The molecules are situated at crystallographic inversion centers, hence any deviations from planarity for the cyclohexa-1,4-diene ring lead to a chair structure. The deviations from planarity are small (each atom lies approximately 0.01 Å from the least-squares plane), but significant in a statistical sense. These results are in good agreement with those of the X-ray study of a glycine derivative of cyclohexa-1,4-diene.[6] It is convenient to redefine the reference plane by the four olefinic (sp^2) carbon atoms and to discuss deviations of the methylenic (sp^3) carbon atoms from this plane since this allows immediate comparison of the boat and chair forms. This structure shows a deviation of 0.03 Å for C-3 for this reference plane. Dallinga and Toneman[5] considered chair, boat, planar, and skew conformations in the preliminary stages of their electron diffraction study but pursued only the planar form to completion. However the suggested deviations from the plane were ≤0.05 Å. On the other hand Oberhammer and Bauer[7] favored the boat conformation with a dihedral angle of 160° giving a deviation of 0.23 Å from the diene plane for the methylenic (sp^3) carbon atoms. While the cyclohexa-1,4-diene ring in this structure is not severely constrained as it would be in a fused ring system it remains a legitimate question as to whether the observed geometry reflects the inherently preferred structure for the cyclohexa-1,4-diene ring or whether it results from either intermolecular forces in the condensed phase or intramolecular forces due to the bulky substituents (particularly the phenyl–phenyl repulsions).

Having established the face-to-face geometry of two phenyl substituents of A, one can readily understand the 236-nm uv maximum of this compound. In a manner analogous to the case of the bicyclobutane system,[18] the two groups in this geometry couple rather strongly through the p-rich σ bond common to the three- and four-membered rings of the system. The carbomethoxy group appears not to exert any significant steric repulsion to distort this unique alignment.[18d,e] The hypsochromic shift of the stilbene chromophore of B is obvious in the geometry shown and requires no further comment.

Acknowledgment. We thank the Research Council of Canada and the Defense Research Board for financial support.

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[18] (a) S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964); (b) for the X-ray analysis of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl *p*-bromobenzoate, see ref 1c; (c) S. Masamune, *Tetrahedron Lett.*, 945 (1965); (d) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4613 (1969); (e) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6654 (1970). In the cases of esters of *exo*-1,3-diphenylbicyclobutanecarboxylic acid, uv maxima are shifted to shorter wavelengths (*ca.* 220 nm) from the normal position (*ca.* 270 nm) apparently due to the steric hindrance between the carbethoxy and phenyl groups.

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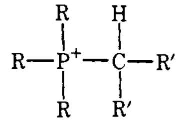
A Stable Pentaalkylphosphorane

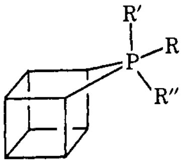
Sir:

Although pentaarylphosphoranes can be prepared by treating tetraarylphosphonium salts with aryllithium reagents,[1] no pentaalkylphosphorane has yet been prepared in this or any other way. Thus, tetramethylphosphonium iodide reacts with methyllithium or phenyllithium in ether to give not the phosphorane, but the ylide,[2] and there are numerous analogous reactions,[3] many of which are the basis of the Wittig reaction.[4] Consider the general phosphonium salt, I, the precursor of anylide, and suppose that two of the substituents, say R and R′, are joined in a ring so small that it strains the carbon–phosphorus–carbon angle. When base approaches this molecule it can relieve the strain if, instead of removing the hydrogen atom from the carbon adjacent to phosphorus, it bonds to the phosphorus instead.[5] This would account, for example, for the stability of the phosphorane IIa[6] and would explain why the phosphonium salt IIIa,[6] unlike tetraphenylphosphonium salts,[7] can be prepared from the phosphine oxide IVa[8] and phenyllithium.[9]

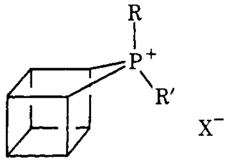


$$R_3P^+\text{—}CH(R')_2$$

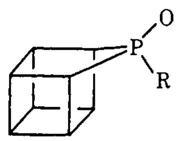
I



IIa, R = R′ = R″ = C_6H_5
b, R = R′ = R″ = CH_3
c, R = C_6H_5; R′ = R″ = CH_3
d, R = R′ = C_6H_5; R″ = CH_3



IIIa, R = R′ = C_6H_5; X = Br
b, R = R′ = CH_3; X = I
c, R = C_6H_5; R′ = CH_3; X = I



IVa, R = C_6H_5
b, R = CH_3

It would also mean that if one of the substituents in the phosphonium salt had a potentially reactive hydrogen atom and two *other* substituents on the phosphorus atom, say the groups labeled R in structure I, were joined in a small ring, base would react not with the hydrogen atom, but would add to the phosphorus instead. We have verified this hypothesis by showing that the phosphoranes IIb, IIc, and IId are easily synthesized and stable at room temperature, and we

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[1] (a) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 187 (1949); (b) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1966).

[2] G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 177 (1949).

[3] (a) G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953); (b) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 2847 (1965); (c) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[4] A. Maercker, *Org. React.*, **14**, 270 (1965).

[5] This hypothesis is derived from Westheimer's account for the rate of hydrolysis of small-ring phosphorus esters: F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **91**, 4143 (1969).

[6] T. J. Katz and E. W. Turnblom, *ibid.*, **92**, 6701 (1970).

[7] (a) G. Wittig and H.-J. Cristau, *Bull. Soc. Chim. Fr.*, 1293 (1969); (b) H. Gilman and G. E. Brown, *J. Amer. Chem. Soc.*, **67**, 824 (1945).

[8] T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *ibid.*, **92**, 734 (1970).

[9] It also accounts for the ease with which bisbiphenylenephosphonium salts can be prepared[10] and for the stability of the alkylbisbiphenylenephosphoranes.[10,11] See also ref 6, footnote 22.

[10] D. Hellwinkel, *Chem. Ber.*, **102**, 548 (1969); **98**, 576 (1965).

[11] M. Schlosser, T. Kadibelban, and G. Steinhoff, *Justus Liebigs Ann. Chem.*, **743**, 25 (1971).

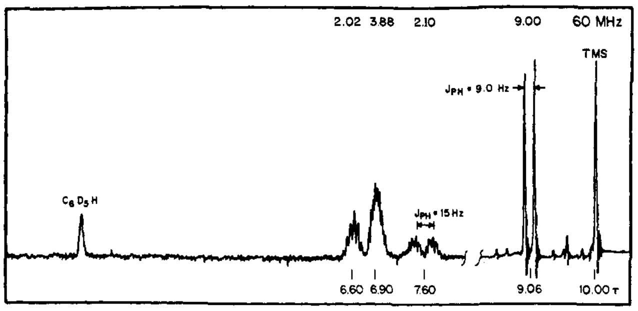

Figure 1. Proton nmr spectrum of IIb in C_6D_6. Intensities are listed above the peaks. The amplification is decreased above τ 8.

have thus prepared the first stable pentaalkylphosphorane.

The methylphosphonium salt IIIc in ether with phenyllithium[12] gives the corresponding phosphorane IId (50% yield), a solid, mp 124–125°, which can be crystallized from ether.[13,14] The dimethylphosphonium salt IIIb with phenyllithium similarly gives IIc, a liquid isolable by distillation (60° $(10^{-6}$ mm),[13] 55% yield), while with methyllithium[15] it gives the trimethylphosphorane IIb, also a distillable liquid (room temperature $(10^{-6}$ mm), 20% yield).[13]

Alternatively, the diphenylmethylphosphorane IId can be prepared by treating the diphenyl salt IIIa with methyllithium (75% yield), but the analogous procedure, the reaction of the phenylmethyl salt IIIc with methyllithium, does not give the simple product IIc cleanly; it gives a mixture of the three phosphoranes IIb, IIc, and IId in the ratio 17:63:20.[16,17] In air IIc decomposed slowly, but IIb and IId were unchanged after a few days. The proton nmr spectrum of the trimethylphosphorane IIb is shown in Figure 1.

To prepare the methylphosphine oxide IVb, the phenyl group in IVa was replaced. Reaction of IVa with methyllithium in ether–benzene at 0° gave IVb directly (66% yield, mp, after crystallization from cyclohexane and sublimation at 90° (0.1 mm), 98.5–100°).[13,14,18] The phosphine oxides IVa and IVb were reduced with Si_2Cl_6 in benzene[19] and quaternized with methyl iodide to give the salts IIIc (95%, mp 195–196°)[20] and IIIb (80%, mp 308–309°).[20]

Like the triphenylphosphorane IIa, the methylphosphoranes IIb, IIc, and IId upon heating fragment to the corresponding phosphines and *syn*-tricyclo[4.2.0.0^{2,5}]-octa-3,7-diene (which rearranges thermally to cyclooctatetraene),[6,21] and the half-lives at 75° decrease with increasing substitution by phenyls from 108 hr for the trimethylphosphorane to 36 hr for the dimethylphenyl-, 23 hr for the methyldiphenyl-, and 7 hr for the triphenylphosphorane, as should be expected if the phenyls conjugatively delocalize electrons freed from two-center bonds.

The trimethylphosphorane IIb absorbs strongly in the ultraviolet, exhibiting a shoulder at 230 nm (log ε 3.45) and strong absorption extending to 300 nm. Photolysis of benzene or cyclohexane solutions through Pyrex fragments the molecule to trimethylphosphine and *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene.

The phosphorane IIb in C_6D_6 shows a ^{31}P resonance at +90 ppm higher magnetic field than 85% H_3PO_4.[22,23] It has a pleasant odor reminiscent of camphor.

Acknowledgments. We are grateful to the National Institutes of Health (MH-08912) for its support and Badische Anilin und Sodafabrik, A.G. for gifts of cyclooctatetraene.

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(12) Phenyllithium in 70:30 benzene–ether from Alfa Inorganics, Inc., Beverly, Mass.

(13) The proton nmr spectrum and the parent peak in the mass spectrum are in accord with the structure.

(14) The analyses for carbon, hydrogen, and phosphorus are satisfactory.

(15) Methyllithium in ether containing 0.4% LiCl from Foote Mineral Co.

(16) The composition of this mixture is indicated by identifying the chemical shifts and the phosphorus coupling constants of the methyl proton nmr resonances with those of pure samples of IIb, IIc, and IId.

(17) The exchange of phenyllithium for methyllithium[11] would account for these products.

(18) For analogies see D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Amer. Chem. Soc.*, **86**, 1100 (1964), and L. Horner and P. Beck, *Chem. Ber.*, **93**, 1371 (1960).

(19) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969).

(20) Satisfactory proton nmr spectra and analyses for carbon, hydrogen, phosphorus, and iodine were obtained.

(21) The final products are the phosphines and cyclooctatetraene, but that tricyclooctadiene is formed initially is suggested by the observation of its proton nmr absorption early in the reaction. The half-life for the conversion of the diene to cyclooctatetraene at 75° is 7.5 hr.[6]

(22) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).

(23) The spectrum was determined by Bruker Physik A.G., Karlsruhe, Germany.

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Optical Activity of Flow-Oriented Deoxyribonucleic Acid[1]

Sir:

We wish to report measurements of the circular dichroism (CD) and absorption spectra of deoxyribonucleic acid (DNA) oriented by flow. The measurements show that the ellipticity θ_{33} of light propagating down the axis of DNA in the B form is more than six times greater than θ_{11} and θ_{22}, the ellipticities for light propagating perpendicular to the helix axis. These results provide new support for the theory of polynucleotide optical activity advanced by Tinoco and coworkers.[2-4]

Salmon sperm DNA (Worthington, MW $\sim 6 \times 10^6$) is oriented by flow through a parallel array of capillaries. Light for the optical measurements propagates parallel to the capillary axes. The circular dichroism θ and absorbance A are determined in the same cell in Cary 6001 and Cary 15 instruments. We verified that residual linear dichroism had negligible effect on the measured CD.[5]

The experimental circular dichroism with and without flow is shown in Figure 1. Under our conditions the 275-nm peak increases with flow by 30 ± 5% and the magnitude of the 245-nm trough increases by 40 ± 5%,

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(1) Supported by U. S. Public Health Service Grant No. NS-07286; S-Y. W. acknowledges support from U. S. Training Grant No. GM 780.

(2) (a) W. C. Johnson and I. Tinoco, Jr., *Biopolymers*, **7**, 727 (1969); (b) I. Tinoco, Jr., *Advan. Chem. Phys.*, **4**, 133 (1962).

(3) I. Tinoco, Jr., *J. Chim. Phys. Physicochim. Biol.*, **65**, 91 (1968).

(4) I. Tinoco, Jr., *J. Amer. Chem. Soc.*, **86**, 297 (1964).

(5) R. Mandel and G. Holzwarth, *Rev. Sci. Instrum.*, **41**, 755 (1970).