

TABLE I

<i>i</i> -Propenylbenzene	Yield, %	B. p., °C.	Mm.	n_D^{20}	Unsatn., %	Analyses, %					
						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 ^a	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_D^{20} 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 arylidimethylcarbinols.

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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	n_D^{20}	<i>p</i> -Chlorostyrene 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

(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).

^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_D^{20} 1.5650, m. p. -13°.

TABLE II
 DECARBOXYLATION OF SUBSTITUTED CINNAMIC ACIDS

Cinnamic acid	Yield from aldehyde %	Expt. ^c cond.	Crude ^e		Styrene		B. p., °C. (mm.)	Lit. n_D^{20}
			Yield, % ^e	n_D^{20}	Fractionated Yield, %	n_D^{20}		
2-Chloro	82	A	50	1.5641	58-59 (7)	1.5648 ^{2a}
3-Chloro	53 ^a	B	67	1.5628	65	1.5630	57.5-57.8 (10)	1.5620 ^{1b}
		E	86	1.5646	1.5619 ^{2a}
4-Chloro	73	A	50-54	1.5675	51	1.5650	60-62 (6.5)	1.5648 ^{1b}
		E	83	1.5664	1.5658 ^{2a}
2,4-Dichloro	70	E ^b	20	1.5828	1.5828 ^{1c}
3,4-Dichloro	81	B	22	1.5847	1.5844 ^{1c}
		E ^b	16	1.5795
3-Bromo	31 ^a	B	56	1.5880	47	1.5900	48.1-48.5 (0.5)	1.5855 ^{1a}
2-Methoxy	68	E	67	1.5568	40	1.5608	60.8-62 (3)	1.556 ¹
4-Methoxy	60	B	75	1.5620	71	1.5612	53-53.8 (2)	1.5608 ^{1d}
		E	85	1.5582	76	1.5620
3,4-Dimethoxy	77	B	10	1.5690	1.5708 ^{1d}
<i>m</i> -Nitro	..	B	0
<i>p</i> -Dimethylamino	50	B ^d	0

^a From *m*-nitrobenzaldehyde (2 steps). ^b Using 260-270° base in place of quinoline. ^c See Table I for significance. ^d In diphenyl ether. ^e Steam distilled product, or distillate after taking up in ether, washing with 2.4 *N* hydrochloric acid to remove base, evaporation of ether.

that the highest yield (83%) was obtained by carrying out the reaction in quinoline with copper powder as a catalyst.

Results on a number of other substituted styrenes are listed in Table II where letters refer to the same experimental conditions as Table I, except that 25 to 200 g. of acid and other reagents in proportion were employed. Here, too, highest yields were obtained by the copper powder-quinoline technique.

From Table II it is evident that, in the case of the monohalo- and monoalkoxystyrenes, decarboxylation of the corresponding cinnamic acids is a very successful means of synthesis, being rapid, simple, and affording high yields. In the other cases listed, however, the method gives either poor or no yields. With the idea that the failure here was due to the high boiling-point of the desired styrenes, which might lead to their polymerization before they could distil, several experiments were carried out at reduced pressure (60-100 mm.) employing copper powder or copper sulfate in a high boiling quinoline base fraction from the Reilly Tar and Chemical Corp. boiling at 100-140° (1 mm.). In no case, however, did these cinnamic acids yield more than traces of the desired styrenes.

The great improvement in yield obtained on carrying out these decarboxylations in the presence of copper salts and quinoline over that obtained on heating the acid alone or in inert solvents is probably due, primarily, to the much lower temperature at which the reaction proceeds. This lowered temperature not only makes it possible to remove the product before it polymerizes but may also avoid some competing decomposition of the acid. The latter is suggested since other decarboxylations have been found to give im-

proved yields in the presence of quinoline and copper powder, a fact first noted by Shepard, Winslow and Johnson⁷ in studying the decarboxylation of halogenated furoic acids. The procedure has been used in the preparation of benzanthrone carboxylic acids,⁸ and has been recommended as a good general technique for decarboxylations by Fieser and Fieser.⁹

The question of how quinoline and a copper salt accelerate the decarboxylation of acids is an interesting one and well worth further study. It is reasonable to expect the base by itself to be a catalyst, since studies on less stable acids such as trichloroacetic indicate that decarboxylation proceeds through the carboxylate ion.^{10,11} A possible function of the copper salt, in turn, is to form a bulky quinoline-copper complex ion having less tendency to form ion pairs with the carboxylate ion than has the quinolinium ion, thus increasing the effective free concentration of the former.^{12,13} In such a scheme, copper powder would function by dissolving to give copper (perhaps cuprous) ion. On the other hand, the effect of copper powder may represent a heterogeneous catalysis by somewhat different mechanism.

(7) Shepard, Winslow and Johnson, *THIS JOURNAL*, **52**, 2083 (1930).

(8) Rule and Smith, *J. Chem. Soc.*, 1096 (1937).

(9) Fieser and Fieser "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 549.

(10) Fairclough, *J. Chem. Soc.*, 1186 (1938).

(11) Johnson and Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A175**, 118 (1940).

(12) A similar suggestion has been made to account for the varying rates of decomposition of different trichloroacetates, by Hall and Verhoek in a paper given before the Division of Physical and Inorganic Chemistry, Atlantic City Meeting, April 8, 1946.

(13) That other metals in conjunction with an aromatic base are effective in catalyzing decarboxylation is suggested by the report by Baker, Lappin, Albisetti and Riegel, *THIS JOURNAL*, **68**, 1267 (1946), that certain nitroquinolinecarboxylic acids are best decarboxylated by heating their silver salts in an inert solvent. Here the acid being decarboxylated supplies its own basic group.

(6) Klages and Eppelsheim, *Ber.*, **36**, 3590 (1903).

Experimental

Aldehydes.—*m*-Chloro- and *m*-bromobenzaldehydes were prepared as described in "Organic Syntheses."¹⁴ The crude aldehydes obtained on steam distillation were used without further purification. 2-Chloro-, 4-chloro-, 2,4-dichloro- and 3,4-dichlorobenzaldehydes were obtained from the Heyden Chemical Corp., the remainder from the Eastman Kodak Co.

Cinnamic Acids.—*m*-Nitrocinnamic acid was obtained from Eastman Kodak Co. The remainder of the acids were prepared by the Doebner reaction. The aldehyde (1.0 mole), malonic acid (1.1 mole), 200 cc. ethanol (either 95% or absolute) and 25 cc. pyridine were heated overnight on the steam bath. In the morning the alcohol which had evaporated was replaced, the mixture cooled and the cinnamic acid filtered off and washed. Recrystallization was generally unnecessary, but additional acid could usually be recovered by concentration of the filtrate. Yields are given in column two of Table II, and at no time was the necessity for anhydrous reagents noted which is mentioned in connection with this reaction when carried out in pyridine as solvent,³ and observation that hardly seems surprising since the condensation itself liberates a mole of water.

In the case of *p*-dimethylaminocinnamic acid no product was obtained by the above procedure. However, when the reaction mixture was merely warmed to solution (50–60°) and then allowed to stand at room temperature for a week the acid crystallized from the mixture in 50% yield.

The two dichlorocinnamic acids have not previously been reported. Melting points and analytical data on samples recrystallized five times from ethanol are given below.

2,4-Dichlorocinnamic acid: m. p. 228.5–229.5° (uncor.). *Anal.* Calcd. for $C_9H_5Cl_2$: C, 49.8; H, 2.79; Cl, 32.7. Found: C, 49.87; H, 2.89; Cl, 32.60.

3,4-Dichlorocinnamic acid: m. p. 217.2–218.2° (uncor.). *Anal.* Found: C, 49.69; H, 2.94; Cl, 32.65.

Decarboxylations were carried out in ordinary Claisen or distilling flasks heated either with a Glass-Col heater or a free flame, the former giving easier control and requiring less attention. From 25 to 200 g. of the cinnamic acids was decarboxylated at a time, usually in the presence of two parts of base and one tenth part of catalyst, both by weight. The size of the run seemed to have no effect on yields and, for the smaller experiments, it was sometimes convenient to use four parts of base. In experiments in quinoline, distillation was carried out at such a rate that during the bulk of the reaction the temperature of the

vapors remained below 220°, and one third to two thirds of the reaction mixture distilled within an hour. The completion of the reaction required usually forty to fifty minutes and was signalled by a rise in the temperature of the vapors to the boiling point of quinoline. In the higher-boiling bases the acid was added in a number of small portions, the heat being adjusted so that, after each addition, the temperature of the vapors rose to 235–240° in two to five minutes, at which point a fresh portion of acid was introduced.

Purification of Products.—The halostyrenes were separated from base by steam distilling from at least a 50% excess of 2.4 *N* hydrochloric acid in the presence of 0.02–0.05 mole per cent. trinitrobenzene as a polymerization inhibitor, and employing a Dean and Stark trap so that the water was continuously recycled. Only traces of polymer remained in the pot and the cloudy steam distillate was dried and clarified with a small amount of drierite, calcium chloride or sodium carbonate. Since the alkoxy-styrenes were found to be unstable toward hot acid, yielding chiefly gummy polymers, they were separated from quinoline by taking up the distillates in ether, washing twice with cold 2.4 *N* hydrochloric acid and water, drying, and removing ether, the last traces under vacuum at room temperature. Subsequent distillations were carried out through short, helices-packed columns at the pressures indicated in Table II. In general, only very small foreruns and high-boiling fractions were obtained, and the yield of purified styrene from crude material was in general more sensitive to the quantity of material available for distillation than to any other variable. Accordingly, in Table II the crude yields probably furnish the best basis for comparing experiments, and many runs, carried out to determine the effect of experimental conditions on yield, were not carried beyond this point.

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Summary

1. A number of halo- and alkoxy-cinnamic acids are converted to the corresponding styrenes in good yield by slow distillation from quinoline in the presence of copper powder.

2. The reaction fails or gives poor yields with 3-nitro-, 4-dimethylamino-, 2,4-dichloro-, 3,4-dichloro- and 3,4-dimethoxycinnamic acids.

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(14) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, 1943, p. 130.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. XXI. Synthesis of Piperazine and C-Substituted Piperazines

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Piperazine, known as long ago as 1853,² has not been readily available, although numerous processes for its synthesis have been described.

A method now is described by which piperazine itself and numerous of its C-substituted homologs readily are derivable by the catalytic cyclodehydration of *N*-(2-hydroxyethyl)-ethenediamine and its C-substituted derivatives. The dehydration is carried out at atmospheric pressure

by refluxing the hydroxyethylethenediamine, alone or with suitable diluent, with catalyst under a fractionating column and collecting water and the piperazine as formed or, better, by carrying out the reaction in an autoclave.

Experimental

Equipment.—Purifications by distillation were carried out with a 15 in. × 19 mm. column packed with glass Raschig rings and having an efficiency of 6-theoretical plates. The column was provided with a head designed for distillation of solids; it had a Hopkins-type condenser made removable by a standard taper connection, enabling

(1) Present address: Firestone Tire and Rubber Co., Akron, Ohio.

(2) Cloëz, *Jahresber. fortschr. Chem.*, 468 (1853).