media cannot therefore be regarded as characteristic of secondary phosphine oxides.

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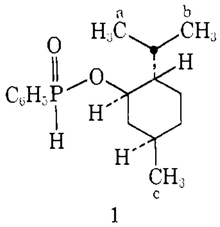
Stereospecific Alkylation of Menthyl Phenylphosphinate[1]

Sir:

Diastereomerically enriched menthyl phosphinates are useful precursors in the synthesis of optically active tertiary phosphine oxides,[2] phosphinamides,[3] and phosphonothioates.[4] We now report a significant broadening of the scope of this method: diastereomerically enriched menthyl alkylarylphosphinates can be conveniently prepared by the stereospecific alkylation of diastereomerically enriched menthyl arylphosphinates, and *a single precursor thus suffices for the synthesis of a wide variety of mixed alkyldiaryl- and aryldialkylphosphine oxides of known absolute configuration.*[5]

Partial separation of the diastereomers (**a** and **b**) of menthyl phenylphosphinate (**1**)[6] was achieved by fractional crystallization.[7] The salient features of the pmr spectra of **1a** and **1b** are listed in Table I. Of particular interest are the isopropyl doublets, H_a and H_b. It has been established[8] in analogous menthyl alkylarylphosphinates (*e.g.*, menthyl methylphenylphosphinate (**2**)[2a]) that both isopropyl doublets of the S_P epimer are shifted upfield relative to the corresponding signals for the R_P epimer, and that the chemical-shift difference is greatest for the H_a (upfield) proton signal. Accordingly, the chirality at phosphorus in **1a** may be assigned as *R*, and that in **1b** as *S*. In support of this conclusion, mixtures diastereomerically enriched in **1a** and **1b** display CD curves which are enantiomeric in type and which correlate well with the corresponding CD curves of $(R)_P$-**2** (**2a**) and $(S)_P$-**2** (**2b**), respectively (Figure 1).[9]



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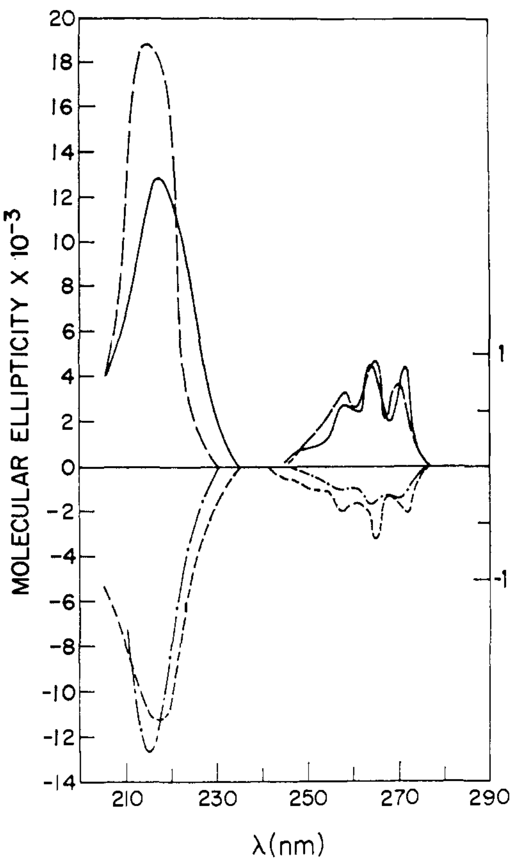

Figure 1. CD spectra (isooctane solution) of menthyl phenylphosphinates: (—) for a 95/5 mixture of **1a**/**1b**; (----) for a 15/85 mixture of **1a**/**1b**; (— —) for **2a**; and (-·-·) for **2b**. The ordinate scale on the right refers to the long-wavelength transition, and the ordinate scale on the left to the short-wavelength transition.

Table I.[a,b] Pmr Chemical Shifts and Coupling Constants of Menthyl Phenylphosphinate (**1**) Diastereomers

	P–H	C–CH₃		
		H_a	H_b	H_c
1a	2.35 (553)	9.13 (7.0)	9.02 (7.0)	9.11 (4.5)
1b	2.34 (556)	9.30 (7.0)	9.11 (7.0)	9.03 (5.0)

[a] Chemical shifts are given in τ units, and coupling constants (in parentheses) are given in hertz. [b] Methyl doublets are assigned by comparison with corresponding signals of analogous menthyl alkylarylphosphinates.[8]

A 95/5 mixture of **1a**/**1b** (1.0 mmol) in dimethylformamide (DMF) was added to a mixture of sodium hydride (1.0 mmol) and methyl iodide (10.0 mmol) in DMF, and the resulting suspension was heated to 50° for 0.5 hr. Work-up of the reaction mixture afforded a 95/5 mixture (by pmr[8]) of **2a**/**2b** in 85% yield. Sim-

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(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) (a) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968); (b) R. A. Lewis and K. Mislow, *ibid.*, **91**, 7009 (1969).

(3) A. Nudelman and D. J. Cram, *ibid.*, **90**, 3869 (1968).

(4) H. P. Benschop, D. H. J. M. Platenburg, F. H. Meppelder, and H. J. Boter, *Chem. Commun.*, 33 (1970).

(5) The extension of this reaction to alkylations of menthyl alkylphosphinates,[4] and thence to the synthesis of mixed aryldialkyl- and trialkylphosphine oxides of known absolute configuration, is readily envisaged.

(6) T. L. Emmick and R. L. Letsinger, *J. Amer. Chem. Soc.*, **90**, 3459 (1968).

(7) An initial crop of crystals of **1** precipitating from *n*-hexane at −78° consisted of a 95/5 mixture of **1a**/**1b**, $[\alpha]^{22}\text{D}$ −21.0° (benzene). The mother liquors, after standing at −20°, deposited a 15/85 mixture of **1a**/**1b**, $[\alpha]^{22}\text{D}$ −89.6° (benzene). Diastereomeric compositions were determined by integration of the low-field half of the characteristic P–H resonances in the pmr spectra (Table I).

(8) R. A. Lewis, O. Korpiun, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4847 (1968).

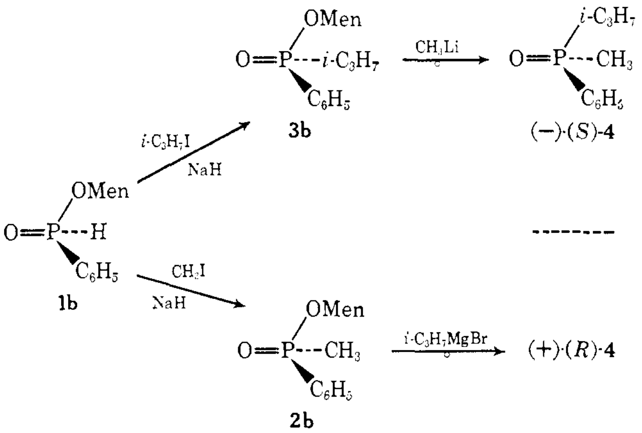
(9) We thank Drs. Franklin D. Saeva and Jeremiah P. Casey for measuring the CD spectra.

ilar treatment of a 30/70 mixture of **1a**/**1b** provided a 30/70 mixture of **2a**/**2b**. The methylation of **1** therefore proceeds stereospecifically with retention of configuration.[10]

Alkylation of **1** with secondary alkyl iodides is illustrated by the reaction of a 30/70 mixture of **1a**/**1b** with isopropyl iodide according to the above procedure. The product, menthyl isopropylphenylphosphinate (**3**), consisted of a 35/65 mixture of **3a**/**3b**, identified as R_P/S_P by the characteristic[8] upfield shift of the H_a proton signal (τ 9.65) in **3b**. Similarly, alkylation of a 95/5 mixture of **1a**/**1b** with isopropyl iodide gave a 90/10 mixture of **3a**/**3b**. Therefore, alkylation of **1** proceeds with predominant retention of configuration.

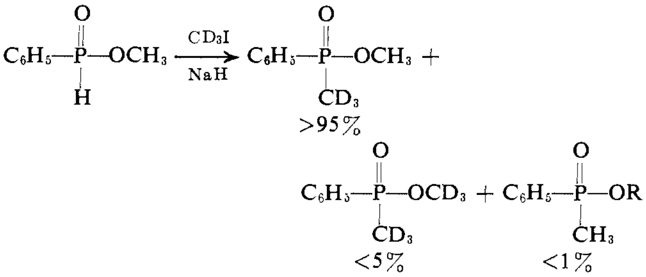
The stereochemistry of this alkylation reaction was confirmed by the chemical correlation of **2b** and **3b** (Chart I). A 30/70 mixture of **3a**/**3b** was treated with methyllithium to provide (−)-isopropylmethylphenylphosphine oxide (**4**),[11] $[\alpha]^{26}\mathrm{D}$ −9.1° (methanol). Reaction of diastereomerically pure **2b** with isopropylmagnesium bromide afforded (+)-**4**, $[\alpha]^{24}\mathrm{D}$ +25.3° (methanol). Since reactions of Grignard[2a] and alkyllithium[2b] reagents with phosphinates proceed with predominant inversion of configuration at phosphorus, the chirality S_P at phosphorus in **3b** and the retention stereochemistry of the alkylation reaction are both corroborated.

Chart I[a]



[a] Men = (−)-menthyl.

The alkylation of alkyl phenylphosphinates under the present conditions is presumed to occur by initial formation of the corresponding anion $[\mathrm{Ph(AlkO)PO}]^-$. Attack on carbon by this anion[12] may in principle occur by either one of two routes: through phosphorus, to give the final product directly, or through oxygen, to give a dialkyl phenylphosphonite intermediate, which then undergoes Michaelis–Arbuzov rearrangement by further reaction with the alkyl halide.[13] The latter pathway was effectively eliminated by the observation that treatment of methyl phenylphosphinate[14] with a tenfold excess of methyl-d_3 iodide gave almost exclusively methyl methyl-d_3-phenylphosphinate



$$\mathrm{C_6H_5{-}P(=O)(H){-}OCH_3 \xrightarrow[NaH]{CD_3I} \underset{>95\%}{C_6H_5{-}P(=O)(CD_3){-}OCH_3} + \underset{<5\%}{C_6H_5{-}P(=O)(CD_3){-}OCD_3} + \underset{<1\%}{C_6H_5{-}P(=O)(CH_3){-}OR}}$$

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[10] The anion derived from **1** is stereolabile under these conditions and significant deviations from the given procedure may therefore lead to epimerization. For example, reaction of a 30/70 mixture of **1a**/**1b** with sodium hydride in DMF, followed by the addition of methyl iodide after hydrogen evolution had ceased, gave an approximately equimolar mixture of **2a** and **2b**.

[11] The pmr spectrum of **4** featured: $\mathrm{PC}H_3$, d, τ 8.30, $^2J_{\mathrm{PH}} = 12.5$ Hz; $\mathrm{C}H_3$, dd, τ 8.92, $^3J_{\mathrm{PH}} = 16$ Hz, $^3J_{\mathrm{HH}} = 7$ Hz; $\mathrm{C}H_3$, dd, τ 8.77, $^3J_{\mathrm{PH}} = 16$ Hz, $^3J_{\mathrm{HH}} = 7$ Hz; $\mathrm{C}H(\mathrm{CH_3})_2$, m, τ 7.60–8.34; $\mathrm{C_6}H_5$, m, τ 2.0–2.6.

[12] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **72**, 4292 (1950). See also: K. Sasse in Houben-Weyl's "Methoden der organischen Chemie," Vol. 12, Part 1, Georg Thieme Verlag, Stuttgart, 1963, pp 446–453.

[13] R. G. Harvey and E. R. De Sombre, "Topics in Phosphorous Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1964, Chapter 3.

[14] A. N. Pudovik and D. Kh. Yarmukhametova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 902 (1952); *Chem. Abstr.*, **47**, 10469c (1953).

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Bicyclo[2.1.1]hexan-5-one *via* the Reaction of 2-Chloronorbornene with Phenyllithium

Sir:

Recently, we reported[1,2] on the unusual reaction of **1** with ethereal methyllithium to yield **2**. As part of our continuing interest in the reactions of vinyl halides with organometallic reagents, we have investigated the reaction of **1** with commercially available phenyllithium.[3] We now wish to report that phenyllithium reacts with **1** in an unprecedented manner to provide the first example of a new type of ring contraction reaction.

When a solution of 2-chloronorbornene (**1**) and phenyllithium in 70:30 benzene–ether[3] was refluxed for 24 hr, a mixture consisting of 90% of 5-benzalbicyclo[2.1.1]hexane (**3**) and 10% of 2-phenylnortricyclane (**4**) was obtained in 69% yield.[4,5] The structural evidence for **3** was obtained through both spectroscopic and chemical means. The ir spectrum of **3** showed a

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[1] P. G. Gassman, J. P. Andrews, Jr., and D. S. Patton, *Chem. Commun.*, 437 (1969).

[2] Certain mechanistic details of the conversion of **1** into **2** through the use of methyllithium remain to be elucidated. However, it has been found that optically active **1** yields optically active **2** with retention of stereochemistry (T. J. Atkins, unpublished work).

[3] Phenyllithium solution which was 2.2 *M* in 70:30 benzene–ether was purchased from Alfa Inorganics, Inc. The reaction was sensitive to the quality of the phenyllithium and to the solvent. The use of pure ether as a solvent results in poorer yields of **3**.

[4] These values represent yields of products isolated after chromatography on activity I basic alumina. Vpc of the crude reaction product *vs.* an internal standard indicated a 87% yield of **3** and a 9% yield of **4**.

[5] Satisfactory elemental analyses have been obtained for all new compounds.