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

Bis-(β-diketones). III. Synthesis and Properties of Compounds of the Type (RCO)(R'CO)CH–Y–CH(COR)(COR')[1,2]

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RECEIVED AUGUST 13, 1958

Bis-(β-diketones) of the type (RCO)(R'CO)CH–Y–CH(COR)(COR'), for which R = R' = CH_3; Y = $(CH_2)_6$, $(CH_2)_{10}$ and 1,4-$(CH_2)_2C_6H_4$, have been prepared by the alkylation of acetylacetone with the appropriate dihalide. The alkylation procedure used in the synthesis of these compounds represents an improvement over existing methods. The infrared and ultraviolet absorption spectra of the bis-(β-diketones) are recorded.

Introduction

During the course of an investigation into the chelation behavior of bis-(β-diketones),[3–5] it was of interest to study the properties of compounds of the type (RCO)(R'CO)CH–Y–CH(COR)(COR'). The bis-(β-diketones) for which the connecting link, Y, is a substituted methylene group CHR'' are prepared readily by the interaction of a β-diketone, $RCOCH_2COR'$, and an aldehyde, R''CHO, in the presence of a suitable catalyst.[6] The bis-(β-diketones) for which the connecting link is simply a bond are prepared by the interaction of the sodium salt of a β-diketone and iodine in absolute ether or ethanol.[7–10] However, apparently only two bis-(β-diketones) have been prepared by the alkylation of a β-diketone with a dihalide. Morgan and Taylor[11] report the preparation of tetraacetylbutane, $(CH_3CO)_2CH(CH_2)_2CH(COCH_3)_2$, by the reaction of sodium acetylacetonate and a large excess of 1,2-dibromoethane (22% yield). The syntheses of 1,4-$[(CH_3CO)_2CHCH_2]_2C_6H_4$ (from sodium acetylacetonate and 1,4-bis-(chloromethyl)-benzene) are claimed,[12] but the experimental procedure is not given, nor are analytical and melting point data.

There are reported here the syntheses and properties of the bis-(β-diketones) for which R = R' = CH_3, Y = $(CH_2)_6$, $(CH_2)_{10}$ and 1,4-$(CH_2)_2C_6H_4$. The alkylation procedure used to prepare these compounds is also applicable to the synthesis of mono-alkylated β-diketones, RCOCHR''COR', as indicated by the preparation of 3-*n*-butyl-2,4-pentanedione.

Experimental

Materials.—The 1,4-bis-(bromomethyl)-benzene (white label grade) was purchased from Distillation Products Industries; 1,6-dibromohexane and 1,10-dibromodecane were obtained from Aldrich Chemical Co. All dihalides were used without further purification.

Tetraacetylethane (m.p. 191°, reported[7] m.p. 191°) and tetrabenzoylethane (m.p. 153–154.5°, reported[10] m.p. 152–153°) were prepared by other workers in this Laboratory.

Alkylation of Acetylacetone (Table I). 1,1,8,8-Tetraacetyloctane, $(CH_3CO)_2CH(CH_2)_6CH(COCH_3)_2$.—Acetylacetone (30.0 g., 0.3 mole) was added during a 10-min. period to a stirred, refluxing solution prepared from potassium (7.8 g., 0.2 g. atom) and 200 ml. of *t*-butyl alcohol. After 30 min., 1,6-dibromohexane (24.4 g., 0.1 mole) was added during a 30-min. period and, 1 hr. after the addition, 4 g. of KI was added. The reaction mixture was stirred and heated at reflux temperature until acidic to moist litmus (*ca.* 46 hr.). After three-fourths of the solvent was distilled, the residue was washed with water and extracted with benzene. The benzene extracts were dried over anhydrous Na_2SO_4 and the solvent and excess acetylacetone were distilled. The residual oil crystallized upon standing in the refrigerator. The product (α-form) (3.5 g.) was filtered and dried. Upon recrystallization from *t*-butyl alcohol–water, short, white needles were obtained.

The filtrate from the α-form was placed in the refrigerator. After about a month, the β-form crystallized as short, white needles (7.5 g.) and was recrystallized from *t*-butyl alcohol–water.

1,1,12,12-Tetraacetyldodecane, $(CH_3CO)_2CH(CH_2)_{10}CH(COCH_3)_2$, was prepared in a similar manner by the interaction of acetylacetone (30.0 g., 0.3 mole), potassium (7.8 g., 0.2 g. atom) and 1,10-dibromodecane (30.0 g., 0.1 mole); yield 11.8 g. Upon recrystallization from benzene–heptane, short, white needles were obtained.

1,4-Bis-(2,2-diacetylethyl)-benzene, 1,4-$[(CH_3CO)_2CHCH_2]_2C_6H_4$, was prepared similarly using 1,4-bis-(bromomethyl)-benzene (26.4 g., 0.1 mole). The reaction was complete within 3 hr. After three-fourths of the solvent was distilled, the solid residue was washed thoroughly with water, filtered and dried; yield 23.5 g. Upon recrystallization from *t*-butyl alcohol, white platelets were obtained.

3-*n*-Butyl-2,4-pentanedione, $(CH_3CO)_2CH(CH_2)_3CH_3$.[13]—The interaction of acetylacetone (30.0 g., 0.3 mole), *n*-butyl bromide (27.4 g., 0.2 mole) and potassium (7.8 g., 0.2 g. atom) afforded 14.3 g. (46%) of the β-diketone, b.p. 98–102° (16–17 mm.), $n^{25}D$ 1.4442; reported[14] b.p. 90–94° (10 mm.). The β-diketone was further characterized by a gray copper chelate, m.p. 185–187° (from methanol); reported[15] m.p. 186° (from benzene).

Infrared Absorption Spectra.—All spectra were obtained with a Perkin–Elmer model 21 recording infrared spectrophotometer. The spectra in the solid phase were made by incorporating the materials in potassium bromide pellets.[16] Tentative assignments are summarized in Table II.

Ultraviolet Absorption Spectra.—All spectra were obtained by means of a Warren Spectracord with a hydrogen lamp light source and using 2-cm. quartz cells. Samples were obtained by dilution of stock solutions containing 10 mg. of bis-(β-diketone) per 100 ml. of 95% ethanol. The ultraviolet absorption maxima and extinction coefficients of the bis-(β-diketones) are listed in Table III.

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[1] This research was supported in whole by the U. S. Air Force under Contract AF 33(616)-2742, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

[2] Based upon a portion of the doctoral dissertation of Dean F. Martin, The Pennsylvania State University, 1958.

[3] E. H. Holst, Doctoral Dissertation, The Pennsylvania State University, August, 1955.

[4] D. F. Martin, M. Shamma and W. C. Fernelius, THIS JOURNAL, **80**, 4891 (1958).

[5] D. F. Martin, M. Shamma and W. C. Fernelius, *ibid.*, **80**, 5851 (1958).

[6] For literature references see ref. 5.

[7] S. P. Mulliken, *Am. Chem. J.*, **15**, 523 (1893).

[8] J. C. Bailar, Jr., *et al.*, WADC Technical Report 57-391 Part II, May, 1958.

[9] E. Fischer and C. Bülow, *Ber.*, **18**, 2131 (1885).

[10] Wesenberg, Dissertation, University of Leipzig, 1898; Beilstein, Vol. 10, 1927, p. 1124.

[11] G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, 43 (1926).

[12] J. P. Wilkins and E. L. Wittbecker (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,659,711 (Nov. 17, 1953).

[13] Prepared by Mrs. Barbara B. Martin.

[14] H. Adkins, W. Kutz and D. D. Coffman, THIS JOURNAL, **52**, 3213 (1930).

[15] G. T. Morgan and E. Holmes, *J. Chem. Soc.*, 760 (1924).

[16] M. M. Stimson and J. D. O'Donnell, THIS JOURNAL, **74**, 1805 (1952); U. Scheidt and H. Reinwein, *Z. Naturforsch.*, **7B**, 270 (1952).

TABLE I

BIS-(β-DIKETONES) OF THE TYPE (RCO)(R'CO)CH-Y-CH(COR)(COR')[a,b]

R	R'	Y	M.p., °C.	Yield, %	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	CH_3	$(CH_2)_6$	45.2–45.4[c]	12	$C_{16}H_{26}O_4$	68.05	68.01	9.28	9.12
			80–82[d]	27	$C_{16}H_{26}O_4$	68.05	67.88	9.28	9.32
CH_3	CH_3	$(CH_2)_{10}$	54.2–54.5	35	$C_{20}H_{34}O_4$	70.97	70.76	10.12	10.47
CH_3	CH_3	1,4-$(CH_2)_2C_6H_4$	111.5–112	78	$C_{18}H_{22}O_4$	71.50	71.52	7.33	7.45

[a] All compounds produced a purple color with methanolic $FeCl_3$. [b] All analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. [c] α-Form. [d] β-Form.

TABLE II

INFRARED ABSORPTION OF BIS-(β-DIKETONES) OF THE TYPE (RCO)(R'CO)CH-Y-CH(COR)(COR') IN THE SOLID STATE

R	R'	Y	Hydroxyl, μ	Carbonyl, μ	Enol-chelate, μ
CH_3	CH_3	...	2.95w[a]		6.27vs,b
C_6H_5	C_6H_5	...		5.87vs 5.93vs 5.98vs	6.27s 6.33m
CH_3[b]	CH_3	CH_2	3.04m	5.88vs	6.20w 6.30w
C_6H_5[b]	C_6H_5	CH_2	2.96w	5.91vs 5.97s,sh	6.25m 6.32m
CH_3[c]	CH_3	$(CH_2)_6$		5.80vs,sh 5.88vs	6.25–6.28m
CH_3[d]	CH_3	$(CH_2)_6$		5.80m,sh 5.88s	6.25m,b
CH_3	CH_3	$(CH_2)_{10}$	2.98w	5.93vs,b	6.28m,sh
CH_3	CH_3	1,4-$(CH_2)_2C_6H_4$	2.98w	5.80vs 5.87vs	6.15–6.30m
$(CH_3CO)_2CH(CH_2)_3CH_3$[e]			2.98w	5.78s,sh 5.83s	6.24m,b

[a] s, strong; m, moderate; w, weak; b, broad; sh, shoulder. [b] Ref. 5. [c] α-Form. [d] β-Form. [e] Thin film spectrum.

TABLE III

ULTRAVIOLET ABSORPTION OF BIS-(β-DIKETONES) OF THE TYPE (RCO)(R'CO)CH-Y-CH(COR)(COR') IN 95% ETHANOL

R	R'	Y	Molarity $\times 10^5$	λ_{max}, μ	I	log ϵ_{max}
CH_3	CH_3	...	2.52	285	0.670	4.12
			5.04	285	1.43	4.15
C_6H_5	C_6H_5	...	1.12	247.5	0.860	4.89
C_6H_5[a]	C_6H_5	CH_2	1.09	249	.910	4.62
				340	.055	3.40
			2.17	249	1.685	4.59
				340	0.040	2.96
CH_3[b]	CH_3	$(CH_2)_6$	3.54	289	0.125	3.25
			5.31	291	.437	3.61
			6.38	291	.595	3.67
			7.08	292	.688	3.69
CH_3[c]	CH_3	$(CH_2)_6$	3.54	291	.363	3.71
			5.31	292	.530	3.70
			6.38	292	.670	3.72
CH_3	CH_3	$(CH_2)_{10}$	2.37	275[d]	.270	3.76
				293	.320	3.83
CH_3	CH_3	1,4-$(CH_2)_2C_6H_4$	1.66	289	.232	3.84

[a] Ref. 5. [b] α-Form. [c] β-Form. [d] Shoulder.

Discussion

Alkylation of β-Diketones.—It might be thought that the procedures used for the alkylation of malonic[17] and acetoacetic esters could be used for the alkylation of β-diketones. This does not appear to be the case. An 80–90% yield of diethyl n-butylmalonate is obtained by interaction of the ester and n-butyl bromide in the presence of ethanolic sodium ethoxide,[18] and ethyl n-butylacetoacetate is similarly prepared (69–72% yield)[19];

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[17] *Cf.* A. C. Cope, H. L. Holmes and H. O. House, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. IX, 9157, Chapter 4.

[18] R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.

[19] C. S. Marvel and F. D. Hager, *ibid.*, p. 248.

but apparently only one alkylated β-diketone, *viz.*, allylacetylacetone, has been prepared by a similar procedure (78% yield).[20]

Generally, alkylated β-diketones, (RCO)(R′CO)-CHR″, have been prepared in a steel or glass bomb by the interaction of the sodium salt of a β-diketone and an alkyl halide.[14,21–23] A second procedure consists in refluxing a mixture of the sodium salt of a β-diketone with an excess of alkyl halide either without solvent[24,25] or using a high-boiling solvent such as nitrobenzene.[26]

Only one description of the alkylation of a β-diketone with a dihalide has been found. The procedure, used to prepare tetraacetylbutane, consisted in refluxing a mixture of sodium acetylacetonate and a 26% excess of 1,2-dibromoethane.[11] The dihalide presumably acts as solvent and provides a high reaction temperature. However, the presence of a large excess of dihalide would be expected to favor the formation of a β-diketone halide, (RCO)(R′CO)CH–Y–X, which might be capable of intramolecular condensation. Furthermore the use of excess dihalide is, in many cases, a prohibitively expensive procedure and is impractical when the dihalide is a high-melting solid.

The alkylation procedure found to be successful consists in the interaction of acetylacetone (three moles) and a dihalide (one mole) in a *t*-butanolic solution of potassium *t*-butoxide (two moles). The reaction mixture is stirred at reflux temperature until acidic to moist litmus.

The alkylation procedure devised for the preparation of bis-(β-diketones) is also applicable to the synthesis of alkylated β-diketones. For example, 3-*n*-butyl-2,4-pentanedione was prepared from acetylacetone, potassium and *n*-butyl bromide (molar ratio 1.5:1:1). The 46% yield thus obtained represents an improvement over the 38% yield obtained by Adkins and co-workers,[14] who carried out the reaction of sodium acetylacetonate and *n*-butyl iodide in a glass bomb.

Infrared Absorption Spectra.—A previous study[4] has shown that bis-(β-diketones) of the type $RCOCH_2CO–Y–COCH_2COR$ exist largely in the enolic form in the solid state. This is evidenced by the presence of hydroxyl absorption bands near 2.95 μ, the presence of strong enol-chelate absorption near 6.2–6.25 μ, and the general absence of carbonyl absorption in the region 5.7–5.9 μ.

By way of contrast, most bis-(β-diketones) of the type $[(RCO)(R'CO)CH]_2CHR''$ (where R″ is not a hydrogen atom) in the solid state have strong carbonyl absorption bands in the 5.75–5.9 μ region and weak to moderate enol-chelate absorption near 6.2 μ.[5] This is interpreted as indicating that bis-(β-diketones) of the type $[(RCO)(RCO)CH]_2CHR''$ have a much lower tendency to exist in the enolic form than compounds of the type $RCOCH_2CO–Y–COCH_2COR$.

The bis-(β-diketones) listed in Table II exist in the enolic form to widely varying extents. This is indicated by the presence of hydroxyl stretching bands near 2.95 μ in the spectra of all the bis-(β-diketones) (except tetraacetyloctane) and the presence of weak to strong enol-chelate absorption bands near 6.2 μ. These bis-(β-diketones have strong carbonyl absorption bands near 5.85 μ. Tetraacetylethane lacks normal carbonyl absorption near 5.85 μ but has a high intensity enol-chelate band at 6.27 μ. Thus only this compound appears to exist largely in the enolic form in the solid state.

It is interesting to compare the spectra of the two forms of tetraacetyloctane. The respective absorption maxima of the two forms occur at about the same positions. The most prominent difference between the two spectra is the intensities of the two carbonyl bands (5.80, 5.88 μ) relative to that of the enol-chelate band (6.25 μ). The α-form has the following relative intensities: 4 (5.80 μ), 4.7 (5.88 μ) and 1 (6.25 μ); the values for the β-form: 1 (5.80 μ), 1.8 (5.88 μ) and 1 (6.25μ). Thus, from the relative intensity values, the enol content of the β-form appears to be greater than that of the α-form.

Ultraviolet Absorption Spectra.—The nature of the connecting link, Y, appears to have a marked influence on the ultraviolet absorption characteristics of the bis-(β-diketones) listed in Table III. The extinction coefficient (log ϵ_{max} 4.13–4.15) of the absorption maximum at 285 mμ of tetraacetylethane is somewhat greater than that of the enol form of acetylacetone which absorbs near 270 mμ (log ϵ_{max} 4.08).[27] Acetylacetone has an enol content of 84% in ethanol.[27] On the basis of the relative extinction coefficients, tetraacetylethane probably has an enol content less than, but comparable to, that of acetylacetone. On the other hand, tetraacetyldodecane, the two forms of tetraacetyloctane and $1,4\text{-}[(CH_3CO)_2CHCH_2]_2C_6H_4$ have extinction coefficients which are less than half that of tetraacetylethane and presumably have much lower enol contents.

Tetrabenzoylethane has a high intensity maximum at 247.5 mμ (log ϵ_{max} 4.89) but lacks absorption near 340 mμ. This is in marked contrast to dibenzoylmethane and tetrabenzoylpropane which absorb near 340 mμ (log ϵ_{max} 4.36 and 3.92, respectively). The intense absorption of dibenzoylmethane near 340 mμ is due to enol-form absorption.[28] Thus although dibenzoylmethane exists almost exclusively in the enolic form in ethanol[28] and tetrabenzoylpropane apparently has an appreciable enol content in 95% ethanol, tetrabenzoylethane apparently has little tendency to exist in the enol form in 95% ethanol.

It is interesting to compare the ultraviolet absorption of the two forms of tetraacetyloctane. The extinction coefficient of the α-form absorption maximum near 290 mμ increases almost linearly with increasing concentration. The extinction of the β-form is greater than that of the α-form and does not vary appreciably with concentration. On

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(20) J. P. English, *et al.*, THIS JOURNAL, **68**, 453 (1946).

(21) G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, 754 (1924).

(22) G. T. Morgan, *ibid.*, 2611 (1925).

(23) H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, THIS JOURNAL, **74**, 3776 (1952).

(24) G. T. Morgan and H. K. Drew, *J. Chem. Soc.*, 731 (1924).

(25) H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, THIS JOURNAL, **78**, 1838 (1956).

(26) H. F. Holtzclaw, Jr., and J. P. Collman, *ibid.*, **79**, 3318 (1957).

(27) P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924); *C. A.*, **19**, 39 (1925).

(28) R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934).

the basis of the extinction coefficients, the β-form has a higher enol content than that of the α-form. The fact that the extinction coefficient of the β-form remains fairly constant over a wide concentration range may be due to the existence of the β-form in a stable configuration.

Acknowledgments.—The authors gratefully acknowledge the help of Mr. Richard E. Dagle who made the infrared absorption spectral measurements and of Mrs. Barbara B. Martin who made the ultraviolet absorption spectral measurements. The authors are indebted to the Union Carbide Chemicals Co. for supplying the acetylacetone and to Dr. Joseph A. Dixon for supplying the 1,10-dibromodecane.

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[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

The Mechanism of the Prins Reaction[1]

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RECEIVED JULY 31, 1958

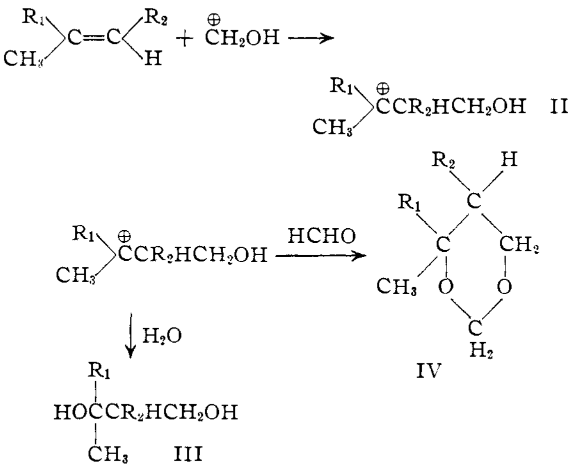
The stannic chloride-catalyzed condensation of some trisubstituted olefins with formaldehyde in chloroform was investigated. The products obtained from 2-methyl-2-butene and from 1-ethoxy-3-methyl-2-butene were 2,3-dimethyl-3-buten-1-ol and 1-ethoxy-2-hydroxymethyl-3-methyl-3-butene, respectively, and their corresponding formals. The structures of these products, established by infrared spectroscopy and chemical degradations, differ from those predicted by a previous mechanism. A mechanism involving general acid catalysis is suggested for the induced condensation of olefins with aldehydes. Catalysts such as anhydrous metal halides and aqueous acids result in different products depending on the solvolytic action of the reaction media.

The condensation of olefins with aldehydes is catalyzed by acids, heat, light and peroxides, and those catalyzed by acids are referred to generally as the Prins reaction. The reaction may be carried out in an aqueous or an anhydrous medium, and the major products consist of a 1,3-dioxane, 1,3-glycol or an unsaturated alcohol depending on the experimental conditions.[2,3] Because of this unusual versatility, the Prins reaction is useful in organic syntheses. It offers a new route to the manufacture of many organic compounds utilizing readily available petroleum products.[4] Despite the fact that the Prins reaction has been employed frequently for synthetic purposes, the condensation in aqueous and anhydrous media was believed to proceed by different mechanisms,[5–7] and different products were derived accordingly. There is some controversy as to the actual mechanism involved and experimental evidence is scarce.[5,6b]

When an olefin is condensed with formaldehyde in an aqueous medium using mineral acids as catalysts, a mixture of a 1,3-dioxane and a 1,3-glycol is produced.[8] If the condensing olefin is trisubstituted, a 1,3-diene is obtained additionally.[9] The acid-catalyzed hydrolysis of a 1,3-dioxane to the corresponding 1,3-glycol and formaldehyde is a reversible process. Since the 1,3-dioxane and the 1,3-glycol are not readily interconvertible under the conditions of the condensation, the two products must be produced independently.[7a] A mechanism (mechanism A) which involves the addition of a protonated formaldehyde molecule to the olefin was postulated.[5] The intermediate adduct II may react with formaldehyde or solvent to give a mixture of the 1,3-dioxane and the 1,3-glycol.

Mechanism A

$$\mathrm{HCHO} + \mathrm{H_3\overset{\oplus}{O}} \rightleftarrows \mathrm{\overset{\oplus}{C}H_2OH} + \mathrm{H_2O}$$



II

IV

III

When the condensation is carried out under anhydrous conditions with stannic chloride as a catalyst, an unsaturated alcohol is produced.[10] This alcohol could be dehydrated readily to the corresponding conjugated diene,[7b] and was claimed to have the general formula VI,[10,11] isomeric with that

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[1] Presented in part at the 133rd Meeting of the American Chemical Society, April, 1958, San Francisco, Calif.

[2] For a review on the Prins reaction, see E. Arundale and L. A. Mikeska, *Chem. Revs.*, **51**, 505 (1952).

[3] A. T. Blomquist, *et al.*, THIS JOURNAL, **79**, 4972 (1957), and later papers.

[4] E. Arundale and L. A. Mikeska, U. S. Patent 2,312,743, *C. A.*, **37**, 4749 (1943); E. Arundale and L. A. Mikeska, U. S. Patent 2,350,485, *C. A.*, **38**, 4957 (1944); E. Rosen, U. S. Patent 2,335,029, *C. A.*, **38**, 3834 (1944).

[5] C. C. Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 45.

[6] (a) J. W. Baker, *J. Chem. Soc.*, 296 (1944); (b) J. W. Baker, *Nature*, **161**, 171 (1948).

[7] (a) Reference 2, p. 516; (b) p. 539.

[8] H. J. Prins, *Pro. Acad. Sci. Amsterdam*, **22**, 51 (1919); H. J. Prins, *J. Chem. Soc.*, **118**, 42 (1920); ref. 2, p. 507.

[9] E. Arundale and L. A. Mikeska, U. S. Patent 2,350,485, *C. A.*, **38**, 4957 (1944); R. Rosen and E. Arundale, U. S. Patent 2,368,494, *C. A.*, **39**, 4529 (1945).

[10] L. A. Mikeska and E. Arundale, U. S. Patent 2,308,192, *C. A.*, **37**, 3450 (1943); L. A. Mikeska and E. Arundale, British Patent 545,191, *C. A.*, **36**, 7030 (1942).

[11] L. A. Mikeska and E. Arundale, U. S. Patent 2,253,342, *C. A.*, **35**, 7974 (1941).