EXPERIMENTAL

The following procedures are typical for the synthesis of aryl fluorides and of aryl fluorosulfonates from phenols.

Reaction of phenol with sulfur oxytetrafluoride. A stainless steel-lined autoclave of 400-ml. capacity was charged with phenol (24 g., 0.25 mole) and evacuated. Sulfur oxytetrafluoride[4] (31 g., 0.25 mole) was introduced, and the reaction mixture was shaken and heated at 150° for 9 hr. The gaseous product (27 g.), principally sulfuryl fluoride, distilled at −49° to −44°. The remainder comprised 27 g. of black, fuming liquid. After washing with aqueous 5% sodium hydroxide and with water, 22 g. of liquid was left. Upon distillation this liquid gave 7 g. (0.07 mole) of fluorobenzene, b.p. 85-87°, f.p. −40°, $n_D^{25.5}$ 1.4624 and 7 g. (0.04 mole) of phenyl fluorosulfonate, b.p. 175-180°, f.p. −21, $n_D^{25.5}$ 1.4628. Fraction 1 was further identified as fluorobenzene by comparison of its infrared absorption with an authentic sample. Fraction 2 had infrared absorption peaks at 3.25 μ, corresponding to $=CH$; at 6.25 μ, 6.3 μ, and 6.7 μ, corresponding to aromatic $-C=C-$; and at 12.3 μ, suggesting an S—F bond.

Anal. of Fraction 2. Calcd. for $C_6H_5SO_3F$: C, 40.91; H, 2.86. Found: C, 41.11; H, 3.06.

The distillation residue weighed 8 g. It was combined with residues of similar experiments, and the composite was distilled to give a fluorine-free distillate (b.p. 145-150°/5 mm., n_D^{25} 1.5483), which was hydrolyzed by hot aqueous sodium hydroxide to phenol and sulfate ion.

Reaction of phenols with sulfuryl chloride fluoride. A solution of 20 g. (0.2 mole) of phenol in 80 ml. of pyridine was stirred in a flask fitted with a condenser cooled by solid carbon dioxide. The mixture was chilled to 0°, and 30 g. of sulfuryl chloride fluoride (0.28 mole) was introduced. The mixture was slowly warmed and held at 40° for 1 hr. It was then poured into iced hydrochloric acid, and the product was extracted with ether. The ethereal extract was washed with water, then with dilute aqueous sodium hydroxide and again, with water. Phenyl fluorosulfonate (30 g., 0.17 mole) was recovered by distillation.

In a similar procedure *p*-methoxyphenol was converted (45%) to *p*-methoxyphenyl fluorosulfonate (b.p. 75° at 2 mm., n_D^{25} 1.4798).

Anal. Calcd. for $C_7H_7O_4SF$: C, 40.77; H, 3.42; S, 15.55. Found: C, 41.06; H, 3.40; S, 15.41.

Similarly, *p*-chlorophenol gave *p*-chlorophenyl fluorosulfonate (50%) (b.p. 61° at 2 mm., n_D^{25} 1.4872).

Anal. Calcd. for $C_6H_4O_3SClF$: S, 15.22; Cl, 16.84; F, 9.02. Found: S, 15.03; Cl, 17.16; F, 9.39.

Infrared absorption spectra were consistent with the proposed formulas.

CONTRIBUTION NO. 679
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON, DEL.

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[4] W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, 82, 3838 (1960).

Preparation of Some Arylalkenes

EDGAR W. GARBISCH, JR.

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In connection with nitration studies of alkenes, the necessity arose for the preparation of a number of arylalkenes. The precursors for most of the arylalkenes were readily dehydrated tertiary arylcarbinols; however, the methods for the dehydration of many of these alcohols which have been described in the literature were found to be time-consuming.[1]

By using warm 20% sulfuric acid–acetic acid (by volume) it was observed that the crude alcohols could be converted within thirty seconds to the corresponding alkenes in over-all yields generally exceeding 70% (based on the carbonyl compound used in the preparation).[2]

This method, as described, does not appear to be applicable to the dehydration of purely aliphatic tertiary alcohols or secondary arylcarbinols, since 1-methylcyclohexene and *trans*-stilbene were prepared in yields of only 20 to 30% from the corresponding tertiary and secondary alcohols respectively.

EXPERIMENTAL

General procedure. In each instance preparation of the carbinol was carried out by adding the carbonyl-containing reagent (Table I) to approximately 10% excess of appropriate Grignard reagent (generally 0.3–0.5 mole scale). The reaction mixture was then poured into cold ammonium chloride solution with stirring and the carbinol extracted with additional ether. The extract was washed with water, dried for a short period over sodium sulfate, and the ether was evaporated under reduced pressure on the steam bath. The resulting crude alcohol melt, while still warm, was treated with freshly prepared (warm) 20% (by volume) sulfuric acid–acetic acid (200 ml./mole of alcohol). The resulting mixture was swirled for 15–30 sec. (two phases separated immediately) and poured into ether–water (600 ml. of ether–1 l. of water per mole of alcohol). The ether was washed with water and dilute potassium bicarbonate, dried over calcium chloride, and evaporated under reduced pressure. The crude arylalkene residue was purified by vacuum distillation. On occasions where the crude alcohol did not melt on the steam bath, the solid was swirled with the sulfuric acid–acetic acid reagent until the solid phase had expired, and for several minutes thereafter. For those solid alkenes where purification by distillation was impracticable (see Table I), the acid dehydration mixture was poured into cold water containing excess sodium acetate. The solid was filtered, washed free of acetic acid, and recrystallized from methanol.

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DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

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[1] Refluxing aqueous sulfuric acid has been widely employed to effect dehydration of tertiary arylcarbinols. See: (a) C. F. H. Allen and S. Converse, *Org. Syntheses*, **Coll. Vol. I**, 266 (1941). (b) H. Adkins and W. Zartman, *Org. Syntheses*, **Coll. Vol. I**, 606 (1943).

[2] Acetic acid–sulfuric acid has been used by a number of previous investigators for dehydrations. The present method resembles most nearly that of R. Lagrave, *Ann. Chim.* (10), **8**, 386 (1927).

TABLE I

PREPARATION OF ARYLALKENES USING SULFURIC ACID–ACETIC ACID

Arylalkene	Carbonyl Reactant[a]	Over-all Yield, %	B.P.(M.P.)	Literature
trans-1,1-Bis(*p*-chlorophenyl)-ethene	[b]	86[b]	(175–176°)	(175–176°)[c]
trans-α-Methylstilbene[d]	Acetophenone	73	(80–81°)	(83°)[e]
1,1-Diphenylethene	Acetophenone	70	92–93°/0.8 mm. n_D^{20} 1.6083	113°/2 mm.[f] n_D^{20} 1.6091[g]
1,1-Di-*p*-tolylethene	*p*-Methylacetophenone	50	125–128°/1.1 mm. (60.5°)	(61°)[h]
1,1-Bis(*p*-chlorophenyl)ethene[d]	*p*-Chloroacetophenone	76	(85–85.5°)	(84–86°)[i]
1,1-Diphenyl-1-propene	Propiophenone	86	93.5–94°/0.8 mm. (48–48.5°)	(48.5°)[j]
1,1-Di-*p*-tolyl-1-propene	Ethyl propionate	58	125/0.7 mm. n_D^{40} 1.5803	168–169°/9 mm. n_D^{40} 1.5790; (37–38°)[k]
1,1-Bis(*p*-chlorophenyl)-1-propene[l]	*p*-Chloropropiophenone	69	137°/0.5 mm.[l] (63.5–64°)	
Triphenylethene[d,m]	Benzophenone	81	(68–68.5°)	(69°)[n]
1,1-Diphenyl-2-methyl-1-propene	Phenyl isopropyl ketone	84	98°/0.5 mm. n_D^{16} 1.5911	150–155°/14 mm. m_D^{16} 1.5910[o]
1,1,3,3-Tetraphenyl-1-propene[d]	1,3,3-Triphenyl-1-propanone	86	(126.5–127°)	(127–128°)[p]
1-α-Naphthyl-1-phenylethene	Acetophenone	44	155–195°/1 mm. (59.5°)	195–196°/7 mm. (60°)[aa]
1-Phenylcyclopentene	Cyclopentanone	67	72–74°/1.5 mm. n_D^{25} 1.5732; (21–24°)	109°/14 mm. n_D^{25} 1.5734; (23)[q]
1-*p*-Tolylcyclopentene	Cyclopentanone	46	96–100°/2.5 mm. (48–50°)	130–133°/21 mm.[r] (52°)
1-*p*-Chlorophenylcyclo-pentene[d,s]	Cyclopentanone	53	(71.5–72°)[s]	
1-Phenylcyclohexene	Cyclohexanone	83	71°/0.6 mm. n_D^{20} 1.5670	102–103°/5 mm.[t] n_D^{20} 1.5670[bb]
1-*p*-Tolylcyclohexene[u]	Cyclohexanone	72	85–86/0.5 mm.[u] n_D^{20} 1.5623	
1-*p*-Chlorocyclohexene[v]	Cyclohexanone	63	(64.5–65°)[v]	
1-*m*-Chlorocyclohexene[w]	Cyclohexanone	80	104–107°/1.2 mm. n_D^{20} 1.5783[w]	
4-Methyl-1-phenylcyclohexene	4-Methylcyclohexanone	81	74.5–75.5°/0.5 mm. n_D^{20} 1.5539	137°/16 mm. n_D^{20} 1.5558[cc]
4-*t*-Butyl-1-phenylcyclohexene[x]	4-*t*-Butylcyclohexanone	80	106–107°/0.4 mm. n_D^{20} 1.5437[x]	
3,4-Dihydro-1-methylnaphthalene	α-Tetralone	68	60–62°/0.9 mm. n_D^{25} 1.5742	84°/5 mm. n_D^{25} 1.5742[y]
7-Chloro-3,4-dihydro-1-methylnaphthalene[z]	7-Chloro-α-tetralone	63	77°/0.4 mm. n_D^{20} 1.5877[z]	

[a] A 10% excess of appropriate Grignard reagent was treated with the carbonyl reactant. [b] 1,2-bis(*p*-chlorophenyl)ethanol was heated with 10% sulfuric acid–acetic acid (8 ml. per gram of alcohol) for 15 min. on a steam bath to effect dehydration. [c] E. Lutz and R. S. Murphey, *J. Am. Chem. Soc.*, **71**, 478 (1949). [d] Following the treatment of the crude alcohol with sulfuric acid–acetic acid, the mixture was poured into excess aqueous sodium acetate and the solid alkene filtered and purified through crystallization from methanol. [e] P. Sabatier and M. Murat, *Compt. rend.*, **155**, 386 (1912). [f] Ref. 1 (*a*). [g] A. Cotton and H. Mouton, *Ann. chim.* (8), **28**, 209 (1913). [h] R. Anschutz and A. Hilbert, *Ber.*, **57**, 1699 (1924). [i] O. Grummith, A. C. Buck, and E. I. Becker, *J. Am. Chem. Soc.*, **67**, 2265 (1945). [j] P. Schorigin, *Ber.*, **41**, 2717 (1908). [k] M. A. Khaimova, *J. Gen. Chem.* (U.S.S.R.), **25**, 367 (1955); *Chem. Abstr.*, **50**, 2509h (1956). [l] *Anal.* Calcd.: C, 68.46; H, 4.60. Found: C, 68.73; H, 4.72. [m] Seeding was necessary to induce crystallization of the alkene. [n] Ref. 1 (b). [o] F. G. Bordwell and G. W. Crosby, *J. Am. Chem. Soc.*, **78**, 5367 (1956). [p] D. Vorlander and C. Seibert, *Ber.*, **39**, 1024 (1906). [q] E. Bauer, *Ann. chim.* (9), **1**, 364 (1914). [r] J. P. Vila and R. Crespo, *Anales real, soc. españ., fís. y. quím.*, **48B**, 273 (1942); *Chem. Abstr.*, **47**, 3802g (1953). [s] *Anal.* Calcd.: C, 73.95; H, 6.21. Found: C, 74.61; H, 6.40. [t] F. O. Rice and M. T. Murphy, *J. Am. Chem. Soc.*, **66**, 765 (1944). [u] *Anal.* Calcd.: C, 90.64; H, 9.36. Found: C, 90.38; H, 9.71. [v] *Anal.* Calcd.: C, 74.80; H, 6.80. Found: C, 74.84; H, 6.62. [w] *Anal.* Calcd.: C, 74.80; H, 6.80. Found: C, 74.76; H, 6.46. [x] *Anal.* Calcd.: C, 89.65; H, 10.35. Found: C, 89.71; H, 10.14. [y] J. English and G. Cavaglieri, *J. Am. Chem. Soc.*, **65**, 1088 (1943). [z] *Anal.* Calcd.: C, 73.95; H, 6.21. Found: C, 74.08; H, 6.03. [aa] R. Stoermer and M. Simon, *Ber.*, **37**, 4167 (1904). [bb] C. R. Noller and G. K. Kaneko, *J. Am. Chem. Soc.*, **69**, 1121 (1947). [cc] H. Pines, A. Edeleanu, and U. N. Ipatieff, *J. Am. Chem. Soc.*, **67**, 2193 (1945).