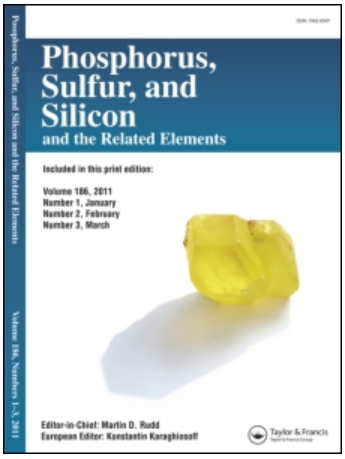

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THIATION OF CARBONYL COMPOUNDS WITH THE DIMER OF *p*-METHOXYPHENYL-THIONOPHOSPHINSULFIDE

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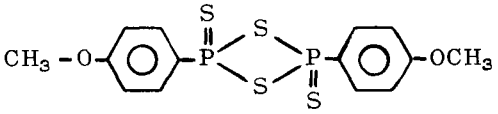
Recent studies on thiation of carbonyl compounds with organic P,S-compounds have shown that *p*-methoxyphenyl-thionophosphinsulfide (1) is the most effective thiation reagent for ketones, carboxamides, esters, and thioloesters hitherto known.



1

Thus a series of aromatic and alifatic ketones such as substituted benzoephenones 2-benzoylthiophene, Michler's ketone, thioxanthon, camphor, and dicyclopropylketone were reacted with 1 (mole ratio of 1:0.6), in anhydrous toluene at 110 °C giving the corresponding thioketones in yields of 95-100%. Dibenzylketone gave 1,3-diphenylpropene-2-thiol (46%) 2- and 4-benzoylpyridine failed to give thioketone but the 3-isomer gave thioketone (32%).

A great number of primary, secondary, and tertiary alifatic and aromatic carboxamides were reacted with 1 (mole ratio 1:0.6) in the temperature range from 80-100 °C using anhydrous toluene or HMPA as solvent. In all cases the corresponding thiocarboxamides were isolated in nearly quantitative yields (95-100%).

Also thioloesters like phenyl-, benzyl-, and tert-butylthiolobenzoate, phenyl- and benzylthioloacetate and ethylthiolopropaneoate were reacted with 1 (mole ratio 1:0.6) in boiling anhydrous toluene. The dithioesters were isolated in yields of 90-100%.

A very surprising result was found in the reaction of 1 with thiobenzoic-S,S'-methylene ester which as product gave 4,5-diphenyl-1,3-dithio-thion (2).

Finally, esters like ethyl-, isopropyl, and benzylbenzoate, α- and β-ethyl naphthoate, benzylpropanoate and ethylheptanoate were reacted with 1 (mole ratio 1:1.2) in anhydrous xylene at 140 °C. In all cases the corresponding thionoesters were isolated in yields of about 90%.