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SYNTHESIS OF THE FIRST STABLE METADITHIOPHOSPHONATE*

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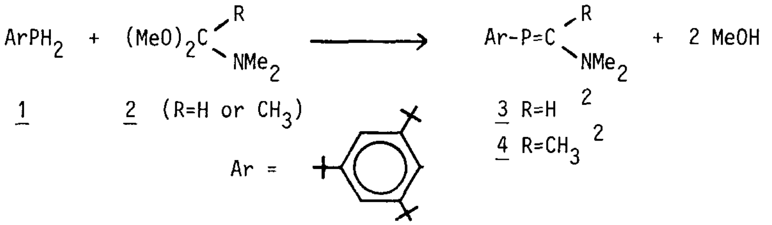
Abstract : Evidence for the formation of the first stable metadithiophosphonate is given.

In connection with our studies on photochemical reactions of phosphaalkenes [1] we prepared new dicoordinated trivalent phosphorus derivatives by reacting triterbutylphenyl phosphine 1 with dimethylamino acetals 2.

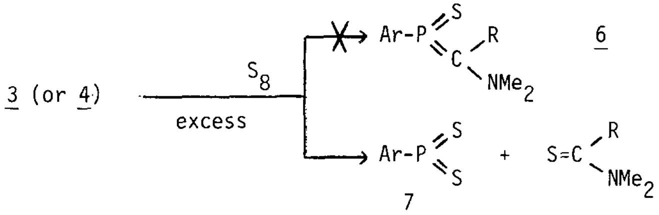


1 2 (R=H or CH_3) 3 R=H [2] 4 R=CH_3 [2]

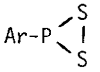
Compounds 3 and 4 are stable and do not dimerize. Photolysis does not generate the corresponding phosphinidene or diphosphene 5 as expected [1]

Ar-P=P-Ar 5

Addition of sulphur to 3 (or 4) does not afford the unknown phosphorus species 6 [3], but surprisingly, in this case, we observed, besides the formation of N,N-dimethylthioformamide, that of the first metadithiophosphonate 7 - a type of derivative often postulated as transient intermediate but never isolated.



7 was obtained as stable yellow crystals m.p 92-93 °C, ^{31}P N.M.R. (C_6D_6, δ) + 295.3(s); ^1H - N.M.R. (C_6D_6, δ) 1.22 (18H) 1.6 (9H) 7.8 (2H) ; mass spectra (field desorption) m/e : 340 ; analysis C.H.P.S. The $\delta^{31}P$ of 7 has a low-field resonance typical of an sp^2 hybridized phosphorus thus excluding a structure of type 8 [4] or 9 ($\delta^{31}P$ of dimers occur between + 14 and + 35 [5])



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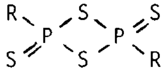

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7 is obtained in better yield (90%) by reacting for 2h phosphine 1 with 3 equimolecular amounts of sulphur in refluxing toluene [6].

$$\underline{1} + 3/8\ S_8 \xrightarrow{-SH_2} \underline{7}$$

Addition of methanol to 7 allowed us to obtain 10 quantitatively [7]. Moreover a [2+4] cycloaddition reaction is observed with 2,3-dimethylbutadiene [8] to give 11 [9].

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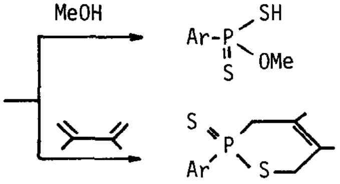

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References

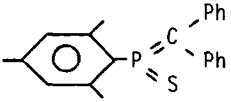
* These results were presented in the International Conference on Phosphorus Chemistry 5-9 sept. 1983 Nice (France).

[1] A. Meriem, J.P. Majoral, M. Revel and J. Navech, Tetrahedron Lett., 24, 1975 (1983).

[2] 3 : yield 55% ; m.p : 96-7 °C ; ^{31}P N.M.R. (C_6H_6,δ) + 85 ppm ; ^1H N.M.R. (C_6D_6,δ) 2.07 (6H, J_{PCNCH} = 3.7 Hz), 7.1 (H, J_{P-C-H} =12.7Hz), 7 (aromatic protons) ;^{13}C N.M.R. ($CDCl_3$, δ) : 30.4 and 32.6 (C) 32.9, 33.9 and 34.0 (CH_3) 41.5 (NCH_3 $J_{P-C-N-C}$ = 21.7 Hz) and 37.5 (NCH_3 , no observable $J_{P-C-N-C}$) 183.9 (C=P J_{PC} =90.5 Hz) ; mass spect. M-1: 333 ; analysis.

4 : yield 40% , oil, ^{31}P N.M.R. (C_6H_6, δ) + 96.3 ppm ; mass spect. M^+ 348.

[3] ^{31}P N.M.R. spectroscopic evidence and chemical proofs of the formation of unstable compound 6' have been recently given : Th. A. Van der knaap and F. Bickelhaupt, International Conference on Phosphorus Chemistry 5-9 sept. 1983 Nice (France).

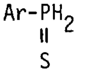


6'

[4] See for ex : E. Niecke and D.A. Wildbredt, J.C.S. Chem. Comm., p. 72 (1981) ; E. Niecke and O.J. Scherer, Nachr. Chem. Tech., 23, 395 (1975).

[5] E. Fluck and H. Binder, Z. Anorg. Allg. Chem., 377, 298 (1970).

[6] When the reaction is carried out at 65 °C, the thiophosphine 12 is formed as well as two other compounds (δ ^{31}P = 17.6 , J_{PH} = 456.5 Hz . δ^{31}P = 49.8 , J_{PH} = 572.3 Hz) not yet identified.



$\underset{S}{\overset{\|}{Ar\text{-}PH_2}}$

12

δ^{31}P = -26 (C_6H_6)

J_{PH} = 469.5 Hz

[7] 10 ^{31}P N.M.R. ($CHCl_3$, δ) + 95.4 ppm ; ^1H N.M.R. ($CDCl_3$,δ) 1.23 (18H) 1.43 (9H) 3.66 (3H. J_{PH} = 15 Hz) 7.2 (2H).

[8] Note that dimers of type 9 give a similar cycloaddition reaction [10]

[9] 11 ^{31}P N.M.R. ($CDCl_3$, δ) + 42.6 ; ^1H N.M.R. ($CDCl_3$,δ) 1.25 (18H) 1.55 (9H) 1.68 (3H) 1.90 (3H) 2.8 and 4.0 (4H, m) 7.6 (2H).

[10] A. Ecker, I. Boie and U. Schmidt, Angew. Chem., Internat. Edit., 10, 191 (1971).

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