catalytic amounts of ammonium acetate (0.2 gram) and acetamide (0.2 gram) was refluxed for 2 hours (*4*). To prepare the 3,4-dichlorobenzylidene derivative (compound 3), benzene was also added and the water removed by azeotropic distillation. The cooled reaction mixture was filtered and the collected solid was washed with water, air-dried, and then recrystallized from the solvent indicated in Table I.

4-HYDROXY-3-IODO-5-METHOXYBENZYLIDENEMALONONITRILE (COMPOUND 4)

This compound was prepared by azeotropic distillation of water from a benzene solution of 5-iodovanillin (0.25 mole), malononitrile (0.26 mole), and piperidine (5 ml) (*3*). The cooled reaction mixture was filtered and the collected solid was purified by continuous extraction of red impurities with ethanol followed by recrystallization from benzene. Elemental and infrared analyses of the red impurity showed it to be the piperidine salt of the title compound.

DIETHYL 2-PYRIDYLMETHYLENEMALONATE (COMPOUND 5)

A benzene solution of 2-pyridinecarboxaldehyde (0.50 mole), diethyl malonate (0.51 mole), piperidine (5 ml), and 2-pyridinecarboxylic acid (a few crystals) was refluxed using a Dean-Stark trap until a constant quantity of water collected (*1*). The solution was concentrated in vacuo and the residue vacuum distilled to yield a bright red oil, bp 159–62° C/1.4–1.7 mm, which solidified on cooling (48 hours) to a beige solid, m.p. 45–7° C (after hexane wash). The solid was further purified by treatment of the benzene solution with charcoal. The benzene was removed in vacuo and the residue triturated in hexane to yield 22 grams (18%) of a beige solid, m.p. 46–8° C. The infrared spectrum was in accord with the assigned structure. Calcd. for $C_{13}H_{15}NO_4$: C, 62.7; H, 6.1; N, 5.6; found: C, 62.8; H, 6.1; N, 5.8.

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LITERATURE CITED

(1) Allen, C.F.H., Spangler, F.W., *Org. Syn.* Coll. Vol. **III**, 377 (1955).
(2) Campaigne, E., Subramanya, R., Maulding, D.R., *J. Org. Chem.* **28**, 623 (1963).
(3) Corson, B.B., Stoughton, R.W., *J. Am. Chem. Soc.* **50**, 2825 (1928).
(4) Horner, L., Klupfel, K., *Ann.* **591**, 69 (1955).

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Synthesis of *N*-Alkyl- and *N*-Arylsulfonylphthalimides from Potassium Phthalimide and Sulfonyl Chlorides

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The facile reaction of potassium phthalimide with sulfonyl chlorides in refluxing acetonitrile to give new *N*-alkyl- and known *N*-arylsulfonylphthalimides is reported

THERE is a paucity of published information on the reaction of potassium phthalimide with sulfonyl chlorides to give *N*-alkyl- and *N*-arylsulfonylphthalimides. Attempts by Evans and Dehn (*1*) to prepare several *N*-aryl derivatives and later by Scott and Lutz (7) to prepare several *N*-alkyl derivatives by this reaction were unsuccessful. More recently, potassium phthalimide was reported to interact with *p*-toluenesulfonyl chloride at 140° C. (*3*) or in dimethylformamide at 5° to 40° C. (*4*) to yield *N*-(*p*-tolylsulfonyl)phthalimide.

Potassium phthalimide readily reacts with both aliphatic and aromatic sulfonyl chlorides in refluxing acetonitrile to give the corresponding *N*-substituted phthalimides. Reactions that involved aliphatic sulfonyl chlorides afforded a series of novel compounds; those that involved aromatic sulfonyl chlorides gave known compounds. The experimental results are summarized in Table I.

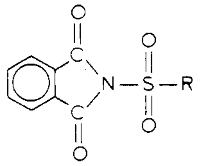
The yields of the *N*-alkylsulfonylphthalimides were consistently slightly lower than those of the corresponding *N*-aryl derivatives. This probably is a result of a side reaction that only the aliphatic sulfonyl chlorides can undergo—namely, attack by the phthalimido ion on the hydrogen atom α to the sulfonyl group to form phthalimide, chloride ion, and a nonisolable sulfene (*5*). Evidence in support of this supposition is that some phthalimide was isolated in several experiments only when aliphatic sulfonyl chlorides were used.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Potassium phthalimide was prepared according to a reported method (*6*). All other reagents were Eastman Kodak Co. chemicals. Acetonitrile was distilled from phosphorus pentoxide. Except for methane- and ethanesulfonyl chlorides, which were distilled, the sulfonyl chlorides were used as received.

Table I. *N*-Alkyl- and *N*-Arylsulfonylphthalimides



R	Recryst. Solvent[a]	Yield, %[b]	M.P., ° C.	Analysis, % N Calcd.	N Found	S Calcd.	S Found
Methyl	*A*	62	229.5–30	6.22	6.26	14.24	14.27
Ethyl	*B*	65	181.5–82	5.85	5.86	13.40	13.55
n-Propyl	*C*	62	139–39.5	5.53	5.51	12.66	12.69
n-Butyl	*C*	60	114.5–15	5.24	5.27	12.00	11.92
Phenyl	*D*	74	202.5–03.5[c]				
p-Tolyl	*E*	75	239–40[d]				
p-Bromophenyl	*E*	70	247–48[e]				
β-Naphthyl	*E*	73	218–19[f]				

[a] *A*, acetonitrile; *B*, acetonitrile-benzene; *C*, benzene; *D*, toluene; *E*, xylenes (b.p. 135–40° C.). [b] Yields are for purified products. [c] Lit. (*2*) m.p. 205° C. [d] Lit. (*2*) m.p. 237° C. [e] Lit. (*2*) m.p. 246° C. [f] Lit. (*2*) m.p. 216° C.

Reaction of Potassium Phthalimide with Sulfonyl Chlorides. All of the compounds listed in Table I were prepared in the same manner. A stirred mixture of 0.0050 mole of potassium phthalimide and 0.0050 mole of the appropriate sulfonyl chloride in 20 ml. of acetonitrile was heated under reflux for 1 hour. After cooling to ambient temperature, the mixture was poured into 100 ml. of cold water. The white solid, which separated immediately, was removed by filtration, washed with water, and dried. The crude products were purified by one or two recrystallizations from the solvents indicated in Table I.

Each *N*-substituted phthalimide was found to be identical with an authentic sample, which was prepared by the reaction of the appropriate sulfonamide with phthaloyl chloride according to the method of Evans and Dehn (*1*), by mixture melting point determination and infrared spectra comparison.

In experiments that involved methane- and butane-1-sulfonyl chlorides, small amounts of a solid—32 and 20 mg., respectively—precipitated from the aqueous filtrates on standing overnight. This solid was identified by mixture melting point determination and infrared spectra comparison as phthalimide.

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LITERATURE CITED

(1) Evans, T.W., Dehn, W.M., *J. Am. Chem. Soc.* **51**, 3651 (1929).
(2) Evans, T.W., Dehn, W.M., *Ibid.*, **52**, 2531 (1930).
(3) Kühle, E., Wegler, R., *Ann.* **616**, 183 (1958).
(4) Nefkens, G.H.L., Tesser, G.I., Nivard, R.J.F., *Rec. Trav. Chim.* **79**, 688 (1960).
(5) Optiz, G., *Angew. Chem. Intern. Ed. Engl.* **6**, 107 (1967).
(6) Salzberg, P.L., Supniewski, J.V., "Organic Syntheses," Coll. Vol. **I**, p. 119, Wiley, New York, 1941.
(7) Scott, R.B., Jr., Lutz, R.E., *J. Org. Chem.* **19**, 830 (1954).

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Synthesis of Seven New Polyphenyl Ethers

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Seven new polyphenyl ethers were synthesized, using a modified Ullmann reaction. Per cent yields, physical properties, and elemental analyses are given.

POLYPHENYL ethers show excellent thermal stability and are used as high-temperature functional fluids, finding application as heat transfer agents. In addition, they have proved useful as the liquid phase in high-temperature chromatographic work (*3–5, 7*). Seven new polyphenyl ethers containing a biphenyl central core were synthesized in these laboratories. The synthetic routes used were similar in each case and involved a modified Ullmann reaction. The mechanism and parameters of this reaction have been studied in detail by a number of workers (*1, 2, 8, 9*). The reaction schemes leading to each compound are depicted below:

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