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1-ARENESULFONYLPYRROLES

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Reactions of organometallic compounds with sulfonyl halides are well known, but their effectiveness as a means of introduction of the sulfonyl group is not generally dependable.(1) We have found that a smooth reaction takes place in tetrahydrofuran between pyrrolylpotassium and arenesulfonyl chlorides with formation of 1-arenesulfonylpyrroles (2) in good yield (Table I). The structure assigned to the products of this reaction is supported by the elemental analysis results and the following spectral evidence:

(a) Except for 1-(p-acetaminobenzenesulfonyl)pyrrole and 1-(p-aminobenzenesulfonyl)-pyrrole, the infrared spectra show no absorption in the 3400-3500 cm^{-1} region (pyrrole N-H stretching) (3) thus ruling out a 2-, or 3-substituted pyrrole structure.

(b) In all cases, the infrared spectrum has a strong band in the 1160-1180 and the 1330-1370 cm^{-1} regions (SO_2-N stretching).(4)

(c) The spectrum of 1-(p-acetaminobenzenesulfonyl)pyrrole shows the expected carbonyl absorption at 1700 cm^{-1}.

(d) The spectrum of 1-(p-aminobenzenesulfonyl)pyrrole contains two absorption bands in the 3350-3450 cm^{-1} region (NH_2 stretching).(4) Further evidence for the structure of this compound is provided by its conversion by acetylation to 1-(p-acetaminobenzenesulfonyl)pyrrole.

In contrast to the easy preparation of the 1-derivatives, our attempts to prepare 2-arenesulfonylpyrroles were unsuccessful. Pyrrolylmagnesium halides are known to yield predominantly or exclusively the 2-substituted pyrroles when they are made to react with alkyl or acid chlorides, respectively.(5) Furthermore, there are examples in the literature of formation of sulfones, although in low yields, by the reaction of organomagnesium halides with sulfonyl halides.(1)(a),(1)(c) In this work, however, pyrrolylmagnesium bromide yielded only tars when treated with arenesulfonyl chlorides under various conditions. Similarly unsuccessful were our attempts to effect Friedel-Crafts type substitution, because polymerization of pyrrole could not be prevented.

TABLE I

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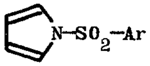

Ar	Solvent of Recrystallization	Mp, °C	Yield,[a] %
Phenyl	Methanol	89-89.5	87
p-Tolyl	Methanol	104.5	84
p-Fluorophenyl	Methanol-water	108-108.5	81
p-Chlorophenyl	95% Ethanol	122	75
p-Bromophenyl	Methanol	136	89
p-Nitrophenyl	Methanol	142-142.5	26
p-Methoxyphenyl	95% Ethanol	124.5-125	71
p-Acetaminophenyl	95% Ethanol	170-171	59
p-Aminophenyl[b]	Methanol-water	130.5	89[c]
α-Naphthyl	Methanol	137-138	81
β-Naphthyl	Methanol	132-132.5	82
8- Quinolyl	2-Propanol	183-184	79

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[a] Material of mp not more than 4° below that of the analytical sample.

[b] By hydrolysis of 1-(p-acetaminobenzenesulfonyl)pyrrole.

[c] On 1-(p-acetaminobenzenesulfonyl)pyrrole.

Pyrrolylpotassium was prepared by refluxing gently a stirred mixture of 0.15 mole of pyrrole, 0.125 g-atom of potassium, and 100 ml of tetrahydrofuran (6) until all of the metal had reacted. Heating was then discontinued, the slurry diluted with 100 ml of solvent, and a solution of 0.10 mole of sulfonyl chloride in 100 ml of tetrahydrofuran (6) added dropwise, over a period of 30 min. After the resulting mixture had been stirred at room temperature overnight (14-18 hr), it was filtered to yield a solution which was evaporated to dryness under reduced pressure, and the solid residue was recrystallized .

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(2) French Patent 1,008,479 (February 20, 1952), *Chem. Abstr.*, **52**, 1229c (1958), covers sulfones of the general formula $H_2NXSO_2YNR_1R_2C(OH)R_3R_4$, where X and Y are aromatic or heterocyclic (pyrrole, among other) rings.

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(6) Toluene was used as solvent in the reaction with p-nitrobenzenesulfonyl chloride.