alkyldiaryl-, and triarylphosphine oxides may in principle be correlated *via* the appropriately substituted phosphinates; such correlations have not been possible by previously existing methods. We are currently exploring the scope and ramifications of this scheme.

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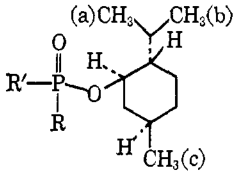
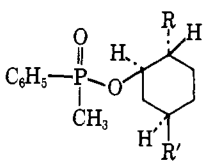
Configurational Correlation of Phosphinates by Nuclear Magnetic Resonance and Optical Rotatory Dispersion[1]

Sir:

Menthyl phosphinates are useful precursors in the synthesis of optically active phosphorus compounds.[2] We now report that the nmr and ord spectra of these esters are characteristic of configuration and are thus important adjuncts to the assignment of chirality at phosphorus in this family of compounds.





1, R = n-C_3H_7; R′ = C_6H_5
2, R = CH_3; R′ = C_6H_5
3, R = CH_3; R′ = C_6H_{11}
4, R = R′ = C_6H_5

5, R = i-C_3H_7; R′ = H
6, R = H; R′ = CH_3

The absolute configuration of the menthyl esters **1** and **2** has been established.[2] As shown in Table I, the epimers of **1** and **2** having the *S* configuration at phosphorus (**1B** and **2B**) exhibit a downfield shift of the H_c doublet and an upfield shift of the isopropyl doublets (H_a and H_b), relative to the corresponding signals for the epimers which have the *R* configuration at phosphorus (**1A** and **2A**). The large upfield shift of the H_a doublet (*ca.* 0.5 ppm) is particularly striking; its location in a region unencumbered by other signals provides an excellent measure of diastereomeric purity since contamination of **A** by **B** can be easily detected and estimated quantitatively.

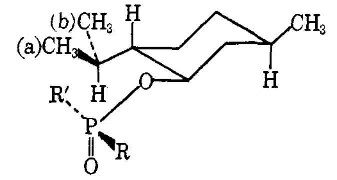
Table I.[a] Pmr Chemical Shifts and Coupling Constants of Phosphinate Esters

Compd	P–CH_3	C–CH_3		
		H_a	H_b	H_c
1A		9.11 (7.0)	9.05 (7.0)	9.25 (4.5)
1B		9.68 (7.0)	9.19 (7.0)	9.10 (5.0)
2A	8.38 (14.5)	9.11 (7.0)	9.05 (7.0)	9.24 (4.5)
2B	8.14 (14.5)	9.66 (7.0)	9.19 (7.0)	9.11 (5.0)
3A	8.64 (13.0)	9.19 (7.0)	9.08 (7.0)	9.10 (5.0)
3B	8.61 (13.0)	9.19 (7.0)	9.08 (7.0)	9.10 (5.0)
4		9.43 (7.0)	9.12 (7.0)	9.15 (5.0)
5A	8.38 (14.5)	9.10 (7.0)	9.05 (7.0)	
5B	8.32 (14.5)	9.59 (7.0)	9.20 (7.0)	
6A	8.42 (14.5)			*Ca.* 9.1 (5.0)
6B	8.42 (14.5)			*Ca.* 9.1 (5.0)

[a] Chemical shifts are given in τ units, and coupling constants (in parentheses) are given in Hz.

The source of the shift experienced by H_a is traceable to the diamagnetic anisotropy of the phenyl ring rather than of the phosphoryl group, as shown by two observations. First, the C–CH_3 protons of the diastereomeric menthyl cyclohexylmethylphosphinates (**3**)[3,4] are indistinguishable at 60 MHz; second, the large upfield shift of H_a is also exhibited by menthyl diphenylphosphinate (**4**).[3] The C–CH_3 proton signals can be assigned by comparison (Table I) of the nmr spectra of esters containing portions of the menthyl group (**5** and **6**) with the spectra of **1–4**. First, both diastereomers of racemic *trans*-2-isopropyl-1-cyclohexyl methylphenylphosphinate (**5**)[3] feature two C–CH_3 doublets with J = 7.0 Hz; second, **5B** exhibits a 0.5-ppm upfield shift of one doublet relative to the corresponding signal in **5A**; third, both diastereomers of *cis*-3-methyl-1-cyclohexyl methylphenylphosphinate (**6**)[3] exhibit a C–CH_3 doublet with J = 5.0 Hz. Consequently, H_a must be located in the isopropyl portion of **1–5** and is diagnostic of configuration. For example, given the 1*R*,2*S*,5*R* configuration of menthol,[5] it can be deduced that **5A** is a mixture of enantiomers, one of which has the *R* configuration at phosphorus and the 1*R*,2*S* configuration in the cyclohexyl moiety, *i.e.*, $(R)_P$-$(1R,2S)_C$, while the other has the $(S)_P$-$(1S,2R)_C$ configuration; similarly **5B** is an equimolar mixture of $(S)_P$-$(1R,2S)_C$ and $(R)_P$-$(1S,2R)_C$ enantiomers.

The remaining question is to decide which of the two diastereotopic[6] methyl groups in the isopropyl portion of **1–5** is associated with the most highly shielded proton, H_a. If we assume minimal conformational strain in the menthol portion and an "up" conformation for the phosphinate ester grouping,[7] the most populated conformation of **1–4** (and, by extension, **5**) may be represented by stereoformula **7**. If this formulation is correct, it follows that when R′ = phenyl, as in **1B**, **2B**, **4**, and $(S)_P$-$(1R,2S)_C$-**5**, the more highly shielded proton (H_a) is located on the methyl group which has the *pro-R* chirality[8,9] and the less highly shielded proton (H_b) on the methyl group which has the *pro-S* chirality.[8]



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[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67.

[2] O. Korpiun and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4784 (1967).

[3] All new compounds gave elemental analyses (C, H, and P) and nmr spectra consistent with their structures.

[4] Prepared from $C_6H_{11}P(Cl)N(C_2H_5)_2$ (K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959)) by the route $(+CH_3OH) \rightarrow C_6H_{11}P(OCH_3)_2$ $(+CH_3I) \rightarrow (C_6H_{11})(CH_3)P(O)OCH_3$ $(+PCl_5) \rightarrow (C_6H_{11})(CH_3)P(O)Cl$ (L. Z. Soborovskij and J. M. Zinovjev, *Zh. Obshch. Khim.*, **24**, 516 (1954)), followed by reaction with (—)-menthol and separation of the epimers by fractional crystallization.

[5] V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

[6] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 1.

[7] T. H. Siddall, III, and C. A. Prohaska, *J. Am. Chem. Soc.*, **84**, 3467 (1962); K. D. Berlin and R. U. Pagilagan, *Chem. Commun.*, 687 (1966); K. D. Berlin and R. U. Pagilagan, *J. Org. Chem.*, **32**, 129 (1967).

[8] K. R. Hanson, *J. Am. Chem. Soc.*, **88**, 2731 (1966).

[9] Similar arguments have been advanced by T. S. Sorensen, *Can. J. Chem.*, **45**, 1585 (1967), in a discussion of the nmr spectra of isoproylcyclopentenones.

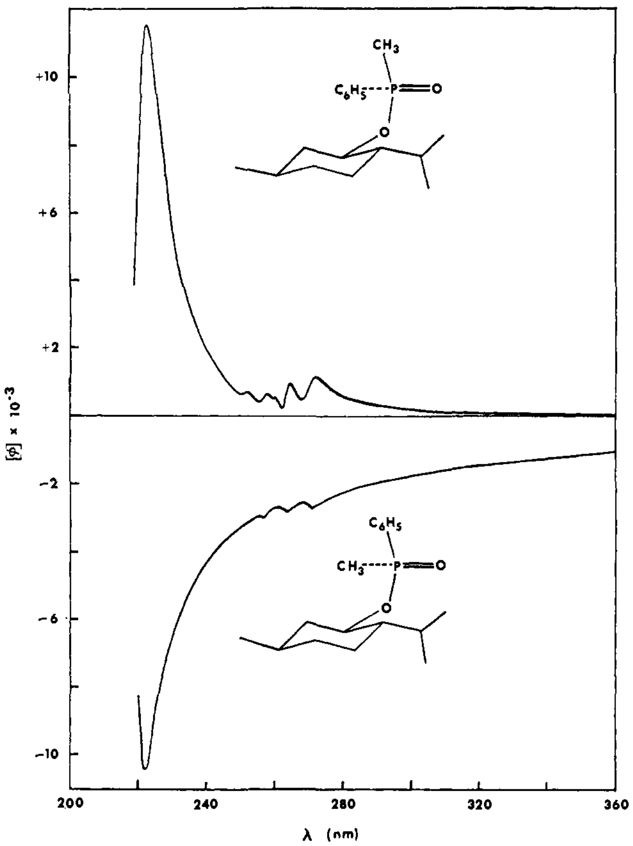

Figure 1.

The ord curves (Figure 1) of **2A** and **2B** are enantiomeric in type, the positive and negative Cotton effects corresponding to the *R* and *S* configurations at phosphorus, respectively. The chirality of the benzenephosphoryl chromophore (λ_{max} 210 nm (ϵ 8300), 217 nm (ϵ 7800)) dominates the ord, as previously found[10] for the analogous *p*-iodobenzenesulfinyl chromophore in the diastereomeric menthyl *p*-iodobenzenesulfinates. Further studies on the correlation of configuration and ord of phosphinates and phosphine oxides[11] are in progress.

[10] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

[11] See also L. Horner and H. Winkler, *Tetrahedron Letters*, 3265 (1964); O. Červinka and O. Kříž, *Collection Czech. Chem. Commun.*, **31**, 1910 (1966).

[12] U. S. Public Health Service Predoctoral Fellow, 1966–1967.

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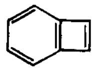
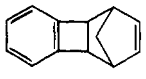
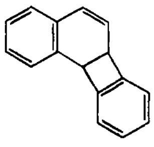
Oxidative Degradation of (Benzocyclobutadiene)iron Tricarbonyl

Sir:

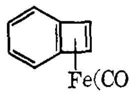
Previous work by Cava[1] and by Nenitzescu[2] and their collaborators has indicated that benzocyclobutadiene (I) is produced upon dehalogenation of dihalobenzocyclobutene with zinc or lithium amalgam. When conducted in the presence of cyclopentadiene, this reaction produces the Diels–Alder adduct II whereas, in the absence of added diene, the hydrocarbon III is formed.[2,3] Compound III is reasoned to be the stable rearrangement product of the intermediate Diels–Alder type dimer of benzocyclobutadiene.

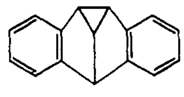

I


II


III

Our previous studies have indicated that cyclobutadiene is liberated upon oxidative degradation of cyclobutadieneiron tricarbonyl.[4] However, as also reported earlier, oxidative decomposition of (benzocyclobutadiene)iron tricarbonyl (IV) using silver ions as the oxidant produced none of the normal dimerization product of I, *viz.* III, but instead gave rise to the isomeric hydrocarbon V;[5] oxidation with ceric ion produced polymeric material. This has then raised the important question as to whether free benzocyclobutadiene is liberated in these oxidative decompositions. In this paper we wish to report evidence indicating that I is indeed produced upon oxidation of IV and to rationalize the anomaly presented by the formation of V.


IV


V

It is now found that oxidative degradation of the complex IV in the presence of cyclopentadiene, using lead tetraacetate in pyridine, produces the hydrocarbon II identical with an authentic sample prepared by the method of Nenitzescu.[2] In the absence of cyclopentadiene this oxidation also produces the normal dimer III in good yield, and none of the isomeric compound V can be detected. Identical behavior is found when ferric nitrate in aqueous ethanol is used as the oxidant. These products parallel exactly the pattern found in the earlier dehalogenation reactions and support the contention that the benzocyclobutadiene is implicated in their formation.

The rate of oxidation of the complex IV is fast and appears to be comparable to that of the oxidation of cyclobutadieneiron tricarbonyl with $Pb(OAc)_4$. Since evidence indicated benzocyclobutadiene to be reactive as a dienophile but not as a diene,[3] this then suggested the intriguing possibility of being able to add cyclobutadiene to benzocyclobutadiene by this technique. This has now proved to be possible; addition of a mixture of cyclobutadieneiron tricarbonyl and the complex IV to $Pb(OAc)_4$ afforded the adduct VI[6] in 75% yield.

[1] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

[2] C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).

[3] M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

[4] J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967), and references therein.

[5] G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

[6] White crystalline solid, mp 17°, nmr absorptions at τ 2.98, 4.28, 6.22–6.77, having areas of 4:2:4, respectively. Elemental analysis and molecular weight are in agreement with the formula $C_{12}H_{10}$.