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SYNTHESIS OF 1-(SUBSTITUTED-ARYL) METHYLTHIOMETHANEPHOSPHONATES BY FRIEDEL-CRAFTS REACTION OF AROMATIC COMPOUNDS WITH CHLORO(METHYLTHIO)METHANEPHOSPHONATE

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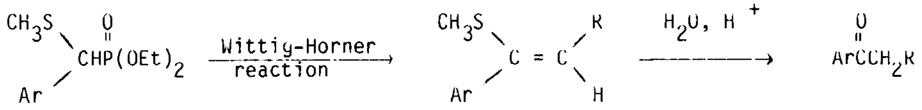
Summary: Friedel-Crafts reaction of aromatic compounds with chloro(methylthio)methane phosphonate(1) under mild condition in the presence of Lewis acid affords 1-(substituted-aryl)methylthiomethanephosphonates(2).

The synthetic utility of alkylthiomethanephosphonate carbanions in the Wittig-Horner reaction has been a subject of interest in organic synthesis because they are reagents in the synthesis of ketones.[1] 1-(Substituted-aryl)methylthiomethanephosphonates(2) are also the intermediate for the conversion under the Wittig-Horner reaction condition into the corresponding α,β-unsaturated sulfide. Subsequent hydrolysis of the intermediate α,β-unsaturated sulfide affords aromatic ketone.[2]



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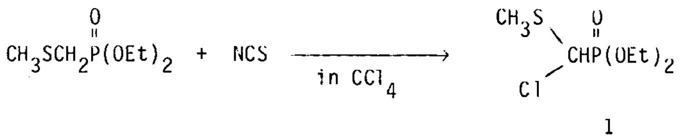
Whereas the synthesis of 1-unsubstituted alkylthiomethanephosphonates is well documented,[3] the preparation of 1-(substituted-aryl)alkylthiomethanephosphates, first reported by Mikolajczyk and co-workers in order to overcome the synthetic limitation of aryl substituent, results from addition of the elemental sulfur[2] or dialkyl disulfide[4] to arylmethanephosphonate carbanions.

In the course of our studies on O,S-thioacetals of formylphosphonate we have recently developed an intermediate, chloro(methylthio)methanephosphonate(1).[5] In an extension of this work we wish to report the synthesis of 1-(substituted-aryl)methylthiomethanephosphonates(2) by the Friedel-Crafts reaction of the aromatic compounds with 1. The Friedel-Crafts reaction was successfully carried out in methylene chloride under mild condition in the presence of one equivalent of stannic chloride($SnCl_4$). The present method gives no polyalkylated product. Further alkylation of 2a or 2j with 1 in the presence of equivalent $SnCl_4$ did not occur. Chloro(methylthio)methanephosphonate(1) (isolated yield by distillation, 85%, b.p. 118-120°C/1.6 mm) was prepared from methylthiomethanephosphonate by the chlorination with one equivalent of N-chlorosuccinimide(NCS). The following procedure is representative for the Friedel-Crafts reaction; To a stirred solution of 1 and benzene (5 eq) in ice bath was added one equivalent of stannic chloride. The reaction mixture was stirred at the room temperature for 40 min. The mixture was quenched by adding water and extracted with chloroform and dried. The solvent was removed, and the crude product was chromatographed on silica gel, using ether as an eluent. The structural assignment of 2a was made on the basis of authentic spectral data.[2]



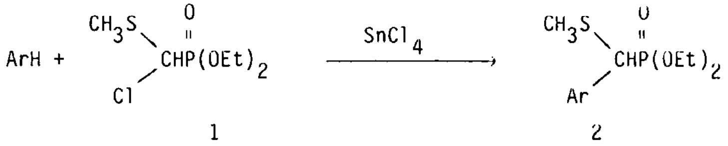


Table. Preparation and ^{31}P NMR Data of 1-(Substituted-aryl)methylthiomethanephosphonates(2).

	ArH	Yield(%)[a]	^{31}P NMR($CDCl_3/H_3PO_4$)[b]	Product(2)
2a	Benzene[c]	85	22.1	Phenyl
2b	Toluene	91	22.2	4-Methylphenyl
2c	Cumene	94	22.3	4-i-Propylphenyl
2d	i-Butylbenzene	99	22.4	4-i-Butylphenyl
2e	t-Butylbenzene	99	22.4	4-t-Butylpenyl
2f	p-Xylene	90	22.8	2,5-Dimethylphenyl
2g	Anisole[d]	88	22.4	4-Methoxyphenyl
2h	Durene	78	25.5	2,3,5,6-Tetramethylphenyl
2i	Isodurene	74	25.1	2,3,4,5-Tetramethylphenyl
2j	p-Diethylbenzene	99	22.8	2,5-Diethylphenyl

[a] Isolated yield by column chromatography [b] The conversion of positive ^{31}P NMR signals to low field from H_3PO_4 was used [c] Solent was benzene in 2a and methylene chloride in othr cases
[d] Reaction temperature was 0°C

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