THE PREPARATION OF SUBSTITUTED STYRENES BY METHODS NOT INVOLVING HYDROCARBON CRACKING

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CONTENTS

I. INTRODUCTION

This review summarizes the methods for preparing nuclear-substituted styrenes and β-nitrostyrenes by those methods which do not involve the cracking of hydrocarbons. In this sense it is a supplement to "The Reactions of Monomeric Styrenes" (43), which reviews the preparation of styrenes substituted in the side chain and the reactions of substituted styrenes. The literature and types of compounds covered are identical with those in the former review.

II. DEHYDRATION OF ALCOHOLS

This method for preparing substituted styrenes has received particular attention during the last few years in connection with the synthetic rubber program of the United States Government. α-Phenethyl alcohols can be obtained easily by the Grignard reaction from the corresponding aryl bromide or iodide or the corresponding aromatic aldehyde. An equally convenient preparation is the reduction of the corresponding acetophenone.

$$ArMgBr + CH_3CHO \rightarrow ArCHOHCH_3$$

$$ArCHO + CH_3MgI \rightarrow ArCHOHCH_3$$

$$ArCOCH_3 \xrightarrow{(H)} ArCHOHCH_3$$

This method is limited only by the availability of these intermediates and obviously is capable of very extensive application.

The earliest method of dehydration, and one that has been used occasionally in recent years, was simply to distil the alcohol slowly. As a matter of fact Bottcher (14) observed that when he decomposed the adduct from piperonal and methylmagnesium iodide with dilute sulfuric acid he obtained the olefin directly,

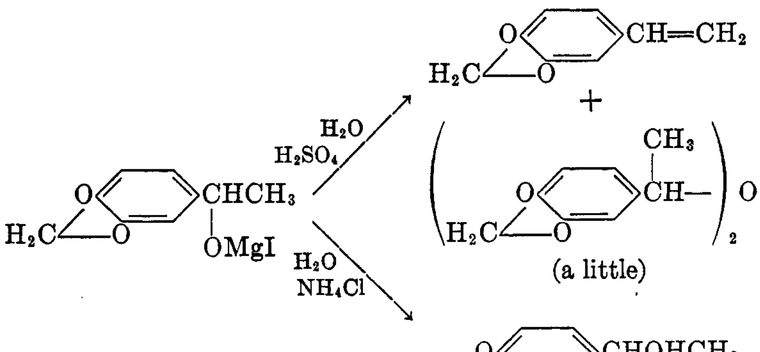
[1] Some additions inserted in manuscript August 15, 1949.

TABLE 1

Dehydration of α-phenethyl alcohols by distillation

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
p-Isopropyl		(94)
p-Methoxy	Good	(118)
		(199)
3,4-Dimethoxy		(9)
		(57)
3,4-Methylenedioxy	82	(141)
		(14)
		(93)
		(116)
		(87)
p-Dimethylamino	45	(125)
	30	(204)
	0	(180)

whereas with aqueous ammonium chloride the carbinol was obtained in 90 per cent yield.



Mannich and Jacobsohn (118) obtained a good yield of p-methoxystyrene when they decomposed the adduct from anisaldehyde and methylmagnesium iodide with dilute sulfuric acid. In table 1 are summarized the preparations of substituted styrenes by the distillation of the corresponding α-phenethyl alcohol.

$$ArCHOHCH_3 \xrightarrow{\text{distil}} ArCH{=}CH_2 + H_2O$$

2,3-Dimethoxystyrene has been prepared by steam distilling the corresponding α-phenethyl alcohol (77).

When *p*-methoxystyrene was obtained directly from the Grignard reaction, some *p*-methoxy-α-phenethyl alcohol also was isolated, as well as some *p*-methoxy-α-phenethyl ether (199). In the case of 3,4-methylenedioxystyrene, besides 3,4-methylenedioxy-α-phenethyl alcohol (116), both 3,4-methylenedioxy-α-phenethyl ether (14) and 3,4-methylenedioxyacetophenone (116) were isolated.

When *m*-benzoxybenzaldehyde was treated with methylmagnesium iodide and the product hydrolyzed with aqueous potassium hydroxide, *m*-hydroxystyrene was produced (77).

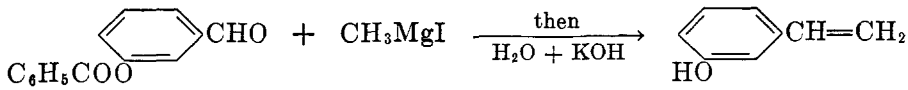
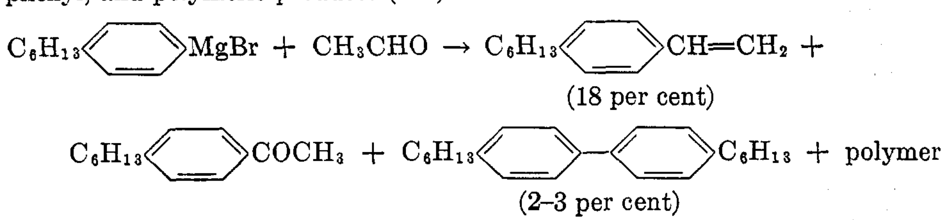


TABLE 2

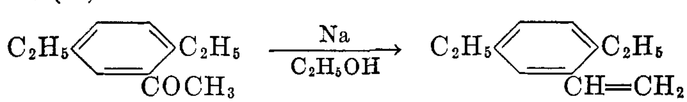
Dehydration of α-phenethyl alcohols with phosphorus pentoxide

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
m-tert-Butyl	40	(120)
m-Bromo	51	(24)
p-Bromo	40–44	(159)
m-Trifluoromethyl	54	(125)
m-Nitro	25	(125)

Acetaldehyde reacted with *p*-hexylphenylmagnesium bromide to give 18 per cent of *p*-hexylstyrene, some *p*-hexylacetophenone, 2–3 per cent of *p*-hexylbiphenyl, and polymeric products (120).



Reduction of 2,5-diethylacetophenone with sodium and alcohol yielded 2,5-diethylstyrene (94).



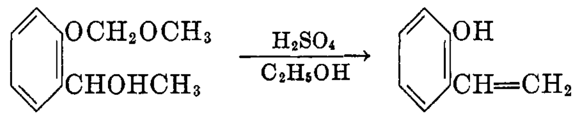
The electrolysis of ether solutions of *p*-methylphenylmagnesium bromide and of *p*-chlorophenylmagnesium bromide yielded the corresponding styrenes (51).

Since the direct distillation of α-phenethyl alcohols usually is not a particularly effective method of dehydration, a variety of dehydrating agents have been employed. In the liquid phase phosphorus pentoxide in boiling benzene has proven to be reasonably useful. In table 2 are listed the substituted styrenes

$$ArCHOHCH_3 \xrightarrow[C_6H_6]{P_2O_5} ArCH{=}CH_2$$

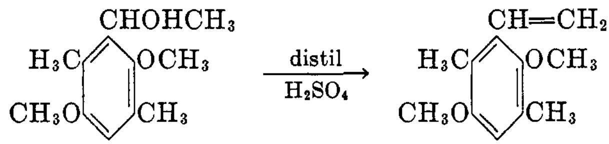
which have been prepared in this manner.

Treatment of *o*-methoxymethyleneoxy-α-phenethyl alcohol with alcoholic sulfuric acid yielded *o*-vinylphenol (76).



Treatment of 2,4,5-trimethyl-α-phenethyl alcohol with phosphoric acid yielded only polymer (92).

A great many substituted styrenes have been prepared by distilling the corresponding α-phenethyl alcohol from a dehydrating agent. Thus, *o*-chlorostyrene was obtained in 80–94 per cent yields in this way from *o*-chloro-α-phenethyl alcohol (215). 2,5-Dimethyl-3,6-dimethoxystyrene was obtained similarly by distilling the corresponding α-phenethyl alcohol from a drop of sulfuric acid (196).



The following styrenes were obtained by distilling the corresponding α-phenethyl alcohols from phosphorus pentoxide: 2,4,6-trimethyl- (92), *m*-trifluoromethyl- (79 per cent yield) (7), *p*-fluoro-*m*-trifluoromethyl- (70 per cent yield) (7), and *o*-bromo-*p*-trifluoromethyl- (7).

Probably the most widely used preparation of substituted styrenes is the distillation of the corresponding α-phenethyl alcohol from sodium bisulfate, potassium bisulfate, or potassium pyrosulfate. This operation usually is conducted at

$$ArCHOHCH_3 \xrightarrow{KHSO_4} ArCH{=}CH_2$$

reduced pressure and at temperatures of 175–230°C. In table 3 are listed the substituted styrenes which have been prepared in this way.

Another widely used method for dehydrating α-phenethyl alcohols is to pass their vapors over activated alumina at 250–450°C. (usually 300–350°C.), generally at reduced pressures.

$$ArCHOHCH_3 \xrightarrow[300\text{–}350°C.]{Al_2O_3} ArCH{=}CH_2 + H_2O$$

This method suffers from the disadvantage that some disproportionation may occur to give the corresponding ethylbenzene and acetophenone.

$$ArCHOHCH_3 \xrightarrow[300\text{–}350°C.]{Al_2O_3} ArCH_2CH_3 + ArCOCH_3$$

Acetophenone has been isolated from such a pyrolysis of methylphenylcarbinol itself (79). When *p*-benzyl- (121), *o*-methoxy- (121), and *p*-phenoxy-styrenes

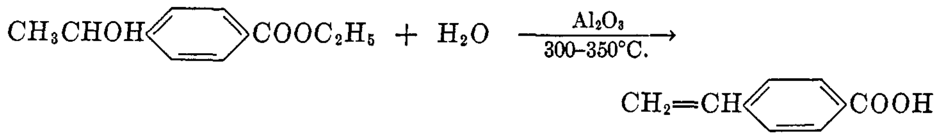
(57) were prepared in this way, they were all contaminated with some of the corresponding ethylbenzene. In the case of *o*-methoxystyrene (121), some *o*-ethylphenol also was isolated, presumably from demethylation of the *o*-ethylanisole. Pyrolysis of (*m*-methylaminophenyl)methylcarbinol gave as the sole product 48 per cent of *m*-(methylamino)ethylbenzene (122). In table 4 are listed those substituted styrenes which have been prepared by dehydration of the corresponding carbinols over activated alumina.

TABLE 3

Dehydration of α-phenethyl alcohols with bisulfates

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE	SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent			*per cent*	
o-Methyl		(41)		86	(23)
m-Methyl	50	(125)	*p*-Chloro	60	(127)
				47	(203)
	72	(206a)			
p-Methyl		(41)	2,3-Dichloro	44	(124)
		(66)	2,4-Dichloro	33	(124)
		(203)	2,5-Dichloro	37	(23)
			2,6-Dichloro	32	(124)
2,4-Dimethyl	71	(126)			
2,5-Dimethyl	88	(126)	3,4-Dichloro	83	(23)
3,4-Dimethyl	80	(126)		64	(124)
3,5-Dimethyl	87	(126)			
			3,5-Dichloro	43	(124)
p-Ethyl	80	(66)	*o*-Bromo		(189)
	72	(206a)	*m*-Bromo	Low	(24)
p-*n*-Butyl	70	(206a)	*p*-Bromo		(189)
m-*sec*-Butyl	61	(120)			(229)
m-*tert*-Butyl	61	(120)			
p-*n*-Heptyl	69	(206a)	*p*-Iodo	60	(204)
p-(2-Ethylhexyl)	30	(206a)	*o*-Methoxy		(189)
o-Fluoro	76	(23)			
m-Fluoro	80	(23)	*p*-Methoxy		(189)
					(203)
p-Fluoro	81	(23)			
	62	(7)	2,6-Dimethoxy	60	(186)
			p-Acetoxy	45	(45)
Chloro		(181)	*p*-Carbomethoxy	49	(44)
o-Chloro	70	(23)	d-*p*-(*sec*-Butoxymethylene)	47	(123)
			o-Amino		(189)
m-Chloro	83	(23)	*p*-Amino		(189)
	23	(127)			

When alumina on pumice was used for the preparation of *p*-ethylstyrene at 300°C., some alcohol was recovered and some *p*-ethyl-α-phenethyl ether was obtained (80). When the vapors of *p*-carbethoxy-α-phenethyl alcohol together with steam were passed over activated alumina at 300–350°C., 8 per cent of *p*-vinylbenzoic acid was isolated along with 35 per cent of its polymer (44).



β-Phenethyl alcohols also are dehydrated very smoothly and in general give purer products than do the *α*-isomers (57, 121). This operation uniformly has been effected by distilling the alcohol from solid potassium hydroxide with a pot temperature of about 200°C., usually in a copper vessel. These alcohols

TABLE 4

Dehydration of α-phenethyl alcohols over activated alumina

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE	SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent			*per cent*	
p-Methyl	83	(134)	3,5-Dichloro		(133)
m-Trifluoromethyl	79	(171)	2,3,4,5,6-Pentachloro	61	(178)
m-Ethyl	93	(134)	*o*-Methoxy		(121)
p-Ethyl	83	(134)	*p*-Methoxy	65	(134)
3,5-Diethyl	83	(134)	*p*-Ethoxy	69	(134)
p-*tert*-Butyl	76	(134)			
p-Hexyl	87	(134)			
p-Benzyl	83	(121)	*p*-Phenoxy	72	(134) (57)
p-Fluoro	89	(171)			
m-Chloro	84	(47)			
2,3-Dichloro		(133)	*p*-Cyano	71	(134)
2,4-Dichloro		(133)	*p*-Amino	20	(134)
2,5-Dichloro		(133)			
2,6-Dichloro		(133)	*p*-Vinyl	83	(134)
3,4-Dichloro	87	(134)		81	(73)

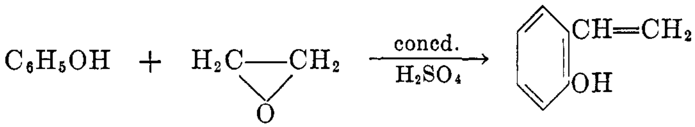
generally are prepared by treating the corresponding arylmagnesium halide with ethylene oxide.

$$ArMgX + H_2C\underset{O}{—}CH_2 \longrightarrow ArCH_2CH_2OH$$

In table 5 are listed the substituted styrenes which have been prepared from alcohols in this manner.

$$ArCH_2CH_2OH \xrightarrow[200°C.]{KOH} ArCH{=}CH_2 + H_2O$$

The dehydration of a *β*-phenethyl alcohol possibly is involved in the reaction of phenol with ethylene oxide in the presence of concentrated sulfuric acid to give 65 per cent of *o*-vinylphenol (195).



(65 per cent)

Treatment of β-hydroxyethyl phenyl ether with concentrated sulfuric acid gave the same product.

III. PYROLYSIS OF ESTERS AND ETHERS

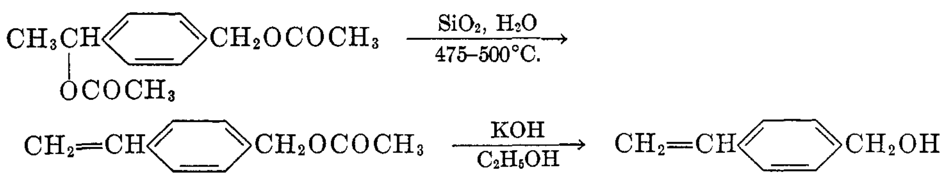
Occasionally the pyrolysis of an ether or ester has proven to be more useful for the preparation of a substituted styrene than the dehydration of the corresponding α-phenethyl alcohol. The following styrenes have been prepared by

TABLE 5

Dehydration of β-phenethyl alcohols with potassium hydroxide

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
o-Methyl		(188)
m-Methyl		(188)
p-Methyl	Good	(128)
p-Methyl		(179)
p-Methyl		(188)
2,4-Dimethyl		(71)
p-Ethyl		(129)
Fluoro		(36)
p-Fluoro	23	(7)
(*o* + *p*)-Chloro		(139)
(*o* + *p*)-Bromo		(139)
m-Trifluoromethyl	72	(7)
o-Methoxy	69	(121)
m-Methoxy	69	(57)
p-Phenoxy	77	(57)

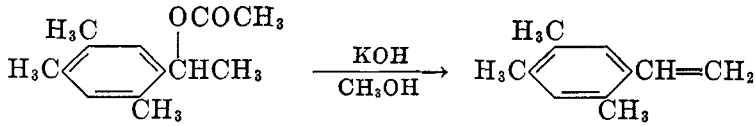
pyrolyzing the α-phenethyl acetates in question over glass at 480–600°C.: 3,4-dichloro- (85 per cent yield) (124), *p*-acetoxy- (90 per cent yield) (2), and *p*-cyano- (76 per cent yield) (138). In the case of *p*-acetoxymethylene-α-phenethyl acetate a silica catalyst was used and steam was used as a carrier to prevent the tube from clogging (46). The yield was 72 per cent. Hydrolysis of this ester with alcoholic potassium hydroxide yielded 38 per cent of *p*-vinylbenzyl alcohol.



(72 per cent)

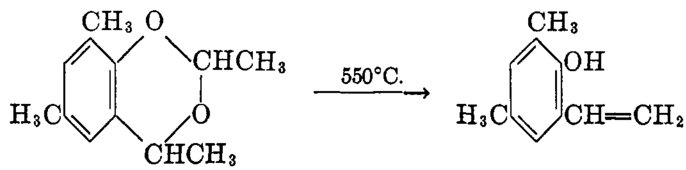
Pyrolysis of *p*-dimethylamino-α-phenethyl acetate was not effective for the preparation of *p*-dimethylaminostyrene (180).

In the case of 2,4,5-trimethyl-α-phenethyl acetate, boiling with potassium hydroxide in methanol yielded 2,4,5-trimethylstyrene (92). With 2,4,6-tri-



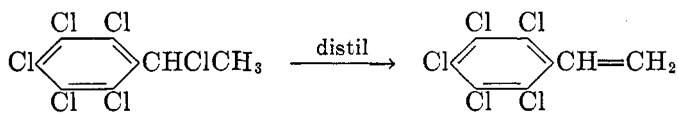
methyl-α-phenethyl acetate only the alcohol was obtained.

When vapors of *p*-phenoxy-α-phenethyl isopropyl ether were passed over alumina at 325–450°C., *p*-phenoxystyrene was obtained (57). Distillation was sufficient to convert 3,4-methylenedioxy-α-phenethyl ether to 3,4-methylenedioxystyrene (14). When the vapors of *o*-methoxy-α-phenethyl ether were passed over activated alumina at 310°C., a 75 per cent yield of *o*-methoxystyrene was obtained (121). At 550°C. in a stream of nitrogen 2-hydroxy-3,5-dimethylstyrene was obtained from 2,4,6,8-tetramethylbenzo-1,3-dioxane (1).

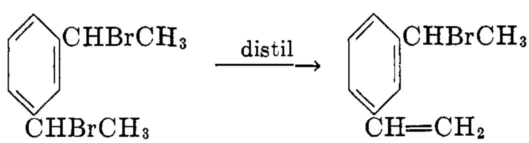


IV. DEHYDROHALOGENATION OF HALIDES

In many cases the dehydrohalogenation of α- or β-phenethyl halides has been used to prepare nuclear-substituted styrenes. The simplest procedure, which has been effective in a few instances, is to distil the halide in question. Thus, trichlorostyrene (114) and 2,3,4,5,6-pentachlorostyrene (86 per cent yield) (113) have been prepared by distilling the corresponding α-phenethyl chlorides three times and twice, respectively. When *o*-ethylphenol was treated with



bromine and then distilled, a crude tribromo-*o*-hydroxystyrene was obtained (206). It was purified by treatment with alcoholic potassium hydroxide. Both *o*- (34) and *m*-vinyl-α-phenethyl bromides (33) have been prepared by distillation.



In table 6 are shown those substituted styrenes which have been prepared by treating a phenethyl halide with alcoholic potassium hydroxide.

$$ArCHXCH_3 \text{ or } ArCH_2CH_2X \xrightarrow[C_2H_5OH]{KOH} ArCH{=}CH_2$$

In the *p*-methylstyrene preparation some *p*-methyl-α-phenethyl ether also was isolated (184).

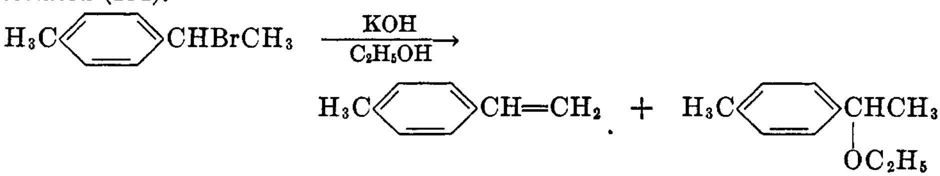


TABLE 6

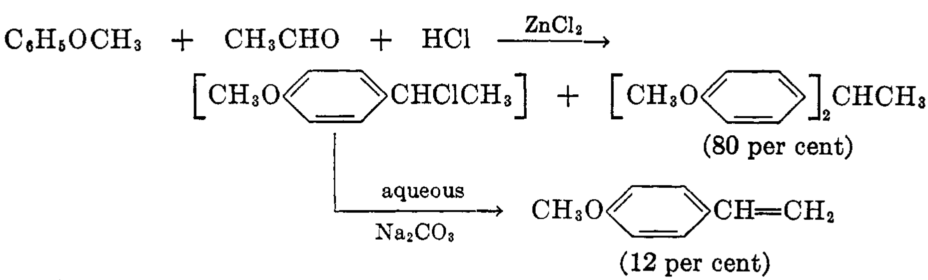
Dehydrohalogenation of phenethyl halides with alcoholic potassium hydroxide

SUBSTITUTED STYRENE OBTAINED	HALIDE USED	YIELD	REFERENCE
		per cent	
p-Methyl	α-Bromo	15	(184)
p-Chloro	α-Chloro	Quantitative	(220a)
(*o* + *p*)-Bromo	α-Bromo		(184)
2,3,4,5,6-Pentachloro	α-Chloro	87	(113)
	α-Chloro	4	(178)
	β-Chloro	60	(178)
p-(*N*,*N*-Dimethylsulfonamido)	β-Bromo	67	(84)

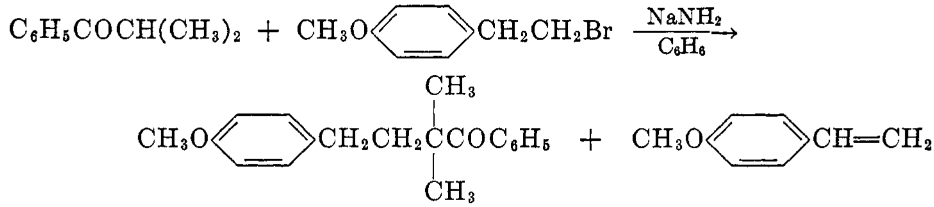
p-Fluorostyrene has been prepared in 72 per cent yield by heating the corresponding β-phenethyl bromide with potassium hydroxide at 220°C. (56).

(72 per cent)

When anisole was treated with acetaldehyde and hydrochloric acid in the presence of zinc chloride and the product was treated with aqueous sodium carbonate, 80 per cent of di(*p*-methoxyphenyl)ethane and 12 per cent of *p*-methoxystyrene were obtained (161). The *p*-methoxystyrene undoubtedly was produced from *p*-methoxy-α-phenethyl chloride, a product of the initial condensation.



When *p*-methoxy-β-phenethyl bromide was condensed with phenyl isopropyl ketone by means of sodium amide in boiling benzene, considerable *p*-methoxystyrene was obtained as a by-product (26).



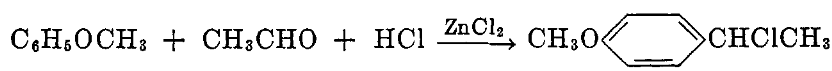
Chlorostyrene has been prepared by passing the vapors of the corresponding α-phenethyl chloride over a supported phosphoric acid–sodium phosphate catalyst (good yield) (82) or over mercurous chloride (92 per cent yield) (37) at 330–370°C. A mixture of dichlorostyrenes was obtained when mixed dichloro-α-chloroethylbenzenes were passed over silica gel in the presence of steam at 250–350°C. (50). When the vapors of α,*m*-dichloroethylbenzene together with steam were passed over calcium sulfate at 425–475°C., a 92.5 per cent yield of *m*-chlorostyrene was obtained (47). The *o*- and *p*-cyanostyrenes have been prepared in 57 per cent and 55 per cent yields, respectively, by passing the vapors of the corresponding α-chloroethylbenzenes over clay at 570–590°C. (220).

The most widely used method for dehydrochlorinating phenethyl halides is to pyrolyze a quaternary ammonium salt or hydroxide. In a great many cases no attempt has been made to isolate the quaternary salt, but instead the phenethyl halide is distilled with some tertiary amine. In table 7 are listed those substituted styrenes which have been prepared by distilling the corresponding α-phenethyl chloride with pyridine.

$$ArCHClCH_3 \xrightarrow{\text{pyridine}} ArCH{=}CH_2$$

The α-phenethyl chlorides usually were prepared by treating the corresponding α-phenethyl alcohol with hydrogen chloride or, in the case of many of the alkoxy compounds, by chloroethylating the phenyl ether in question.

$$ArCHOHCH_3 \xrightarrow{HCl} ArCHClCH_3$$



Treatment of *p*-dimethylamino-α-phenethyl alcohol with phosphorus pentachloride gave a mixture unsuitable for dehydrochlorination with pyridine (180).

2,4,6-Trimethylstyrene was obtained in low yield by heating 2,4,6-trimethyl-α-phenethyl chloride with aniline (92). Under the same conditions 2,4,5-trimethyl-α-phenethyl chloride yielded only polymer. *p*-Nitrostyrene was obtained in 85–91 per cent yield by heating *p*-nitro-β-phenethyl bromide with triethanolamine (204).

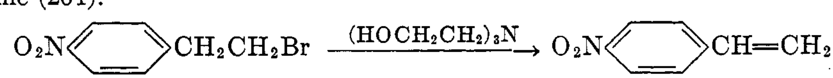


TABLE 7

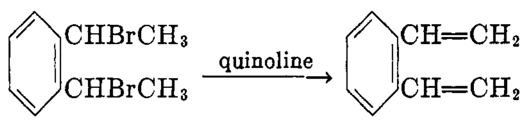
Dehydrochlorination of α-phenethyl chlorides with pyridine

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
Methyl	90	(81)
p-Methyl	73	(94) (91)
2,4-Dimethyl		(94) (91) (198)
2,5-Dimethyl	78	(94)
2,4,5-Trimethyl		(94)
2,4,6-Trimethyl		(94) (91)
p-Ethyl	70	(94) (91)
2,4,5-Triethyl		(94)
Chloro	90	(35)
o-Methoxy	80	(93) (167)
m-Methoxy		(93)
p-Methoxy		(93) (160) (162) (163) (164) (197) (198)
2-Methoxy-5-methyl		(57) (160) (162) (165)
2-Methyl-4-methoxy		(57) (160) (162) (165)
3-Methyl-4-methoxy		(57) (160) (162) (165)

TABLE 7—*Continued*

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
2-Methoxy-5-isopropyl		(166)
2-Methyl-4-methoxy-5-isopropyl		(57) (160) (162) (165)
3,4-Dimethoxy		(57) (119)
3,4-Methylenedioxy		(9)
p-Ethoxy		(93)
p-Phenoxy	17	(57)
Divinylbenzene	82	(35)

Both *o*- (33) and *p*-divinylbenzenes (83, 112) have been prepared by distilling the corresponding bis-α-phenethyl bromides with quinoline. The *m*-isomer was



prepared by distilling *m*-vinyl-α-phenethyl bromide with quinoline (33).

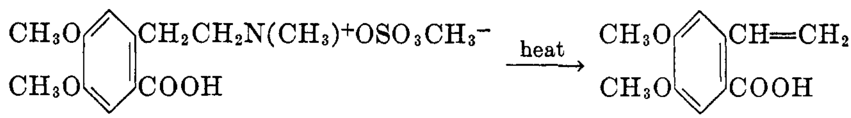
Another convenient method for preparing substituted styrenes is to pyrolyze a quaternary hydroxide. In practice this has been effected either by isolating the

$$ArCH_2CH_2N(CH_3)_3^+OH^- \rightarrow ArCH{=}CH_2 + (CH_3)_3N + H_2O$$

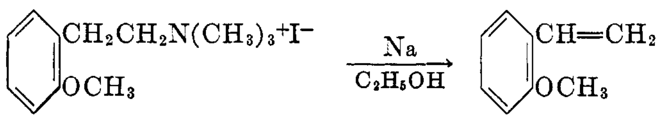
quaternary hydroxide and heating it in the dry state or by steam distilling a quaternary halide with a strong base. In table 8 are listed those substituted styrenes which have been prepared in this manner. The yields in this table when listed for a quaternary base invariably are based on the halide precursor. In the preparation of *o*-dimethylaminomethylstyrene from the quaternary iodide, some *N*-methyltetrahydroisoquinoline also was isolated (53). The identity of the bis-β-(*o*-phenylene)ethylamine used as the starting material for the preparation of *o*-dimethylaminoethylstyrene (21) has been questioned (61). When the methiodide from this *o*-dimethylaminoethylstyrene was treated with silver oxide and then heated, trimethylamine and a tar were the only products obtained.

The quaternary base and iodide from which *p*-nitrostyrene was obtained decomposed very easily (78). When (*p*-nitro-β-phenethyl)dimethylamine was treated with β-phenethyl chloride, the quaternary salt could not be isolated (69). *p*-Nitrostyrene was obtained directly from the reaction mixture.

2-Carboxy-4,5-dimethoxystyrene has been prepared by heating the methosulfate of the corresponding β-phenethyldimethylamine (101).



o-Methoxystyrene has been prepared by treating (*o*-methoxy-β-phenethyl)trimethylammonium iodide with sodium and ethanol.



V. DECARBOXYLATION OF CINNAMIC ACIDS

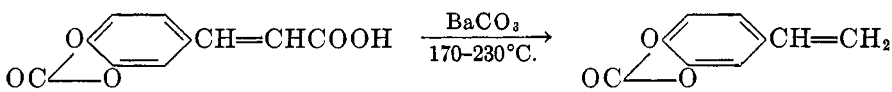
A great many substituted styrenes have been prepared by heating the corresponding cinnamic acids. In table 9 are listed those styrenes which have been

$$ArCH{=}CHCOOH \rightarrow ArCH{=}CH_2 + CO_2$$

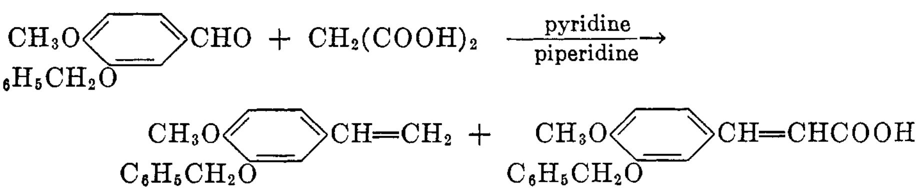
prepared in this manner.

In several cases this decarboxylation has been facilitated by the use of catalysts. These preparations are summarized in table 10.

3-Methoxy-4-hydroxystyrene was obtained in 48 per cent yield by distilling the corresponding cinnamic acid with soda (169). *p*-Hydroxystyrene was prepared in very low yield by pyrolyzing the barium salt of *p*-hydroxycinnamic acid (12). 3,4-Carbonyldioxystyrene was obtained in 33 per cent yield by heating 3,4-carbonyldioxycinnamic acid with barium carbonate.



When 3-benzyloxy-4-methoxybenzaldehyde was treated with malonic acid in the presence of pyridine and piperidine, some 3-benzyloxy-4-methoxystyrene was obtained along with the principal product, 3-benzyloxy-4-methoxycinnamic acid (173).



A number of substituted styrenes have been prepared by treating the corresponding halogenated phenylpropionic acid with aqueous sodium carbonate.

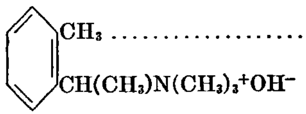
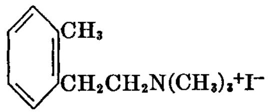
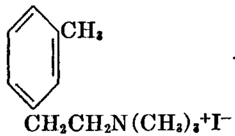
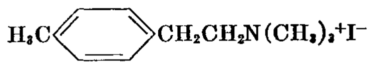
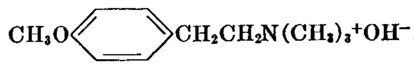
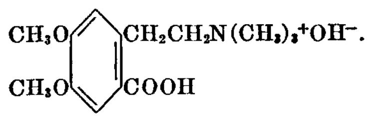
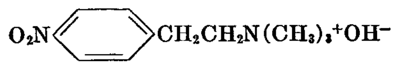
$$ArCH{=}CHCOOH \xrightarrow{HX} ArCHXCH_2COOH \xrightarrow[Na_2CO_3]{aqueous} ArCH{=}CH_2$$

These preparations are summarized in table 11.

In one preparation, besides the 10 per cent of *o*-nitrostyrene obtained, there

TABLE 8

Pyrolysis of quaternary hydroxides

STARTING MATERIALS	SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
		per cent	
	*o*-Methyl		(22)
 + KOH + H_2O	*o*-Methyl		(42)
 + KOH + CH_3OH	*m*-Methyl		(212)
 + KOH + CH_3OH	*p*-Methyl		(212)
	*p*-Methoxy	92	(111)
	2-Carboxy-4,5-dimethoxy		(99)
	*p*-Nitro		(78)

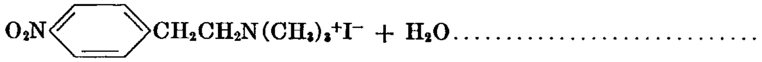
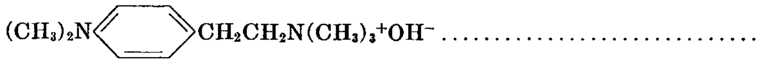
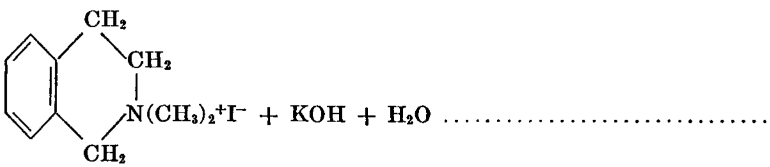
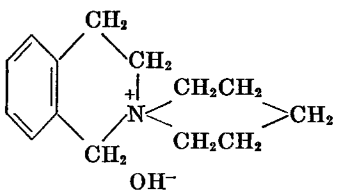
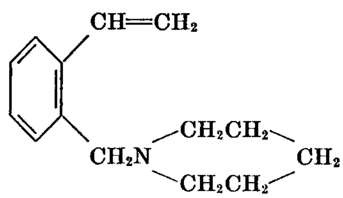
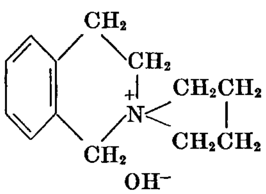
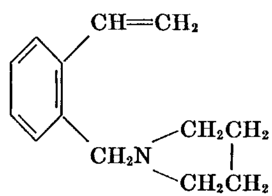
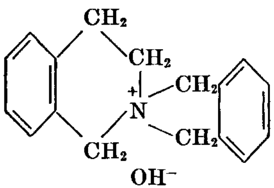
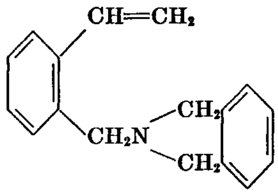
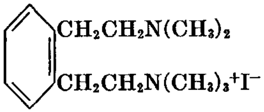
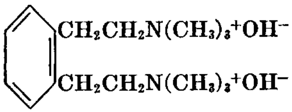
	*p*-Nitro		(78)
	*p*-Dimethylamino	75	(19)
	*o*-Dimethylaminomethyl	80 77	(18) (42)
	*o*-Dimethylaminomethyl		(52, 53)
			(17)
			(17)

TABLE 8—*Concluded*

STARTING MATERIALS	SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
		per cent	
			(17)
 + NaOH + H_2O	*o*-(β-Dimethylaminoethyl)	25–30	(21)
	*o*-Divinylbenzene		(61)

also were isolated 42 per cent of *o*-nitro-β-hydroxyphenylpropionic acid and 16 per cent of *o*-nitrocinnamic acid (38).

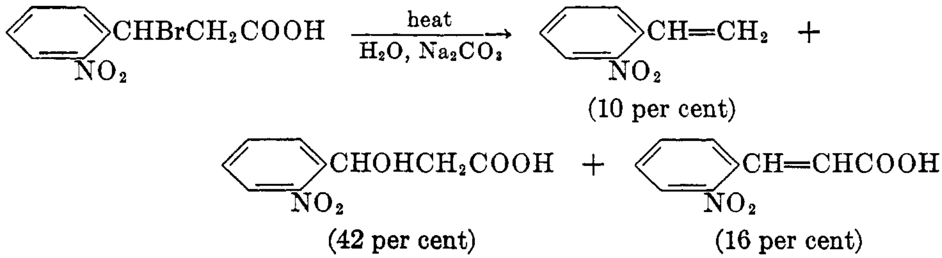


TABLE 9

Decarboxylation of cinnamic acids

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
Isopropyl		(143)
p-Isopropyl		(142)
o-Methoxy		(6)
p-Methoxy		(143)
		(144)
		(145)
o-Hydroxy	Quantitative	(106)
	50	(62)
		(6)
		(105)
3,4-Dihydroxy	75	(104)
		(210)
3-Hydroxy-4-methoxy		(211)
3-Methoxy-4-hydroxy	19	(152)
p-Amino	Almost quantitative	(12)

In a *m*-nitrostyrene preparation where the yield was 30 per cent, 10 per cent of the β-hydroxyphenylpropionic acid and 20 per cent of the cinnamic acid were isolated (155). In the *p*-nitrostyrene preparation the yield of *p*-nitro-β-hydroxyphenylpropionic acid was 65 per cent (10). Some of the β-hydroxyphenylpropionic acid likewise was isolated in the 2-nitro-4-isopropylstyrene preparation (40).

A few substituted styrenes have been prepared by heating the corresponding β-hydroxyphenylpropionic acid lactone alone or in glacial acetic acid. These

$$\underset{\lfloor\_\_\_O\_\_\_\rfloor}{ArCHCH_2CO} \xrightarrow{heat} ArCH{=}CH_2 + CO_2$$

compounds are listed in table 12.

TABLE 10

Catalyzed decarboxylation of cinnamic acids

SUBSTITUTED STYRENE OBTAINED	CATALYST USED	YIELD	REFERENCE
		per cent	
o-Fluoro	Quinoline + copper powder	66	(121)
o-Chloro	Quinoline + copper sulfate	0	(216)
m-Chloro	Quinoline + copper powder	86	(216)
	Lepidine + copper sulfate	67	(216)
p-Chloro	Quinoline + copper powder	83	(216)
	Quinoline + copper acetate	71	(216)
	Lepidine + copper sulfate	58	(216)
	Quinoline + copper sulfate	50–54	(216)
2,4-Dichloro	Higher quinoline base + copper powder	20	(216)
3,4-Dichloro	Lepidine + copper sulfate	22	(216)
	Higher quinoline base + copper powder	16	(216)
m-Bromo	Lepidine + copper sulfate	56	(216)
o-Methoxy	Quinoline + copper powder	67	(216)
	Quinoline + copper powder		(121)
m-Methoxy	Copper chromite	27	(77)
p-Methoxy	Quinoline + copper powder	85	(216)
	Lepidine + copper sulfate	75	(216)
3,4-Dimethoxy	Lepidine + copper sulfate	10	(216)
3-Methoxy-4-hydroxy	Quinoline + copper powder	74	(169)
3-Methoxy-4-acetoxy	Quinoline + copper bronze	25	(172)
3,4-Dihydroxy	Aniline		(28)
p-Formyl	Quinoline + copper powder	52	(219a)
o-Cyano	Quinoline + copper bronze	30	(121)
m-Cyano	Quinoline + copper powder	51	(219b)
m-Nitro	Quinoline + copper powder	60	(219c, 219d)
	Lepidine + copper sulfate	0	(216)
p-Dimethylamino	Lepidine + copper sulfate	0	(216)
p-Vinyl	Quinoline + copper powder	45	(219a)

When *p*-methyl-β-hydroxyphenylpropionic acid was heated with dilute sulfuric acid some *p*-methylstyrene was isolated along with the main product, *p*-methylcinnamic acid (4).

TABLE 11

Styrenes from halogenated phenylpropionic acids

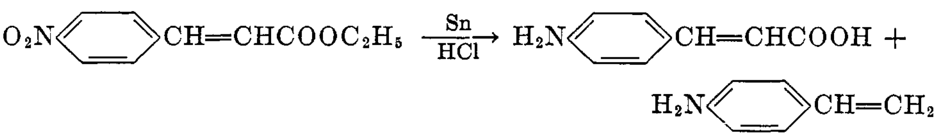
SUBSTITUTED STYRENE OBTAINED	HALOGEN IN PHENYLPROPIONIC ACID	YIELD	REFERENCE
		per cent	
o-Methyl	β-Bromo		(6)
m-Methyl	β-Bromo		(135)
p-Methyl	β-Bromo	51	(5)
Isopropyl	α-Bromo		(143)
p-Isopropyl	β-Bromo		(145)
p-Chloro	β-Bromo		(20)
p-Bromo	β-Bromo		(20)
o-Methoxy	β-Iodo		(148)
	β-Iodo		(147)
	β-Iodo		(146)
p-Methoxy	β-Iodo		(146)
	β-Iodo		(147)
o-Nitro	β-Bromo	10	(38)
	β-Bromo		(98)
	β-Bromo		(150)
m-Nitro	β-Bromo	59	(98)
	β-Bromo	30	(155)
	β-Bromo		(150)
p-Nitro	β-Bromo	29	(10)
2-Nitro-4-isopropyl	β-Bromo		(40)
o-Arsonic acid	β-Bromo		(30)
	β-Bromo		(31)

TABLE 12

Pyrolysis of β-hydroxyphenylpropionic acid lactones

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
o-Nitro		(38)
m-Nitro		(155)
p-Nitro	70	(98)
		(10)

Reduction of ethyl *p*-nitrocinnamate with tin and hydrochloric acid yielded both *p*-aminocinnamic acid and *p*-aminostyrene (11).



Treatment of 3,4-dibromomethylenedioxycinnamic acid dibromide with aqueous potassium hydroxide has been reported to yield both α- and β-bromo-3,4-dibromomethylenedioxycinnamic acids, 3,4-dibromomethylenedioxystyrene, and 3,4-dibromomethylenedioxy-α-bromostyrene (149).

When α-iodo-β,p-dimethoxyphenylpropionic acid was heated with aqueous ammonia at 100°C., the product was p-methoxystyrene (185).

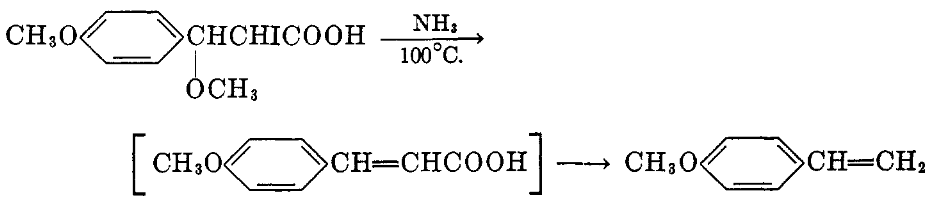
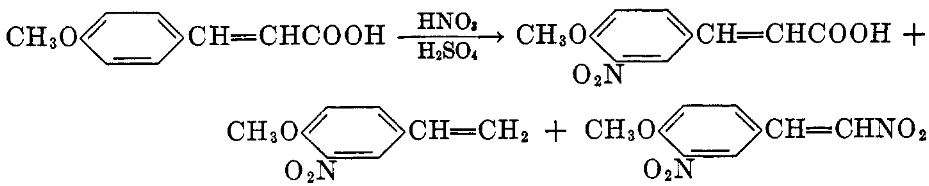


TABLE 13

Dehalogenation of styrene dibromides

SUBSTITUTED STYRENE OBTAINED	DEHALOGENATING AGENT	YIELD	REFERENCE
		per cent	
o-Ethyl	Mg	70	(61)
2-Hydroxy-3,5-dibromo	Zn + HCl		(63)
4-Hydroxy-3,5-dibromo	Zn + HBr		(230)
4-Hydroxy-2,3,5-tribromo	Zn + HBr		(231)

Nitration of p-methoxycinnamic acid yielded three products, as shown in the following equation (39):



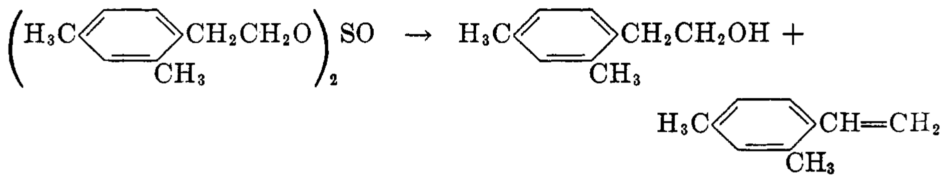
When o-methoxycinnamic acid was treated with sodium hypochlorite, a mixture of mono- and di-chlorinated derivatives of o-methoxystyrene was obtained (148).

VI. MISCELLANEOUS METHODS

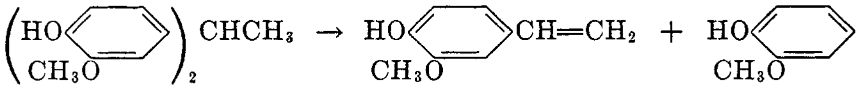
A few substituted styrenes have been prepared by treating the corresponding styrene dibromide with a metal or a metal and acid in ether solution. The styrenes prepared in this way are listed in table 13.

$$ArCHBrCH_2Br \xrightarrow{heat} ArCH{=}CH_2$$

Pyrolysis of the sulfite of 2,4-dimethyl-β-phenethyl alcohol yielded, besides the alcohol, some 2,4-dimethylstyrene (71).

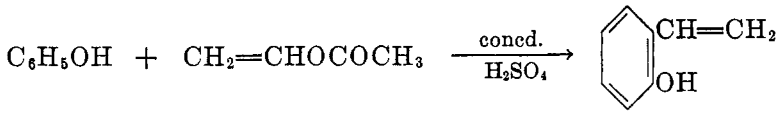


When the vapors of bis(3-methoxy-4-hydroxyphenyl)ethane were passed over "Tonsil" at 230°C., 55 per cent of 3-methoxy-4-hydroxystyrene and 88 per cent of catechol monomethyl ether were obtained (183).

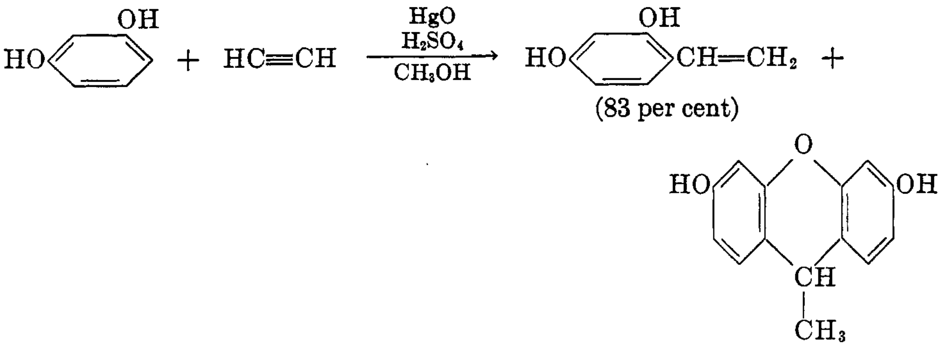


(55 per cent) (88 per cent)

When phenol was treated with vinyl acetate in the presence of concentrated sulfuric acid, *o*-hydroxystyrene was obtained (137).



Similarly, treatment of resorcinol with acetylene yielded 83 per cent of 2,4-dihydroxystyrene and 10 per cent of a substituted dibenzopyran (55). 2,4-Di-



(83 per cent)

methoxystyrene was prepared by the same method.

A mixture of *m*- and *p*-vinylphenylisocyanates and 2-methyl-5-vinylphenylisocyanate were prepared in 71 per cent and 31 per cent yields, respectively, by treating the corresponding aminostyrenes with phosgene (103a).

VII. β-NITROSTYRENES

This subject has been reviewed previously to a limited extent (72). β-Nitrostyrene itself was prepared first by Simon in 1839 (190), who obtained it in extremely small yield by distilling styrene with nitric acid. Styrene also has been nitrated by treating its nitrogen trioxide adduct with sulfuric acid (214).

$$C_6H_5CH{=}CH_2 \xrightarrow[CH_3COOH]{NaNO_2} C_6H_5CH{=}CH_2 \cdot N_2O_3 \xrightarrow{H_2SO_4} C_6H_5CH{=}CHNO_2$$

The first satisfactory synthetic method was that of Priebs (1883), who heated benzaldehyde and nitromethane at 160°C. in the presence of zinc chloride (156).

$$C_6H_5CHO + CH_3NO_2 \xrightarrow[160°C.]{ZnCl_2} C_6H_5CH{=}CHNO_2$$

For an 8-hr. run his yield amounted to 30–40 per cent (60 per cent with recycle) (157). He also obtained a 28 per cent yield by nitrating styrene by means of nitrogen pentoxide in ether. It was Priebs who first showed that the nitrostyrene of earlier investigators (3, 13, 190) was β-nitrostyrene. β,*o*-Dinitrostyrene and β,*m*-dinitrostyrene have been prepared by Priebs' method (157).

In 1899 Thiele (208) showed that benzaldehyde reacted with nitromethane in the presence of alcoholic potassium hydroxide. The reaction mixture was treated with acid in order to obtain the β-nitrostyrene. Since then this general method has been utilized for the synthesis of a tremendous number of β-nitrostyrenes, either with or without the isolation of the intermediate nitrophenethyl alcohol.

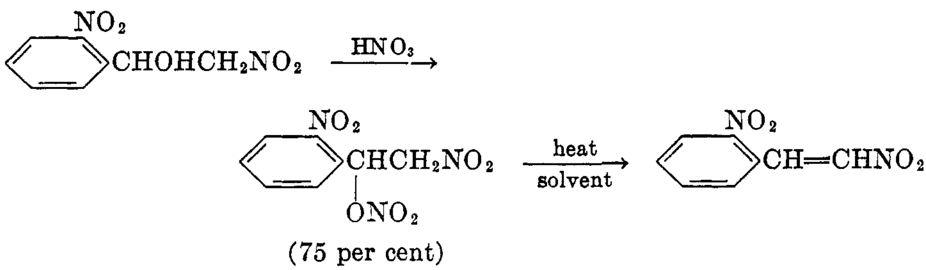
$$ArCHO + CH_3NO_2 \xrightarrow{OH^-} ArCHOHCH_2NO_2 \xrightarrow{H^+} ArCH{=}CHNO_2$$

In table 14 are summarized these β-nitrostyrene preparations.

In one *p*-acetoxy-β-nitrostyrene preparation, besides the 11 per cent of the product obtained, there also was isolated 15 per cent of *p*-hydroxy-β-nitrostyrene (68).

In a few instances the intermediate β-nitro-α-phenethyl alcohols have been isolated and used as intermediates for further synthetic work. Since these compounds are so closely related to the β-nitrostyrenes, their preparation is summarized in table 15. In general they are isolated by acidifying the original condensation mixture with acetic acid rather than with a mineral acid.

In the preparation of 3,4-methylenedioxy-β-nitro-α-phenethyl alcohol both the alcohol and 3,4-methylenedioxy-β-nitrostyrene were obtained, as shown in tables 14 and 15 (132). The β,*o*-dinitro-α-phenethyl alcohol and the β,2,4-trinitro-α-phenethyl alcohol were prepared as intermediates for obtaining the corresponding nitrostyrenes (54). The nitrates of these alcohols were prepared in 75 per cent and 73 per cent yields, respectively, and then converted to the corresponding styrenes by heating in a solvent.



(75 per cent)

Several investigators tested different condensing and dehydrating agents for the preparation of β-nitrostyrenes. The best yield obtained by the investigator

TABLE 14

β-Nitrostyrenes from aldehydes and nitromethane

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
	$NaOH + CH_3OH$	HCl	80–83	(221)
	$C_2H_5ONa + C_2H_5OH$	Dilute H_2SO_4	91.5	(75)
	$KOH + CH_3OH$	Dilute H_2SO_4	80	(209)
	$C_5H_{11}NH_2$		75	(96)
	$KOH + C_2H_5OH$	H^+		(208)
	$KHCO_3$	HCl in C_2H_5OH	14	(89)
p-Methyl	$C_5H_{11}NH_2$		60	(223)
o-Fluoro	$(C_2H_5)_3N$		60	(228)
o-Chloro	$(C_2H_5)_3N$		70	(222)
	$(C_2H_5)_3N$			(224)
	$NaOH + CH_3OH$	HCl	Good	(27)
m-Chloro	$NaOH + CH_3OH$	HCl	Good	(27)
p-Chloro	$NaOH + CH_3OH$	HCl	Good	(27)
	$KOH + C_2H_5OH$	Dilute HCl		(170)
o-Bromo	$(C_2H_5)_3N$		60	(227)
	Piperidine + $C_4H_9NH_2$		50	(27)
m-Bromo	$KOH + CH_3OH$	HCl		(100)
p-Bromo	$C_5H_{11}NH_2$		67	(222)
o-Iodo	$(C_2H_5)_3N$		65–70	(226)
o-Nitro	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH		(16)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH		(15)
m-Nitro	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	76	(194)
	$(C_2H_5)_3N$		47	(222)
	$KOH + C_2H_5OH$	H^+		(208)
	$KOH + C_2H_5OH$	HCl		(32)
p-Nitro	$KOH + C_2H_5OH$	H^+		(208)
m-Cyano	$KOH + H_2O + C_2H_5OH$	HCl	43	(192)
m-Carbomethoxy	$KOH + H_2O + C_2H_5OH$	HCl	70	(192)
m-Carbethoxy	$KOH + H_2O + C_2H_5OH$	HCl	63	(192)
p-Carbomethoxy	$KOH + H_2O + C_2H_5OH$	HCl	62	(192)
p-Carbethoxy	$KOH + H_2O + C_2H_5OH$	HCl	64	(192)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
o-Hydroxy	$NaOH + H_2O + CH_3OH$	HCl	35	(68)
	$KOH + C_2H_5OH$	Dilute HCl		(170)
2-Hydroxy-3-nitro	$KOH + C_2H_5OH$	Dilute HCl		(170)
2-Hydroxy-3-carboxy	$KOH + C_2H_5OH$	Dilute HCl		(170)
2-Hydroxy-3-carbethoxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
2-Hydroxy-3-carboxy-5-nitro	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
o-Methoxy	$(C_2H_5)_3N$			(225)
m-Hydroxy	$NaOH + H_2O + CH_3OH$	HCl	66	(68)
	$KOH + C_2H_5OH$	Dilute HCl		(170)
m-Methoxy	$KOH + H_2O + CH_3OH$	Dilute H_2SO_4		(187)
m-Carbethoxymethyleneoxy	$KOH + C_2H_5OH$	Dilute HCl		(170)
m-Carboxymethyleneoxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
p-Hydroxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
3-Nitro-4-hydroxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
3-Carbethoxy-4-hydroxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
3-Carboxy-4-hydroxy-5-nitro	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
p-Methoxy	$(CH_3NH_3)_2CO_3$		86	(96)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH	80	(16)
	$KOH + C_2H_5OH$	10% HCl	76	(102)
	$KOH + C_2H_5OH$	H^+	68	(174)
	$C_5H_{11}NH_2$		62	(222)
	C_2H_5ONa	HCl		(86)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH		(15)
	$(CH_3NH_3)_2CO_3$			(95)
3-Bromo-4-methoxy	$KOH + C_2H_5OH$	HCl		(100)
3-Nitro-4-methoxy	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	74	(194)
	$KOH + C_2H_5OH$	Dilute HCl		(170)
p-Benzyloxy	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
p-Acetoxy	$NaOH + H_2O + CH_3OH$	HCl	11	(68)
	$KOH + C_2H_5OH$	Dilute HCl		(170)
2-Nitro-5-acetoxy	$KOH + C_2H_5OH$	$(CH_3CO)_2O + CH_3COONa$	82	(10a)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
2-Nitro-6-acetoxy	$KOH + C_2H_5OH$	$(CH_3CO)_2O + CH_3COONa$	Almost theoretical	(10a)
p-Benzoxy	$KOH + C_2H_5OH$	Dilute HCl		(170)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
p-Ethoxycarboxy	$CH_3ONa + CH_3OH$	Dilute HCl		(177)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
p-Carboxymethyleneoxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
p-Carbethoxymethyleneoxy	$KOH + C_2H_5OH$	Dilute HCl		(170)
2-Hydroxy-4-methoxy	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
2,4-Dimethoxy	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
	$KOH + CH_3OH$	Dilute H_2SO_4		(117)
2,4-Dimethoxy-5-nitro	CH_3NH_2		Good	(168)
2-Ethoxy-4-methoxy	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
2,5-Dimethoxy	$(CH_3NH_3)_2CO_3$		76	(205)
3,4-Dihydroxy	$KOH + C_2H_5OH$	Dilute HCl	0	(170)
3-Hydroxy-4-methoxy	$NaOH + H_2O + CH_3OH$	HCl	96	(67)
3-Methoxy-4-hydroxy	$(CH_3NH_3)_2CO_3$		90	(96)
	$NaOH + CH_3OH$		84	(68)
	$C_5H_{11}NH_2$		80	(222)
	CH_3ONa	HCl		(177)
	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
3-Methoxy-4-hydroxy-5-bromo	CH_3NH_2		73	(115)
3,4-Dimethoxy	$(CH_3NH_3)_2CO_3$	CH_3COOH	83	(191)
	$KOH + CH_3OH$	HCl	68	(175)
	$KOH + C_2H_5OH$	Dilute HCl		(173)
	$KOH + CH_3OH$	Dilute HCl		(99)
	$KOH + CH_3OH$	Dilute HCl		(101)
	CH_3ONa	HCl		(8)
3,4-Dimethoxy-5-bromo	$KOH + C_2H_5OH$		41	(213)
3,4-Dimethoxy-5-nitro	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	76	(194)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
3-Methoxy-4-ethoxy...	$KOH + H_2O + C_2H_5OH$	Dilute HCl	100	(201)
	$KOH + CH_3OH$	10 per cent HCl		(103)
				(182)
3,4-Diethoxy..........	$(CH_3NH_3)_2CO_3$	CH_3COOH	94	(191)
3-Methoxy-4-benzyloxy...............	$NaOH + C_2H_5OH$	HCl	97	(107)
	CH_3NH_2		89	(97)
	$KOH + H_2O + C_2H_5OH$	10 per cent HCl	88	(202)
3-Benzyloxy-4-methoxy................	$(CH_3NH_3)_2CO_3$		85	(173)
	$KOH + H_2O + C_2H_5OH$	10 per cent HCl	40	(202)
3-Methoxy-4-methoxymethyleneoxy.......	$(CH_3NH_3)_2CO_3$			(97)
3,4-Methylenedioxy...	$C_5H_{11}NH_2$		96	(222)
	$(CH_3NH_3)_2CO_3$	CH_3COOH	94	(191)
	OH^-	Dilute HCl	93	(207)
	$(CH_3NH_3)_2CO_3$		93	(96)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH	75	(16)
	$NaOH + C_2H_5OH$	HCl	74	(107)
	$KOH + C_2H_5OH$	Dilute H_2SO_4	38	(136)
	$KHCO_3$	HCl in C_2H_5OH	34	(89)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH		(15)
	$CH_3ONa + CH_3OH$	H^+		(132)
	$KOH + CH_3OH$	HCl		(175)
3-Methoxy-4-acetoxy...	$KHCO_3$	HCl in C_2H_5OH	27	(89)
3-Methoxy-4-benzoxy .	$(CH_3NH_3)_2CO_3$		75	(213)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
3,4-Diacetoxy.........	$KHCO_3$	HCl in C_2H_5OH	70	(89)
3,4-Dibenzoxy........	$CH_3ONa + CH_3OH$	Dilute HCl		(177)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
3,4-Di(ethoxycarboxy).	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
2,3,4-Trimethoxy......	$KOH + C_2H_5OH$	Dilute HCl	73	(193)
2,4,5-Trimethoxy.....	$KOH + H_2O + C_2H_5OH$	HCl		(85)
	$KOH + H_2O + C_2H_5OH$	HCl		(86)

TABLE 14—*Concluded*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
3,5-Dimethoxy-4-hydroxy	$KOH + C_2H_5OH$			(130)
3,4,5-Trimethoxy	$KOH + C_2H_5OH$	10 per cent HCl	80	(200)
	$KOH + C_2H_5OH$	Dilute HCl	79	(193)
	$KOH + C_2H_5OH$			(130)
3,4,5-Triethoxy	$KOH + C_2H_5OH$	Dilute HCl	55	(193)
2,5-Dimethoxy-3,4-methylenedioxy	$KOH + CH_3OH$			(117)

in question has been given in table 14. In table 16 are shown for purposes of comparison the various conditions tried.

Worrall (222) showed that β-nitro-α-phenethyl alcohol was converted quantitatively to β-nitrostyrene by distillation from acids. The use of molar quantities of diethylamine or amylamine in the benzaldehyde–nitromethane reaction gave only tar. Good yields of β-nitrostyrene were obtained from nitromethane and benzalbutylamine or benzalamylamine. Nitromethane reacted with benzalaniline to give an adduct which yielded β-nitrostyrene on heating with hydrochloric acid (131).

$$C_6H_5CH{=}NC_6H_5 + CH_3NO_2 \rightarrow C_6H_5\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}HCH_2NO_2 \rightarrow C_6H_5CH{=}CHNO_2$$

Treatment of this adduct with benzaldehyde also gave β-nitrostyrene (222).

$$C_6H_5\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}HCH_2NO_2 + C_6H_5CHO \rightarrow$$

$$C_6H_5CH{=}CHNO_2 + C_6H_5CH{=}NC_6H_5 + H_2O$$

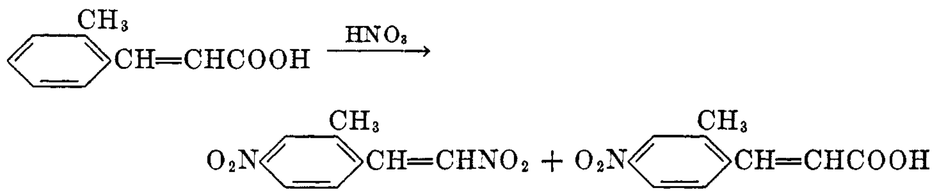
Quite a few β-nitrostyrenes have been prepared by nitrating cinnamic acids.

$$ArCH{=}CHCOOH \xrightarrow{HNO_3} ArCH{=}CHNO_2$$

The aromatic nucleus may or may not be nitrated in the process. The β-nitrostyrenes prepared by this means are listed in table 17.

Nitric acid or a mixture of nitric and sulfuric acids was used for all of these nitrations except in the case of cinnamic acid itself, where nitrogen dioxide in ether (49), hot aqueous sodium nitrate (49), and nitrous and sulfuric acids (154) were found to be effective.

In the nitration of *o*-methylcinnamic acid, some 2-methyl-4-nitrocinnamic acid was obtained as well as the 2-methyl-β,4-dinitrostyrene (58). Likewise, as



mentioned in a previous section, the nitration of *p*-methoxycinnamic acid yielded, besides 4-methoxy-β,3-dinitrostyrene, 3-nitro-4-methoxystyrene and 3-nitro-4-methoxycinnamic acid (151).

TABLE 15
β-Nitro-α-phenethyl alcohols

SUBSTITUTED β-NITRO-α-PHENETHYL ALCOHOL OBTAINED	CONDENSING AGENT	YIELD	REFERENCE
		per cent	
o-Nitro	CH_3ONa	84	(76)
	$CH_3ONa + CH_3OH$		(176)
	$(C_2H_5)_3N$		(54)
	$KOH + C_2H_5OH$		(208)
2,4-Dinitro	$(C_2H_5)_3N$	41	(54)
p-Methoxy	$CH_3ONa + CH_3OH$		(176)
3,5-Dinitro-4-methoxy	$KOH + C_2H_5OH$		(170)
p-Benzoxy	$CH_3ONa + CH_3OH$		(176)
p-Ethoxycarboxy	$CH_3ONa + CH_3OH$		(176)
2,5-Dihydroxy	$CH_3ONa + CH_3OH$		(170)
3,4-Dihydroxy	$NaHSO_3 + NaOH + H_2O$	93	(88)
3,4-Dimethoxy	$CH_3ONa + CH_3OH$		(176)
3,4-Methylenedioxy	CH_3ONa		(132)
3,4-Dibenzoxy	$CH_3ONa + CH_3OH$		(176)
3,4-Di(ethoxycarboxy)	$CH_3ONa + CH_3OH$		(176)

These cinnamic acid nitrations are believed to proceed through an intermediate of the type:

$$\left(ArCH{=}C\begin{matrix}NO_2\\COOH\end{matrix}\right)$$

which loses carbon dioxide on treatment with water (109). Treatment of such a compound with concentrated sulfuric acid below 10°C. yielded the corresponding β-nitrostyrene (60).

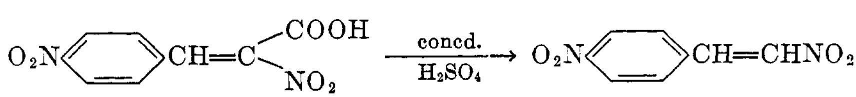


TABLE 16

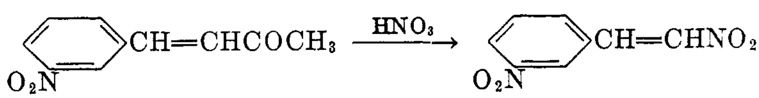
Comparison of β-nitrostyrene preparations

SUBSTITUTED β-NITROSTYRENE OBTAINED	CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
	5% concentrated aqueous NH_3		14	(222)
	5% hydrobenzamide		14	(222)
	5% n-$C_4H_9NH_2$		54	(222)
	5% $HOCH_2CH_2NH_2$		54	(222)
	5% $CH_2{=}CHCH_2NH_2$		57	(222)
	5% $C_6H_5CH_2NH_2$		61	(222)
	5% n-$C_5H_{11}NH_2$		64	(222)
	5% piperidine		14	(222)
	5% pyridine		Trace	(222)
	5% $(C_2H_5)_2NH$		38	(222)
	5% $(C_6H_5CH_2)_2NH$		Poor	(222)
	5% $(n$-$C_4H_9)_2NH$		Poor	(222)
	5% $(HOCH_2CH_2)_2NH$		Poor	(222)
	5% $(C_2H_5)_3N$		52	(222)
	5% $(HOCH_2CH_2)_3N$		53	(222)
	10% $C_6H_5NH_2$		32	(222)
	10% *o*-toluidine		4	(222)
	10% *m*-toluidine		38	(222)
	10% *p*-toluidine		41	(222)
	10% *p*-chloroaniline		23	(222)
	10% *p*-anisidine		57	(222)
	10% *p*-aminodimethylaniline		54	(222)
	10% α-naphthylamine		<1	(222)
	10% β-naphthylamine		24	(222)
	$C_5H_{11}NH_2$		75	(96)
	$C_2H_5NH_2$		25	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)
o-Chloro	$C_5H_{11}NH_2$		3–4	(222)
	$(C_2H_5)_2NH$		50	(222)
	$(C_2H_5)_3N$		70	(222)
p-Bromo	$C_5H_{11}NH_2$		67	(222)
	$(C_2H_5)_3N$		50	(222)
m-Nitro	$C_5H_{11}NH_2$		9	(222)
	$(C_2H_5)_3N$		47	(222)
	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	76	(194)
	CH_3NH_2		32	(194)
p-Carbomethoxy	$KOH + H_2O + C_2H_5OH$	HCl	62	(192)
	CH_3NH_3Cl		33	(192)
o-Hydroxy	$NaOH + H_2O + CH_3OH$	HCl	35	(68)
	$CH_3NH_2 \cdot CH_3COOH$		28	(68)

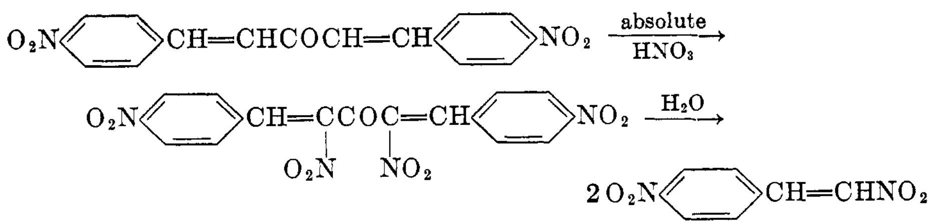
TABLE 16—*Concluded*

SUBSTITUTED β-NITROSTYRENE OBTAINED	CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
p-Methoxy	$C_5H_{11}NH_2$		62	(222)
	$(C_2H_5)_3N$		39	(222)
	$(CH_3NH_3)_2CO_3$		86	(96)
	$KOH + CH_3OH$	H^+	65	(96)
	$C_2H_5NH_2$		0	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)
2-Hydroxy-4-methoxy	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
	CH_3NH_3Cl		Low	(168)
3-Methoxy-4-hydroxy	$(CH_3NH_3)_2CO_3$		90	(96)
	$KOH + CH_3OH$	H^+	0	(96)
	$C_2H_5NH_2$		0	(96)
	$C_5H_{11}NH_2$		80	(222)
	$(C_2H_5)_3N$		0	(222)
	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
	CH_3NH_3Cl		Good	(168)
3,4-Dimethoxy-5-nitro	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	76	(194)
	CH_3NH_2		30	(194)
3,4-Methylenedioxy	$C_5H_{11}NH_2$		80	(222)
	$(C_2H_5)_3N$		0	(222)
	$KOH + CH_3OH$	H^+	95	(96)
	$(CH_3NH_3)_2CO_3$		93	(96)
	$C_2H_5NH_2$		25	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)

Nitration of *m*- and *p*-nitrostyryl methyl ketones and of *m*- and *p*-nitrodistyryl ketones yielded the corresponding β-nitrostyrenes (110). In the case of the



p-nitrodistyryl ketone an intermediate nitro compound was isolated which decomposed to give β,*p*-dinitrostyrene on treatment with water.



A similar compound derived from *p*-methoxystyryl methyl ketone decomposed on treatment with aqueous sodium hydroxide to give *p*-methoxy-β-nitrostyrene (218).

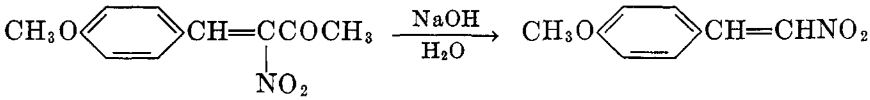


TABLE 17

β-Nitrostyrenes by nitration of cinnamic acids

SUBSTITUTED CINNAMIC ACID USED	SUBSTITUTED β-NITROSTYRENE OBTAINED	YIELD	REFERENCE
		per cent	
		38	(154)
		15	(49)
			(48)
	(*o* + *p*)-Nitro		(109)
o-Methyl	2-Methyl-4-nitro		(58)
p-Methyl	3-Nitro-4-methyl		(70)
p-Chloro	(2 + 3)-Nitro-4-chloro	67	(109)
p-Bromo	(2 + 3)-Nitro-4-bromo	66	(109)
3,4,5-Tribromo	2-Nitro-3,4,5-tribromo		(25)
o-Nitro	*o*-Nitro	50	(109)
	o-Nitro		(108)
m-Nitro	*m*-Nitro	70	(109)
	m-Nitro		(59)
p-Nitro	*p*-Nitro	75	(109)
	p-Nitro	22	(151)
2-Nitro-4-chloro	2-Nitro-4-chloro	60	(109)
3-Nitro-4-chloro	3-Nitro-4-chloro	60	(109)
2-Nitro-4-bromo	2-Nitro-4-bromo	70	(109)
3-Nitro-4-bromo	3-Nitro-4-bromo.	70	(109)
p-Methoxy	3-Nitro-4-methoxy		(39)
p-Amino	2-Nitro-4-amino		(59)
p-Acetamino	3-Nitro-4-acetamino		(65)

α-Ethoxy-β-nitrostyrene was obtained in 25–30 per cent yields by a similar procedure (217).

$$\underset{\substack{|\quad\ \ |\\ C_2H_5O\ \ NO_2}}{C_6H_5CHCHCOC_6H_5} \xrightarrow[C_2H_5OH]{KOH} \underset{\substack{|\\ OC_2H_5}}{C_6H_5C{=}CHNO_2}$$

A dinitro derivative behaved similarly (219).

$$\underset{\substack{|\quad\ \ |\\ O_2N\ \ NO_2}}{C_6H_5CHCHCOCH{=}CHC_6H_5} \xrightarrow[CH_3OH]{KOH}$$

$$C_6H_5CH{=}CHNO_2 + NH_4NO_2 + C_6H_5CH{=}CHCOOH$$

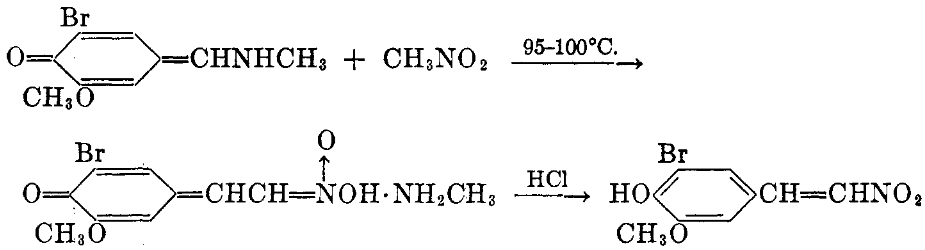
Sodium nitromethane reacted with benzil in ethanol solution to give ethyl benzoate and sodium β-nitro-α-phenethyl alcohol (64, 90). The latter compound yielded β-nitrostyrene on treatment with acid. Yields of 56–58 per cent were obtained (64).

$$C_6H_5COCOC_6H_5 + CH_2{=}NO_2Na + C_2H_5OH \rightarrow$$

$$\underset{(58\text{ per cent})}{C_6H_5COOC_2H_5} + C_6H_5CHOHCH{=}NO_2Na \xrightarrow{H^+} \underset{(56\text{ per cent})}{C_6H_5CH{=}CHNO_2}$$

Under the same conditions (nitromethane and sodium ethoxide in pyridine) phenyl furyl diketone yielded β-nitrostyrene, ethyl benzoate, and ethyl furoate but no α-furyl-β-nitroethylene (64).

Nitromethane reacted with the quinoid forms of vanillylidenemethylamine and of 5-bromovanillylidenemethylamine to give methylamine salts of the corresponding β-nitrostyrenes (115). Treatment with hydrochloric acid liberated the β-nitrostyrene.



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