menasylate in 80 ml of dimethylformamide was added dropwise over a 15-min period 9 ml of thionyl chloride at room temperature. After stirring for an additional 5 min, the reaction solution was poured into ice-water. Precipitates were filtered and dried. Recrystallization from ligroin gave 15.7 g of the pure chloride, mp 98.0–99.0° (lit.[6] mp 97–98°).

Preparation of Menasylates. Menasylates were prepared by standard procedures from menasyl chloride and alcohols at 0° in pyridine as a solvent.

2-Phenylethyl menasylate (**1**) had mp 101.9–102.5° (from ligroin).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56; S, 9.82. Found: C, 69.98; H, 5.29; S, 9.71.

2-(*p*-Methoxyphenyl)ethyl menasylate (**2**) had mp 112.8–113.3° (from ligroin-benzene).

Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66; S, 9.00. Found: C, 67.30; H, 5.46; S, 8.80.

2-(*p*-Nitrophenyl)ethyl menasylate (**3**) had mp 135.0–135.8° (from carbon tetrachloride-chloroform).

Anal. Calcd for $C_{19}H_{17}NO_5S$: C, 61.44; H, 4.61; N, 3.77; S, 8.63. Found: C, 61.31; H, 4.47; N, 3.58; S, 8.78.

Trifluoroacetolysis Media. Trifluoroacetic acid and its 2 vol % of trifluoroacetic anhydride were refluxed for 2 hr. The solution was then distilled through a 85-cm vacuum-jacketed column packed with glass helices. The middle cut (bp 71.5–72.0°) was redistilled through the same column. To this middle cut (bp 71.5–72.0°) was added 1 wt % of freshly distilled trifluoroacetic anhydride. Sodium trifluoroacetate (17.0 g, 0.125 mol) was dissolved with the previous solution in a 1000-ml volumetric flask to prepare buffered medium.

Kinetic Procedure. The required amount of menasylate for making a 0.05 *M* solution was weighed in a volumetric flask and diluted with the trifluoroacetolysis media prepared as above. For the reactions above 50°, 1.5-ml portions of this solution were sealed in 5-ml glass ampoules, which were placed together in a thermostatic bath at the desired temperature (±0.02°). At the appropriate intervals, the tubes were quenched in ice-water successively. Each was warmed to room temperature and opened, and 1.00 ml of the solution was pipetted into *ca.* 48 ml of 95% ethanol in a 50-ml volumetric flask, followed by 95% ethanol up to the mark. The absorbance of the resulting solution was measured at the maximum of 326 nm, using a Hitachi Perkin-Elmer 139 uv-visible spectrophotometer. A Beer's law for the concentration of ethyl menasylate was shown to be linear over the range used for the kinetics.

The reaction of **3** was followed using a 0.025 *M* solution. For the reaction of **2** at 24°, 1-ml aliquots were pipetted out from a reaction flask placed in a thermostatic bath.

Registry No.—**1**, 51751-79-2; **2**, 51751-80-5; **3**, 51751-81-6; menasylic acid, 29181-96-2; 2-methylnaphthalene, 91-57-6; menasyl chloride, 1875-72-5; sodium menasylate, 13035-04-6; 2-phenylethanol, 60-12-8; 2-(*p*-methoxyphenyl)ethanol, 702-23-8; 2-(*p*-nitrophenyl)ethanol, 100-27-6; trifluoroacetic acid, 76-05-1.

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Friedel–Crafts Alkylations with Aromatic Aldehydes

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Received February 20, 1974

Friedel–Crafts reactions of benzaldehyde with aromatic substrates have been reported to produce either triarylmethanes or anthracene derivatives depending on the catalyst, substrate, and reaction conditions.[1] In the reaction of substituted benzaldehydes with benzene in the presence of aluminum chloride to produce anthracenes it was found that the aldehyde served only to supply the meso carbon atoms in the anthracene molecule[2] *via* decarbonylation to carbon monoxide. Benzoic acid[3] and "traces" of diphenylmethane[4] have also been reported as products of the reaction of benzaldehyde with benzene in the presence of aluminum chloride.

During the course of a study of Tishchenko reactions catalyzed by boron compounds[5] a new modification of the Friedel–Crafts reaction of benzaldehydes with aromatics has been found. When boron trifluoride etherate is used as catalyst at elevated temperatures the major products are diphenylmethane derivatives along with low yields of the corresponding benzoic acids. If the assumption is correct that the initial reaction step is disproportionation of the aldehyde to benzyl benzoate, the following reaction stoichiometry would be expected.

$$2\mathrm{ArCHO} \xrightarrow{\mathrm{BF_3}} \mathrm{ArCO_2CH_2Ar} \xrightarrow[\mathrm{BF_3}]{\mathrm{Ar'H}} \mathrm{ArCH_2Ar'} + \mathrm{ArCO_2H}$$

Table I summarizes the results observed under typical conditions using excess aromatic hydrocarbon as solvent.

Although good yields of diphenylmethane derivatives were usually obtained, the corresponding carboxylic acid was generally found in only 10–15% yield by basic extraction. In addition to the products isolated there were rather substantial quantities of heavy tars produced. Dibenzylated materials were found in some cases but there was no indication of incorporation of the bulk of the benzoic acid in the form of volatile carbonyl-containing compounds; however, minor quantities of ethyl benzoate were detected (control experiments showed that benzoic acid in benzene solution reacted with boron fluoride etherate to give ethyl benzoate at 150°). Benzylation of benzene and toluene with benzyl benzoate in the presence of catalytic quantities of boron fluoride etherate was found to give high yields of both diphenylmethane and benzoic acid. Treatment of benzaldehyde with boron fluoride etherate in cyclohexane gave no reaction at reflux and tars under more forcing conditions. Pure benzyl benzoate when refluxed with boron fluoride in cyclohexane was converted to polymer (polybenzyl) and benzoic acid. Benzene did not react with carbon monoxide at 200° and 1800 psig in the presence of boron fluoride. Stannic chloride was completely ineffective as a catalyst for the reaction using method B; the starting materials were recovered unchanged. Because of the differences in reaction products between benzaldehyde and benzyl benzoate cited the equation above undoubtedly represents an oversimplification. Although mechanisms can be written which would account for the observed products, they would be speculative at this time; a competition between other routes and a Tishchenko disproportionation, followed by alkylation, may also be occurring.

Isomer distributions of the benzyltoluenes from the reaction of benzaldehyde with toluene were determined by capillary glc and found to be substantially the same for all three methods of preparation: 49–51% para, 7–8% meta, and 41–43% ortho. Reaction of *p*-tolualdehyde with benzene gave *p*-benzyltoluene of >99.5% purity and *p*-chlorobenzaldehyde with benzene gave 4-chlorodiphenylmethane, also in very high purity. Where the requisite aldehydes are available this method may provide a useful synthetic procedure for the preparation of substituted diphenylmethanes,[6] since the experimental procedure, par-

Table I

$$2ArCHO + Ar'H \xrightarrow{BF_3} ArCH_2Ar' + ArCO_2H$$

Registry no.		Ar	Mol	Ar'	Ml	Method[a]	Aldehyde conver-sion, %	Diphenyl-meth-ane[b] yield, %	$ArCH_2Ar'$ registry no.
ArCHO'	Ar'H								
100-52-7	71-43-2	C_6H_5	1.89	C_6H_5	400	A	8	85	101-81-5
		C_6H_5	1.89	C_6H_5	400	B	16	91	
		C_6H_5	1.89	C_6H_5	300	C	47	55	
	108-88-3	C_6H_5	1.89	$CH_3C_6H_4$	400	A	16	81	
		C_6H_5	1.89	$CH_3C_6H_4$	400	B	36	82	
		C_6H_5	1.89	$CH_3C_6H_4$	300	C	51	57	
	108-38-3	C_6H_5	1.89	m-$(CH_3)_2C_6H_3$	300	C	53	67	38094-29-0
104-87-0		p-$CH_3C_6H_4$	1.89	C_6H_5	300	C	48	33	620-83-7
104-88-1		p-ClC_6H_4	1.00	C_6H_5	300	C	66	79	14310-22-6

[a] In method A the indicated quantities were refluxed under nitrogen with 25 ml of boron fluoride etherate for 24 hr, method B used 48-hr reflux, and in method C the reaction mixtures were heated for 6 hr at 150° in an autoclave. [b] Based on reacted aldehyde.

ticularly using method B, is simple and product isolation is easily accomplished by distillation.

Experimental Section[7]

Reaction of Benzaldehyde with Toluene (Method B). A mixture of 200 g (1.89 mol) of benzaldehyde, 25 ml of boron fluoride etherate, and 400 ml of toluene was refluxed for 48 hr. After cooling, the reaction mixture ws washed with water (100 ml) and extracted with saturated sodium carbonate solution. The organic layer was dried ($MgSO_4$) and filtered, and the toluene was removed on a 36-in. column. Distillation of the residue through the same column gave 127.3 g (64% recovery) of benzaldehyde, bp 80–82° (20 mm), and 51.1 g (82%) of a mixture of benzyltoluenes, bp 160–164° (18 mm), which was found to contain 42% ortho, 7% meta, and 51% para isomer by glc analysis (150 ft × 0.01 in. Carbowax 20M column programmed from 150 to 200° at 5°/min). The sodium carbonate extracts were filtered, acidified with concentrated HCl, collected on a filter, and air dried to give 5.4 g (13%) of benzoic acid, mp 119–120°, identified by its infrared spectrum.

Reaction of *p*-Chlorobenzaldehyde with Benzene (Method C). A 1-l. Magnedrive autoclave[9] constructed of Hastelloy C was charged with 140.5 g (1.0 mol) of *p*-chlorobenzaldehyde, 300 ml of benzene, and 25 ml of boron fluoride etherate. The autoclave was flushed with nitrogen and heated at 150° for 6 hr. After work-up as in method B there was obtained 48.2 g (34%) of unreacted *p*-chlorobenzaldehyde, bp 98–100° (15 mm), and 52.9 g (79%) of 4-chlorodiphenylmethane, bp 116–117° (3 mm).

Anal. Calcd for $C_{13}H_{11}Cl$: C, 77.04; H, 5.43; Cl, 17.5. Found: C, 76.88; H, 5.35; Cl, 17.4.

Acidification of the sodium carbonate extracts gave 10.3 g (10%) of *p*-chlorobenzoic acid, mp 232–234°, identified by comparison of the infrared spectrum with that of an authentic sample.

Registry No.—*o*-Benzyltoluene, 713-36-0.

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Reaction of Carbon Disulfide with 4-Hydrazinoquinazoline

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Received April 11, 1974

During the course of our studies on quinazolines we observed an unusual reaction between carbon disulfide and 4-hydrazinoquinazoline.