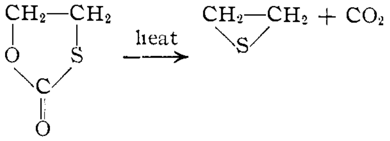
starting materials are readily available, but, after a long preparation which involves a low temperature reaction, ether extractions, and purification by distillation, a low yield is obtained. Yields ranging from 25–50% have been reported, but the method has met with little success in these Laboratories. A method has now been discovered whereby ethylene sulfide can be obtained in high yield by decomposition of monothiolethylene carbonate. The reaction is



The ethylene sulfide is pure as obtained since the only by-product is carbon dioxide. The reaction is not accompanied by polymerization and there is practically no residue. The monothiolethylene carbonate is prepared readily by the reaction of commercially available 2-mercaptoethanol with phosgene.

Among other advantages of the process is the fact that the monothiolethylene carbonate is a high-boiling, stable liquid which can be prepared and kept until ethylene sulfide is needed. Then it is only necessary to heat this intermediate in a suitable apparatus in which the ethylene sulfide can be collected. Since ethylene sulfide cannot be kept because of its tendency to polymerize, this provides a quick and convenient source of it.

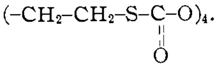
The monothiolethylene carbonate can serve as a mercaptoethylating reagent, as will be shown in a subsequent publication.

The addition of a small amount of an alkaline catalyst, such as sodium carbonate, during the preparation of ethylene sulfide results in a smooth and rapid decomposition. On the other hand, the addition of, *e.g.*, 1% *p*-toluenesulfonic acid inhibits the decomposition. The optimum amount of sodium carbonate is 1%, based on the monothiolethylene carbonate. Larger quantities cause too rapid decomposition and polymerization. Volatile catalysts cause polymerization of the ethylene sulfide in the distillation column.

When the procedure for preparing monothiolethylene carbonate is modified by stirring the pyridine, 2-mercaptoethanol, and ethyl acetate together and adding the phosgene–ethyl acetate solution, the yield of monothiolethylene carbonate is decreased and the amount of polymer is increased accordingly. If the pyridine and pyridine hydrochloride are not thoroughly removed by washing, the monothiolethylene carbonate may decompose near the end of the step in which the ethyl acetate is being removed.

Experimental

Monothiolethylene Carbonate.—Two hundred and thirty seven grams of pyridine and one hundred grams of ethyl acetate were stirred together at 10°. A solution of 150 g. of phosgene in 300 ml. of ethyl acetate was cooled to −15° and 158 g. of 2-mercaptoethanol was added to it. This cold solution was added gradually to the stirred pyridine solution. The reaction temperature was maintained at 15–20°. After all the phosgene had been added, the reaction mixture was stirred for an additional 30 minutes at 35°, after which it was washed by stirring rapidly in an equal volume of cold water containing 10 ml. of concentrated hydrochloric acid. The ethyl acetate layer was washed with an equal volume of cold water, dried over anhydrous magnesium sulfate, and then ethyl acetate was removed by distillation under reduced pressure. The oily residue was then distilled through a 10-in. Vigreux column equipped with a variable-reflux take-off head; yield, 80 g., b.p. 50–60° at 1.0–1.5 mm., n^{25}_D 1.5104; residue of polymer 47 g. Redistillation of the monothiolethylene carbonate gave 75 g. (48.1%), b.p. 47–50° at 0.08 mm., n^{25}_D 1.5104. Analysis indicated the polymer is



$$(\text{-}CH_2\text{-}CH_2\text{-}S\text{-}\underset{\underset{O}{\|}}{C}\text{-}O)_4.$$

Anal. Calcd. for $C_3H_4SO_2$: C, 34.6; H, 3.8; S, 30.7. Found: C, 34.6; H, 3.9; S, 31.1. Found for the polymeric residue: C, 34.4; H, 4.2; S, 30.1; mol. wt., 415.

Ethylene Sulfide.—Thirty-six grams of monothiolethylene carbonate and 0.36 g. of anhydrous sodium carbonate was heated to 200°. The decomposition proceeded smoothly to yield ethylene sulfide which was collected in a Dry-Ice trap (19.0 g., 88%, n^{25}_D 1.4898). There was no polymerization and practically no residue remaining in the flask.

Numerous other runs were made in which the yields varied from 80–88%.

Rochester, N. Y.

[Contribution from the Petroleum and Chemical Research Department of the M. W. Kellogg Co.]

The Chemistry of *p*-Xylylene.[1] I. The Preparation of Solutions of Pseudodiradicals[2]

By L. A. Errede[3] and B. F. Landrum

Received March 29, 1957

A method has been developed for the preparation of relatively stable solutions of pseudodiradicals such as *p*-xylene, 2-chloro-*p*-xylylene and 2-methyl-*p*-xylylene. It involves the fast flow pyrolysis of the parent aromatic hydrocarbon under low pressure and subsequent instantaneous condensation of the pyrolysis products into a solvent maintained at 78°. Polymerization occurs rapidly when the solutions are warmed to room temperature. The corresponding *p*-xylylene diiodides are obtained, however, when these solutions are added at −78° to an excess of iodine.

Introduction

Szwarc[4] was the first to observe that the fast flow pyrolysis of *p*-xylene at low pressure leads to the formation of a white polymeric material having the postulated structure of poly-*p*-xylylene. He suggested[5] that the polymer is formed *via* a series of gas phase reactions whereby C–H bonds of *p*-xylene are cleaved thermally to give *p*-xylyl radicals that disproportionate on collision to produce

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(1) Also named *p*-quinodimethane and 1,4-dimethylene-2,5-cyclohexadiene.

(2) Presented at the 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957.

(3) To whom inquiries should be sent, Minnesota Mining and Manufacturing Co., St. Paul 6, Minn.

(4) M. Szwarc, *Nature*, **160**, 403 (1947).

(5) M. Szwarc, *J. Chem. Phys.*, **16**, 319 (1951).

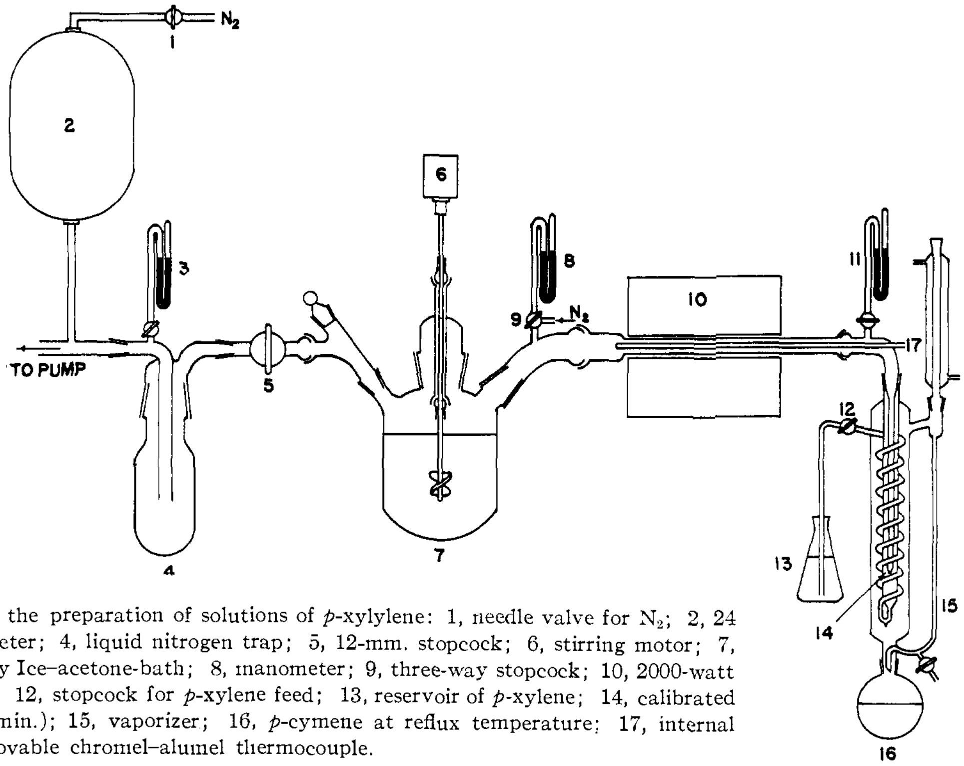
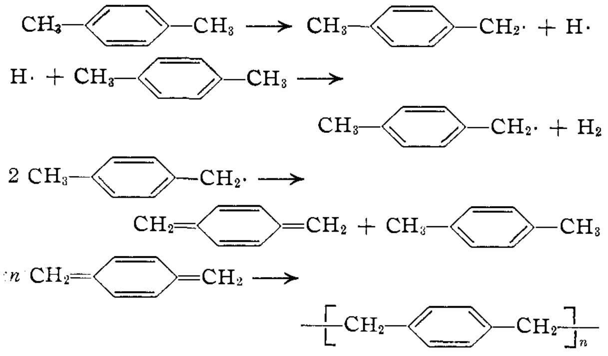


Fig. 1.—Apparatus for the preparation of solutions of *p*-xylylene: 1, needle valve for N_2; 2, 24 L surge tank; 3, manometer; 4, liquid nitrogen trap; 5, 12-mm. stopcock; 6, stirring motor; 7, monomer receiver in a Dry Ice–acetone-bath; 8, manometer; 9, three-way stopcock; 10, 2000-watt furnace; 11, manometer; 12, stopcock for *p*-xylene feed; 13, reservoir of *p*-xylene; 14, calibrated capillary (*ca.* 0.03 mole/min.); 15, vaporizer; 16, *p*-cymene at reflux temperature; 17, internal thermowell containing movable chromel–alumel thermocouple.

p-xylene and *p*-xylylene, which subsequently polymerizes on condensation.



Szwarc demonstrated the existence of *p*-xylylene in gas phase by injecting iodine vapor into the pyrolysate as it emanated from the furnace and thus obtaining *p*-xylylene diiodide.[6]

The calculations of Coulson[7] and others[8] indicate that an energy difference of only 12 kcal. separates the singlet and triplet states of *p*-xylylene and that the molecule in the ground state has a resonance energy of 38 kcal./mole. This implies that the molecules at room temperature are virtually all in the quinoidal form. They point out, however, that the electron availability at the terminal methylene groups of *p*-xylylene is almost as high in the singlet state as it is in the triplet state which accounts for the extreme reactivity of these molecules in condensed phase. Consistent with these calculations are the many publications[9–14] reporting that *p*-xylylene can only exist in gas phase and that polymerization occurs at the moment of condensation even at −190°.[10]

Results and Discussion

The work carried out in our laboratory has shown that *p*-xylylene is stable in condensed phase at extremely low temperature as well as in gas phase. This was demonstrated when a satisfactory method was devised for transferring *p*-xylylene from one stable state to the other in such a way that polymerization did not occur during the critical transition period.

The original apparatus of Szwarc[5,9] was modified as shown in Fig. 1, and *p*-xylylene, produced *via* fast flow pyrolysis of *p*-xylene, was condensed at 4 mm. pressure in hexane kept at −78°. A portion of this solution was added to an excess of iodine and *p*-xylylene diiodide was obtained in good yield. Another portion was warmed to room temperature and a copious precipitate formed throughout the solution. The polymer produced in this way was in a highly swollen state. Once dried, however, it could not be made to swell again. The infrared spectrum and X-ray diffraction pattern of this material indicated that it is the α-form of

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[6] M. Szwarc, *Disc. Faraday Soc.*, **2**, 46 (1947).

[7] C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *ibid.*, **2**, 36 (1947).

[8] Namiot, Diatkina and Syrkin, *Compt. rend. U.S.S.R.*, **48**, 233 (1945).

[9] M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

[10] L. A. Auspos, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, *ibid.*, **15**, 9 (1955).

[11] L. A. Auspos, C. W. Burman, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, *ibid.*, **15**, 19 (1955).

[12] J. R. Schaefgen, *ibid.*, **15**, 203 (1955).

[13] M. H. Kaufman, H. F. Mark and R. B. Mesrobian, *ibid.*, **13**, 3 (1954).

[14] R. S. Corley, H. C. Haas, M. W. Kane and D. I. Livingston, *ibid.*, **13**, 137 (1954).

poly-*p*-xylylene as classified by Brown and Farthing.[15]

This newly developed technique of instant quenching is a general method for the preparation of pseudodiradical solutions.[16] Thus, solutions of 2-methyl-*p*-xylylene and 2-chloro-*p*-xylylene are prepared in this way, and the corresponding diiodides are obtained when the respective solutions are added to an excess of iodine. Copolymers of these unusual monomers are prepared by mixing the appropriate solutions at −78° and then warming the resulting solution to room temperature.

p-Xylylene concentrations of 0.12 mole in toluene are produced easily since the solvent protects the accumulated pseudodiradical solute from the activating effects of the incoming hot molecules of the pyrolysate. The usual formation of poly-*p*-xylylene, however, develops on the unprotected surface of the flask above the level of the liquid. It is particularly important to avoid even a small amount of splashing of the rotating solution onto the exposed upper surface, since this creates nuclei for polymerization that continues when the splashings wash back into the monomer solution. If the formation of polymerization sites is not prevented, the concentration of monomer increases to a maximum and then falls steadily despite continued pyrolysis as shown in Fig. 2. The kinetics of polymerization are first order with respect to monomer (Fig. 3), but the specific rate of polymerization varies from one solution to another. Although the half-life of such a *p*-xylylene solution at −78° is about 21 hr., the polymerization can be arrested if the solution is frozen at −190°.

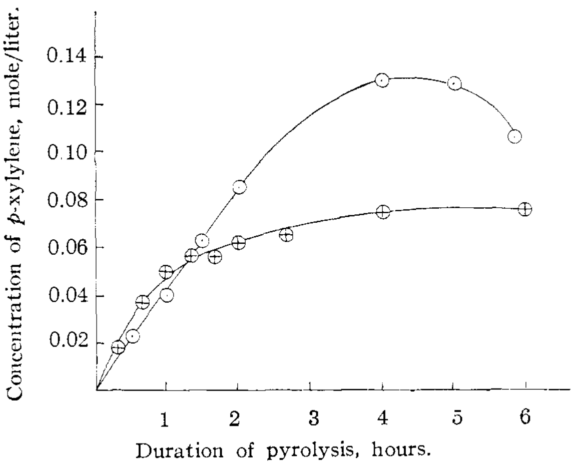

Fig. 2.—The accumulation of *p*-xylylene as a function of duration of pyrolysis: ⊙, in toluene; ⊕, in a 1:1 mixture of $CHCl_3$ and CCl_4.

When a relatively poor solvent for *p*-xylylene, such as a 1:1 mixture of $CHCl_3$ and CCl_4, is used as the liquid coolant in the monomer receiver, a saturation point is reached and the pseudodiradical co-precipitates with *p*-xylene. Under these circumstances the concentration of *p*-xylylene remains constant in spite of continued pyrolysis as shown in Fig. 2. The slurry can be separated by filtration, and the monomer, dispersed and immobilized in crystalline *p*-xylene, can be preserved indefinitely so long as the temperature is low enough to prevent melting.

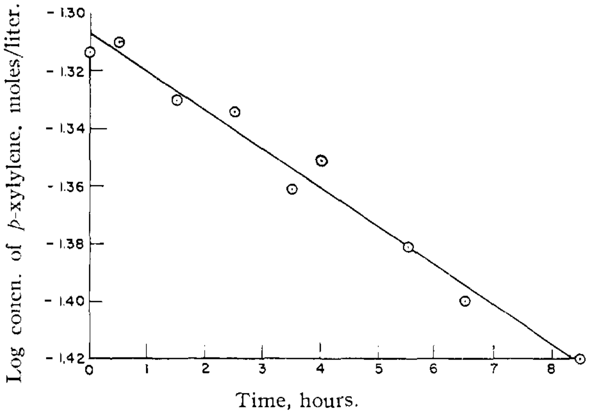

Fig. 3.—Polymerization of *p*-xylylene at −78°.

The stability of *p*-xylylene solutions is not improved by addition of the usual inhibitors even if they are present as a major component of the solvent. The free radical reactivity of the pseudodiradical is so much greater than that of the inhibitor that polymerization occurs just as if the monomer were in an inert medium.

Experimental

General Procedure.—*p*-Xylene was metered into the evacuated system shown in Fig. 1 at the rate of 0.03 mole/min. Fast flow pyrolysis occurred at 1000°, 4 mm. pressure and 0.008 sec. residence time, and the pyrolysate was condensed in 4 liters of hexane at −78°. Pyrolysis was continued until the concentration was roughly 0.1 molar (about 3 hr.). The apparatus was equilibrated to atmospheric pressure under nitrogen and a 25-cc. aliquot sample was removed by means of a rapid delivery pipet that had been pre-chilled to −78°. The sample was added to a known excess of iodine dissolved in CCl_4. The solution was warmed to room temperature and the excess iodine was back titrated with aqueous $Na_2S_2O_3$. If the concentration was not high enough, pyrolysis was resumed. Otherwise the monomer receiver was disengaged from the rest of the apparatus and the contents were separated by filtration. The clear amber solution of the filtrate was stored at −78°. The concentration of monomer was redetermined by iodometric titration of an aliquot sample just prior to its use. The concentration of monomer in the receiver as a function of duration of pyrolysis was followed by the periodic iodometric titration of a 25-cc. aliquot sample. The same technique was used to determine the half-life of a *p*-xylylene solution stored at −78° and at −190°.

***p*-Xylylene Diiodide.**—A half-liter of *p*-xylylene (0.05 molar) in hexane was added at −78° to an excess of iodine. The excess iodine was reduced with aqueous $Na_2S_2O_3$. The organic layer was washed with water and carefully evaporated to dryness under a stream of nitrogen. The residue was recrystallized from hexane to yield 3.5 g. of crude *p*-xylylene diiodide. The crude product was recrystallized from MeOH in the form of light amber needles (m.p. 176–177°; no depression with authentic sample prepared *via* the metathetical reaction of *p*-xylylene dibromide with KI in acetone). *Anal.* Calcd. for $C_8H_8I_2$: I, 70.91. Found: I, 70.9.

2-Chloro-*p*-xylylene Diiodide.—The same procedure was used to prepare 2-chloro-*p*-xylylene diiodide from 2-chloro-*p*-xylylene. The crude product was purified by recrystallization from methanol followed by sublimation under vacuum. The compound melted at 146.5–147.0°. *Anal.* Calcd. for $C_8H_7ClI_2$: C, 24.47; H, 1.80; Cl, 9.05; I, 64.68; mol. wt., 392.5. Found: C, 24.5; H, 1.84; Cl, 8.74; I, 64.4; mol. wt., 385.

2-Methyl-*p*-xylylene Diiodide.—The same procedure was used to prepare the corresponding diiodide from 2-methyl-*p*-

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(15) C. J. Brown and A. C. Farthing, *J. Chem. Soc.*, 3276 (1953).

(16) L. A. Errede and B. F. Landrum, U. S. Patent 2,777,005.

xylylene. The compound was recrystallized from methyl alcohol in the form of lemon yellow needles (m.p. 152.0–154.5° dec.). *Anal.* Calcd. for $C_9H_{10}I_2$: C, 29.04; H, 2.71; I, 68.23; mol. wt., 372.1. Found: C, 28.8; H, 2.65; I, 68.3; mol. wt., 345.

WESTFIELD, N. J.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF FRIBOURG. SWITZERLAND, AND ST. JOSEPH'S COLLEGE, INDIANA]

Reactivity of Methyl Groups in Some Derivatives of *m*-Xylene and Toluene

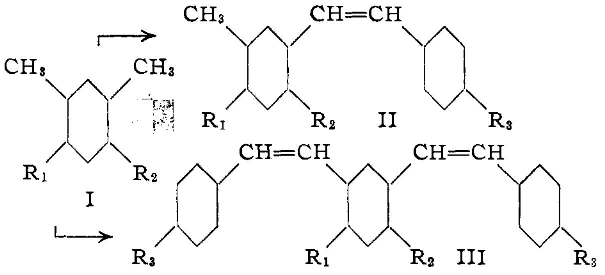
BY LOUIS CHARDONNENS AND WILLIAM J. KRAMER[1]

RECEIVED APRIL 22, 1957

Several *o*- and *p*-substituted *m*-xylenes were condensed with aromatic aldehydes. Included are condensations of some substituted toluenes, particularly some not bearing nitro groups.

It is well known that the methyl group, which is relatively inert in pure hydrocarbon compounds, becomes more reactive in the vicinity of certain substituents in the molecule. Among the rich possibilities in this field are the condensations of substituted toluene and *m*-xylene with aromatic aldehydes in the catalytic presence of piperidine to produce substituted stilbenes.[2] The present paper extends the study of these condensations in two ways: it investigates some derivatives of *m*-xylene, a study begun by Borsche[3]; and it establishes the possibility of carrying out such condensations in both toluene and *m*-xylene derivatives without the presence of the nitro group as an activating substituent.

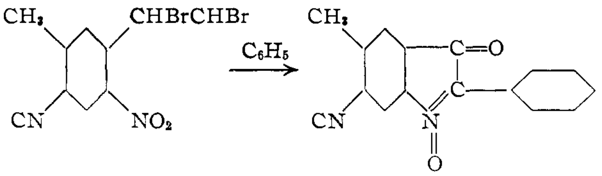
The *m*-xylene derivatives employed bore activating substituents (R_1, R_2) in *o*- and *p*-positions relative to a methyl group, the *m*-position being of little value.[4] Among the most likely substituents nitro, nitrile, benzenesulfonyl, benzoyl, *p*-nitrobenzoyl, only the first three were used with success. When R_1 and R_2 are different, two isomeric monocondensation products are possible, but only one was ever found in a particular reaction. Consistently better yields were obtained from *p*-dimethylaminobenzaldehyde than from benzaldehyde. Yields were for the most part considerably poorer than those obtained from the corresponding toluene derivatives.



Borsche had condensed 5-nitro-2,4-dimethylbenzonitrile (I, R_1 = CN, R_2 = NO_2) with benzaldehyde at 190–200° and obtained a 6% yield of a monocondensation product for which he did not establish the relative positions of the substituents. Subsequent experience has shown that better results are obtained with a longer reaction time at lower temperatures and by a more generous use of the catalyst piperidine. The reaction was therefore repeated at 145–150°, and it yielded 15% of a monocondensation product together with 4% of a double condensation product, the latter being 5-nitro-2,4-distyrylbenzonitrile.

The monocondensation product proved identical by mixed melting point with that obtained by following Borsche's directions. Its formula was determined by its ultraviolet absorption spectrum, which was compared with those of the two possible homologs 2-nitro-4-stilbenecarbonitrile[5] and 4-nitro-2-stilbenecarbonitrile.[5] The inverted chromophores –CN and –NO_2 in these two substances produce widely differing spectra, whereas the methyl group in the substance in question affected the spectrum but slightly. Borsche's compound, corresponding to the former of the two homologs, is therefore 2-nitro-5-methyl-4-stilbenecarbonitrile (II, R_1 = CN, R_2 = NO_2, R_3 = H).

It was possible in this case to check the method of proof by a reaction requiring a nitro and styryl group adjacent to each other. Addition of bromine to the stilbene double bond and exposure of the product to sunlight in pyridine produced an isatogen[6] derivative, 2-phenyl-5-methyl-6-cyanoisatogen.



The condensation of 5-nitro-2,4-dimethylbenzonitrile with *p*-dimethylaminobenzaldehyde gave a 14% yield of the double condensation product, 5-nitro-2,4-bis-(*p*-dimethylaminostyryl)-benzonitrile (III, R_3 = NMe_2). In addition there was a 13% yield of a monocondensation product. Analogy with the product just described would suggest that the methyl group adjacent to the nitro group had reacted. That the contrary had taken

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[1] St. Joseph's College; Collegeville, Ind., to whom all inquiries should be addressed.

[2] *Cf.* L. Chardonnens and H. Thomann, *Helv. Chim. Acta*, **39**, 1892 (1956), for the most recent publication on this subject.

[3] W. Borsche, *Ann.*, **386**, 351 (1912); *cf.* P. Ruggli, A. Zimmermann and R. Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).

[4] L. Chardonnens and P. Heinrich, *ibid.*, **22**, 1471 (1939).

[5] F. Ullmann and M. Gschwind, *Ber.*, **41**, 2291 (1908).

[6] P. Pfeiffer, *ibid.*, **45**, 1810, 1819 (1912); *Ann.*, **411**, 72 (1916); P. Ruggli and R. Thouvay, *Helv. Chim. Acta*, **14**, 1256 (1931); *cf.* J. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).