Stereospecific Trisubstituted Olefin Synthesis *via* Interconversion of Allylic Sulphoxides and Sulphenates

By PAUL A. GRIECO

(*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania* 15213)

Summary α-Substituted methallyl *p*-tolyl sulphoxides undergo a [2,3]-sigmatropic rearrangement to allylic sulphenate esters (II) which can be intercepted by suitable nucleophiles, thus providing a new stereospecific route to trisubstituted olefins.

WE report a version of the allylic sulphoxide–sulphenate interconversion[1] which is completely stereospecific and results in the synthesis of trisubstituted olefins (III)

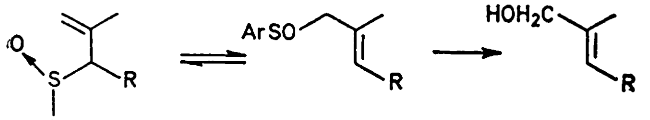

FIGURE. a; R = Bu, b; R = Et, c; R = Me, d; R = H, Ar = *p*-C_6H_4Me.

Treatment of (IIId) with BuLi (−20°, THF), followed by treatment with *p*-toluenesulphenyl chloride[2] gave (IId) which was smoothly transformed into (Id), b.p. 107—109°/*ca.* 0·15 mm [ν_{max} (neat) 1050 (sulphoxide) and 898(=CH_2) cm^{-1}]. This interconversion represents a typical example of a generalized class of [2,3]-sigmatropic rearrangements.[3] Treatment of (Id) with BuLi at −50 °C in dry THF followed by the addition of BuI (3 equiv.) afforded (Ia) (90%). Subsequent treatment of (Ia) with thiophenoxide[4] in MeOH (7 h, 60 °C) produced the *trans* allylic alcohol (IIIa) [$\delta(CCl_4)$ 5·30(t, =$CHCH_2$)[5] 3·90(s, CH_2OH), 1·60(s, C=CCH_3)[5] p.p.m.] in *ca.* 90% yield. (IIIa) was further identified by comparison of its n.m.r. and i.r. spectra and its retention time on g.l.c. with those of a sample prepared by an alternate route.[6] Less than 1% of the corresponding *cis* isomer† could be detected by g.l.c.

The allylic sulphoxides (Ib) and (Ic) lead, also in high yield, to the olefins (IIIb) and (IIIc) respectively.†

The present method of synthesizing trisubstituted olefins as a result of the concerted nature of the sulphoxide-sulphenate rearrangement complements the existing methods of olefin synthesis.[8]

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the Science Development Program of the National Science Foundation for support of this research.

(*Received*, 10*th April* 1972; *Com.* 601.)

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† Satisfactory analytical and/or spectral data, have been obtained for all new compounds.

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[6] (IIIa) was prepared by SeO_2 oxidation of 2-methylhept-2-ene followed by reduction with $NaBH_4$ (U.T. Bhalerao and H. Rapoport, *J. Amer. Chem. Soc.*, 1971, **93**, 4835).

[7] The *cis* isomer was synthesized *via* the β-oxido ylide procedure of Corey (E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 226).

[8] For a recent review of trisubstituted olefin syntheses, see D. J. Faulkner, *Synthesis*, 1971, 175.