

produced. After the mixture had been allowed to stand overnight in the ice box, large clusters of needle-shaped crystals had separated. These melted at approximately 250° with decomposition. The yield of the oxime was 0.70 g. or 66%.

Recrystallization of the crude product from reagent alcohol (35 cc. per g.) gave lustrous plates, m. p. 256–257° (with dec.), and rotating¹⁰ -97.8° (c , 1.6; pyridine).

Anal. Calcd. for $C_9H_{15}O_2N$: N, 6.46. Found: N, 6.32, 6.53.

aldehydo-2,4,3,5-Diethylidene-L-xylose Dimethone.—Crude diethylidene-L-xylose (0.85 g.) was dissolved in a few cc. of water and added to a nearly boiling solution of 1.6 g. of dimethyldihydroresorcinol in 200 cc. of water. Within two minutes solid began to separate. After the mixture had been allowed to stand for ten minutes, 200 cc. of water was added, and the mixture was placed in the ice box overnight to complete the crystallization. The solid product was recrystallized from the smallest possible amount of a boiling mixture of reagent alcohol and water (5 parts to 3 by volume). This gave 0.76 g. of white needles, m. p. 196–200° (dec.). The yield was 39%.

Further recrystallization gave a product melting at 196–199° (dec.), and rotating¹⁰ $+40.3^\circ$ (c , 1.2; $CHCl_3$).

The product was soluble in dilute alkali and gave a coloration with ferric chloride in alcohol. It is, therefore, the dimethone rather than the dimethone "anhydride."

Anal. Calcd. for $C_{25}H_{36}O_8$: C, 64.7; H, 7.77. Found: C, 63.3, 63.6; H, 8.58, 8.14.

Summary

A method for preparing L-xylose from sorbitol by way of a diethylidenesorbitol which is oxidized by lead tetraacetate, has been restudied and the yields improved at every stage. Following oxidations in aqueous solution, the free sugar has been isolated directly in addition to the two derivatives which were obtained by the previous author. The *aldehydo-2,4,3,5-diethylidene-L-xylose* presumed previously to be an intermediate in the preparation has been isolated in a crystalline state and further characterized by preparation of two derivatives a crystalline oxime and dimethone which are described.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Vinyl Aromatic Compounds. IV. *i*-Propenylchlorobenzenes¹

BY DAVID T. MOWRY, W. FREDERICK HUBER² AND EUGENE L. RINGWALD

Recently Brooks³ has described the synthesis of a series of mono- and dichloro-styrenes. The present paper briefly describes the preparation and properties of a similar series of homologous compounds, the *o*-, *m*- and *p*-monochloro- and the 2,5- and 3,4-dichloroisopropenylbenzenes.

These materials were all prepared by the dehydration of the appropriate aryl dimethylcarbinols by the action of acetic anhydride in the presence of a trace of sulfuric acid. This is a convenient method for the dehydration of tertiary aryl carbinols of this type but does not always give high yields because of the tendency to form dimers and low molecular weight polymers.⁴ Thus, in the preparation of 3,4-dichloroisopropenylbenzene this method gave a 37% yield, while the vapor phase dehydration technique described earlier⁵ gave an 85% yield. The properties and analytical data for the unsaturated compounds are given in Table I.

The carbinols used were prepared by conventional methods by the action of methylmagnesium iodide on the appropriate acetophenone or benzoic ester. *m*-Chlorophenyldimethylcarbinol was prepared from *m*-chlorophenylmagnesium bromide and acetone. In some cases the carbinols were not isolated in a state of analytical purity because of a tendency to dehydrate upon distillation.

Experimental

Dimethylphenylcarbinols.—The preparation of 3,4-dichlorophenyldimethylcarbinol is typical. Methyl iodide (206 g., 1.46 moles) was converted to the Grignard reagent using 1 liter of dry ether and 35 g. of magnesium. Then 260 g. (1.0 mole) of 3,4-dichloroacetophenone,⁶ m. p. 74–75°, was slowly added with stirring at reflux temperature and the mixture was allowed to stand overnight. The ether solution was hydrolyzed with ice and ammonium chloride solution, washed with dilute sulfuric acid and dried over calcium chloride. Rapid distillation gave 238 g. (85%) of 3,4-dichlorophenyldimethylcarbinol, b. p. 128° (6.5 mm.), n_D^{25} 1.5519.

By similar methods were prepared 2,5-dichlorophenyldimethylcarbinol⁷ which was dehydrated in the crude form. *o*-Chlorophenyldimethylcarbinol, b. p. 112–114° (3 mm.), n_D^{25} 1.5396, was prepared by the action of the methyl Grignard reagent on methyl *o*-chlorobenzoate in 94% yield.⁸ The Grignard reagent from *m*-chlorobromobenzene reacted in the conventional manner with acetone at 5–10° to give a 78% yield of *m*-chlorophenyldimethylcarbinol,⁹ b. p. 119–120° (19 mm.), n_D^{25} 1.5352.

***i*-Propenylbenzenes.**—The dehydration of 2,5-dichlorophenyldimethylcarbinol is typical of the method used. A mixture of the carbinol (337 g., 1.64 moles), 500 g. (4.9 moles) of acetic anhydride and 1 cc. of concentrated sulfuric acid was refluxed for fifteen hours. It was quenched in several volumes of water, and the layers separated. The water layer was neutralized with sodium hydroxide and extracted with benzene. Distillation of the combined organic portions gave 272 g. (89%) of 2,5-dichloro-*i*-propenylbenzene, b. p. 63–64° (3 mm.), n_D^{25} 1.5492.

The results of similar dehydrations are given in Table I.

(6) Glynn and Linnell, *Quart. J. Pharm. Pharmacol.*, **5**, 480 (1932).

(7) Similarly prepared but not isolated by Ellingboe and Fuson, *THIS JOURNAL*, **55**, 2960–2966 (1933).

(8) Bradsher and Wert, *ibid.*, **65**, 1643 (1943), report b. p. 94° (8 mm.), for a similar preparation in 82% yield.

(9) Bergmann and Weizmann, *Trans. Faraday Soc.*, **32**, 1327 (1936), report b. p. 124–126° (18 mm.), for a sample prepared from methyl *m*-chlorobenzoate and the methyl Grignard reagent.

(1) Preceding paper of this series, *THIS JOURNAL*, **68**, 1159 (1946).

(2) Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

(3) Brooks, *ibid.*, **66**, 1295 (1944).

(4) See Staudinger and Breusch, *Ber.*, **62**, 442 (1929).

(5) Mowry, Renoll and Huber, *THIS JOURNAL*, **68**, 1105 (1946).

TABLE I

<i>i</i> -Propenylbenzene	Yield, %	B. p.,		<i>n</i> _D ²⁰	Unsatn., % ^e	Analyses, ^d %					
		°C.	Mm.			Carbon		Hydrogen		Chlorine	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>o</i> -Chloro-	50	72-73	14	1.5324	98.8	70.8	70.8	5.95	6.32	23.2	23.4
<i>m</i> -Chloro- ^a	42	98-100	24	1.5506	96.5
<i>p</i> -Chloro- ^b	77	88-89	15	1.5543	99.1
2,5-Dichloro-	89	64	3	1.5492	33.0 ^f	57.8	57.8	4.27	4.58	37.9	38.3
3,4-Dichloro-	85 ^e	92-93	4	1.5733	98.4	57.8	57.6	4.27	4.35	37.9	38.3

^a Bergmann and Weizmann, ref. 9, give b. p. 105-108° (26 mm.). ^b Ellingboe and Fuson, ref. 7, report b. p. 89° (14 mm.), *n*_D²⁰ 1.5527. ^c By bromide-bromate titration, see Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935). This procedure gives values in excess of 99% for very pure *i*-propenylbenzene. ^d Microanalyses by the Arlington Laboratories, Fairfax, Va. ^e By the vapor phase method. The acetic anhydride method gave a 37% yield. ^f Certain chlorostyrenes also give erratic and anomalously low values, see ref. 5.

Summary

ortho-, *meta*- and *para*-monochloro- and 2,5- and 3,4-dichloro-*i*-propenylbenzenes have been

synthesized by acetic anhydride dehydration of the appropriate aryldimethylcarbinols.

DAYTON, OHIO

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Substituted Styrenes. I. The Decarboxylation of Substituted Cinnamic Acids

BY CHEVES WALLING AND KATHERINE B. WOLFSTIRN

Recent descriptions of the synthesis of substituted styrenes by Marvel and co-workers¹ and by others² have, in almost every case, involved the dehydration of the appropriate phenylmethylcarbinol either in the liquid phase with potassium bisulfate or phosphorus pentoxide, or in the vapor phase over alumina. Although the method possesses great generality and frequently affords high yields, particularly when carried out over alumina,^{2b} it involves the preliminary synthesis of the carbinol, either by reduction of the appropriate acetophenone or through the Grignard reaction. We have investigated the alternative synthesis of a number of substituted styrenes through the decarboxylation of the appropriate cinnamic acids and find that, while the reaction lacks the generality of the dehydration of the phenylmethylcarbinols, in several cases it gives excellent yields. Here, since the cinnamic acids are readily obtained,³ decarboxylation represents probably the shortest and simplest laboratory method of preparation.

Although cinnamic acid may be converted to styrene in 38-41% yields by simple slow distillation,⁴ Galimberti⁵ has reported that almost quantitative yields are obtained by slow distillation of the acid with quinoline in the presence of anhydrous copper sulfate. In a series of preliminary

experiments Galimberti's observation has been confirmed and the required presence of both base and copper salt established. On refluxing alone (300°) or in the presence of copper salts cinnamic acid decomposes only slowly, while on boiling in diphenyl ether or quinoline (237°) there is no evidence of carbon dioxide evolution. However, the addition of 0.1 part by weight of copper sulfate to the acid in boiling quinoline results in an enormous increase in the rate of decarboxylation with almost quantitative conversion to styrene in less than an hour.

Next, a series of experiments was carried out modifying the base and copper salt employed to determine the optimum conditions for the decarboxylation. For this purpose *p*-chlorocinnamic acid was chosen since it gives only moderate yields of *p*-chlorostyrene by the quinoline-copper sulfate technique. Decarboxylations were carried out by slowly distilling 50 g. of acid in 100 cc. of base in the presence of 5 g. of copper salt. Results are listed in Table I, where it may be seen

TABLE I
DECARBOXYLATIONS OF *p*-CHLOROCINNAMIC ACID

Ref.	Conditions Solvent	Catalyst	Yield, % ^c	<i>p</i> -Chlorostyrene <i>n</i> _D ²⁰	M. p.
A	Quinoline	CuSO ₄	50	1.5675	-14.8°
B	Lepidine	CuSO ₄	58	1.5650	-15.2
C ^a	260-270° fraction ^b	CuSO ₄	61	1.5670	-19.5
D ^a	Quinoline	Cu(OAc) ₂	71	1.5661	-15.9
E	Quinoline	Cu powder	83	1.5664	-14.4

^a Acid added in portions over forty minutes. ^b A quinoline base fraction boiling 260-270° kindly supplied by the Reilly Tar and Chemical Corp. ^c Determined upon product obtained on steam distillation of distillate. Physical constants of pure *p*-chlorostyrene are *n*_D²⁰ 1.5650, m. p. -13°.

(1) (a) Brown and Marvel, *THIS JOURNAL*, **59**, 1176 (1937); (b) Marvel and Schertz, *ibid.*, **65**, 2054 (1943); (c) Marvel, Overberger, Allen, Johnston, Saunders, and Young, *ibid.*, 861 (1946); (d) Frank, Adams, Allen, Gander and Smith, *ibid.*, 1365 (1946).

(2) (a) Brooks, *ibid.*, **66**, 1295 (1944); (b) Mowry, Renoll and Huber, *ibid.*, 1105 (1946).

(3) The syntheses of cinnamic acids have been recently reviewed by Johnson, "The Perkin Reaction and Related Reactions," in "Organic Reactions," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1942, pp. 210-265.

(4) Abbott and Johnson, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, New York, N. Y., 1941, p. 440.

(5) Galimberti, *Bull. sci. facoltà chim. ind. Bologna*, 351 (1940).