Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1995, **5(1)**, 14–15
Mendeleev Communications

Cleavage of P—P Bonds in Phosphorus. An Efficient Method for the Preparation of Primary Alkylphosphines

Lambert Brandsma,*[a] Johanes A. van Doorn,[b] Robert-Jan de Lang,[a] Nina K. Gusarova[c] and Boris A. Trofimov*[c]

[a]*Department of Preparative Organic Chemistry, University of Utrecht, 3584 CH Utrecht, The Netherlands.*
[b]*Koninklijke/Shell Laboratory, Amsterdam, The Netherlands. E-mail: pocket@cc.ruu.nl*
[c]*Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 466 434; e-mail: trofimov@dir.iochem.irkutsk.su*

Effective cleavage of P–P bonds in red (and yellow) phosphorus can be brought about by adding *tert*-butyl alcohol to a mixture of phosphorus, lithium and liquid ammonia; subsequent addition of alkyl halides gives primary phosphines in good to excellent yields.

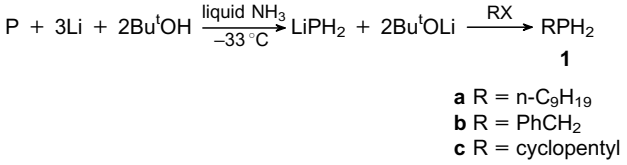
Cleavage of S–S, Be–Se and Te–Te bonds in the elements with alkali metals in liquid ammonia proceeds very easily, affording at will MX_2 or M_2X_2 depending on the molar ratio of the alkali metal M and the chalcogen X.[1] The alkali chalcogenides may be used for further conversions, either in liquid ammonia or after replacement of the ammonia by another solvent.

Prior to our investigations[2] the possibility of generation of phosphide and phosphinite ions from elemental phosphorus in the presence of strong bases had been reported in only a few publications.[3]

Russian investigators[4] achieved the cleavage of P–P bonds in red phosphorus by performing a sequence of alternating treatments with sodium in liquid ammonia and addition of alkyl halides, and ultimately obtained tertiary phosphines (isolated as phosphine sulfides) in low to moderate yields.

We succeeded in accomplishing effective cleavage of all P–P bonds in the phosphorus molecule in a single operation with the stoichiometry shown in Scheme 1.

Subsequent reaction with alkyl halides was carried out to intercept the very reactive phosphide anion. The higher, non-volatile representative n-$C_9H_{19}PH_2$ was isolated in excellent yield.† The reaction also successfully proceeded with yellow phosphorus, but its experimental performance was much more troublesome, as the finely divided phosphorus (made



Scheme 1

† *General experimental details*. All operations were scrupulously carried out under an atmosphere of inert gas (preferably argon). A slurry of red phosphorus (0.25 mol, 7.8 g) in 30 ml of dry THF was introduced into 700 ml of liquid ammonia, followed by addition of freshly cut lithium (0.75 mol, 5.3 g) (~ 0.2 g pieces) during 10 min. A mixture of dry *tert*-butyl alcohol (0.5 mol, 37 g) and 30 ml diethyl ether was added dropwise over 30 min with efficient stirring. After disappearance of the blue colour the alkyl halide (n-$C_9H_{19}Br$, benzyl chloride and cyclopentyl bromide, 0.20 mol) was added to the slightly yellowish suspension over 20 min with vigorous stirring. The ammonia was then removed by placing the flask in a water bath at ~ 40 °C. After addition of water (500 ml) to the residue the product was extracted with an ether–pentane mixture and the extract was washed with water and dried over $MgSO_4$. After removal of solvent the remaining liquid was distilled *in vacuo*. The yield of the phosphines **1** (calculated from the amount of RX) was, respectively, 87%, 72% and 72%, *i.e.* 27.8, 17.9 and 14.7 g (purities by GLC and ^{31}P NMR at least 97%). The physical constants of the phosphines **1** corresponded to the literature data.[5]

by *in vacuo* removal of the solvent from a concentrated solution in carbon disulfide) and brown products of partial cleavage constantly deposited on the wall of the flask.

References

1 L. Brandsma and H. E. Wijers, *Recl. Trav. Chim. Pays-Bas*, 1963, **82**, 68.

2 (*a*) B. A. Trofimov, N. K. Gusarova, S. F. Malysheva, T. N. Rakhmatulina, M. G. Voronkov, V. I. Dmitriev and S. I. Shaikhudinova, *Sulfur and Silicon*, 1991, **55**, 271; (*b*) B. A. Trofimov, T. N. Rakhmatulina, N. K. Gusarova and S. F. Malysheva, *Usp. Khim.*, 1991, **116**, 2619 (*Russ. Chem. Rev.*, 1991, **116**, 1360) (*Chem. Abstr.*, 1992, **116**, 106343t).

3 (*a*) M. M. Rauhut, *Topics in Phosphorus Chemistry*, eds. M. Grayson and E. J. Griffith, Interscience, New York, 1964, vol. 1, p. 1; (*b*) L. Maier, *Fortschr. Chem. Forsch.*, 1971, **19**, 1; (*c*) L. Maier, *Helv. Chim. Acta*, 1966, **49**, 2458; (*d*) C. Brown, R. F. Hudson and G. A. Wartew, *Phosphorus and Sulfur*, 1978, **5**, 67.

4 (*a*) G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, 1966, **36**, 1505 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1966, **36**, 1510] (*Chem. Abstr.*, 1967, **66**, 10995y); (*b*) G. M. Bogolyubov and A. A. Petrov, *Dokl. Akad. Nauk SSSR*, 1967, 1076 [*Dokl. Chem. (Engl. Transl.)*, 1967, 329] (*Chem. Abstr.*, 1967, **67**, 90887e); compare also (*c*) E. R. Bornancini, R. A. Alonsa and A. R. Rossi, *J. Organometal. Chem.*, 1984, **270**, 177.

5 (*a*) H. Schindlbaner and E. Steininger, *Monatsh. Chem.*, 1961, **92**, 869; (*b*) P. Pass, E. Steininger and H. Zorn, *Monatsh. Chem.*, 1962, **93**, 230; (*c*) N. Kreutzkamp, *Chem. Ber.*, 1954, **87**, 919; (*d*) L. Horner, H. Hoffman and P. Beck, *Chem. Ber.*, 1958, **91**, 1583.

Received: Moscow, 2nd August 1994
Cambridge, 17th October 1994; Com. 4/04835K