Tetrahedron Letters No. 2, pp. 51-53, 1962. Pergamon Press Ltd. Printed in Great Britain.

SYNTHESIS OF DIPHENYLARSENONITRIDE TETRAMER

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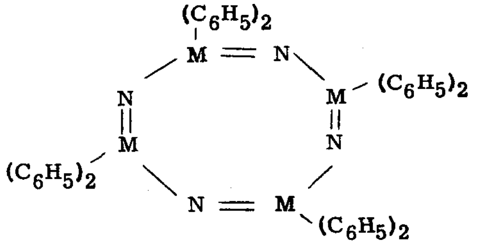
(Received 29 December 1961)

DIPHENYLPHOSPHONITRIDE tetramer (I, m.p. 321°) has been prepared by several investigators.[1,2,3,4] This communication describes the preparation of the unknown arsenic analog (II, m.p. 316-317°), the first member of the arsenonitride family.



(I) M = P

(II) M = As

Diphenylarsenous azide (III) was prepared by refluxing diphenylarsenous chloride (b.p. 174-177°/6 mm Hg; found: Cl, 13.1, 13.1. $C_{12}H_{10}AsCl$ requires: Cl, 13.44%) with dry lithium azide in anhydrous pyridine. Removal of the

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[1] D.L. Herring, Chem. & Ind. 717 (1960).

[2] H. Bode and R. Thamer, Ber. Dtsch. Chem. Ges. 76, 121 (1943).

[3] C.P. Haber, D.L. Herring and E.A. Lawton, J. Amer. Chem. Soc. 80, 2116 (1958).

[4] V.V. Korshak, I.A. Gribova, T.V. Artamonova and A.N. Bouschmarina, Vysokomol. Soedin. 2, 377 (1960).

solvent in vacuo, extraction of the residue with hexane, filtration, and removal of this solvent left a yellow oil whose infrared spectrum (neat) had the typical monosubstituted phenyl absorptions next to a sharp and intense band at 2075 cm^{-1}, presumably due to the azide group (Found: C, 54.48; H, 3.75; As, 21.79; N, 12.48. $C_{12}H_{10}AsN_3$ requires: C, 53.11; H, 3.69; As, 27.70; N, 15.50%). The analyses indicate an 80% purity of (III), the remainder was presumably unreacted chloride. In view of the unstable nature of some azides, it was decided not to attempt purification (the compound could not be induced to crystallize).

This impure azide (III) was thermally decomposed (neat) in a device designed to simultaneously measure the evolved nitrogen. Two runs yielded smooth reactions; nitrogen was evolved following a first-order rate law: temp. 191-2°, $k_1 = 6.4 \times 10^{-3}$ min^{-1}, temp. 197-9°, $k_1 = 9.3 \times 10^{-3}$ min^{-1}. In the first case, the total volume of gas expelled was 83% of theory for:

$$(C_6H_5)_2AsN_3 \longrightarrow (C_6H_5)_2AsN + N_2$$

The residue was a dark brown solid. Charcoal treatment and several recrystallizations from boiling benzene yielded colorless crystals (about 19% yield, well purified), m.p. 316-317° (Found: C, 59.00, 58.94; H, 4.31, 4.09; As, 30.78, 31.01; N, 5.91, 5.95; mol. wt., 976, ebullioscopic in CH_2Cl_2. $C_{12}H_{10}AsN$ requires: C, 59.27; H, 4.11; As, 30.85; N, 5.77; mol. wt., 972, tetramer). The infrared absorption spectrum (KBr pressed disk) showed the following bands: 3080 (w), 1970 (vw), 1900 (vw), 1830 (vw), 1775 (vw), 1593 (vw), 1485 (w), 1440 (m), 1308 (w), 1180 (w), 1160 (vw), 1087 (s), 1065 (w), 1036 (w), 1020 (m), 943 (vs broad), 738 (s), 691 (s), 680 (m) cm^{-1}. The intensity of the band at 943 cm^{-1} was about five times that of the next strongest band at 691 cm^{-1}. This 943 cm^{-1} absorption is, no doubt, the As = N vibration [the P = N band[5] is also very intense and occurs at

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[5] L.W. Daasch, J. Amer. Chem. Soc. 76, 3403 (1954).

1220 cm^{-1} in (I)]. The remainder of the bands are due to monosubstituted phenyl groups.[6]

(II) appears to be stable to atmospheric moisture; thermally gradual decomposition takes place at 350-400°. The crystal liquors yielded no other compound excepting a small amount of diphenylarsenic acid. It is interesting to observe that (III) decomposes at 190° at about the same rate as the interaction product of diphenylphosphinous chloride and lithium azide in pyridine does at 0° (presumably the diphenylphosphinous azide). An explanation for this abnormal difference in decomposition rates is not apparent [(III) does not decompose in boiling pyridine].

(II) appears to be the first arsenic analog of the phosphonitrides[7] prepared to date. The physical properties and infrared spectrum of (II) indicate strongly that the bonding here is similar to that of the phosphonitrides;[8,9] namely, a strong $2p_N$-$4d_{As}\pi$ bond superimposed on the usual sigma bond system.

Professor L.F. Dahl of the University of Wisconsin is currently examining (II) by X-ray in order to determine the crystal structure.

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[6] M.C. Henry and J.G. Noltes, J. Amer. Chem. Soc. **82**, 555 (1960).

[7] N.L. Paddock and H.T. Searle, Advances in Inorganic Chemistry and Radiochemistry Vol. I, p. 347. Academic Press, New York (1959).

[8] D.P. Craig, J. Chem. Soc. 997 (1959).

[9] M.J.S. Dewar, E.A.C. Luken and M.A. Whitehead, J. Chem. Soc. 2423 (1960).