Synthesis of Substituted, 1,1-Diarylethanes

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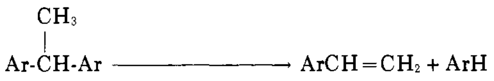
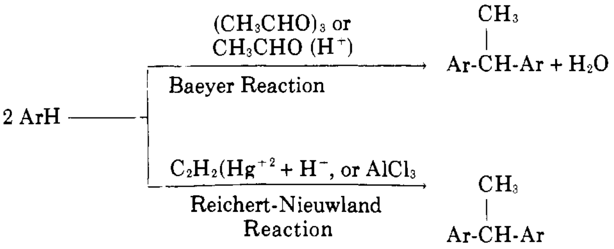
1,1-Diarylethanes have been conveniently synthesized from benzenes substituted with alkyl, halo, hydroxy, methoxy, and amino groups and from several other aromatic compounds by means of the Baeyer reaction with acetaldehyde or the Reichert-Nieuwland reaction with acetylene.

A DIRECT and efficient method of preparing ring-substituted styrenes utilizes 1,1-diarylethanes as intermediates which are cracked over siliceous catalysts to produce the styrene in high yield (*2, 7, 10*).



$$\mathrm{Ar{-}\overset{CH_3}{\overset{|}{C}}H{-}Ar \longrightarrow ArCH{=}CH_2 + ArH}$$

Among the numerous methods of preparing diarylethanes, the two routes employed here give the highest yields from the simplest reactants in one step. These comprise the treatment of an aromatic compound with paraldehyde (or acetaldehyde) in the Baeyer reaction (*1*) and with acetylene in the Reichert-Nieuwland reaction (*8*).



The present work summarizes the best conditions for the preparation of a number of diarylethanes from benzene, mono-, di-, and tri-substituted benzenes, naphthalene, and thiophene.

RESULTS

The experiment results have been grouped in Tables I to IV according to type of aromatic starting material. Previous publications (*2, 6*) noted that Baeyer 1,1-diarylethanes differ greatly from Reichert-Nieuwland 1,1-diarylethanes in isomeric composition. In the tables, these compositions are indicated in cases where they have been determined.

Results with aromatic hydrocarbons are summarized in Table I. In all cases, the catalyst was 95 to 97% H_2SO_4 and reactions were run at 0° to 10° C. unless otherwise indicated. Yields are based on the aromatic consumed. Acetylene syntheses always employed Hg^{+2} cocatalyst, usually added in the form of 23% $HgSO_4$in 15% H_2SO_4. The product isomer distribution was determined by infrared analysis; in some cases only the total amount of each type of substitution was determined.

The diarylethanes from the Baeyer reaction were observed to have higher para/ortho ratios than those from the Reichert-Nieuwland reaction. For example, in the case of *m*-xylene, no 2,6-substituted products could be detected with acetaldehyde while 20% of the acetylene derived product consisted of 2,6-substituted diarylethanes. Differences with toluene and ethylbenzene were also quite striking. When the Baeyer reaction, in which para substitution is preferred, was carried out with *p*-xylene a very low yield of diarylethane was obtained compared with the yield from the Reichert-Nieuwland reaction. The Baeyer reaction did not require a mercuric salt catalyst. Moreover, a larger amount of more dilute sulfuric acid gave highest yields. Higher yields were also obtained and product isolation simplified when an excess of aromatic was employed so that only 25 to 40% was reacted with aldehyde (*9*).

The diarylethanes listed in Table II were prepared from highly reactive aromatics such as phenols and their ethers. In all cases, only Baeyer synthesis conditions were used with these compounds. The reaction temperature range was 30° to 45° C.

The halogenated benzenes listed in Table III were converted to diarylethanes by condensation with acetylene in the presence of a Lewis acid catalyst, $HAlCl_4$. The temperature range was 70° to 80° C.

Experiments with several aromatic amines, thiophene, thiophenol, and ethyl phenylacetate are summarized in Table IV. Acetaldehyde was used with aniline; acetylene with thiophenol and ethylphenylacetate; and paraldehyde with the other compounds. Ethanol solvent was used for *N,N*-dimethylaniline. Only in the case of *N,N*-dimethylaniline was good yield of diarylethanes obtained. In addition to those reported in Table IV, condensations were carried out successfully with toluene using formaldehyde and propionaldehyde giving ditolylmethane and 1,1-ditolylpropane, respectively, and with *ortho-* and *meta*-cresol using acetone in the presence of $HCL\text{-}HSCH_2COOH$ to give 2,2-dicresylpropanes.

During our studies an approximate correlation was useful for estimating the optimum acid concentration for the Baeyer condensation of several substituted benzenes. When aqueous solutions of strong acids were employed as catalysts, the acidity, expressed as H_o (*4*), required for maximum yield of diarylethanes was directly related to the substituent constant σ (*4*). The correlation was especially useful when sulfuric acid was employed as the acid catalyst since one of the major side reactions was sulfonation of both the starting aromatic and the product diarylethane.

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Table I. 1,1-Diarylethanes from Aromatic Hydrocarbons

Aromatic Reactant	Yield, % Using: Acetylene A	Yield, % Using: Paraldehyde B	Theoretical Conversion,[a] %: A	Theoretical Conversion,[a] %: B	Product Isomer Distribution: A	Product Isomer Distribution: B	B.P., ° C./Mm. Hg	M.P., ° C.
Benzene	14[b]	...	30	...			153/20	
Toluene	89	95	30	36	30% *p*, *p* 70% *o*, *p*	77% *p*, *p* 22% *o*, *p*	178/20, 300/760	
o-Xylene, 100%	87	95[c,d]	36	36	80% 3, 4 20% 2, 3	100% 3, 4	201/20	
p-Xylene, 97%	75[e]	22[b,d]	15	30	>95% 2, 5		200/20	60.5-61.0 from MeOH
m-Xylene, 97%	86	92	36	33	80% 2, 4 20% 2, 6	100% 2, 4	195/20	
Ethylbenzene	89	83	36	25	62% *p* 21% *m* 17% *o*	94% *p*, *p*	198-200/20	
Isopropylbenzene	88[f]	19[g,h]	33	30	60% *o* 40% *p*		174/5	
tert-Butylbenzene	79	<1[g]	28	33	10% *o*, *p* 90% *p*, *p*		194/10	96.5-97.0 from MeOH
Cyclohexylbenzene	19[d,i]	...	33	...	...		220-5/1	
Naphthalene	...	70[j]	...	...	Mostly β		231/11	83-86

[a] Refers to molar equivalent of acetylene or aldehyde to aromatic. [b] Low yield due to formation of polymeric materials. [c] Reaction temperature: −14° C. [d] Used 5 grams of AEROSOL[R] C-25 emulsifying agent from American Cyanamid Company. [e] Reaction temperature: 17° C. [f] Used trace of $NaClO_4$ as additional cocatalyst. [g] Alkylating agent reacted poorly. Low yield due to material losses in work-up. [h] Acetic acid solvent; 107% H_2SO_4 catalyst. [i] $BF_3 \cdot CH_3COOH + HgO$ catalyst system at 60° C. gave low yield of product. [j] Used HF catalyst and chlorobenzene solvent.

Table II. 1,1-Diarylethanes from Phenols and Phenol Ethers with Paraldehyde

Aromatic Reactant	Yield, %	Theoretical Conversion, %	Catalyst	B.P., ° C./Mm. Hg	M.P., ° C.
Phenol	90	50	37% HCl		99–103[a,b] 120–122[c]
p-Cresol	90	50	37% HCl	glass, not distillable[d]	
o-Cresol	97	50	37% HCl	glass, not distillable[d]	
Anisole	96	40	65% H_2SO_4	215/15	67–68
Resorcinol di-Me-Ether	89	36	65% H_2SO_4	240/10	

[a] The m.p. of 99–103° C. is for the *p*,*p* product containing one mole of phenol of crystallization. The higher melting point is for solvent-free product. The complex was isolated on crystallization in the reaction vessel after removal of excess phenol and catalyst by steam distillation. The complexed phenol was removed from the product by a second steam distillation with superheated steam. [b] Lit. m.p. 100–102° C. (*5*). [c] Lit. m.p. 122° C. (*3*). [d] Also isolated from reaction vessel after removal of excess cresol and catalyst by steam distillation.

Table III. 1,1-Diarylethanes from Halogenated Aromatics with Acetylene

Substituted Benzene Reactant	Yield,[b] %	Theoretical Conversion[c], %	B.P., ° C./Mm. Hg	M.P., ° C.	Remarks
—Cl	67	28	204/22		$d_4^{25} = 1.210$ $\eta_D^{25} = 1.5889$
1—CH_3—2—Cl	51	40	165–166/2		Colorless liq. 3—Me—4—Cl
1,2—Di—Cl	73	28	225/12		$d_4^{25} = 1.38$ $\eta_D^{25} = 1.6114$
1,4—Di—Cl	36	28	210/10		
1,2,3—Tri—Cl	56	40	195–205/0.15	142–3(EtOH)	Colorless prisms, [a] s. sol. EtOH
1,2,4—Tri—Cl	56	50	180–200/0.25	133–5(EtOH)	Yellow Oil[b] before cryst.; sol acetone
—F	37	46	173/50		45% *o,p*; 45% *p,p*; 10% *m*-mixture

[a] Anal.Calcd. for $C_{14}H_8Cl_6$: Cl, 54.7; Found, Cl, 54.5%.

Anal. Calcd. for $C_{14}H_8Cl_6$: Cl, 54.7; Found, Cl, 54.97%.

Table IV. 1,1-Diarylethanes from Amines and Miscellaneous Compounds

Aromatic Reactant	Yield, %	Catalyst	Theoretical Conversion, %	Reaction Temp., ° C.	B.P., ° C./Mm. Hg	M.P., ° C.
N,N-Dimethyl aniline	92	18% H_2SO_4	100	55	270–80/15/20	67–58
Aniline	16	37% HCl	100	130	170–190/0.6 360–380/760	
N,N-Dimethylbenzylamine	0	55% or 97% H_2SO_4	37	40	...	
Thiophene	23	37% HCl + HCl gas	100	75	140–5/9	
Thiophenol	0	97% H_2SO_4	40	0	...	
Ethyl phenylacetate	0	97% H_2SO_4 or $HAlCl_4$	30	0 or 55	...	

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Synthesis of *N*-Carboalkoxy-ε-Aminocaproic Acid Esters

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Two procedures for the synthesis of *N*-carboalkoxy-ε-aminocaproates starting with ε-caprolactam are described. The first method involves hydrolysis, treatment with a chloroformate, and esterification. The second procedure involves alcoholysis, phosgenation, and treatment with an alcohol. Physical properties of the compounds and their intermediates are listed.

STRUCTURAL SIMILARITY between *N*-carboalkoxy-ε-aminocaproic acid esters (I) and diesters of aliphatic dicarboxylic acids (II), prompted the synthesis of a variety of such urethane-esters and the evaluation of them in areas where the diesters find wide applications—plasticizers, synthetic lubricants, polymer intermediates.

$$\mathrm{ROOCNH\text{-}(CH_2)_5COOR} \qquad \mathrm{ROOC\text{-}(CH_2)_n\text{-}COOR}$$

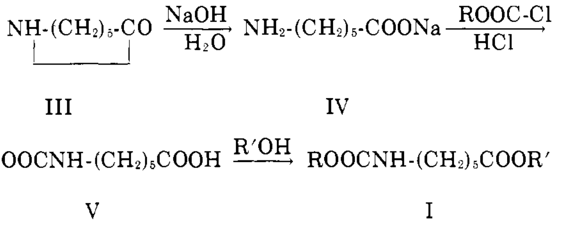
I II

The higher homologues of the urethane-esters were effective plasticizers for poly(vinyl chloride) resins and exhibited little tendency towards migration. Polymers containing both urea and amide linkages were prepared by condensing a urethane-ester with an aliphatic diamine.

Treibs and Hauptmann (*4*) prepared methyl *N*-carbomethoxy-ε-aminocaproate via a Hofmann degradation by treating 6-carbomethoxyhexanoic acid amide with bromine and alkali in the presence of methanol. Adamson and Kenner (*1*) synthesized ethyl *N*-carboethoxy-ε-aminocaproate from ethyl-ε-aminocaproate. The disadvantage of the latter method is that a relatively unstable intermediate (the free amino ester) must be used.

Two convenient methods for the synthesis of the *N*-carboalkoxy-ε-aminocaproates starting with ε-caprolactam were developed.

Chloroformate Method.



$$\mathrm{NH\text{-}(CH_2)_5\text{-}CO} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} \mathrm{NH_2\text{-}(CH_2)_5\text{-}COONa} \xrightarrow[\mathrm{HCl}]{\mathrm{ROOC\text{-}Cl}}$$

III IV

$$\mathrm{ROOCNH\text{-}(CH_2)_5COOH} \xrightarrow{\mathrm{R'OH}} \mathrm{ROOCNH\text{-}(CH_2)_5COOR'}$$

V I

Refluxing ε-caprolactam (III) with an aqueous solution of sodium hydroxide effects the ring opening (IV), following which an alkyl chloroformate is added at room temperature. Upon acidification, the *N*-carboalkoxy-ε-aminocaproic acid (V) is obtained. The latter is esterified with an alcohol in the usual manner to give the *N*-carboalkoxy-ε-aminocaproic acid ester (I).

Table I lists a variety of urethane acids prepared by this method.

Isocyanate Method.