Addition of Acetyl Hypobromite to Styrene and Its Derivatives[1]

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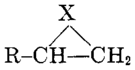
The product of the reaction of acetyl hypobromite with styrene, *p*-methylstyrene, and *p*-chlorostyrene is the 1-aryl-2-bromoethyl acetate. On distillation the 1-aryl-2-bromoethyl acetates are isomerized in part to the corresponding 2-aryl-2-bromoethyl acetates. The product of the addition of acetyl hypobromite to *p*-nitrostyrene is largely (or possibly entirely) 1-(*p*-nitrophenyl)-2-bromoethyl acetate. Some of the factors presumably involved in determining the direction of addition of the acetyl hypobromite are discussed.

Nucleophilic attack on molecules of the general formula Ia occurs preferentially at the less hindered primary position. Under conditions of acid catalysis a greater proportion of nucleophilic attack at the secondary position is observed. This pattern of relative reactivities is well established for epoxides[3] (Ia and b). In the case of styrene oxide nucleophilic attack on the positively charged species (Ib, R = C_6H_5) occurs predominantly or almost exclusively at the secondary position owing to extensive "bond-breaking" (*i.e.*, S_N1 character) in the transition state.[4]



Ia, X = O
b, X = OH^+; R = C_6H_5
c, X = Br^+; R = C_6H_5

A similar situation should be expected for the addition of positive halogen compounds to styrene, which may involve intermediates of type Ic (R = C_6H_5). For example the addition of acyl hypobromites to styrene in carbon tetrachloride has been reported to give the bromo ester corresponding to nucleophilic attack at the secondary position.[5] Similar results have been obtained in the addition of iodine monochloride[6] and the addition of aqueous *t*-butyl hypochlorite[7] to styrene.

It might be anticipated that the extent of bond breaking in the transition states for nucleophilic attack on styrene halonium ions (Ic) would be influenced by substituents on the phenyl ring. In particular electron-withdrawing substituents could be expected to reduce the tendency for incipient benzylic carbonium ion formation during nucleophilic attack and therefore promote more attack at the primary position. This effect should be most readily observed in relatively nonpolar solvents.

The addition of acetyl hypobromite to styrene and to *p*-chloro, *p*-methyl, and *p*-nitrostyrene was carried out in order to determine what control, if any, the substituents would exert on the direction of addition. Substituents in the *para* position could be expected to exert a polar effect on the reaction without appreciably altering the steric situation.[8] Abbott and Arcus[5] have reported that the reaction of styrene with acetyl hypobromite gave 1-phenyl-2-bromoethyl acetate (II) although few experimental details concerning product analysis were given.

The acetyl hypobromite additions were carried out essentially by the method of Abbott and Arcus.[5] This involves the reaction of an olefin with the reagent formed from equimolar amounts of dry silver acetate and bromine (the Prévost reaction[9]) to form the bromoacetate (eq. 1).

$$RCO_2Ag + X_2 + R'CH{=}CHR'' \longrightarrow R'CH(OCOR)CHXR'' + AgX \quad (1)$$

It has been established[9] that the product of the reaction between a dry silver salt of a carboxylic acid and halogen is an acyl hypohalite (eq. 2).

$$RCO_2Ag + X_2 \longrightarrow RCO_2X + AgX \quad (2)$$

Attempts were made to prepare independently the anticipated isomeric products of the reaction of styrene with acetyl hypobromite, namely 1-phenyl-2-bromoethyl acetate (II) and 2-bromo-2-phenylethyl acetate (III). The reaction sequences used are summarized in eq. 3 and 4.

$$C_6H_5COCH_2Br \xrightarrow{NaBH_4} C_6H_5CHOHCH_2Br \xrightarrow[(2)\ \text{distillation}]{(1)\ CH_3COCl} \underset{II}{C_6H_5CH(OCOCH_3)CH_2Br} + \underset{III}{C_6H_5CHBrCH_2OCOCH_3} \quad (3)$$

$$C_6H_5CH_2CO_2H \xrightarrow[(2)\ C_2H_5OH]{(1)\ Br_2 + P} C_6H_5CHBrCO_2C_2H_5 \xrightarrow[AlCl_3]{NaBH_4} C_6H_5CHBrCH_2OH \xrightarrow[(2)\ \text{distillation}]{(1)\ CH_3COCl} II + III \quad (4)$$

These synthetic approaches (eq. 3 and 4) led to mixtures of both isomers II and III. The mixtures had identical infrared spectra and each was reduced with lithium aluminum hydride in tetrahydrofuran to an alcohol mixture containing roughly equal amounts of 1-phenylethanol and 2-phenylethanol. It was subsequently shown that each bromoacetate isomer (II and III) rearranged to a mixture of both isomers on distillation. For example, when crude bromoacetate (II) was not distilled but was reduced directly with lithium aluminum hydride, only 1-phenylethanol was formed.[10]

The addition of acetyl hypobromite to styrene followed by hydride reduction of the crude, undistilled product yielded 1-phenylethanol as the only carbinol.

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(3) (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 106.

(4) For example, see ref. 3b, p. 112.

(5) D. C. Abbott and C. L. Arcus, *J. Chem. Soc.*, 1515 (1952).

(6) C. K. Ingold and H. G. Smith, *ibid.*, 2742 (1931); S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).

(7) W. E. Hanby and H. N. Rydon, *J. Chem. Soc.*, 114 (1946).

(8) R. Fuchs and C. A. VanderWerf, *J. Am. Chem. Soc.*, **76**, 1631 (1954).

(9) For a review see C. V. Wilson, *Org. Reactions*, **9**, 332 (1957).

(10) Identification of the phenylethanols obtained on lithium aluminum hydride reduction of the bromoacetates was generally made by gas chromatographic analysis, refractive index, and infrared spectral comparison with authentic samples.

When the bromoacetate was distilled prior to hydride reduction, approximately equal amounts of 1-phenylethanol and 2-phenylethanol were formed.[11] Addition of acetyl hypobromite to *p*-methylstyrene and *p*-chlorostyrene also gave 1-aryl-2-bromoethyl acetate without any detectable amount of its isomer, 2-aryl-2-bromoethyl acetate, as shown by reduction of the crude bromoacetate to the corresponding 1-arylethanol. In the case of the *p*-methylstyrene reaction, it was demonstrated that distillation of the bromoacetate followed by hydride reduction led to appreciable amounts of 2-(*p*-tolyl)ethanol in addition to the expected 1-(*p*-tolyl)ethanol. A similar situation is assumed to exist with the *p*-chlorostyrene system. These results are summarized in eq. 5–7.

$$p\text{-}XC_6H_4CH{=}CH_2 + CH_3CO_2Br \xrightarrow{CCl_4} \underset{\text{IV}}{p\text{-}XC_6H_4CH(OCOCH_3)CH_2Br} \quad (5)$$

$$X = H, CH_3, Cl$$

$$\text{IV} \xrightarrow{\text{LiAlH}_4,\ \text{THF}} p\text{-}XC_6H_4CHOH{-}CH_3 \quad (6)$$

$$\text{IV} \xrightarrow[\text{2. LiAlH}_4,\ \text{THF}]{\text{1. distillation}} p\text{-}XC_6H_4CHOHCH_3 + p\text{-}XC_6H_4CH_2CH_2OH \quad (7)$$

The addition of acetyl hypobromite to *p*-nitrostyrene was also investigated. Since the hydride reduction technique could not be utilized, the two bromoacetate isomers V and VI were synthesized (eq. 8 and 9) for comparison with the product of the addition reaction. Isomer V was a crystalline solid, m.p. 121–123°,

$$p\text{-}NO_2C_6H_4COCH_2Br \xrightarrow{NaBH_4} p\text{-}NO_2C_6H_4CHOHCH_2Br \xrightarrow[C_5H_5N]{CH_3COCl} \underset{\text{V}}{p\text{-}NO_2C_6H_4CH(OCOCH_3)CH_2Br} \quad (8)$$

$$p\text{-}NO_2C_6H_4CH_2CO_2H \xrightarrow[\text{3. } C_2H_5OH]{\text{1. } SOCl_2,\ \text{2. } Br_2} p\text{-}NO_2C_6H_4CHBrCO_2C_2H_5 \xrightarrow[AlCl_3]{NaBH_4} p\text{-}NO_2C_6H_4CHBrCH_2OH \xrightarrow[C_5H_5N]{CH_3COCl} \underset{\text{VI}}{p\text{-}NO_2C_6H_4CHBrCH_2OCOCH_3} \quad (9)$$

while isomer VI was a liquid which was not distilled in order to avoid rearrangement. The infrared spectra of V and VI were similar, although VI showed a strong band at 9.65 μ absent in isomer V.

The reaction of *p*-nitrostyrene with acetyl hypobromite gave a crude solid bromoacetate the infrared spectrum of which was essentially identical with that of isomer V. No absorption at 9.65 μ characteristic of VI was present. The bromoacetate formed appears to be predominantly, if not exclusively, isomer V (see Experimental).

The addition of acetyl hypobromite to olefins in carbon tetrachloride has been interpreted as involving initial attack by Br^+ to give an intermediate-bridged bromonium ion which is then opened by attack of acetate ion.[12,13] Formation of bromonium ion–acetate ion pairs which rapidly collapse to product accounts for the absence of polystyrene in the product. The 1-aryl-2-bromoethyl acetate isolated is logically the product of an ionic addition. It seems clear that there must be a considerable degree of bond breaking in the transition state involved in the attack of acetate ion on the bromonium ion.[14] This appears to be true even with a *p*-nitro substituent. Stabilization of a positive charge by a *p*-nitrophenyl group leading to attack by acetate ion at the benzylic position is favored over SN2 attack at the less sterically hindered primary position.[15]

The isomerizations encountered on heating the styrene bromoacetates are specific examples of a rather general behavior of 1,2-bromocarboxylates. For example 2,3-dibromo-1-propyl benzoate and 1,3-dibromo-2-propyl benzoate are interconverted on heating above 100°.[16] This rearrangement was shown to be truly thermal and not to require acid catalysis. Many other examples are known in the steroid field.[17]

Experimental[18]

Reaction of Styrene with Acetyl Hypobromite.—A solution of bromine (38 g., 0.24 mole) in 50 ml. of carbon tetrachloride was added over 105 min. to a stirred suspension of silver acetate (41.2 g., 0.247 mole) in 250 ml. of carbon tetrachloride. The temperature was kept at −15 ± 5° during the addition. After stirring for an additional 50 min., a solution of freshly distilled styrene (25.2 g., 0.242 mole) in 50 ml. of carbon tetrachloride was added over 15 min. at −5 ± 5°. On addition of the styrene solution the deep orange reaction mixture decolorized. After warming to room temperature the silver bromide was separated by filtration. The filtrate was washed with 10% sodium bisulfite and water and dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure leaving 49.3 g. of a pale yellow liquid residue. The lithium aluminum hydride reduction of 10 g. of this crude unheated bromoacetate is described in detail below. The remainder of the bromoacetate (39 g.) was distilled and about 30 g. of styrene bromoacetate was collected, b.p. 92–93° (0.4 mm.), $n^{20}D$ 1.5418. A residue of 2.5 g. was dissolved in carbon tetrachloride and gave no precipitate of polystyrene on addition to methanol.

The distilled styrene bromoacetate was further heated for 3 hr. under nitrogen to a maximum temperature of 131°. An aliquot was reduced with lithium aluminum hydride and the product consisted of a phenylethanol mixture (95%) and styrene (5%) as shown by gas chromatographic analysis (see below for chromatographic conditions). The alcohol mixture consisted of 50.1% 1-phenylethanol and 49.9% 2-phenylethanol. Relative areas were determined by peak height–half-width measurement.

In similar additions of acetyl hypobromite to styrene it was found that distilled styrene bromoacetate fractions with considerable refractive index variations (*e.g.*, $n^{20.5}D$ 1.5388, $n^{27}D$ 1.5381)

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[11] The fact that on hydride reduction of the distilled bromoacetate both phenylethanols were formed and that reduction of crude (not heated) bromoacetate consistently gave only 1-phenylethanol precludes the possibility that a common intermediate, such as the epoxide, is involved in the reduction of both styrene bromoacetate isomers.

[12] For example, see S. G. Levine and M. E. Wall, *J. Am. Chem. Soc.*, **81**, 2826 (1959).

[13] For a modified view of the nature of bromonium ions, see P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 443 (1962).

[14] The formation of a benzylic carbonium ion intermediate rather than a bromonium ion can equally well explain the observed results. However, the addition of benzoyl hypobromite to stilbene has been shown to occur in a stereospecific *trans* manner, and therefore likely involved a bromonium ion or similar type intermediate: see K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 6256 (1957). It therefore is reasonable to propose that by analogy a simple benzylic carbonium ion is not involved in additions of acyl hypohalites to styrene.

[15] E. L. Eliel, A. H. Goldkamp, L. E. Carosino, and M. Eberhardt [*J. Org. Chem.*, **26**, 5188 (1961)] have reported that *p*-nitrostyrene gave only 1-(*p*-nitrophenyl)ethyl bromide on reaction with HBr.

[16] J. H. C. Nayler, *J. Chem. Soc.*, 189 (1959).

[17] D. H. R. Barton and J. F. King, *ibid.*, 4398 (1958).

[18] All melting and boiling points are uncorrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The substituted styrenes were obtained from Monomer–Polymer Laboratories, Borden Chemical Co., Philadelphia 24, Pa.

had correct C, H, Br analyses and were obviously mixtures of styrene bromoacetate isomers.

Lithium Aluminum Hydride Reduction of the Crude Styrene Bromoacetate.—Lithium aluminum hydride (2.3 g., 0.06 mole) was stirred with 20 ml. of tetrahydrofuran (purified by storing over KOH and distilling from lithium aluminum hydride). A solution of 10 g. of the above crude bromoacetate in 5 ml. of tetrahydrofuran was added dropwise. The reaction mixture was then heated under reflux for 3 hr. and 45 min., cooled, and hydrolyzed with ice–water and dilute hydrochloric acid. The acid solution was saturated with salt and extracted with ether. After washing the ether extract with sodium bicarbonate and salt solution, drying over magnesium sulfate, and evaporation of the ether, the residue was distilled and 4.0 g. (80% based on bromoacetate) of 1-phenylethanol was collected, b.p. 83–84° (8 mm.). Gas chromatographic analysis of the reduction product on a 2-m. Perkin-Elmer K column at a temperature of 190° identified the product as 1-phenylethanol with a minor amount of styrene.[19] A smaller amount of unidentified material at low retention time was also present. There was no trace of 2-phenylethanol. This reduction procedure is typical of the hydride reductions of other bromoacetates carried out in this work.[20]

Attempted Preparation of 2-Bromo-2-phenylethyl Acetate.—Ethyl α-bromophenylacetate was prepared in 81% yield by the method of Anschütz,[21] b.p. 93–94° (0.8 mm.), $n^{20}\text{D}$ 1.5396; lit.[22] b.p. 103–104° (2 mm.), $n^{20}\text{D}$ 1.5395.

Reduction of ethyl α-bromophenylacetate with a mixture of sodium borohydride and aluminum chloride[23] in diglyme–ether afforded 2-bromo-2-phenylethanol. This bromohydrin was unstable on attempted distillation and was reacted directly with acetyl chloride to give a bromoacetate, b.p. 89° (0.7 mm.), $n^{26}\text{D}$ 1.5361.

Anal. Calcd. for $C_{10}H_{11}BrO_2$: C, 49.40; H, 4.56; Br, 32.87. Found: C, 49.56; H, 4.61; Br, 32.62.

Hydride reduction of the bromoacetate gave a mixture consisting of about equal amounts of 1- and 2-phenylethanol based on infrared analysis.

Attempted Preparation of 1-Phenyl-2-bromoethyl Acetate.—1-Phenyl-2-bromoethanol was prepared by the reduction of phenacyl bromide with sodium borohydride in aqueous dioxane. The bromohydrin had b.p. 100° (1.7 mm.), $n^{25}\text{D}$ 1.5772; lit.[24] b.p. 109–110° (2 mm.), $n^{17}\text{D}$ 1.5800.

Anal. Calcd. for C_8H_9BrO: C, 47.79; H, 4.53; Br, 39.73. Found: C, 47.52; H, 4.45; Br, 39.90.

Acetylation of the bromohydrin with acetyl chloride gave a bromoacetate, b.p. 94–94.5° (0.7 mm.), $n^{20}\text{D}$ 1.5388; lit.[25] b.p. 105–107° (3 mm.), $n^{20}\text{D}$ 1.5380.

Anal. Calcd. for $C_{10}H_{11}BrO_2$: C, 49.40; H, 4.56; Br, 32.87. Found: C, 49.63; H, 4.67; Br, 33.03.

Hydride reduction of the bromoacetate gave a mixture consisting of about 64% 1-phenylethanol and 36% 2-phenylethanol based on infrared analysis.

Experiments in which the product from the acetylation of 1-phenyl-2-bromoethanol was not distilled but was reduced directly with hydride gave only 1-phenylethanol with no detectable amount of 2-phenylethanol by gas chromatographic analysis.

Reaction of *p*-Methylstyrene and *p*-Chlorostyrene with Acetyl Hypobromite.—The reactions of *p*-methylstyrene and *p*-chlorostyrene with acetyl hypobromite were carried out in the same manner as that described for styrene. In both cases hydride reduction of the crude undistilled bromoacetate gave only the 1-arylethanol as shown by gas chromatographic analysis. In the case of *p*-methylstyrene, distillation of the bromoacetate followed by hydride reduction gave a mixture of 1- and 2-*p*-tolylethanols.

For gas chromatographic comparison purposes, 1-*p*-tolylethanol was prepared in 90% yield by the reduction of *p*-methylacetophenone with sodium borohydride in aqueous methanol, b.p. 98.5–99.5° (9 mm.), $n^{25}\text{D}$ 1.5211; lit.[26] b.p. 105–106° (13 mm.), $n^{25}\text{D}$ 1.5203. 2-*p*-Tolylethanol was prepared by a procedure adapted from that of Speer and Hill[27] and had b.p. 103° (6 mm.), $n^{25}\text{D}$ 1.5261; lit.[28] b.p. 105° (4 mm.), $n^{21}\text{D}$ 1.5275. Reduction of *p*-chloroacetophenone with sodium borohydride in aqueous methanol afforded 1-*p*-chlorophenylethanol in 77% yield, b.p. 106.5–107° (6 mm.). 2-*p*-Chlorophenylethanol, b.p. 117–124° (8 mm.), was obtained by reduction of *p*-chlorophenylacetic acid with lithium aluminium hydride.

1-*p*-Nitrophenyl-2-bromoethyl Acetate.—1-*p*-Nitrophenyl-2-bromoethanol was prepared by the reduction of *p*-nitrophenacyl bromide with sodium borohydride in aqueous dimethoxyethane. Recrystallization from benzene–Skellysolve B gave pale yellow crystals, m.p. 85.5–88°, lit.[29] m.p. 86–87°.

Anal. Calcd. for $C_8H_8BrNO_3$: C, 39.05; H, 3.28; Br, 32.47. Found: C, 39.30; H, 3.34; Br, 32.31.

Acetylation of the bromohydrin with acetyl chloride in pyridine gave on recrystallization from benzene–Skellysolve B pale yellow crystals, m.p. 121–123°.

Anal. Calcd. for $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.51; N, 4.86; Br, 27.73. Found: C, 41.87; H, 3.49; N, 4.66; Br, 27.71.

2-*p*-Nitrophenyl-2-bromoethyl Acetate.—*p*-Nitrophenylacetyl chloride, prepared as described by Fourneau and Nicolitch[30] was converted to ethyl *p*-nitrophenyl-α-bromoacetate by reaction with bromine followed by ethanol. Distillation gave the bromoacetate, b.p. 138–141° (0.2 mm.).

Anal. Calcd. for $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.51; N, 4.86; Br, 27.73. Found: C, 41.75; H, 3.61; N, 5.00; Br, 27.67.

Ethyl *p*-nitrophenyl-α-bromoacetate (7.1 g., 0.025 mole) was dissolved in a mixture of 20 ml. of dry ether and 10 ml. of diglyme. Sodium borohydride (0.93 g.) was added. A solution of 1.15 g. of aluminum chloride in 17 ml. of ether was added dropwise to the cooled reaction mixture. The temperature was kept below 25° during the addition. The reaction mixture was then heated for about 4 hr. at 40°, cooled, and poured into dilute hydrochloric acid. Ether extraction followed by washing and drying gave 5.2 g. of a yellow liquid. An infrared spectrum of the product showed that reduction was complete. The bromohydrin was converted to the bromoacetate with acetyl chloride in pyridine. The infrared spectrum was very similar to that of the isomer 1-*p*-nitrophenyl-2-bromoethyl acetate but differed in having a strong band at 9.65 μ.

Reaction of *p*-Nitrostyrene with Acetyl Hypobromite.—The commercial *p*-nitrostyrene[18] was purified in the following manner. The styrene was cooled to 0° and the liquid portion was decanted. The solid was dissolved in methanol, undissolved material was filtered, and the filtrate was cooled to −40°. The precipitated *p*-nitrostyrene was dried under vacuum at 0°.

A solution of bromine (4.4 g.) in 10 ml. of carbon tetrachloride was added to a stirred slurry of silver acetate (4.5 g., 0.027 mole) in 80 ml. of carbon tetrachloride at −10 to −15°. The reaction mixture was stirred at this temperature for 40 min., and a solution of *p*-nitrostyrene (4.0 g., 0.027 mole) in 20 ml. of carbon tetrachloride was added over 5 min. The reaction mixture was stirred at room temperature for 12.5 hr. and the silver bromide separated by filtration. The filtrate was washed with sodium thiosulfate solution, water, and dried. Evaporation of the solvent left 4.4 g. of a pale yellow solid. The infrared spectrum of this solid was very similar to that of 1-*p*-nitrophenyl-2-bromoethyl acetate with some differences in the relative intensities of certain bands, particularly at 9 μ. No strong absorption at 9.65 μ indicative of the isomeric 2-*p*-nitrophenyl-2-bromoethyl acetate was present. Extraction of the silver bromide precipitate with ether led to the recovery of 2.8 g. of white solid, which had an infrared spectrum identical with that of 1-*p*-nitrophenyl-2-bromoethyl acetate. The residual silver bromide weighed 4.7 g. (calculated, 5.1 g.). Recrystallization of the product from benzene–hexane gave 3.3 g. of 1-*p*-nitrophenyl-2-bromoethyl acetate, m.p. 120–121°.

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[19] The styrene observed in the gas chromatograph may have been formed by dehydration of 1-phenylethanol on the column. A commercial sample of 1-phenylethanol under the same chromatographic conditions, analyzed for 83% 1-phenylethanol and 17% styrene had exactly the same composition as found in the reduction product. A sample of 2-phenylethanol showed no styrene. The infrared spectrum of the 1-phenylethanol reduction product did not show any styrene and was almost identical with an authentic sample.

[20] In many of the hydride reductions lithium hydride was used together with lithium aluminum hydride; *cf.* J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 3664 (1948).

[21] R. Anschütz, C. Hahn, and P. Walter, *Ann.*, **354**, 126 (1907).

[22] V. M. Rodionov, N. N. Suvorov, and K. S. Mikhailov, *Akad. Nauk S.S.S.R. Inst. Organ. Khim., Sintezy Organ. Soedin., Sb.*, **2**, 162 (1952); *Chem. Abstr.*, **48**, 579*d* (1954).

[23] For reductions with $NaBH_4$–$AlCl_3$, see H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 3164 (1955); **78**, 2582 (1956).

[24] J. Read and W. G. Reid, *J. Chem. Soc.*, 1487 (1928).

[25] C. S. Marvel and N. S. Moon, *J. Am. Chem. Soc.*, **62**, 45 (1940).

[26] D. Mowry, M. Renoll, and W. F. Huber, *ibid.*, **68**, 1105 (1946).

[27] J. H. Speer and A. J. Hill, *J. Org. Chem.*, **2**, 139 (1937).

[28] N. V. Shorygina, *J. Gen. Chem. USSR*, **21**, 1273 (1951).

[29] C. O. Guss and H. G. Mautner, *J. Org. Chem.*, **16**, 887 (1951).

[30] E. Fourneau and V. Nicolitch, *Bull. soc. chim. France*, **43**, 1232 (1928).