[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Tribenzotropone from a 1,3-Rearrangement[1]

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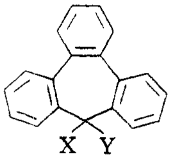
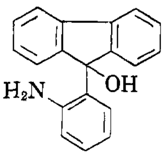
The decomposition, in acid solution, of the diazonium salt from 9-*o*-aminophenyl-9-fluorenol yields tribenzotropone (I), whose structure was determined by conversion to 4-phenylfluorenone. The properties of I and the corresponding carbinol (II) indicate that the tribenzotropylium ion (III) possesses little if any of the stabilization present in the parent tropylium system.

In connection with our interest in the properties of compounds containing carbon atoms with unusual bond angles we have attempted the synthesis of derivatives of indeno[1,2,3-*jk*]fluorene.[2] This paper describes an unusual rearrangement which was observed in the course of one such attempt. The product of this rearrangement, tribenzotropone (I), and the corresponding carbinol (II) have been examined briefly for evidence of the basic properties associated with other tropone derivatives.

The amino alcohol (IV) was obtained by a method suggested by the work of Gilman and Stuckwisch,[3] who prepared 2,*N*,*N*-trilithioaniline and converted it to anthranilic acid by carbonation. We found that the mixture of organolithium compounds formed when a 3:1 ratio of *n*-butyllithium and *o*-bromoaniline are stirred together at room temperature could be treated with excess fluorenone to yield a complex mixture of products from which IV could be obtained in low yield. The amino alcohol could not be obtained by acid extraction of an ethereal solution of the product, but by hot acid extraction of the tarry residue. This fact may merely reflect the demonstrated low solubility of IV in aqueous acids, but it may mean that IV can be isolated only after the hydrolysis of some condensation product between IV and the excess fluorenone.

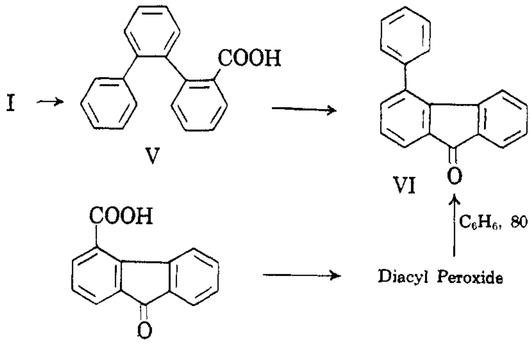


I, X + Y = O
II, X = OH; Y = H
III, X = +; Y = H



IV

The diazonium sulfate of IV decomposed slowly at room temperature and very rapidly on the steam bath to produce, in addition to the usual phenolic product, a 24% yield of tribenzotropone (I). This ketone was identified by alkali fusion to *o*-terphenyl-2-carboxylic acid (V), which could be dehydrated by thionyl chloride to 4-phenylfluorenone (VI).[4] A sample of 4-phenylfluorenone for comparison purposes was prepared by a method which we had previously found suitable for preparing 1-phenylfluorenone, *i.e.* the decomposition of the diacyl peroxide from the appropriate fluorenonecarboxylic acid. Since this appears to be the first example of the use of a ketoperoxide as an arylating agent and since the synthesis of the 1-phenyl isomer was studied in more detail, both reactions are described in the Experimental section.



The work of DeTar[5] indicates that the decomposition of aryldiazonium salts in acid solution to give cyclic products or phenols involves ionic intermediates. Thus, the rearrangement of the hydroxy diazonium salt, which further work has shown occurs in a number of related compounds,[6] appears to be an example of the 1,3-shift of an aryl group to an electron-deficient carbon atom, a type of rearrangement which, so far as we know, has not been reported before. A discussion of the detailed mechanism of this reaction including the factors responsible for its occurrence will be de-

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(1) Presented before the Division of Organic Chemistry at the 131st Meeting, AMERICAN CHEMICAL SOCIETY, Miami, Fla., April 6–12, 1957.

(2) The synthesis of the closely related but less strained 2,2a,3,4-tetrahydro-1*H*-cyclopent[*cd*]indene has recently been reported by H. Rapoport and J. Z. Pasky [*J. Am. Chem. Soc.*, **78**, 3788 (1956)] who have reviewed the prior attempts to prepare these compounds.

(3) H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **71**, 2933 (1949).

(4) K. Alder, J. Haydn, K. Heimbach, K. Neufang, G. Hansen, and W. Gerhard, *Ann.*, **586**, 110 (1954).

(5) D. F. DeTar and S. V. Sagmanli, *J. Am. Chem. Soc.*, **72**, 965 (1950); D. F. DeTar and D. I. Relyea, *J. Am. Chem. Soc.*, **76**, 1680 (1954).

(6) Unpublished results of Anthony J. Sisti in this laboratory.

ferred until later. It seems clear that in the present case, however, the cyclization was effectively prevented by the severe strain which would be present in the resulting ring system. It is anticipated that the rearrangement may occur to a major extent only in compounds which cannot readily cyclize.

The properties of tribenzotropone (I) are in accord with the theoretical prediction[7] and the other experimental observations[8,9] that fusion of benzene nuclei onto the 7-membered ring decreases the stabilization provided by the 7-carbon π-electron system. In Figs. 1 and 2 the ultraviolet absorption curves of I in ethanol and in formic acid are seen to be similar, and those of the carbinol (II) in these two solvents nearly identical. In this respect I and II differ sharply from derivatives of 2,3- and 4,5-benzotropones,[10,11] which are decidedly basic toward formic acid. Both I and II are colored in concentrated sulfuric acid solution (yellow and rose, respectively). The intensity of the visible absorption bands (410 and 560 mμ) of the solutions of II in sulfuric acid more dilute than 90% is distinctly less than that of the solution in concentrated acid, indicating that pK_{R^+}[12] is approximately −15.[13] This lack of stability for the tribenzotropylium ion (III) compared to tropylium[14] (pK_{R^+} 4.8), benzotropylium[10] (pK_{R^+} 1.6), dibenzo[*ae*]tropylium[9] (pK_{R^+} −3.7) and diphenylcarbonium[12] (pK_{R^+} −13.3) ions is much more pronounced than would have been expected on electronic grounds. It is suggested that an important factor is the resistance to planarity arising from interference of the *ortho*- hydrogens as well as from the angular strain of a planar 7-membered ring.

The infrared spectrum of I indicates that the carbonyl group (1668 cm.$^{-1}$) differs little from that in 2,3,6,7,-dibenzotropone[15] and normal diaryl ketones[16] and does not resemble the highly polar carbonyl group apparently present in tropone[17] (1638 cm.$^{-1}$), 2,3-benzotropone[11] (1644 cm.$^{-1}$), 4,5-benzotropone[11] (1633), and 2,7-dimethyl-4,5-benzotropone[11] (1625 cm.$^{-1}$).

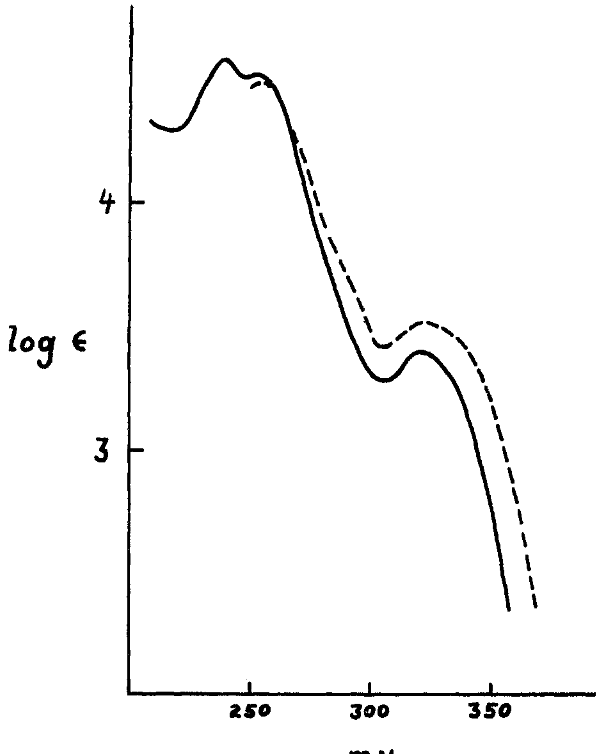

FIG. 1. ULTRAVIOLET SPECTRUM OF I IN 95% ETHANOL (——) AND IN FORMIC ACID (- - -)

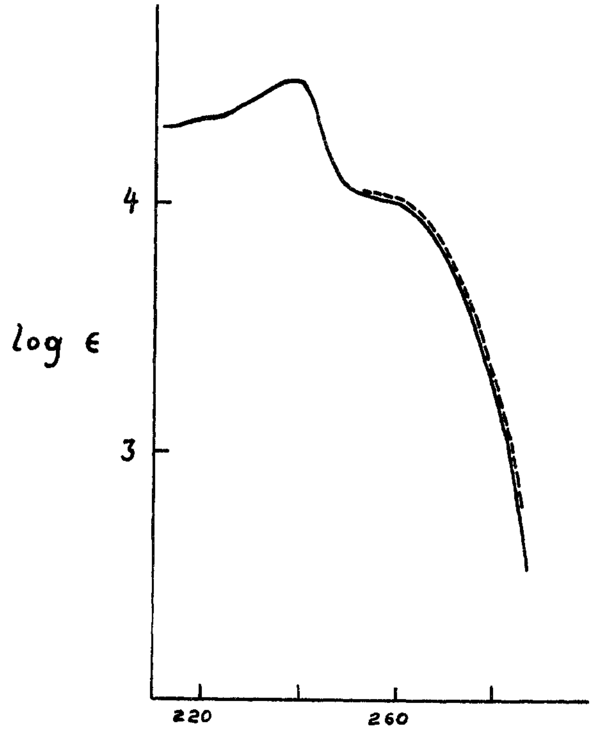

FIG. 2. ULTRAVIOLET SPECTRUM OF II IN 95% ETHANOL (——) AND IN FORMIC ACID (- - -)

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(7) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(8) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

(9) G. Berti, *J. Org. Chem.*, **22**, 231 (1957).

(10) H. H. Rennhard, E. Heilbronner, and A. Eschenmoser, *Chemistry and Industry*, 415 (1955).

(11) E. Kloster-Jensen, N. Tarköy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).

(12) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3047 (1955).

(13) A more accurate determination of pK_{R^+} was prevented by the behavior of the solutions on standing; see Experimental.

(14) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(15) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, 689 (1951).

(16) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley & Sons, Inc., New York, 1954, p. 114.

(17) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).

EXPERIMENTAL[18]

9-o-Aminophenyl-9-fluorenol. Under an atmosphere of dry nitrogen 365 ml. (0.398 mole) of a 1.09*M* ethereal solution of *n*-butyllithium[19] was added with stirring to 25.8 g. (0.150 mole) of *o*-bromoaniline in 100 ml. ether over a 1-hr. period at room temperature. The vigorous gas evolution slackened abruptly after the addition of 140 ml. of solution and the rate of addition was greatly increased at this point. The brown solution was stirred for an additional 30 min. before the addition of 36 g. (0.20 mole) of fluorenone dissolved in 500 ml. ether. The addition of the ketone required 1 hr. The mixture was allowed to stand overnight prior to hydrolysis by the addition of water. The ether layer was separated, washed with water, and extracted with 500 ml. of 10% HCl in five portions. No solid material was obtained from the acid extract upon treatment with excess alkali.

The dried ether solution was evaporated to a thick brown residue which was digested with a mixture of 100 ml. alcohol and 400 ml. 10% HCl on the steam bath for 30 min. The hot acid solution was decanted, treated with charcoal, filtered, cooled, and made alkaline. The digestion was repeated with fresh portions of acid as long as significant quantities of amine were extracted. The amine was taken up in ether and dried, and the solution was evaporated to 6.4 g. of a thick oil. The oil crystallized from benzene to give 2.28 g. of light crystalline powder, m.p. 141–143°. The analytical sample, m.p. 142.5–143.0°, was colorless.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.50; H, 5.53; N, 5.13. Found: C, 83.39; H, 5.48; N, 5.02.

Deamination of 9-o-aminophenyl-9-fluorenol. The amino alcohol (2.05 g., 0.0075 mole) was finely powdered and suspended in 70 ml. of 10% sulfuric acid. Diazotization by the addition of a portion of 0.52 g. (0.0075 mole) sodium nitrite in 5 ml. water was very slow at 0°, so most of the solution was added at room temperature, over a 45-min. period. Under these conditions some nitrogen was evolved and a small amount of oil separated during the diazotization. The mixture was then heated on the steam bath until the evolution of nitrogen ceased. The precipitated oil was taken up in ether, washed with water, and extracted with 150 ml. of 5% NaOH in three portions. The neutral material obtained by evaporation of the dried ether solution was dissolved in 1:1 benzene-petroleum ether and adsorbed on a column of alumina. Elution with more of the same solvent yielded 0.457 g. of colorless crystals of I melting at 178–179° after crystallization from benzene. λ_{max}^{EtOH} 238 (log ϵ 4.58), 254 (4.52), 321 (3.40).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 89.05, 89.15; H, 5.02, 4.72.

The *oxime*, prepared in the usual way and recrystallized from benzene, melted at 196–197°.

Anal. Calcd. for $C_{19}H_{13}NO$: N, 5.16. Found: N, 4.91, 4.87.

The alkaline extract of the crude deamination product yielded, upon acidification, 0.604 g. of resinous material, presumably *9-o-hydroxyphenyl-9-fluorenol*, which crystallized from chloroform-petroleum ether as light amber prisms, m.p. 133–134°. Material of this melting point could be obtained only with considerable loss in weight, and its purity is apparently low.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.59; H, 5.32.

Alkali fusion of tribenzotropone. The ketone (0.121 g., 0.00047 mole) was added in portions to 2 g. molten KOH at a temperature just high enough to maintain the flux. After cooling, the solid was dissolved in water and the solution was filtered and acidified. The crude acid was taken up in ether, dried, and isolated as 0.080 g. (61%) of a thick, nearly colorless oil. *S-benzylthiuronium salt,* m.p. 154.5–155.0°.

Anal. Calcd. for $C_{27}H_{24}N_2O_2S$: C, 73.61; H, 5.49; N, 6.36. Found: C, 73.68; H, 5.61; N, 6.40.

On the basis of the following experiment the acid was assigned the structure *o-terphenyl-2-carboxylic acid,* IV.

Ring closure of the acid, IV. Treatment of 0.080 g. (0.00029 mole) of IV with 2 ml. of thionyl chloride on the steam bath overnight produced, after removal of excess $SOCl_2$, a yellow residue which was adsorbed on 4 g. of alumina. Elution with a 1:2 mixture of benzene-petroleum ether yielded 0.043 g. of yellow crystals, m.p. 116–117° alone and when mixed with a sample of 4-phenylfluorenone prepared as described below. The two samples exhibited the same infrared spectrum.

1-Phenylfluorenone. Fluorenone-1-carboxylic acid[20] was converted to the acid chloride, m.p. 134–135°, as described by Goldschmiedt[21] who reported the melting point as 140°. The acid chloride (3.60 g., 0.0148 mole) was dissolved in the minimum quantity of chloroform and treated for 1.5 hr. at 0° with a cold solution of excess Na_2O_2. The precipitated crude product was washed with cold water, methanol, and chloroform, and dried in air. The yellow *peroxide* melted at 157° with decomposition, and was very slightly soluble in the common organic solvents. Recrystallization was therefore impractical. Iodometric titration required 75–80% of the theoretical quantity of thiosulfate.

The crude peroxide (2.21 g.) was suspended in benzene and refluxed 48 hr., at which time the yellow solid had disappeared. After extraction of the dark benzene solution with alkali, chromatography on alumina yielded 0.796 g. of yellow crystalline material which melted at 120–121° after crystallization from ethanol. λ_{max}^{EtOH} 253 (log ϵ 4.71), 273 (4.34), 329 (3.45).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.04; H, 4.72; Mol. Wt., 256. Found: C, 89.47, 89.26; H, 5.24, 5.21; Mol. Wt. (Rast), 266.

The *oxime* melted at 235–236°.

Anal. Calcd. for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.92; H, 5.01; N, 5.09.

From the alkaline extract of the crude product there was obtained 0.857 g. of fluorenone-1-carboxylic acid, m.p. 199–201°.

4-Phenylfluorenone, V. Fluorenone-4-carboxylic acid[22] was converted to the acid chloride[23] which, when treated in the manner described above, gave a 65% yield of yellow crystals, m.p. 116–117° when crystallized from methanol (reported[4] m.p. 112°). λ_{max}^{EtOH} 250 (4.53), 258 (4.60), 304 (shoulder, 3.52), 333 (shoulder, 3.15).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 89.15; H, 4.75.

The intermediate *peroxide*, m.p. 167° (dec.), was not purified.

Tribenzotropyl alcohol (II). The ketone (I) was reduced by sodium borohydride in either methanol or 95% ethanol to yield fine colorless needles, m.p. 118–119° (80%); λ_{max}^{alc} 222 (shoulder, log ϵ 4.34), 238 (4.51), 256 (shoulder, 4.04). Principal infrared bands of a chloroform solution were at 3577, 1487, 1479, 1438, 1190, 1126, 1063, and 1047 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.46. Found: C, 88.26; H, 5.47.

Solutions of II *in sulfuric acid.* In order to measure pK_{R^+}, solutions of II were prepared in 6 different concentrations of sulfuric acid, ranging from 84 to 96%, and the absorption

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(18) Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(19) H. Gilman and R. G. Jones, *Org. Reactions*, **6**, 352 (1951). The concentration of alkyllithium was determined as described by H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(20) J. Forrest and S. H. Tucker, *J. Chem. Soc.*, 1137 (1948); L. F. Fieser and A. Seligman, *J. Am. Chem. Soc.*, **57**, 2174 (1935).

(21) G. Goldschmiedt, *Monatsh.*, **23**, 886 (1902).

(22) R. Götz, *Monatsh.*, **23**, 32 (1904).

(23) C. Graebe and Ch. Aubin, *Ber.*, **20**, 845 (1887).

at 410 mμ was measured in 1-cm. cells with a Cary Model 11 Spectrophotometer. It was found that the absorption of solutions in 92–96% H_2SO_4 increased over a period of hours and then slowly fell. The maximum value of A/c for each solution was in the range $(0.9–1.2) \times 10^4$ liters/mole. Solutions of II in 86–89% H_2SO_4 absorbed more weakly and the intensity of the 410 mμ band began to decrease immediately, falling to nearly zero over a period of a few hours. The color of a solution in 84% H_2SO_4 was barely discernible, $A/c = 6 \times 10^2$ at 410 mμ. An approximate value of -15 for pK_{R^+} may be calculated from these data. A more precise determination was not attempted due to poor reproducibility. Similar behavior has been reported[12] for other rather unstable carbonium ions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Certain Alkylations with the Methiodide of *N*,*N*-Dimethylaminomethylferrocene. Synthesis of an α-Amino Acid Having the Ferrocene Group[1]

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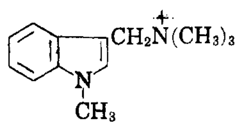
Alkylations of sodio malonic ester and sodio ethyl acetamidocyanoacetate with the methiodide of *N*,*N*-dimethylaminomethylferrocene were effected, and the products hydrolyzed and decarboxylated to form the corresponding monocarboxylic acids. The latter overall reaction produced an α-amino acid having the ferrocene group, which may be regarded as an analogue of phenylalanine.

Certain quaternary ammonium ions have been more available than the corresponding alkyl halides, and have been employed successfully in the alkylations of the sodium derivatives of active hydrogen compounds.[2] For example, quaternary ammonium ion I, which is prepared by the methylation of 1-methylgramine, has been used in the alkylation of sodio malonic ester to form II (after saponification).[3]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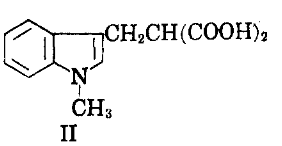
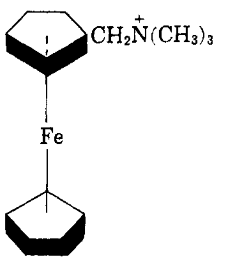
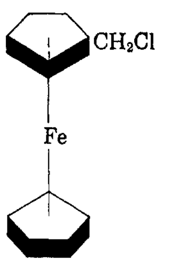

II

In the present investigation quaternary ammonium ion III was employed in the alkylations of sodio malonic ester and sodio ethyl acetamidocyanoacetate. This quaternary ammonium ion was readily prepared by the aminomethylation of ferrocene, followed by the methylation of the resulting tertiary amine.[4] On the other hand attempts to prepare the corresponding chloride (IV) by treatment of hydroxymethylferrocene[4] with thionyl chloride or hydrogen chloride produced material that failed to give the Beilstein test for halogen. Similarly the product from hydroxymethylferrocene and phosphorus tribromide appeared not to contain halogen.


III


IV

The alkylation of sodio malonic ester with quaternary ion III was effected in ethanol, and the resulting alkylation product was saponified to form dicarboxylic acid V in 67% yield. This dicarboxylic acid was decarboxylated to give monocarboxylic acid VI in 85% yield, the overall yield from III being 57%.

Similarly the alkylation of sodio ethyl acetamidocyanoacetate was effected with quaternary ion III, and the alkylation product hydrolyzed and decarboxylated to form amino acid VII in 67% yield. This α-amino acid was isolated as the monohydrate and in the anhydrous condition. It may be considered as an analog of phenylalanine.

It should be mentioned that sodio acetonitrile, prepared by means of sodium amide in a mixture of liquid ammonia and ether, failed to undergo alkylation with quaternary ammonium ion III within one hour in this medium (at −33°). Since the quaternary ammonium salt was recovered, higher temperatures appear to be required for such alkylations.

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(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) See H. R. Snyder, C. W. Smith, and J. M. Stewart, *J. Am. Chem. Soc.*, 66, 200 (1944).

(3) H. R. Snyder and E. L. Eliel, *J. Am. Chem. Soc.*, 71, 663 (1949); *see also, Org. Reactions*, VII, 99 (1953).

(4) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 22, 355 (1957).