

The angle, ω , is defined by the projection along the bond around which ω represents the torsional angle, looking from the lower-numbered to the higher-numbered atom. ω is negative if taken clockwise, positive if taken counterclockwise, from the projection of the front bond to that of the rear bond, as shown in the diagram. In any formula for the distance, r , between atoms 1 and n there will be $(3n-6)$ variables (d , θ and ω terms).

$$n = 3$$

$$r^2 = d_1^2 + d_2^2 - 2d_1d_2\cos\theta_1 \quad (1)$$

$$n = 4$$

$$r^2 = d_1^2 + d_2^2 + d_3^2 - 2d_1d_2\cos\theta_1 - 2d_2d_3\cos\theta_2 + 2d_1d_3(\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\omega_1) \quad (2)$$

$$n = 5$$

$$r^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2$$

$$(x_2 - x_1) = (d_3 - d_4\cos\theta_3)\cos\theta_2 + d_4\sin\theta_2\sin\theta_3\cos\omega_2 - (d_2 - d_1\cos\theta_1)$$

$$(y_2 - y_1) = (d_3 - d_4\cos\theta_3)\sin\theta_2 - d_4\cos\theta_2\sin\theta_3\cos\omega_2 - d_1\sin\theta_1\cos\omega_1$$

$$(z_2 - z_1) = -d_4\sin\theta_3\sin\omega_2 - d_1\sin\theta_1\sin\omega_1 \quad (3)$$

$$n = 6$$

$$r^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2$$

$$(x_2 - x_1) = d_5[\cos\theta_4(\cos\theta_2\cos\theta_3 - \sin\theta_2\sin\theta_3\cos\omega_2) -$$

$$\sin\theta_4(\sin\theta_2\sin\omega_2\sin\omega_3 + \cos\theta_2\sin\theta_3\cos\omega_3 + \sin\theta_2\cos\theta_3\cos\omega_2\cos\omega_3)] - d_4(\cos\theta_2\cos\theta_3 - \sin\theta_2\sin\theta_3\cos\omega_2) + d_3\cos\theta_2 - d_2 + d_1\cos\theta_1$$

$$(y_2 - y_1) = d_5[\cos\theta_4(\sin\theta_2\cos\theta_3 + \cos\theta_2\sin\theta_3\cos\omega_3) + \sin\theta_4(\cos\theta_2\sin\omega_2\sin\omega_3 - \sin\theta_2\sin\theta_3\cos\omega_3 + \cos\theta_2\cos\theta_3\cos\omega_2\cos\omega_3)] - d_4(\sin\theta_2\cos\theta_3 + \cos\theta_2\sin\theta_3\cos\omega_2) + d_3\sin\theta_2 - d_1\sin\theta_1\cos\omega_1$$

$$(z_2 - z_1) = d_5[-\sin\theta_4\cos\theta_3\sin\omega_2 + \sin\theta_4(\cos\omega_2\sin\omega_3 - \cos\theta_3\sin\omega_2\cos\omega_3)] + d_4\sin\theta_3\sin\omega_2 + d_1\sin\theta_1\sin\omega_1 \quad (4)$$

$n = 7$

$$r^2 = (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2$$

$$(x_2 - x_1) = d_6[\cos\theta_5(\cos\theta_2\cos\theta_4 - \sin\theta_2\sin\theta_4\cos\omega_4) - \sin\theta_5(\sin\theta_2\sin\omega_2\sin\omega_4 + \cos\theta_2\sin\theta_4\cos\omega_4 + \sin\theta_2\cos\theta_4\cos\omega_3\cos\omega_4)] - d_5(\cos\theta_2\cos\theta_4 - \sin\theta_2\sin\theta_4\cos\omega_4) + d_4\cos\theta_3 - d_3 + d_2\cos\theta_2 - d_1(\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\omega_1)$$

$$(y_2 - y_1) = d_6[\cos\theta_5(\sin\theta_2\cos\theta_4 + \cos\theta_2\sin\theta_4\cos\omega_4) + \sin\theta_5(\cos\theta_3\sin\omega_2\sin\omega_4 - \sin\theta_2\sin\theta_4\cos\omega_4 + \cos\theta_3\cos\theta_4\cos\omega_3\cos\omega_4)] - d_5(\sin\theta_2\cos\theta_4 + \cos\theta_2\sin\theta_4\cos\omega_4) + d_4\sin\theta_3 - d_2\sin\theta_2\cos\omega_2 + d_1[\cos\omega_2(\cos\theta_1\sin\theta_2 + \sin\theta_1\cos\theta_2\cos\omega_1) + \sin\theta_1\sin\omega_1\sin\omega_2]$$

$$(z_2 - z_1) = d_6[-\sin\theta_4\cos\theta_5\sin\omega_3 + \sin\theta_5(\cos\omega_3\sin\omega_4 - \cos\theta_3\sin\omega_3\cos\omega_4)] + d_5\sin\theta_4\sin\omega_3 + d_2\sin\theta_2\sin\omega_2 - d_1[\sin\omega_2(\cos\theta_1\sin\theta_2 + \sin\theta_1\cos\theta_2\cos\omega_1) - \sin\theta_1\sin\omega_1\cos\omega_2] \quad (5)$$

Alternatively, computation of the distance between any number of atoms may be accomplished in an iterative process, progressing one atom at a time using these equations to derive the coordinates of the new (n th) atom from those of the last; the over-all distance from atom 1 to n is then $r = \sqrt{x_n^2 + y_n^2 + z_n^2}$.

$$x_n = d_{n-1} - x_{n-1}\cos\theta_{n-2} - y_{n-1}\sin\theta_{n-2}\cos\omega_{n-3} + z_{n-1}\sin\theta_{n-2}\sin\omega_{n-3}$$

$$y_n = x_{n-1}\sin\theta_{n-2} - y_{n-1}\cos\theta_{n-2}\cos\omega_{n-3} + z_{n-1}\cos\theta_{n-2}\sin\omega_{n-3}$$

$$z_n = y_{n-1}\sin\omega_{n-3} + z_{n-1}\cos\omega_{n-3}$$

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Contraction of Medium Size Rings¹

By A. T. BLOMQUIST AND F. W. SCHLAEFER

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With the object of providing an auxilliary sequence to the acyloin cyclization, irradiation of α -diazo ketones derived from simple nine-, ten- and eleven-membered rings have been studied. In solvent aqueous dioxane they all have been found to contract smoothly and in fair yield to the corresponding cycloalkylcarboxylic acids, which contain one ring member less than the starting diazo ketone. This simple ring contraction thus provides an entree to strained carbocycles unavailable directly *via* the acyloin cyclization. Degradation of the cycloalkylcarboxylic acids, thus formed, to the related simple cycloalkanones has been done easily and in good yield with cyclononancarboxylic acid to give cyclononane.

Although the acyloin cyclization has proved to be a superior method for obtaining many cyclic systems, including the medium size rings, it has been found to fail in efforts to realize certain rather interesting cyclic systems. Illustrative of the latter are carbocycles such as [8]paracyclophane, 1,6-cyclodecadiyne and *trans*-5-cyclononane. It seemed desirable, therefore, to examine a synthetic route which could be used to prepare cyclic compounds of the type mentioned.

In view of the fact that little, if any, attention has been given to contraction of medium sized rings, it seemed useful here to study the photolysis

of α -diazo ketones of such rings as a synthetic method. In smaller ring systems it has been possible to obtain very highly strained rings by this method.²⁻⁴

Contraction of simple nine-, ten- and eleven-membered carbon rings has been done with fair success as outlined (Fig. 1).

Preparation of the tosylhydrazones, compounds IV, was straightforward. The α -diazoketones, compounds V, were irradiated with an ultraviolet source immediately following their preparation. The yields of pure distilled carboxylic acids were: VIa, 23%; VIb, 33%; VIc, 31%.

(2) L. Horner and E. Spietscka, *Ber.*, **88**, 934 (1954).

(3) M. P. Cava, R. L. Little and R. D. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

(4) J. Meinwald and P. Gassman, *ibid.*, **82**, 2857 (1960).

(1) This is the twenty-fourth publication concerned with the chemistry of large carbon rings. For the preceding paper in this series see A. T. Blomquist, R. E. Stahl, Y. C. Meinwald and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961).

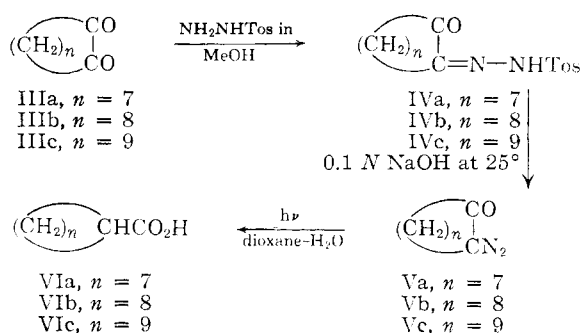
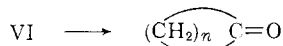


Fig. 1.

With the cycloalkylcarboxylic acids, compounds VI, available, it was of interest to work out a satisfactory degradation to the corresponding cycloalkanones. Cyclic ketones thus obtained would be useful intermediates in several studies which are of current interest to us.



A successful degradation scheme based on a rather classical sequence of transformations was worked out for the conversion of cyclononancarboxylic acid (VIb) to cyclononanone (XII) (Fig. 2).

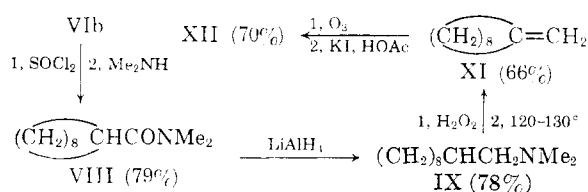


Fig. 2.

Several attempts to obtain the ketone XII directly from the acid VIb by reaction with basic permanganate were unsuccessful.⁴

Subsequent to the study reported above [9] paracyclophane-4,5-dione has been contracted to [8]-paracyclophane-4-carboxylic acid.⁵ The details of the latter transformation will be presented in a succeeding publication.

Experimental Section

Materials.—Azeloins (IIa), sebacoins (IIb) and 2-hydroxycyclohexadecanone (IIc) were all prepared by a conventional acyloin cyclization⁶ of the appropriate diethyl ester. Diethyl hendecanedioate was obtained by ethanolysis of hendecanedinitrile. The latter nitrile was in turn obtained from 1,9-nonanediol *via* 1,9-dibromononane.

A standard cupric acetate-acetic acid method⁷ was used to prepare the several cyclic diketones. Thus obtained were 1,2-cyclononanedione (IIIa) which had n_D^{25} 1.4728 and b.p. 47.5–48° (0.3 mm.) [reported⁷ n_D^{25} 1.4750 and b.p. 80–82° (3 mm.)], 1,2-cyclodecanedione (IIIb) which had b.p. 73° (0.3 mm.) and m.p. 43–44° [reported⁸ m.p. 44°] and 1,2-cyclohexadecanedione (IIIc) which had n_D^{25} 1.4720 and b.p. 79–81° (0.7 mm.) [reported⁹ n_D^{25} 1.4683 and b.p. 56–60° (0.1 mm.)].

(5) Ling-Fai Chow, private communication, Cornell University.
(6) A. T. Blomquist, R. E. Burge and A. C. Sucsy, *J. Am. Chem. Soc.*, **74**, 3636 (1952).

(7) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

(8) V. Prelog, L. Frenkiel, M. Kobelt and P. Barnum, *Helv. Chim. Acta*, **30**, 1741 (1947).

(9) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).

1,2-Cyclononanone 2-Tosylhydrazone (IVa).—A mixture of the diketone IIIa (4.3 g.) and 5.0 g. of *p*-toluenesulfonylhydrazine was refluxed 4 hr. in 50 ml. of methanol. The precipitate which resulted, after flash evaporation of 40 ml. of the methanol, was filtered, washed with 30–60° petroleum ether, and dried *in vacuo*. There thus was obtained 8.3 g. (92%) of the monohydrazone derivative IVa, m.p. 140° dec. Four recrystallizations of this product from absolute methanol gave pure IVa, m.p. 141–142° dec.

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$: C, 59.59; H, 6.89. Found: C, 59.81; H, 7.09.

1-Diazo-2-cyclononanone (Va).—In a slowly stirred mixture of 300 ml. of 0.1 *N* sodium hydroxide solution and 150 ml. of petroleum ether (b.p. 30–60°) 8.3 g. of the hydrazone IVa was stirred for 12 hr. Flash evaporation, at room temperature, of the separated petroleum ether layers gave the diazo compound Va (crude) as a yellow oil. The infrared spectrum of the latter (neat) showed bands at 4.83 and 6.12 μ .

Cyclooctanecarboxylic Acid (VIa).—The impure diazo compound Va, obtained from 8.3 g. of the hydrazone IVa, dissolved in a solution of 1000 ml. of spectrograde *p*-dioxane, 200 ml. of water and 4 g. of sodium bicarbonate was irradiated as described.⁴ Nitrogen evolution ceased in 12 hr. After flash evaporation of all solvent, the residue was diluted with 12 ml. of water. The aqueous layer obtained was acidified with 25% hydrochloric acid and extracted with ether. From the dried ether extracts there was obtained 0.91 g. (23% based on the IVa used) of the acid VIa, n_D^{20} 1.4850, b.p. 56–58° (0.04 mm.) [reported¹⁰ n_D^{20} 1.480, b.p. 142–145° (11 mm.)].

The *p*-bromophenacyl ester of the acid VIa, prepared in the usual manner,¹¹ was isolated after two recrystallizations from methanol as white needles, m.p. 88–89°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{21}\text{O}_3\text{Br}$: C, 57.79; H, 6.00. Found: C, 57.68; H, 5.87.

The 2-Tosylhydrazones of 1,2-Cyclodecanedione and 1,2-Cyclohendecanedione (Compounds IVb and IVc).—The two hydrazones were prepared by the method described for the realization of the hydrazone IVa. From 109.5 g. of sebacin and 125 g. of *p*-tosylhydrazine there was obtained 195.5 g. (89%) of the derivative IVb, m.p. 149° dec., which after three recrystallizations from methanol showed m.p. 151–152° dec.

Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$: C, 60.68; H, 7.20; S, 9.53; N, 8.32. Found: C, 60.67; H, 7.33; S, 9.48; N, 8.14.

Similarly, from 18 g. of 1,2-cyclohendecanedione (IIIc) there was obtained 29.0 g. (84%) of the monohydrazone IVc, which after two recrystallizations from methanol, had m.p. 160° dec.

Anal. Calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$: C, 61.67; H, 7.49; S, 9.15; N, 7.99. Found: C, 61.45; H, 7.37; N, 8.19; S, 9.25.

The 1-Diazo Derivatives of 2-Cyclodecanone and 2-Cyclohendecanone (Compounds Vb and Vc).—The procedure used for these two crude diazo ketones was identical with that previously described. From 54.0 g. of the hydrazone IVb, the diazo compound Vb, m.p. 56.5–57°, which showed absorption in the infrared (Nujol mull) at 4.83 and 6.13 μ was obtained. It, Vb, slowly liquified on standing at room temperature over a period of a week.

The preparation of the diazo compound Vc, only isolated as a yellow oil, showed infrared absorption (neat) at 4.84 and 6.12 μ .

Cyclononancarboxylic Acid (VIb) and Cyclodecanecarboxylic Acid (VIc).—Irradiation of the appropriate crude α -diazoketones Vb or Vc under conditions described previously afforded the expected cycloalkylcarboxylic acids. The crude diazoketone Vb, obtained from 54.0 g. of the tosylhydrazone IVb, gave 8.87 g. (33%) of cyclononancarboxylic acid VIb, n_D^{20} 1.4815, b.p. 95° (0.05 mm.) [reported¹² b.p. 114–115° (0.1 mm.)].

Anal. Calcd. for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.53; H, 10.68. Found: C, 70.64; H, 10.42.

(10) L. Ruzicka, P. Barnum and V. Prelog, *ibid.*, **34**, 401 (1951).

(11) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 200.

(12) K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953).

The *p*-bromophenacyl ester of VIb had m.p. 89–90°. *Anal.* Calcd. for $C_{18}H_{25}O_3Br$: C, 58.85; H, 6.32; Br, 21.76. Found: C, 59.06; H, 6.08; Br, 21.62.

Similarly, the crude diazoketone Vc, formed from 15.0 g. of the hydrazone VIc, produced 2.42 g. (31%) of cyclo-decanecarboxylic acid (VIc) as a white, waxy solid of b.p. 95° (0.05 mm.) and m.p. 52° (reported¹⁰ m.p. 53°).

The *p*-bromophenacyl ester of VIc was obtained as white needles, m.p. 82.5–83°.

Anal. Calcd. for $C_{19}H_{25}O_3Br$: C, 59.84; H, 6.62. Found: C, 59.63; H, 6.53.

N,N-Dimethylcyclononancarboxamide (VIII).—After 24.0 g. of thionyl chloride had been added slowly (1 hr.) to a solution of 12.0 g. of the acid VIb in 100 ml. of benzene, the total mixture was allowed to stand 12 hr. and then refluxed 2 hr., the benzene and thionyl chloride then were removed *in vacuo*. To this mixture there finally was added 25 ml. of benzene and 500 ml. of anhydrous ether, then dimethylamine was gradually passed into the slowly stirred ethereal solution, cooled to 0°. After initial removal of the amine hydrochloride, which separated, and the solvents, there was finally obtained 10.93 g. (79%) of the amide VIII, n_D^{25} 1.4939, b.p. 105–106°, and solid at 0°. The amide VIII, purified by five recrystallizations from hexane, liquefied at room temperature.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.02; H, 11.77; N, 7.10. Found: C, 73.24; H, 11.84; N, 7.09.

N,N-Dimethylaminomethylcyclononane (IX).—A solution of 6.9 g. of the amide VIII in 50 ml. of anhydrous ether was added slowly (1 hr.) at 0° to a stirred slurry of 1.5 g. of lithium aluminum hydride in 50 ml. of dry ether at 0°. After the entire mixture had been stirred for 24 hr., the excess hydride was decomposed with a solution of saturated am-

monium chloride. A standard work-up gave 5.00 g. (78%) of the amine IX, n_D^{25} 1.4700, b.p. 90° (2.4 mm.).

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.59; H, 13.77; N, 7.64. Found: C, 78.33; H, 13.58; N, 7.60.

The N-oxide (X) of the amine IX was prepared by essentially the same method previously described.¹³ The picrate derivative of X, prepared by a standard method,¹⁴ showed m.p. 119° after three recrystallizations from 95% ethanol and two from absolute methanol.

Anal. Calcd. for $C_{12}H_{25}NO_3$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.44; H, 6.60; N, 12.97; 13.07.

Methylenecyclononane (XI).—A solution of 3.60 g. of the amine oxide X in 5 ml. of water was placed in a flask filled with glass wool. The products formed upon heating this filled flask at 120–130° (3 mm.) were collected in a trap cooled to –5°. The usual simple work-up of the product gave 1.79 g. (66%) of the olefin XI, n_D^{25} 1.4782, b.p. 82° (36 mm.) [reported¹⁵ n_D^{19} 1.4808, b.p. 169°].

Cyclononanone (XII).—A solution of 1.15 g. of the exo-olefin XI in 100 ml. of absolute ethanol was treated with dry ozonized air (3% ozone) for 1 hour. Upon isolation of the ozonolysis products 0.81 g. (70%) of the ketone XII was obtained which had n_D^{25} 1.4708 and b.p. 45–47° (10 mm.) [reported⁷ n_D^{20} 1.4768 and b.p. 101–101.5°].

The semicarbazone derivative of the ketone XII, m.p. 180–181°, did not depress the m.p. of an authentic sample of cyclononanone semicarbazone¹⁶ upon admixture.

(13) A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(14) R. L. Shriner, R. C. Fuson and D. Y. Curtin, ref. 11, p. 229.

(15) F. Sorn and J. Beranek, *Chem. listy*, **47**, 708 (1953).

(16) R. L. Shriner, R. C. Fuson and D. Y. Curtin, ref. 11, p. 218

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Selective Reductions. I. The Partial Reduction of Tertiary Amides with Lithium Aluminum Hydride. A New Aldehyde Synthesis *via* the 1-Acylaziridines^{1,2}

BY HERBERT C. BROWN AND AKIRA TSUKAMOTO³

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The partial reduction of tertiary amides by lithium aluminum hydride was explored as a possible synthetic route to aldehydes. Among the amide derivatives which were examined, the 1-acylaziridines exhibited unusually favorable characteristics for this synthesis, producing the corresponding aldehydes in excellent yields. It was demonstrated that the 1-acylaziridine could be synthesized from the acid chloride and ethylenimine, and utilized *in situ* for the aldehyde synthesis. N,N-Diisopropylamides proved to be relatively resistant to reduction by lithium aluminum hydride at 0°, indicating that this group may provide a convenient means of protecting the carboxylic acid grouping from reduction in polyfunctional molecules.

The reduction of tertiary amides by lithium aluminum hydride under ordinary conditions, *i.e.*, with an excess of the reducing agent present, usually produces the corresponding tertiary amines with the same number of carbon atoms.⁴ In some cases reductive cleavage to an alcohol and a secondary amine has been observed.⁵ The controlled reduction of selected tertiary amides by lithium aluminum hydride, followed by hydrolysis, has been utilized for the synthesis of aldehydes.⁶ Thus Wittig and Hornberger obtained a series of un-

saturated aldehydes, $C_6H_5(CH=CH)_nCHO$ ($n = 1, 2, 4$ and 5) from the partial reduction of the corresponding N-acylcarbazoles with lithium aluminum hydride.⁷ Similarly, Weygand and his co-workers demonstrated that the N-methylanilides could be utilized to produce a wide variety of aldehydes in good yields (60–90%).⁸ Cyclohexanecarboxaldehyde was obtained in 80% yield by the reduction of N-cyclohexanecarboxylpiperidine.⁹ Finally, Ried and Konigstein recently have shown that the partial reduction of the 1-acyl-3,5-dimethylpyrazoles gives a general synthetic route to aldehydes from the carboxylic acids.¹⁰

(1) Previous studies in this general area have appeared in connection with other series. For a summary of these earlier publications see H. C. Brown, *J. Chem. Educ.*, **38**, 173 (1961). A preliminary communication of some of these results has been published: H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 2016 (1961).

(2) Based upon a thesis submitted by Akira Tsukamoto in June, 1959, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research assistant on a grant provided by the Eli Lilly and Co., 1957–1959.

(4) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

(5) V. M. Micović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(6) E. Mosettig, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 218–237.

(7) G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

(8) (a) W. Weygand and E. Eberhardt, *Angew. Chem.*, **64**, 458 (1952); (b) W. Weygand, E. Eberhardt, H. Linden, F. Schofer and H. Linden, *ibid.*, **65**, 525 (1953); (c) W. Weygand and H. Linden, *ibid.*, **66**, 174 (1954).

(9) M. Mousseron, R. Jacquier, M. Mousseron-Conet and R. Zagdown, *Bull. soc. chim. France*, **19**, 1042 (1952).

(10) W. Ried and F. J. Konigstein, *Angew. Chem.*, **70**, 165 (1958).