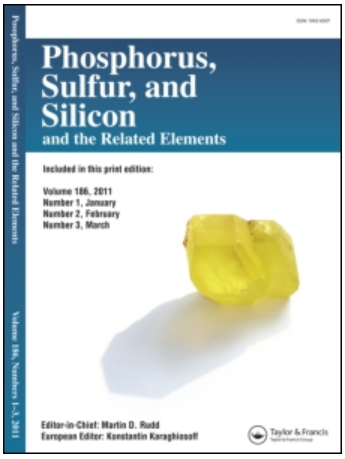

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New Reactions of Olefins with Tetraphosphorus Decasulfide, Thiophosphoryl Trichloride, and Phosphorus Trichloride

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New Reactions of Olefins with Tetraphosphorus Decasulfide, Thiophosphoryl Trichloride, and Phosphorus Trichloride

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In contrast to difficultly characterizable products of olefins with P_4S_{10} alone, the reactions of olefins with P_4S_{10} in the presence of $PSCl_3$ (and in some cases, PCl_3) afforded distillable products amenable to characterization. Ethylene with P_4S_{10}, $PSCl_3$, and PCl_3 gave 1,2-ethanediylbis(phosphonothioic dichloride) in good yield. Propylene with P_4S_{10} and $PSCl_3$ afforded several open-chain phosphonothioic chlorides and at higher temperatures 2-chloro-1,2-thiaphospholane 2-sulfide. 1- or 2-Butene yielded the 5-methyl homolog. Cyclohexene yielded 7-chloro-6-thia-7-phosphabicyclo [3.2.1] octane 7-sulfide and 4-methylcyclohexene yielded the 5-methyl homolog. Norbornene gave stereoisomeric 3-chloro-2-thia-3-phosphatricyclo $[4.3.0.0^{4,8}]$ nonane 3-sulfides. Norbornadiene gave 3-chloro-2-thia-3-phosphatricyclo $[4.3.0.0^{4,8}]$ non-6-ene 3-sulfide. Camphene reacted with P_4S_{10} and $PSCl_3$ in good yield at ambient pressure and moderate heating to produce a characteristic Wagner-Meerwein rearrangement product, 3-chloro-3-phospha-4-thia-10,10-dimethyltricyclo-$[5.2.1.0^{1,5}]$ decane 3-sulfide. Butadienes with P_4S_{10} and $PSCl_3$ afforded Diels-Alder-like 2-chloro-3,6-dihydro-2H-1,2-thiaphosphorins. These products were characterized by nmr and, in some instances, by hydrolysis to characterizable products. The products are generally consistent with electrophilic mechanisms.