

Atropisomeric Sulphur Compounds in Organic Synthesis: Generation and Reactions of the Carbanions of Dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine and its Oxides

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Oxidation of dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine (**2**) gives a single diastereoisomeric sulfoxide (**1**) which reacts diastereospecifically with electrophiles at variance with the unoxidized substrate (**2**) and other combinations of oxides (**4**), (**6**), and (**7**) which afford diastereoisomeric mixtures of products.

We have recently studied a few applications of optically active vinyl sulfoxides obtained *via* a self-induced diastereoselective oxidation mediated by chiral auxiliaries containing an hydroxy group.¹ Here we describe the conceptually related reagent dinaphtho[2,1-*d*:1',2'-*f*][1,3]dithiepine *S*-oxide (**1**) (m.p. 199–200 °C from PrOH/MeOH) in which the chirality of the sulphur atom has been transferred with complete selectivity and virtually quantitative yield from the intrinsically chiral binaphthyl unit of the thioacetal (**2**) (m.p. 158 °C from PrOH/MeOH)² *via* oxidation with *m*-chloroperbenzoic acid (*m*-CPBA). Both reagents (**1**) and (**2**) are atropisomeric chiral variants to the vast class of dithiomethylene compounds³ (and oxides)⁴ which are well-known carbonyl anion equivalents and reagents of established utility.

Compared to the previously described hydroxy derivatives,¹ (**1**) presents several additional features, *i.e.*: the sulphur atom is aryl substituted implying reactions at a single side; the aryl substitution allows a simple reductive elimination of the sulphur functionality from the product; the transfer of chirality from the substrate to the sulphur atom is largely given by the rigid geometry of the system, thus rigorous reaction conditions are not required. Further qualities are a rapid detection under u.v. light, a high crystallinity and a rapid monitoring of adventitious racemizations by ¹H n.m.r. spectroscopy.

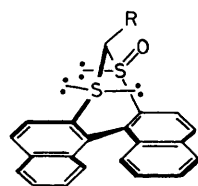
Treatment of a solution of (**1**) in tetrahydrofuran (THF) at –78 °C with *n*-butyl-lithium followed by quenching of the anion with methyl iodide afforded a single (200 MHz ¹H n.m.r. >98% estimated sensitivity) crystalline diastereoisomer (**3**) (m.p. 214–216 °C from PrOH). Similarly alkylated are the thioacetal (**2**) and the disulphone (**4**) (m.p. 321–322 °C from MeOH) but the products are not diastereoisomeric because the methylenic protons of the substrates are sterically equivalent. Trapping of the anion derived from (**1**) and generated as before with benzaldehyde again afforded a single diastereoisomer (**5**) (m.p. 190–192 °C from PrOH). Overall in this adduct, three contiguous chiral centres

have been constructed stereospecifically from the single asymmetric unity of the binaphthyl residue. The same reaction applied to the *C*₂-symmetric dithioacetal (**2**) afforded a mixture of the two possible diastereoisomers in a *ca.* 3 : 1 ratio, while the *C*₂-symmetric tetraoxide (**4**) proved unreactive even under BF₃ catalysis.⁵ Of the two other possible unsymmetric combinations of oxides, *i.e.* the sulphone–sulphide (**6**) [from KMnO₄ oxidation of (**1**), m.p. 233–234 °C from AcOEt/MeOH] and the sulphone–sulfoxide (**7**) [from *m*-CPBA oxidation of (**6**), m.p. 260–261 °C from PrOH], the former afforded with benzaldehyde variable mixtures of the four diastereoisomers while the latter did not react.

The stereochemistry of the sulfoxide oxygen was suggested by the analysis of molecular models and confirmed by the X-ray structure determination of adduct (**5**).[†] The configuration of the two newly formed carbon centres in (**5**) corresponds to the one expected on the basis of a transition state of the type (**8**) which has been postulated for acyclic dithioacetal oxides.⁷ Of the two possible conformations possessing an equatorial phenyl group, (**8**) is favourite over (**8'**) because in the latter the aldehyde hydrogen would approach too close to the naphthyl residue.

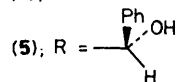
It has to be pointed out that the very strictly related acyclic formaldehyde ditolylthioacetal *S*-oxide (TolSOCH₂STol) is reported to afford in the reaction with benzaldehyde a mixture of three out of the four possible diastereoisomers in 5 : 3.5 : 1.5 ratio.⁶

Although the preliminary experiments so far examined have been performed on racemic substrates, the reagents are available in optically active form by known methodologies⁷ or *via* kinetic resolution in the oxidation with modified Sharpless reagents.⁸ The synthetic strategy presented in this communication is now going to be applied to other chiral frameworks

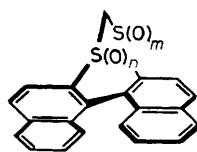


(1); R = H

(3); R = Me



(5); R =

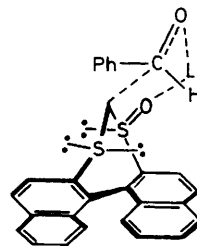


(2); n = m = 0

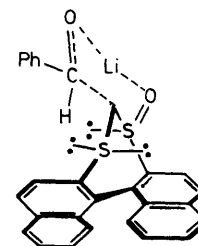
(4); n = m = 2

(6); n = 2, m = 0

(7); n = 2, m = 1



(8)



(8')

[†] The diffractometric analysis was performed by Dr. G. Valle (Centro Studi Biopolimeri del C.N.R., via Marzolo 1, I-35131 Padova, Italy). Details will be published in the full paper.

derived from optically active natural products possessing C_2 symmetry such as tartaric acids and sugar derivatives.

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