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ARYLATION OF α-PHOSPHORYL SULFIDES VIA THEIR PUMMERER REARRANGEMENT INTERMEDIATES GENERATED FROM THE CORRESPONDING SULFOXIDES

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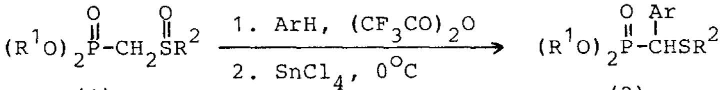
Abstract: Various aryl groups were introduced directly into the α-position of α-phosphoryl sulfides by treating their sulfoxides with trifluoroacetic anhydride and then with tin(IV) chloride in the presence of excess of the aryl compound.

In previous publications[1], we have described the use of Pummerer intermediates in the functionalization of aromatic compounds. These intermediates, which offer a versatile juxtaposition of functionality for further structural manipulations[1c], have been generated from activated and nonactivated sulfoxides. In the case of activated sulfoxides[1a], the activating group was either a carbonyl (of a ketone or ester) or a nitrile group, and the yields of the products were high.

Alkyl or aryl thiomethylphosphonates are useful reagents in the Horner Wittig reaction for the preparation of vinyl sulfides[2]. Furthermore Corey and Shulman have used these vinyl sulfides for the synthesis of unsymmetrical carbonyl compounds[3] and in the thio-Claisen rearrangement[4]. Therefore the above wide synthetic utility of thioalkylphosphonates and the scarsity of general methods to introduce directly a desired aryl group into their α-position[5], prompted us to turn our attention toward this direction. The activation properties of a phosphonate group, the characteristic segment in the Horner Wittig reagents, facilitates the abstraction of a proton in the α-position by a weak base such as the trifluoroacetate anion to give rise to the Pummerer intermediate quantitatively. These phosphoryl intermediates are vulnerable to the nucleophilic attack by an aromatic compound in the presence of Lewis acids such as the tin(IV) chloride under mild conditions.

The α-phosphoryl sulfides used in these experiments are readily available by the Arbuzov reaction[2a,6] of α-chlorosulfides with excess[7] of trialkyl phosphites. Subsequent oxidation of the α-phosphoryl sulfides either with $NaIO_4$[8], or Br_2[9], and chromatography on silica gel using chloroform containing ethanol (1-2% for $R^1=C_2H_5$, $R^2=C_6H_5$; 5% for $R^1=C_2H_5$, $R^2=CH_3$; 10% for $R^1=R^2=CH_3$) as eluent gave pure sulfoxides.



$$(R^1O)_2\overset{O}{\overset{\|}{P}}-CH_2\overset{O}{\overset{\|}{S}}R^2 \xrightarrow[2.\ SnCl_4,\ 0^oC]{1.\ ArH,\ (CF_3CO)_2O} (R^1O)_2\overset{O}{\overset{\|}{P}}-\overset{Ar}{\overset{|}{C}}HSR^2$$

(1) (2)

In general, the sulfoxide (5 mmol) was dissolved in a mixture of dry dichloromethane[10] (10 ml) and excess of dry aryl compound (4-6 equiv.) cooled at 0°C under argon atmosphere. Trifluoroacetic anhydride (5.5 mmol) was added dropwise, followed after 4-5 min. with tin(IV) chloride (5 mmol). The mixture was stirred for an hour at 0°C, quenched with chloroform-water, washed with water and with sodium hydrogen carbonate-water solution, dried (Na_2SO_4), and the solvent evaporated. The residual oil was chromatographed on silica gel (Merck, 70-230 mesh, type 60) using benzene-ethyl acetate or ether-hexane mixtures, or ether. The products were obtained as colorless oils except for the product 2h which was crystallized (neat) as a white solid m.p. 80-2°C. Structural assignments were based on spectral data. Compounds 2a, 2b, 2c, and 2d were also prepared via published procedures[5] and their spectra were compared.

Table: The preparation of α-aryl-thiomethylphosphonates

No.	R^1	R^2	ArH	Ar in Product	% Yield	Ref.
2a	C_2H_5	CH_3	Benzene	Phenyl	92	5a
2b	C_2H_5	CH_3	Toluene	4-Methylphenyl	90	5b
2c	C_2H_5	CH_3	t-Butylbenzene	4-t-Butylphenyl	91	5b
2d	C_2H_5	C_6H_5	Benzene	Phenyl	87	5a
2e	C_2H_5	C_6H_5	Mesitylene	2,4,6-Trimethylphenyl	79	present work
2f	C_2H_5	C_6H_5	p-Xylene	2,5-Dimethylphenyl	84	"
2g	C_2H_5	C_6H_5	iso-Propylbenzene	4-iso-Propylphenyl	85	"
2h	CH_3	CH_3	Cyclohexylbenzene	4-Cyclohexylphenyl	88	"
2i	CH_3	CH_3	n-Butylbenzene	4-n-Butylphenyl	91	"
2j	CH_3	CH_3	Ethylbenzene	4-Ethylphenyl	80	"

References and Notes

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