavage of methyl pentamethylethyl ketone calculated from the equation of two successive first-order reactions. [e] Calculated from the rate of approach of pentamethylacetone to equilibrium and the equilibrium constant.

The rates of the two consecutive reactions do not vary in the same manner with the concentration of sulfuric acid. Therefore, the maximum concentration of methyl pentamethylethyl ketone and the relative time at which this maximum is reached are functions of the acid concentration (Fig. 2). The rates of cleavage of pure methyl pentamethylethyl ketone measured independently at several concentrations of sulfuric acid were in excellent agreement with those calculated from the rearrangement data by the equation for two consecutive first-order reactions (Table I). Only methyl pentamethylethyl ketone exhibited the cleavage reaction. In this instance, the cleaved group is stabilized by maximum hyperconjugation. The

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(1) This investigation was supported by a grant from The Pennsylvania State University Council on Research.

(2) H. D. Zook and S. C. Paviak, THIS JOURNAL, **77**, 2501 (1955).

(3) S. Barton, F. Morton and C. R. Porter, *Nature*, **169**, 373 (1952).

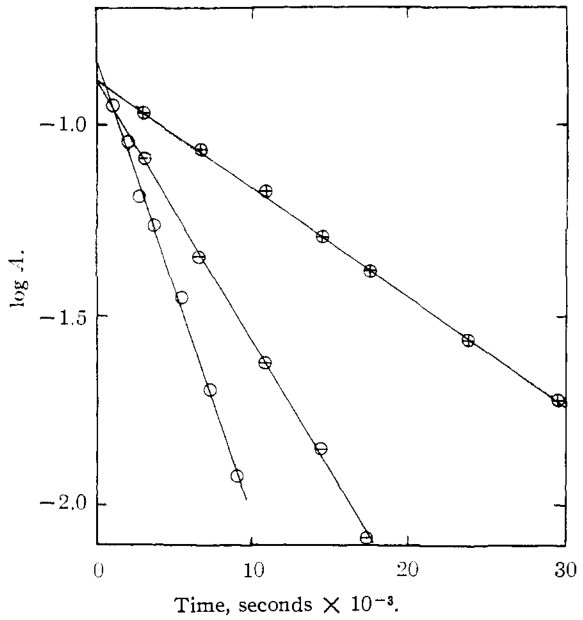

Fig. 1.—Rearrangement of hexamethylacetone; log A *vs.* time: ○, 93.7% sulfuric acid; ⊖, 87.2% sulfuric acid; ⊕, 83.6% sulfuric acid.

β-fission of this ketone is analogous to similar β-elimination of relatively stable groups during the dehydration of alcohols[4] and glycols[5] and accompanying the Schmidt and similar rearrangements.[2]

Effect of Structure on Equilibria.—Several rearrangements of pentamethylacetone in 92–96% sulfuric acid led to an equilibrium mixture containing 86.1 mole % 3,3,4-trimethyl-2-pentanone and 13.9 mole % pentamethylacetone corresponding to an equilibrium constant of 6.2 for the reaction

$$(CH_3)_3CCOCH(CH_3)_2 \underset{k_{-1}}{\overset{k}{\rightleftarrows}} (CH_3)_2CHC(CH_3)_2COCH_3$$

Specific rates of approach to equilibrium were obtained from plots of log $A_0 - A_e/A - A_e$ *versus* time, where A_0, A_e and A are initial, equilibrium and instantaneous concentrations of ketone, respectively (Fig. 3). The constants obtained from the slopes of these lines are equal to the sum of the specific rates for the forward and reverse reactions. From these and the fact that $k_1/k_{-1} = 6.2$, specific rates for the forward and reverse reactions were evaluated. These values are in agreement with specific rates obtained from plots of log A *versus* time over the first 20% of the reaction.

Similarly, rearrangement of ethyl *t*-butyl ketone in 93% sulfuric acid gave a mixture of methyl *t*-amyl ketone and ethyl *t*-butyl ketone corresponding to an equilibrium constant of 5. The equilibrium then was approached by rearrangement of methyl *t*-amyl ketone. After 127 hr., a mixture containing 15.3 mole % ethyl *t*-butyl ketone and corresponding to a constant of 5.5 was obtained.

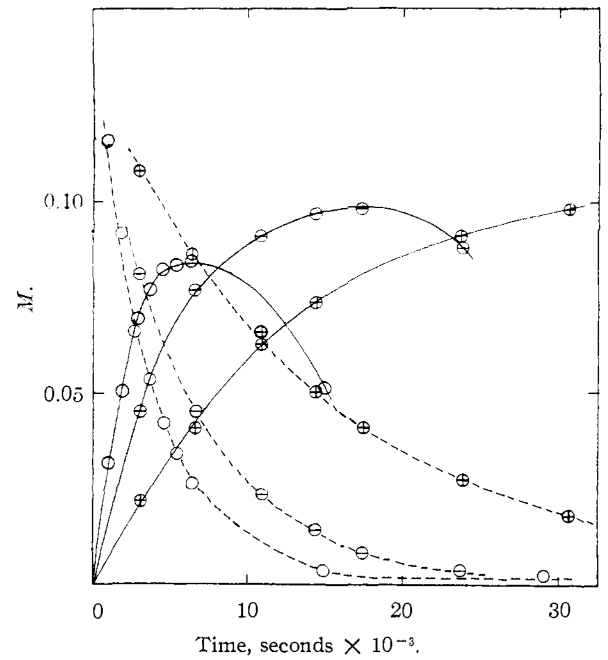

Fig. 2.—Formation and cleavage of methyl pentamethylethyl ketone. Molar concentration of ketone *vs.* time. Solid lines represent methyl pentamethylethyl ketone, broken lines show the corresponding concentrations of hexamethylacetone: ○, 95.7% sulfuric acid; ⊖, 87.2% sulfuric acid; ⊕, 83.6% sulfuric acid.

An equilibrium constant for the conversion of hexamethylacetone to methyl pentamethylethyl ketone could not be determined because of the fission of the latter compound. However, the equilibrium is extremely far to the right. No hexamethylacetone could be detected during the cleavage reactions of pure methyl pentamethylethyl ketone.

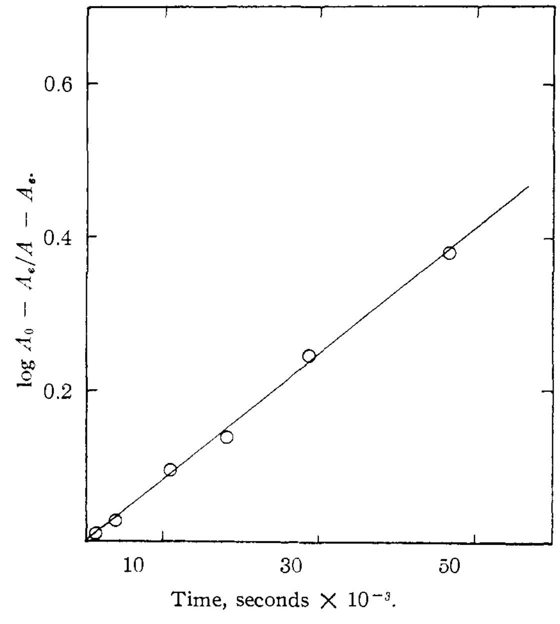

Fig. 3.—Rate of approach of pentamethylacetone to equilibrium; log $A_0 - A_e/A - A_e$ *vs.* time

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(4) F. C. Whitmore and E. E. Stahly, THIS JOURNAL, **55**, 4153 (1933); F. C. Whitmore, *Chem. Eng. News*, **26**, 671 (1948).

(5) L. Schmerling, B. S. Friedman and V. N. Ipatieff, THIS JOURNAL, **62**, 2446 (1940); Kalischev, *J. Russ. Phys. Chem. Soc.*, **46**, 427 (1914).

TABLE II

EXTINCTION COEFFICIENTS OF KETONES RCOR'

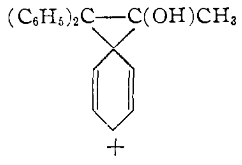
R	R'	λ[a]	k[b]	λ[a]	k[b]	λ[a]	k[b]
$(CH_3)_3C-$	$(CH_3)_3C-$	9.50	95	8.97	1.1	8.75	1.3
$(CH_3)_3C—C(CH_3)_2$	CH_3-	8.97	97	9.50	1.7	8.75	9.5
$(CH_3)_2CH-$	CH_3-	8.75	72.4	9.50	3.2	8.97	19.8
$(CH_3)_3C-$	$(CH_3)_2CH-$	9.15	29.3	8.92	2.5		
$(CH_3)_2CHC(CH_3)_2$	CH_3-	8.92	90	9.15	14.9		
$(CH_3)_3C-$	CH_3CH_2-	9.05	91	8.80	5.1		
$C_2H_5(CH_3)_2C-$	CH_3-	8.80	103	9.05	4.9		
$(C_6H_5)_3C-$	CH_3-	5.82	120				
$(C_6H_5)_2CCH_3$	C_6H_5-	5.94	105				

[a] Wave length in microns. [b] Extinction coefficient (absorbancy index) in ml. g.$^{-1}$ mm.$^{-1}$.

Diisopropyl ketone gave no evidence of rearrangement after 294 hours at 30° in 95.5% sulfuric acid.

Although all ketones which gave rearrangement contained a neopentyl system, the products of rearrangement also contained this system. The driving force of the rearrangement cannot be attributed to the internal strain of this system,[6] for even greater internal strain would be predicted within the more highly branched systems in the products. The series in which the hydrogen atoms of pinacolone are progressively substituted by methyl groups is of interest. Protonated hexamethylacetone is not stabilized by resonance, whereas three contributing hyperconjugation structures are involved in the protonated rearranged product. Pentamethylacetone and methyl *t*-butyl ketone have one and two α-hydrogen atoms, respectively, which results in a corresponding decrease in the extent of the rearrangement equilibria.

Methyl triphenylmethyl ketone is completely rearranged in 15 minutes to α,α-diphenylpropiophenone. The ketones contain similar neopentyl systems. Although methyl triphenylmethyl ketone is stabilized by hyperconjugation, the rearranged product is stabilized by first-order resonance involving the carbonyl and the two α-phenyl groups. The extremely high rate of this rearrangement may be explained by the ease with which the phenyl group can form phenonium ions,[7] thus lowering the energy of the transition state by resonance involving structures such as



Effect of Acid Media.—Plots of the log of the specific rates *versus* the concentration of sulfuric acid or H_0 were far from linear. It is unlikely that the protonation of these ketones is rate controlling, for the more acidic ketone, acetophenone, is completely protonated in 80–96% sulfuric acid.[8] Neither hexamethylacetone nor methyl triphenylmethyl ketone rearranged in 85% phosphoric acid.

Experimental

Materials.—Hexamethylacetone, ethyl *t*-butyl ketone and methyl *t*-amyl ketone were described previously.[2] Pentamethylacetone, b.p. 131° at 725 mm., $n^{25}D$ 1.4046, was prepared by the oxidation[9] of isopropyl-*t*-butylcarbinol and twice fractionated through a 12-plate column. 3,3,4-Trimethyl-2-pentanone was obtained by dehydration of 2,3,4-trimethyl-2,3-pentanediol.[10] The material used in this study, b.p. 149° at 735 mm., $n^{24.8}D$ 1.4209–1.4210, was obtained by refractionation of a sample prepared in this Laboratory by C. R. Enyeart. Sulfuric acid solutions were prepared by diluting Baker Analyzed Reagent with distilled water. Concentrations were determined by dilution and titration with standard base. Carbon tetrachloride was fractionated through a 35-plate column to remove carbon disulfide.

Methyl Pentamethylethyl Ketone (3,3,4,4-Tetramethyl-2-pentanone).—To 1 l. of 88% sulfuric acid at 27° was added 20.5 g., 25 ml., of hexamethylacetone. The mixture was shaken, allowed to stand 4 hr. at 30° and poured onto 5 l. of crushed ice. The ketone was extracted into three 50-ml. portions of carbon tetrachloride and steam distilled along with the solvent to remove traces of sulfuric acid. Fractional distillation through a 12-plate column gave 13.1 g. (64%) of methyl pentamethylethyl ketone, b.p. 164–167°, m.p. 54–60°, containing 15% of hexamethylacetone (infrared). Two additional refractionations were required to give material boiling at 165° at 728 mm., m.p. 61–63°, free of hexamethylacetone. Purification probably would have been easier had the reaction been allowed to continue for 8 hr. Then the main impurity would have been the lower-boiling methyl isopropyl ketone.

Kinetic Studies.—A standard procedure was used for most of the experiments. Sulfuric acid (200.0 ml.) was measured at 30.0° and cooled to 27° in a 250-ml. volumetric flask. After addition of 5.00 ml. of ketone, the mixture was shaken and held at 30.0 ± 0.05° in a constant-temperature bath. Eight 25.0-ml. aliquots were removed at suitable intervals, quenched in 125 ml. of crushed ice and extracted with carbon tetrachloride in 10-ml., 10-ml. and 5-ml. portions. The first 20 ml. of extract was washed with 10 ml. of distilled water and the last 5 ml. used to wash the water layer. The extract was made up to 25.0 ml. and dried with 1 g. of Drierite. A 1:1 dilution of this solution in a 0.52-mm. cell was suitable for infrared analysis. A Perkin-Elmer model 21 spectrophotometer was employed. Analyses were made by determination of a base line with solvent in two matched cells, then by substitution of the solution for the solvent in one cell. Absorbance was measured at frequencies characteristic of each ketone present, and concentrations were determined by solution of simultaneous equations. Extinction coefficients were obtained from the slopes of absorbance curves determined from four or five concentrations of each pure ketone (Table II). Known mixtures of ketones were analyzed to a precision of ±5%.

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

(7) D. J. Cram, *ibid.*, **71**, 3863, 3875, 3883 (1949).

(8) L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **57**, 2103 (1935).

(9) L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 340.

(10) R. Locquin and L. Leers, *Bull. soc. chim. France*, **39**, 433 (1926); C. R. Enyeart, Ph.D. Thesis, The Pennsylvania State University, 1942.

This is the same precision encountered in the over-all process including extraction as was shown by a comparison of concentrations calculated from zero-time aliquots and from the weights of the samples. Because of a decrease in total ketone concentration, probably due to sulfonation, rates were not determined beyond the second half-life.

Specific rates for the rearrangements of hexamethylacetone and methyl triphenylmethyl ketone and for the cleavage of methyl pentamethylethyl ketone were determined from the slopes of log A *versus* time plots. Rate constants for the cleavage reaction also were obtained from the expression

$$k' = \frac{-2.3}{t} \log \left[\frac{A}{A_0} - \frac{B}{A_0}\left(\frac{k'}{k} - 1\right) \right]$$

where A and B are the concentrations of hexamethylacetone and methyl pentamethylethyl ketone at time t, A_0 is the initial concentration of hexamethylacetone and k is the specific rate of the rearrangement. Values were assigned to k', both sides of the equation were plotted against k' and the intersection of the two curves was determined. The values of k' were fairly constant for points near the maximum concentration of methyl pentamethylethyl ketone.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Syntheses with Triarylvinylmagnesium Bromides. α,γ-Bisdiphenylene-β-phenylallyl, a Stable Free Radical

BY C. F. KOELSCH

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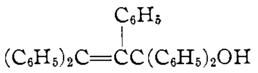
Unlike α,α,β,γ,γ-pentaphenylallyl alcohol, α,γ-bisdiphenylene-β-phenylallyl alcohol can be converted into a chloride because its geometry hinders it from cyclization to an indene. The chloride has been converted into the corresponding free radical, a substance which is highly dissociated and remarkably stable to oxygen.

Ziegler's[2] tetraphenylallyl radical, $(C_6H_5)_2C{=}CH{-}C(C_6H_5)_2$, and its substituted derivatives are particularly remarkable in that although they contain only two aryl groups on the methane carbon atom, molecular weight determinations show them to be largely monomolecular. Their deep colors in solution or in the solid state, and their sensitivity toward oxygen also attest their high degree of dissociation. This degree of dissociation, so much exceeding that of triphenylmethyl, was explained by Ziegler on the ground that as 1,1-diphenylethylene is more unsaturated than benzene, diphenylvinyl has a larger "valence requirement" than phenyl.

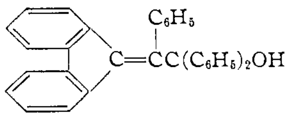
The completely phenylated allyl radical, pentaphenylallyl, as yet unknown, is of interest because of the intermediate position of the constituent triphenylvinyl group between tetraphenylethylene, whose double bond does not add bromine, and 1,1-diphenylethylene, which adds bromine readily.

A previous paper[3] described the difficulties which were encountered when an attempt was made to synthesize the pentaphenylallyl radical and suggested a means for avoiding these. When pentaphenylallyl alcohol (I) is treated with any acidic reagent, a necessary step in its conversion into a radical, it loses water to form 1,1,2,3-tetraphenylindene. α,α,β-Triphenyl-γ-diphenyleneallyl alcohol (II) is unable to lose water directly, but acidic reagents cause it to undergo an allylic rearrangement followed by the formation of 1-diphenylene-2,3-diphenylindene. α,γ-Bisdiphenylene-β-phenylallyl alcohol (III) is hindered in indene formation, since no matter whether the hydroxyl group is on carbon 1 or 3 the same steric effect tends to prevent the approach of this atom to an *ortho* position of a diphenylene group. Linkage of these positions is therefore difficult.[4] The present paper describes the successful conversion of this alcohol into a radical.

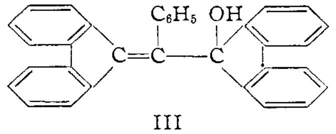


$$(C_6H_5)_2C{=}\overset{C_6H_5}{\overset{|}{C}}C(C_6H_5)_2OH$$

I



II



III

α,γ-Bisdiphenylene-β-phenylallyl alcohol treated with dilute methyl or ethyl alcoholic sulfuric acid gave nearly quantitative yields of the expected ethers. With hydrogen chloride in benzene, α,γ-bisdiphenylene-β-phenylallyl chloride was formed.

The ethers were of no value in the preparation of the radical. When they were treated with sodium amalgam in ether, they yielded deep blue solutions, believed to contain the expected sodio deriva-

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[1] The experimental work in the present paper was done in the Converse Memorial Laboratory of Harvard University in 1931–1932, when the author was a National Research Council fellow. A paper describing the work was submitted to THIS JOURNAL June 9, 1932, but it was not accepted for publication. The referee held that the properties of the chief compound, α,γ-bisdiphenylene-β-phenylallyl, could not be those of a radical.

Recent quantum mechanical calculations by M. M. Kreevoy (to be published in *J. Chem. Phys.*), however, now indicate that a radical of the structure named would be unusually resonance-stabilized, and that the properties reported for the substance in question would be not at all inconsistent with the structure claimed. A study of the thermodynamics of addition of sodium to the substance [N. B. Keevil, THIS JOURNAL **59**, 2104 (1937)] hinted that the compound might be unusually stable as a radical. And finally, recent studies by J. E. Wertz and J. L. Vivo, using electron spin resonance methods (briefly reported in OSR Technical Note 55-203, May 1955, p. 133, and to be published in detail in *J. Chem. Phys.*) indicate that the substance is highly dissociated, has an unusually narrow line-width, and is very stable. A sample kept in air 23 years is unchanged in appearance and shows a high free-radical content.

Because the structure originally suggested appears to be confirmed, and because many requests for samples and preparational details are being received, it appears desirable to publish the work now. In the interest of historical accuracy, the only important changes in the original paper are the additions of footnotes 5, 6 and 8.

[2] K. Ziegler and C. Ochs, *Ber.*, **55**, 2257 (1922); K. Ziegler, *Ann.*, **434**, 34 (1923).

[3] C. F. Koelsch, THIS JOURNAL, **54**, 3384 (1932).

[4] C. F. Koelsch, *ibid.*, **54**, 4744 (1932).