

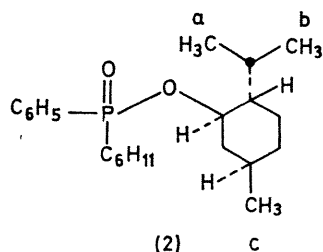
## Stereospecific Free-radical Addition of Menthyl Phenylphosphinate to Cyclohexene: Evidence for Retention of Configuration at Phosphorus

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**Summary** In contradistinction to a recent report that the free-radical addition of menthyl methylphosphinate to alkenes proceeds with inversion of configuration at phosphorus, dibenzoyl peroxide-catalysed addition of menthyl phenylphosphinate to cyclohexene occurs with retention of configuration.

THE recent claim by Benschop and Platenburg<sup>1</sup> that the free-radical addition of menthyl methylphosphinate to alkenes provides the first evidence for inversion of configuration in a free-radical process<sup>2</sup> prompts us to report analogous studies with menthyl phenylphosphinate (**1**) which appear to contradict this conclusion. Our results are summarized in the Scheme.

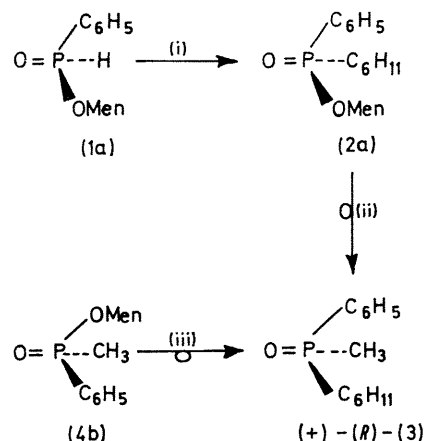


The absolute configurations of the epimers of menthyl phenylphosphinate have been established by both chemical and spectroscopic means as (*R*)<sub>P</sub> for (**1a**) and (*S*)<sub>P</sub> for (**1b**).<sup>3</sup> Menthyl cyclohexylphenylphosphinate (**2**),<sup>†</sup> isolated in 80% yield from the addition of dibenzoyl peroxide (10 mol %) to a solution of a 85/15 mixture of (**1a**)/(**1b**) and cyclohexene in *n*-heptane at 80°, consisted of a 85/15 mixture of (**2a**)/(**2b**). Similar treatment of a 40/60 mixture of (**1a**)/(**1b**) gave a 40/60 mixture of (**2a**)/(**2b**). Arguments presented below conclusively show that the chirality at phosphorus in (**2a**) is *R*, and in (**2b**) is *S*, and that therefore the free-radical addition of (**1**) to cyclohexene proceeds with retention of configuration.

The chirality at phosphorus in the epimers of (**2**) follows from the chemical correlation of (**2a**) and menthyl (*S*)<sub>P</sub>-methylphenylphosphinate (**4b**). Treatment of a 85/15

<sup>†</sup> Satisfactory elemental analyses obtained.

mixture of (**2a**)/(**2b**) with methyl-lithium afforded (+)-cyclohexylmethylphenylphosphine oxide (**3**), [ $\alpha$ ]<sub>D</sub> + 14.2° (methanol). As previously reported,<sup>4</sup> reaction of diastereomerically pure (**4b**) with cyclohexylmagnesium bromide



**SCHEME.** Men = (–)-menthyl. Reagents: (i) cyclohexene in *n*-heptane with 10 mol % of dibenzoyl peroxide for 25 h at 80°; (ii) methyl-lithium in benzene for 12 h at reflux; (iii) C<sub>6</sub>H<sub>11</sub>MgBr in benzene for 44 h at reflux.

gives (+)-(**3**), [ $\alpha$ ]<sub>D</sub> + 19° (methanol). Since reactions of Grignard<sup>4</sup> and alkyl-lithium<sup>5</sup> reagents with phosphinates proceed with predominant inversion of configuration at phosphorus, the chirality at phosphorus in (**2a**) is *R*. Independent support of this conclusion comes from analysis

<sup>1</sup>H *n.m.r.* chemical shifts and coupling constants of menthyl cyclohexylphenylphosphinate (**2**) diastereomers<sup>a,b</sup>

	H <sub>a</sub>	C-CH <sub>3</sub> H <sub>b</sub>	H <sub>c</sub>
( <b>2a</b> )	9.12(7.0)	9.04(7.0)	9.29(4.9)
( <b>2b</b> )	9.67(6.9)	9.18(7.0)	

<sup>a</sup> Chemical shifts are given in  $\tau$  units, and coupling constants (in parentheses) are given in hertz. <sup>b</sup> Methyl doublets are assigned by comparison with corresponding signals of analogous menthyl alkylarylphosphinates.<sup>6</sup>

of the  $^1\text{H}$  n.m.r. spectra of (2a) and (2b) (Table). In analogous menthyl alkylarylphosphinates it has been established<sup>6</sup> that both isopropyl methyl doublets of the ( $S$ )<sub>P</sub> epimer are shifted upfield relative to the corresponding signals for the ( $R$ )<sub>P</sub> epimer, and that the chemical-shift difference is greatest for the  $\text{H}_a$  (upfield) proton signal.

Comparison of these results with those of Benschop and Platenburg<sup>1</sup> allow for but two alternatives: either the free-radical additions of menthyl *p*-phenylphosphinate and menthyl methylphosphinate to alkenes follow opposite

stereochemical paths, or the tentative assignment by Meppelder, Benschop, and Kraay<sup>7</sup> of the ( $R$ )<sub>P</sub> configuration to the starting isomer, *i.e.*, the diastereomer of menthyl methylphosphinate with m.p. 42°, is in error. We would find it surprising if the former alternative were the case, and therefore opt for the latter.

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<sup>1</sup> H. P. Benschop and D. H. J. M. Platenburg, *Chem. Comm.*, 1970, 1098.

<sup>2</sup> The report of a free-radical reaction proceeding with inversion of configuration is not unique; *e.g.*, see L. J. Altman and B. W. Nelson, *J. Amer. Chem. Soc.*, 1969, **91**, 5163.

<sup>3</sup> W. B. Farnham, R. K. Murray, jun., and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 5809.

<sup>4</sup> O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4842.

<sup>5</sup> R. A. Lewis and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7009.

<sup>6</sup> R. A. Lewis, O. Korpiun, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4847.

<sup>7</sup> F. H. Meppelder, H. P. Benschop, and G. W. Kraay, *Chem. Comm.*, 1970, 431.