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Publisher Taylor & Francis

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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Hennig, Heinz-Werner , Neu, Peter and Sartori, Peter(1987) 'Carboxylphosphanes and Carboxyphosphane Chalcogenides', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 725

To link to this Article: DOI: 10.1080/03086648708079219 URL: http://dx.doi.org/10.1080/03086648708079219

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Carboxylphosphanes and Carboxyphosphane Chalcogenides

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Low temperature reactions of organo chloro phosphanes with carboxylic acids and their salts allow the preparation of carboxyphosphanes - mixed anhydrides of carboxylic acids with phosphinic acids. These are subject to thermal rearrangement reaction of the Michaelis-Arbusov-type. Molecular oxygen converts them into carboxy-phosphorane oxides. These compounds are also obtainable by reacting organochlorophosphane oxides with carboxylates. Their thermal stability is higher than that of the P(III)compounds. Analoguous reactions of P-sulfides and selenides give the corresponding thio and seleno phosphoranes with higher thermal stability. At elevated temperatures a number of rearrangement reactions occur, thus producing phosphane oxides and phosphinic acid phosphinyl alkaryl ester. The reaction products of the following reaction sequences are discusses with regard to their NMR-, IR-, MS-spectra and hydrolytic and thermal properties:

$$R_{2}PC\ell + R'COOX \qquad \frac{-\frac{XC\ell}{< 0^{\circ}C}}{80^{\circ}C \rightarrow 180^{\circ}} \qquad R_{2}POC(0)R' \xrightarrow{0_{2}} \qquad R_{2}P(0)OC(0)R'$$

$$3 R_{2}PC\ell + R'COOH \qquad \frac{+2 H_{2}O}{80^{\circ}C \rightarrow 180^{\circ}} \qquad R_{2}P(0)CH_{2}R' + [R_{2}P(0)]_{2}O$$

$$R_{2}PC\ell + R'COOH \qquad \frac{-XC\ell}{< 0^{\circ}C} \rightarrow \qquad R_{2}P(0)CH_{2}R' + R_{2}P(0)C_{R'} - OR(0)R_{2}$$

$$R_{2}P(0,S,Se)C\ell + R'COOX \qquad \frac{-XC\ell}{< 0^{\circ}C} \rightarrow \qquad R_{2}P(0,S,Se)OC(0)R'$$

$$RPC\ell_{2} + 2 R'COOX \qquad \frac{-2 XC\ell}{< 0^{\circ}C} \rightarrow \qquad RP(OC(0)R')_{2}$$

$$RP(0,S,Se)C\ell_{2} + 2 R'COOX \qquad \frac{-2 XC\ell}{< 0^{\circ}C} \rightarrow \qquad RP(0,S,Se)(OC(0)R')_{2}$$

$$RP(0,S,Se)C\ell_{2} + 2 R'COOX \qquad \frac{-2 XC\ell}{< 0^{\circ}C} \rightarrow \qquad RP(0,S,Se)(OC(0)R')_{2}$$

$$RP(0,S,Se)C\ell_{2} + 2 R'COOX \qquad \frac{-2 XC\ell}{< 0^{\circ}C} \rightarrow \qquad RP(0,S,Se)(OC(0)R')_{2}$$

$$RP(0,S,Se)C\ell_{2} + 2 R'COOX \qquad \frac{-2 XC\ell}{< 0^{\circ}C} \rightarrow \qquad RP(0,S,Se)(OC(0)R')_{2}$$