Anal. Calcd. for $C_{10}H_{11}O_2SCl_3$: Cl, 35.27. Found: Cl, 35.48.

The benzoate of trichloromethyl-2-thienylcarbinol was prepared according to the usual procedures of the Schotten–Baumann reaction. In this manner there was obtained from 5 g. of the carbinol 5 g. of a highly viscous oil, b. p. 175–177° at 3 mm. After standing the product began to solidify. The solid mass, crystallized twice from ethanol, yielded a white crystalline compound, m. p. 74.5°.

In a like manner the benzoate of 2,2,3-trichloro-1-(2-thienyl)-1-butanol was prepared in 60% yield. The ester distilled as a highly viscous oil, b. p. 188–191° at 1 mm., but solidified after standing for one day. Two crystallizations from ethanol gave a white crystalline product, m. p. 102°.

Anal. Calcd. for $C_{15}H_{13}O_2SCl_3$: Cl, 29.25. Found: Cl, 29.30.

Summary

1. Chloral and butyl chloral react normally with 2-thienylmagnesium bromide.

2. The secondary alcohols trichloromethyl-2-thienylcarbinol and 2,2,3-trichloro-1-(2-thienyl)-1-butanol have been synthesized via the Grignard reaction. The acetates and benzoates of these carbinols have been prepared.

AKRON, OHIO RECEIVED APRIL 14, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Some 2-Aryl-1,3-butadienes[1a]

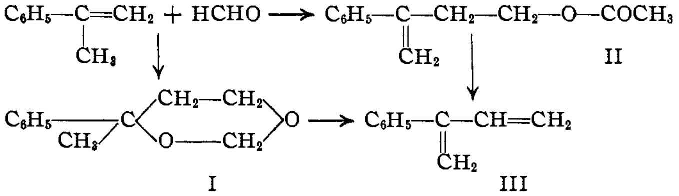
BY CHARLES C. PRICE, F. LEE BENTON AND CLAUDE J. SCHMIDLE[1b]

The synthesis of 2-phenyl-1,3-butadiene has been reported but the methods involve the use of Grignard reagents and are therefore limited in scope.[1c,2] The reaction of α-methylstyrene with formaldehyde followed by pyrolysis of the condensation products appeared to offer a more convenient and practical method of preparing 2-aryl-1,3-butadienes and the results of this investigation are herein described. While this work was in progress, Baker[3] reported that the reaction of α-methylstyrene with formaldehyde in glacial acetic acid containing 13% of sulfuric acid gave the formal of 3-phenylbutane-1,3-diol (I), the diacetate of 3-phenyl-1,3-butanediol, considerable polymeric material and an unidentified fraction.

By employing milder reaction conditions, this reaction gives fairly good yields of products which can be converted into the desired 2-phenyl-1,3-butadiene. When the amount of sulfuric acid is reduced to 0.17%, a mixture is obtained which consists chiefly of 4-phenyl-4-methyl-1,3-dioxane (I), 2-phenyl-4-acetoxy-1-butene (II) and 2-phenyl-4-acetoxy-2-butanol. In the absence of sulfuric acid, 2-phenyl-4-acetoxy-1-butene is obtained by refluxing the crude product with acetic anhydride. Substitution of orthophosphoric acid for the sulfuric acid gives 4-phenyl-4-methyl-1,3-dioxane.

2-Phenyl-1,3-butadiene (III) was obtained from the acetoxybutene by pyrolysis at 530°, by pyrolysis over a heated nichrome filament or by the action of molten potassium hydroxide and was also obtained from the dioxane by pyrolysis over a heated nichrome filament, by pyrolysis over a phosphoric acid catalyst or by heating the dioxane to 150° with sodium bisulfate. The butadiene was characterized by quantitative hydrogenation and through its Diels–Alder adduct with 1,4-naphthoquinone.

The above methods applied to *p*-methyl-α-methylstyrene and 3,4-dichloro-α-methylstyrene gave the corresponding butadienes.



Acknowledgment.—The authors are indebted to the General Tire and Rubber Company for financial assistance in the form of a fellowship (C. J. S.) and for supplying the *p*-methyl-α-methylstyrene and 3,4-dichloro-α-methylstyrene used in this investigation.

Experimental[3a]

Reactions of α-Methylstyrenes with Formaldehyde. A. Using Acetic Acid and Sulfuric Acid.—A solution of 3.6 ml. of concentrated sulfuric acid in 2250 ml. of glacial acetic acid was added to a well-stirred mixture of 330 g. of paraformaldehyde and 1180 g. of α-methylstyrene maintained at a temperature of 35–40° for three hours. The reaction mixture was poured into 3 l. of water and extracted with 2 l. of benzene. The benzene layer was washed with one l. of water, and one l. of 6 *N* sodium carbonate, 1 l. of water and then dried by azeotropic distillation. The benzene and unreacted α-methylstyrene were removed by distillation under reduced pressure and the crude product was then fractionally distilled. The fractions and some of their properties are listed in Table I. Fraction 1 crystallized upon standing at room temperature and consisted of 4-phenyl-4-methyl-1,3-dioxane. Fraction 2 was a mixture while fraction 3 con-

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(1a) Abstracted from a Ph.D. dissertation presented to the Graduate School of the University of Notre Dame by Claude J. Schmidle.

(1b) Present address: Rohm and Haas Co., Philadelphia, Pennsylvania.

(1c) Carothers and Berchet, THIS JOURNAL, **55**. 2813 (1933).

(2) Backer and Strating, *Rec. trav. chim.*, **53**, 539 (1934).

(3) Baker, *J. Chem. Soc.*, 89 (1948).

(3a) The analyses, by Micro Tech Laboratories of Skokie, Illinois, are recorded in tabular form.

TABLE I

Fraction	Weight, g.	B. p., °C. (5 mm.)	n^{20}D
1	360	87- 88	1.5246
2	156	88- 96	1.5246
3	108	97- 99	1.5244
4	50	99-111	1.5287
5	44	111-129	1.5287
6	126	129-130	1.5228
7	64	130-136	1.5198

TABLE II

ANALYTICAL RESULTS

Substance[a]	Carbon, %		Hydrogen, %		Chlorine, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
I, Phenyl[b]	74.13	73.92	7.92	7.65		
I, *p*-Tolyl	74.96	74.97	8.39	8.53		
II, Phenyl[c]	75.76	75.42	7.42	7.36		
II, *p*-Tolyl	76.44	76.08	7.90	8.07		
II, 3,4-Dichlorophenyl					27.65	27.45
III, *p*-Tolyl	83.41	82.74	6.00	6.21		
III, 3,4-Dichlorophenyl	67.21	67.33	3.95	4.06	19.85	19.66
IV, Phenyl	84.49	84.84	4.25	4.41		
IV, *p*-Tolyl	84.55	84.17	4.73	4.80		
IV, 3,4-Dichlorophenyl	67.97	68.12	2.85	3.01	20.08	20.00
V[d]	69.21	70.26	7.75	7.82		

[a] I denotes 4-aryl-4-methyl-1,3-dioxanes; II, 2-aryl-4-acetoxy-1-butenes; III, 2-aryl-1,4,4a,9a-tetrahydroanthraquinones; IV, 2-arylanthraquinones; V, 2-phenyl-4-acetoxy-2-butanol. [b] Calcd.: mol. wt., 178. Found: mol. wt., 175. [c] Calcd.: sapn. equiv., 190. Found: sapn. equiv., 196. [d] Calcd.: sapn. equiv., 208; mol. wt., 208. Found: sapn. equiv., 214; mol. wt., 220.

sisted mainly of 2-phenyl-4-acetoxy-1-butene, as indicated by saponification equivalent and quantitative hydrogenation. The separation of fraction 6, consisting largely of 2-phenyl-4-acetoxy-2-butanol and α-methylstyrene dimer, by distillation was unsatisfactory but a fairly pure sample of the butanol was obtained as a colorless liquid, b. p. 141° (6 mm.), n^{20}D 1.5161. Its identity was established by two methods. The butanol was hydrolyzed by refluxing 15 g. of it with a solution of 30 g. of sodium hydroxide in 100 ml. of water and 150 ml. of 95% ethanol for two hours, giving 8 g. of 3-phenyl-1,3-butanediol (67%), b. p. 108-110° (0.5 mm.), n^{20}D 1.5349 [lit.,[4] b. p. 130° (1 mm.), n^{20}D 1.5341]. Dehydration of 50 g. of the butanol by heating it with 100 g. of acetic anhydride and 10 g. of anhydrous sodium acetate under reflux for two hours gave 14 g. (30%) of 2-phenyl-4-acetoxy-1-butene.

A mixture of 279 g. of **3,4-dichloro-α-methylstyrene**, 60 g. of paraformaldehyde, 480 ml. of glacial acetic acid and 48 g. of concentrated sulfuric acid was stirred at 35-40° for one hour. The mixture was poured into one l. of water, the lower layer separated, washed with 500 ml. of water, 500 ml. of 6 *N* sodium carbonate, 500 ml. of water, and finally dried by azeotropic distillation with 100 ml. of benzene. The crude product was refluxed with 300 g. of acetic anhydride for three hours and then distilled under reduced pressure to yield 185 g. of 2-(3,4-dichlorophenyl)-4-acetoxy-1-butene, b. p. 135-140° (4 mm.), n^{20}D 1.5480.

B. Using Acetic Acid and Phosphoric Acid.—A mixture of one l. of glacial acetic acid, 1416 g. of **α-methylstyrene**, 336 ml. of 85% phosphoric acid and 800 g. of paraformaldehyde was stirred for two hours at 35° in a 5-l. flask. The clear solution was poured into 2 l. of water and extracted with one l. of benzene. The benzene layer was washed with one l. of water, one l. of 6 *N* sodium carbonate, one l. of water and the benzene was then removed by distillation. Vacuum distillation of the residue gave 90 g. of α-methylstyrene and 1460 g. of 4-phenyl-4-methyl-1,3-dioxane, b. p. 130-135° (15 mm.), which crystallized in colorless needles and had a camphor-like odor. The dioxane melted at 39-40° after recrystallization from low boiling petroleum ether.

A mixture of 89 g. of **p-methyl-α-methylstyrene**, 35 g. of paraformaldehyde, 150 ml. of glacial acetic acid and 20 ml. of phosphoric acid, treated as above, gave 49 g. of 4-(*p*-tolyl)-4-methyl-1,3-dioxane, b. p. 89-97° (1 mm.), which crystallized as colorless needles, m. p. 42-43°, from low petroleum ether.

C. Using Acetic Acid.—A mixture of 110 g. of paraformaldehyde, 354 g. of **α-methylstyrene** and one l. of glacial acetic acid was refluxed for three hours. Five hundred ml. of the acetic acid was removed by distillation and replaced by 500 ml. of acetic anhydride. After three hours of refluxing, the acetic acid, acetic anhydride and 40 g. of α-methylstyrene were removed by distillation under reduced pressure. Vacuum distillation of the crude product gave 350 g. of 2-phenyl-4-acetoxy-1-butene, b. p. 85-95° (1 mm.) and 140-145° (15 mm.), n^{20}D 1.5251. Hydrolysis of a sample of the butene in hot aqueous alkali gave an 85% yield of 2-phenyl-1-buten-4-ol, b. p. 89-91° (4 mm.), n^{20}D 1.5580 [lit.,[4] b. p. 123° (10 mm.), n^{20}D 1.5577].

The above procedure, applied to 130 g. of **p-methyl-α-methylstyrene**, 33 g. of paraformaldehyde and 330 ml. of glacial acetic acid, gave 96 g. of 2-(*p*-tolyl)-4-acetoxy-1-butene, b. p. 94-96° (2 mm.), n^{20}D 1.5246.

Preparation of the Butadienes.—One hundred grams of **2-phenyl-4-acetoxy-1-butene** was distilled slowly under 20 mm. pressure through a pyrolysis column, 20 mm. i. d. and 66 cm. long, packed with 0.25-inch Berl saddles and maintained at 550°. The crude product (62 g.) was redistilled, giving 33 g. of 2-phenyl-1,3-butadiene, b. p. 55-60° (15 mm.), n^{20}D 1.5484. By catalytic hydrogenation at atmospheric pressure with platinum oxide catalyst, 0.890 g. of the butadiene absorbed 302 ml. of hydrogen (corrected), amounting to 1.97 moles of hydrogen per mole of butadiene.

The pyrolysis of 30 g. of **2-(p-tolyl)-4-acetoxy-1-butene** at 500° gave 14 g. of 2-(*p*-tolyl)-1,3-butadiene, b. p. 50-55° (5 mm.), n^{20}D 1.5455.

The pyrolysis of 32 g. of **2-(3,4-dichlorophenyl)-4-acetoxy-1-butene** at 550° and 35 mm. pressure gave 11 g. of 2-(3,4-dichlorophenyl)-1,3-butadiene, b. p. 90-100° (3 mm.), n^{20}D 1.5753.

Tetrahydroanthraquinones.—A mixture of 4 g. of 1,4-naphthoquinone and 4 g. of 2-phenyl-1,3-butadiene was heated for two hours at 95°. The product was recrystallized six times from 95% ethanol, giving 2 g. of 2-phenyl-1,4,4a,9a-tetrahydroanthraquinone, m. p. 144° (lit., 142.5-143.5°,[2] 146-147°[1]).

The corresponding derivatives of 2-(*p*-tolyl)-1,3-butadiene and 2-(3,4-dichlorophenyl)-1,3-butadiene melted at 154 and 172°, respectively.

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[4] St. Pfau and Plattner, *Helv. Chim. Acta*, **15**, 1250 (1932).

Anthraquinones.—Oxygen was bubbled through a solution of 1 g. of 2-phenyltetrahydroanthraquinone in 25 ml. of 0.2 N alcoholic sodium hydroxide for one hour; the dark red color of the solution was discharged and a yellow precipitate of 2-phenylanthraquinone appeared. Upon recrystallization from 95% ethanol, the product melted at 162–163° (lit.,[1,2] 162–163°).

2-(p-Tolyl)-anthraquinone, melting at 176°, and 2-(3,4-dichlorophenyl)-anthraquinone, melting at 228°, were also prepared by the above method.

4-Phenyl-Δ^4-tetrahydrophthalic Anhydride.—The anhydride was prepared by heating 2 g. of maleic anhydride, 3 g. of 2-phenyl-1,3-butadiene and 10 ml. of anhydrous benzene at 90° for four hours. Recrystallization from benzene gave a melting point of 105° (lit.,[2] 105–105.5°).

Summary

Procedures have been developed for the preparation of 4-aryl-4-methyl-1,3-dioxanes and 2-aryl-4-acetoxy-1-butenes by the reaction of formaldehyde with α-methylstyrenes in acetic acid solution. The corresponding 2-aryl-1,3-butadienes have been prepared by the pyrolysis of these compounds, and have been characterized by their Diels–Alder adducts with 1,4-naphthoquinone.

NOTRE DAME, INDIANA RECEIVED DECEMBER 17, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aliphatic Aldehydes. I. Lauryl Aldehyde and Some New Aspects of the Stephen Reaction[1]

BY EUGENE LIEBER

Since Stephen[2] announced his "new synthesis of aldehydes" in 1925, there has been some controversy concerning its general applicability, particularly with regard to the higher aliphatic aldehydes.[3,4] In the Stephen procedure[2] anhydrous stannous chloride[5] is suspended in dry ether and saturated with dry hydrogen chloride gas until it dissolves. The nitrile is added and the criterion of the success of the reaction is based upon the precipitation from the reaction mixture of a crystalline "aldimine stannichloride," $(RCH{:}NH{\cdot}HCl)_2SnCl_4$. The complex is generally separated from the reaction mixture, washed with ether (hence *removing all ether soluble materials*) and then hydrolyzed with water or acid, usually by reflux, and the aldehyde recovered by distillation or extraction. Accordingly, failure to obtain an ether insoluble precipitate has been taken to indicate inapplicability of the Stephen reaction to the nitrile under consideration. The original Stephen procedure[2] has been modified at various times[6] because the tin complex was not obtained in the form and at the stage indicated in the original procedure. These modifications have been directed to inducing the formation of the ether insoluble complex.

The present paper summarizes the results of a study which has been made on the preparation of lauryl aldehyde (dodecyl aldehyde) from lauryl nitrile by means of the Stephen reaction. The main results of the study which will be discussed have revealed some new aspects of the Stephen reaction in which the prior criterion of an insoluble "aldimine stanni-complex" in this particular case is definitely misleading since, depending on the manner in which the reaction is conducted, both "liquid" and "solid" type lauryl nitrile–stannic chloride–hydrogen chloride complexes, which are, respectively, ether soluble and insoluble, can be isolated. Further, there seems to be no need for an *a priori* isolation of any complex whatsoever since the clear ether *solution* of a mixture of stannous chloride, hydrogen chloride and lauryl nitrile yields dimeric and trimeric lauryl aldehyde polymers when worked up after decomposition with water. The work has demonstrated the importance of examining the ether (or other solvent) solution of a Stephen reaction mixture, regardless of whether a precipitate has formed or not. The reduction of lauryl nitrile by the Stephen reaction has not been previously studied and this is the first recorded preparation of lauryl aldehyde by that means.

In the present study on the variables of the Stephen reaction the mode of attack and the main results obtained are summarized by Flow Plans A and B. Preliminary qualitative tests showed that anhydrous stannous chloride was quite insoluble in lauryl nitrile; however, by passing dry hydrogen chloride into the mixture, solution of the stannous chloride took place rapidly and the product was totally soluble in ether. By decomposing with water the presence of lauryl aldehyde was quite evident. Only a limited quantity of stannous chloride can be dissolved in lauryl nitrile, in the absence of solvent, by dry hydrogen chloride, the solution becoming very viscous, making further dissolution difficult. Quantitative experiments showed that this stage was reached at molar proportions of lauryl nitrile to hydrogen chloride to

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[1] Presented at the 115th meeting of the American Chemical Society, San Francisco, California, March 28, 1949.

[2] H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

[3] J. W. Williams, THIS JOURNAL, **61**, 2248 (1939).

[4] A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 818.

[5] H. Stephen, *J. Chem. Soc.*, 2786 (1930).

[6] (a) F. E. King and R. Robinson, *J. Chem. Soc.*, 273 (1933); (b) C. R. Harrington and R. C. G. Moggridge, *ibid.*, 443 (1939); (c) F. E. King, P. L'Ecuyer and H. T. Openshaw, *ibid.*, 352 (1936); (d) F. E. King, J. W. Clifton and H. T. Openshaw, *ibid.*, 424 (1942); (e) G. Wittig, R. Kethur, A. Klein and R. Wietbrock, *Ber.*, **69B**, 2078 (1936); (f) G. Wittig and H. Hartmann, *ibid.*, **72B**, 1387 (1939).