is also given to Dr. J. Nagyvary for the use of his Corey–Pauling models.

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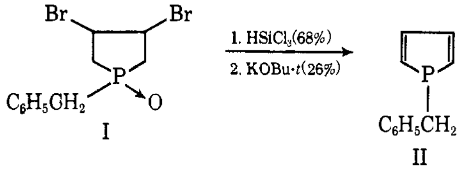
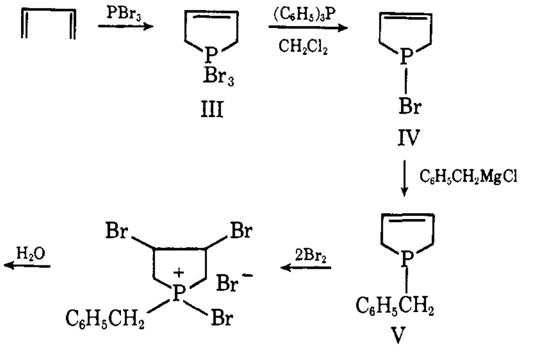
Molecular Structure of 1-Benzylphosphole by X-Ray Analysis[1]

Sir:

We wish to report the first determination of the molecular parameters of a phosphole. The synthesis of 1-benzylphosphole (II) resembled that already employed for 1-methylphosphole,[2] and made use of 1-benzyl-3,4-dibromophospholane oxide (I, mp 159–160°, analyzing correctly) as the key intermediate. As before, some of the corresponding 3-phospholene was formed but was removed on extraction with 2 *N* hydrochloric acid. Several methods of obtaining I were devised; that which proved most successful is shown below.





The reduction of the butadiene–phosphorus tribromide cycloadduct[3] (III) to form 1-bromo-3-phospholene [IV, 34%, bp 64–67° (27 mm), ^{31}P nmr signal −111.4 ppm relative to 85% phosphoric acid] is a new reaction of considerable synthetic value in phospholene chemistry; details on the procedure will be published elsewhere.[4] Compound V was identified by quaternization with methyl bromide to form the same salt obtained from 1-methyl-3-phospholene with benzyl bromide.[5]

1-Benzylphosphole was considerably more stable than 1-methylphosphole and distilled without decomposition at 71–72° (0.2 mm); it had mp 34–34.5° and gave the correct analysis. It resembled 1-methylphosphole in having low basicity, a uv maximum in 95% ethanol at 286 mμ (log ε 3.65), and a ^{31}P nmr signal (−7.9 ppm) showing considerable deshielding relative to the corresponding 3-phospholene (V, +23.5 ppm). Its ring protons were similarly strongly deshielded (multiplet, δ 6.3–7.3 ppm, partly merged with phenyl protons), and the benzylic CH_2 group (δ 3.01 ppm) was not detectably coupled with phosphorus. Its mass spectrum confirmed its monomeric character (M^+ at *m*/*e* 174, 38.8% of $C_7H_7^+$ base peak). It is sensitive to oxygen and can be quaternized with alkyl halides.

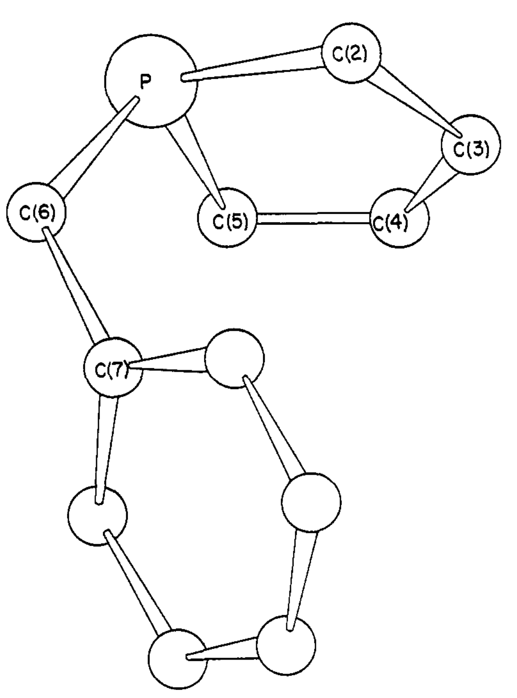


Figure 1. Molecular structure of 1-benzylphosphole. Molecular dimensions are P–C_2 = 1.786, P–C_5 = 1.780, P–C_6 = 1.858, C_2–C_3 = 1.343, C_3–C_4 = 1.438, C_4–C_5 = 1.343, C_6–C_7 = 1.506, mean phenyl C–C = 1.382 Å; C_2PC_5 = 90.7°, C_2PC_6 = 106.1°, C_5PC_6 = 105.9°, PC_2C_3 = 109.9°, PC_5C_4 = 110.1°, $C_2C_3C_4$ = 114.1°, $C_3C_4C_5$ = 114.1°, PC_6C_7 = 116.4°. Standard deviations of distances are ±0.005 Å for P–C bonds and ±0.006 Å for C–C bonds, while those for angles are ±0.2° for CPC angles and ±0.4° for CCC angles.

Crystals of II obtained from a melt have cell dimensions a = 17.62, b = 14.60, c = 7.67 Å, and belong to the orthorhombic system with eight units of $C_{11}H_{11}P$ occupying general positions of space group *Pbca*. A total of 1351 independent structure amplitudes were derived from visually estimated intensities recorded by equiinclination Weissenberg photography of the *hk*0–7 layers. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations[6] to the present conventional *R* of 0.073. The molecular dimensions are given in the legend of Figure 1.

Comparison of the phosphole dimensions with those of the heteroaromatics furan, pyrrole, and thiophene is of particular interest. The average P–C_{sp^2} bond length 1.783 Å is significantly less[7] than the sum of the single-bond radii (1.10[8] and 0.74[9] Å, respectively), the

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(1) Supported in part by Public Health Service Research Grant No. CA-05507 from the National Cancer Institute.

(2) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, 91, 3308 (1969).

(3) U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron Lett.*, 19, 1563 (1963).

(4) D. K. Myers and L. D. Quin, manuscript in preparation.

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(6) Full details of the crystal structure analysis will be published elsewhere.

(7) A bond order of 1.5 has been suggested for the P–C length of 1.743 ± 0.005 Å in 2,6-dimethyl-4-phenylphosphorin: J. C. J. Bart and J. J. Daly, *J. Chem. Soc. A*, 567 (1970).

(8) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224.

(9) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 5, 166 (1959).

contraction being of the same order of magnitude as those found in the other heteroaromatics.[10] The phosphorus d orbitals may be involved in this situation. The C—C and C=C bonds in the phosphole ring have similar lengths to those of the other heteroaromatics, although the average C=C distance of 1-benzylphosphole is closer to the ethylene value[11] (1.334 Å) and not significantly different from it (1.5σ). The ring angles are very similar to those in thiophene.

Microwave spectral studies have indicated that furan, pyrrole, and thiophene are planar species and that the nitrogen proton in pyrrole is in the plane of the ring.[10b] Significant differences of the phosphole ring are a slight puckering of the ring and retention of pyramidal configuration at phosphorus. The latter feature is consistent with the conclusion of other workers[12] based on nmr studies of the barrier to inversion about phosphorus in 1-isopropyl-2-methyl-5-phenylphosphole. The phosphorus and C_6 are displaced by 0.21 and 1.36 Å, respectively, to opposite sides of the least-squares plane through C_2–C_5 which are accurately planar (root-mean-square deviation 0.0018 Å). The significant increase in the PC_6C_7 angle to 116.4 (±0.4°) from tetrahedral (109° 28′) may be ascribed to intramolecular van der Waals repulsions between the phosphole and phenyl rings. The puckering at phosphorus may result, at least in part, from this interaction. The difference between the phosphole and pyrrole systems with regard to the noncoplanarity of the hetero substituent with the ring atoms in the former may be associated with the configurational stability of phosphorus, whereas nitrogen inverts rapidly. Clearly, quantitative treatment of the bonding in the phosphole system would be desirable.

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(10) See, for example (a) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, pp 30–39; (b) R. M. Acheson, "Introduction to the Chemistry of Heterocyclic Compounds," 2nd ed, Interscience, New York, N. Y., 1967, Chapter 3, and references cited therein.

(11) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, 27, 1414 (1957).

(12) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970).

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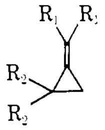
Nickel(0)-Catalyzed Reaction of Methylenecyclopropanes with Olefins. A Novel [$_\sigma 2 + _\pi 2$] Cycloaddition

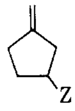
Sir:

The [2 + 2] cycloaddition reaction is not readily attainable in noncatalyzed, ground-state reactions,[1] and few examples of the addition of cyclopropane to olefins to form carbocyclic five-membered rings are known.[2] We wish to report a novel cycloaddition of methylenecyclopropanes across carbon–carbon double bonds under the influence of nickel(0) catalyst.

A solution of methylenecyclopropane (**1a**)[3] (10 mmol) in excess methyl acrylate (15 ml) in the presence of bis(acrylonitrile)nickel(0)[4] (0.3 mmol) was heated in a sealed tube at 60° for 48 hr under a nitrogen atmosphere. The usual work-up and distillation gave the 1:1 adduct, methyl 3-methylenecyclopentanecarboxylate (**2a**), in 82% yield.[5,6] The spectral data were in accord with the assigned structure: mass *m/e* 140 (M^+); ir (neat) 1735 (C=O) and 880 cm^{-1} (exocyclic methylene); nmr (CCl_4, TMS) δ 1.7–2.9 (m, 7 H, ⩾CH and >CH_2), 3.67 (s, 3 H, $COOCH_3$), and 4.90 (m, 2 H, =CH_2). Ozonolysis of **2a** afforded known methyl 3-oxocyclopentanecarboxylate (**3**).[7] $Ni(CH_2{=}CHCN)_2[P(C_6H_5)_3]_n$ (*n* = 1 or 2)[4] also effects the cycloaddition, but in lower yield. No reactions were observed in the absence of the nickel catalysts even at 100°. Employing methyl vinyl ketone[6] or acrylonitrile as substrates gave rise to the corresponding methylenecyclopentanes **2b** and **2c** in moderate yields. Both **2b** and **2c** were identified by converting to **3** using ordinary procedures.

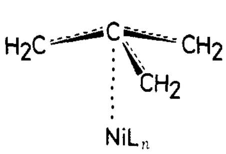


1a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$



2a, $Z = COOCH_3$
b, $Z = COCH_3$
c, $Z = CN$

The fixation of trimethylenemethane, a highly reactive bond isomer of **1a**, on transition metals is well known,[8] and treatment of methylenecyclopropane derivatives with diiron nonacarbonyl produces the corresponding trimethylenemethaneiron tricarbonyl complexes.[9] Recently photolysis of trimethylenemethaneiron tricarbonyl in cyclopentene was reported to afford 3-methylenebicyclo[3.3.0]octane though in poor yield.[10] These facts led us to consider as a mechanism for this cycloaddition the intervention of the nickel(0) complex **4** (L = $CH_2{=}CHZ$) in which the trimethylenemethane ligand has a C_{3v} symmetry.[11] This possibility, however, was ruled out by the following experiments. Reaction of 2,2-dimethylmethylenecyclopropane (**1b**)[12] with methyl acrylate afforded the adduct **5** in 60% yield: mass *m/e* 168 (M^+); ir (neat) 1735



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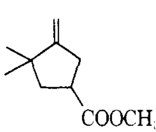

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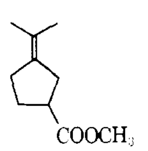

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(5) All new compounds gave satisfactory elemental analyses.

(6) A trace amount of the acrylonitrile adduct **2c** was obtained.

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