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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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Online publication date: 27 October 2010

To cite this Article Hoge, Berthold and Thösen, Christoph(2002) 'Novel Addition of Diphosphanes to Carbonyl Compounds', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 177: 8, 2151 — 2152

To link to this Article: DOI: 10.1080/10426500213437

URL: <http://dx.doi.org/10.1080/10426500213437>

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NOVEL ADDITION OF DIPHOSPHANES TO CARBONYL COMPOUNDS

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(Received July 29, 2001; accepted December 25, 2001)

During our attempts to synthesize chiral bidentate bis(trifluoromethyl)-phosphane containing ligands, we found a bis(trifluoromethyl)-phosphanide induced formal insertion of acetone into tetrakis(trifluoromethyl)diphosphane.

The bis(trifluoromethyl)phosphanide ion, $\text{P}(\text{CF}_3)_2^-$,¹ decomposes slowly above -30°C in CH_2Cl_2 and THF solution. In solvents with an electrophilic center such as DMF and acetone an increase of thermal stability is observed. This increase in thermal stability can best be explained by a donor acceptor adduct formation. Treatment of a [18-Crown-6-K]P(CF₃)₂ solution in acetone with tetrakis(trifluoromethyl)diphosphine causes a nucleophilic cleavage of the diphosphine by the intermediately formed alcoholate ion (I).

The resulting phosphane phosphinite system (II) proves the intermediary formation of the alcoholate ion (I). The nucleophilic cleavage of (CF₃)₂PP(CF₃)₂ causes the formation of a $\text{P}(\text{CF}_3)_2^-$ ion which reacts with excess acetone to the alcoholate (I) and in turn brings about further nucleophilic cleavage (CF₃)₂PP(CF₃)₂. The eventual result is a $\text{P}(\text{CF}_3)_2^-$ induced formal insertion of acetone into (CF₃)₂PP(CF₃)₂. Besides the $\text{P}(\text{CF}_3)_2^-$ ion a variety of nucleophiles such as cyanide salts or even pyridine are suitable to induce the formal acetone insertion reaction.

We are grateful to Prof. Dr. D. Naumann for his generous support. We thank the Fonds der Chemischen Industrie for financial support.

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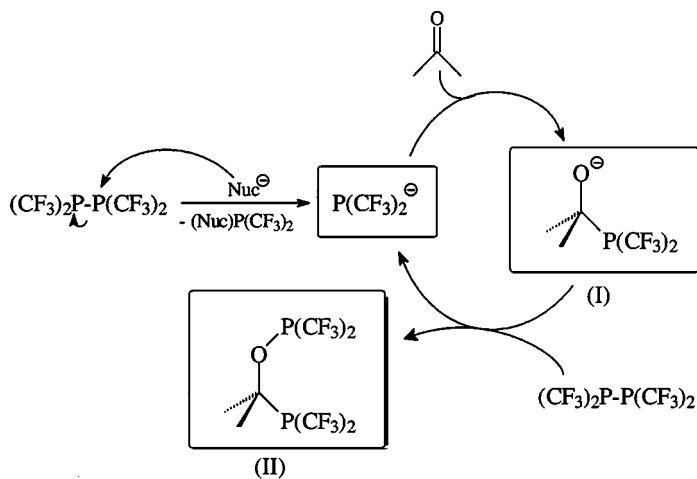


FIGURE 1

REFERENCE

- [1] B. Hoge and C. Thösen, *Inorg. Chem.*, **40**, 3113 (2001).