Reactions of Grignard Reagents with 2,4-Diphenylthietan Monoxides

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RECENT communications[1] on the rearrangements of vinylsulphonium ylids prompt us to report related rearrangements observed in the reactions of Grignard reagents with sulphoxides. *cis*-2,4-Diphenylthietan 1-oxide (I)† was readily prepared by oxidation (HCO_3H–MeOH) and then isomerization (NaOMe–MeOH) of a mixture of *cis*- and *trans*-2,4-diphenylthietan.[2] Treatment of (I) with methylmagnesium iodide yielded 1,2-diphenylcyclopropane (III)[2,3] (21% yield; *cis*:*trans* ratio 0·60), *cis*-2,4-diphenyltetrahydrothiophen (IV) (17% yield), and 1,3,4,5-tetrahydro-3-phenyl-2-benzothiepin (V) (6% yield).

The structure of (IV), m.p. 73—74°, was

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† Of the three possible isomeric, optically inactive, 2,4-diphenylthietan 1-oxides, only two are known to us. Throughout this Communication, *cis*- and *trans*- refer to the configurations of the phenyl groups. We believe that the 1-oxygen of the *cis*-isomer (I) is *trans* to the phenyl groups.

assigned initially from the carbon and hydrogen analysis, the mass spectrum of the compound (molecular ion and base peak, *m/e* 240), and from an analysis of the n.m.r. (CCl_4) spectrum, τ 2·81 (s with broad base, 10·2H, phenyl protons), 5·43 (q, $J_{1,2}$ 5·5, $J_{1,3}$ 11·5 c./sec., 0·8H, –S–C*H*Ph–), 6·43—8·00 (complex m, 4·9H). Compound (IV) was oxidized to *cis*-2,4-diphenyltetrahydrothiophen dioxide (VI), m.p. 192—193°; ν_{max} (KBr) 1115, 1301 cm.$^{-1}$; mass spectrum, *m/e* 208 ($M - 64$), 104 (base peak). Since this sulphone (VI) was recovered quantitatively after treatment at reflux temperature with sodium methoxide in methanol, it and compound (IV) were assigned the *cis*-configuration. The structure of the sulphone (VI) was determined definitively by independent synthesis.

Reduction of methyl β-benzoyl-α-phenylpropionate[4] with lithium aluminum hydride in ether yielded 1,3-diphenylbutane-1,4-diol, which was converted directly into the dimethanesulphonate. This, on reaction with sodium sulphide in dimethylformamide and oxidation of the diphenyltetrahydrothiophen so formed with performic acid, yielded 2,4-diphenyltetrahydrothiophen dioxide, m.p. 183—186°. Repeated crystallizations from light petroleum (b.p. 60—68°)–chloroform raised the melting point to 187—189°. Isomerization of this material with sodium methoxide in methanol yielded (VI), m.p. 192—192·5°, identical with the product described above. The difficulty experienced in purifying (VI) prepared from 1,3-diphenylbutane-1,4-diol probably resulted from the presence of some of the *trans*-isomer and was circumvented by isomerization. Since (VI) prepared from (I) was easily purified, we believe that the rearrangement depicted below (Chart 2) is stereoselective.

Compound (V), m.p. 140—142°; ν_{max} (KBr) 692, 721, 747, and 758 cm.$^{-1}$; (mass spectrum, molecular ion and base peak, *m/e* 240), was oxidized with performic acid to the dioxide (VII), m.p. 267—269°; ν_{max} (KBr) 687, 718, 728, 750, 772, 1119, and 1301 cm.$^{-1}$; mass spectrum, *m/e* 208 ($M - 64$), 104 (base peak). Critical examination of the i.r. spectra of (V) and (VII) in the 1680—2000 cm.$^{-1}$ region suggested the presence of a 1,2-di- as well as a monosubstituted benzene ring in these compounds. Compound (V), m.p. 143—144°, was synthesized from phthalidylmethyl phenyl ketone[5] by reduction [Pd–C in aqueous sodium hydroxide, then lithium aluminium hydride in ether] to 3-(*o*-hydroxymethylphenyl)-1-phenylpropanol which was converted into (V) by the procedure for making cyclic sulphides as described above. Compound (V) so synthesized was then oxidized to the sulphone (VII), m.p. 270—271°.

From the reaction of *trans*-2,4-diphenylthietan 1-oxide (II) with methylmagnesium iodide we isolated only a mixture of *cis*- and *trans*-diphenylcyclopropanes (III) and *trans*-2,4-diphenylthietan (VIII). Reaction of either (I) or (II) with phenylmagnesium bromide yielded, along with other compounds, a mixture of *cis*- and *trans*-1,2-diphenylcyclopropyl phenyl sulphides (IX) and (X). These were separated and identified as the corresponding sulphones; (XI) m.p. 211—212°; (XII) m.p. 155—156·5°. Structures and stereochemistry of (XI) and (XII) are verified by elementary analyses and detailed analyses of the n.m.r. spectra. *cis*-1,2-Diphenylcyclopropyl phenyl sulphone (XI) was independently synthesized from *cis*-α-phenylsulphonylstilbene by the method of Truce and Badiger.[6]

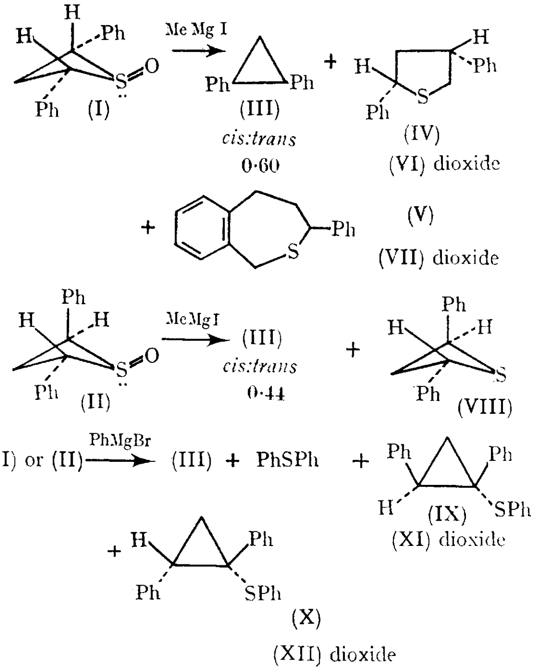

Chart 1

We believe that the formation of (IV) and (V) from reaction of (I) with methylmagnesium iodide proceeds *via* the rearrangement of the sulphonium ylid (XIII) (Chart 2). Compound (IV) is formed by a 1,2-rearrangement while compound (V) is formed by a rearrangement similar to that recently proposed for vinylsulphonium ylids[1] (see arrows). The formation of methyl *o*-methylbenzyl sulphide[7] (XIV) from benzylmagnesium chloride and dimethyl sulphoxide may have proceeded by a similar mechanism (Chart 2). The formation of

(IX) and (X) may also proceed *via* the sulphonium ylid (XV) (drawn as the zwitterion). That Grignard reagents react with sulphoxides to form intermediates of the types depicted has been previously demonstrated by the formation of triarylsulphonium salts on treatment of diaryl sulphoxides with arylmagnesium halides.[8] Formation of sulphonium ylids by reaction of dimethyl sulphoxide with phenylmagnesium bromide has been postulated by Sekera, Fawvet, and Rumpf.[9]

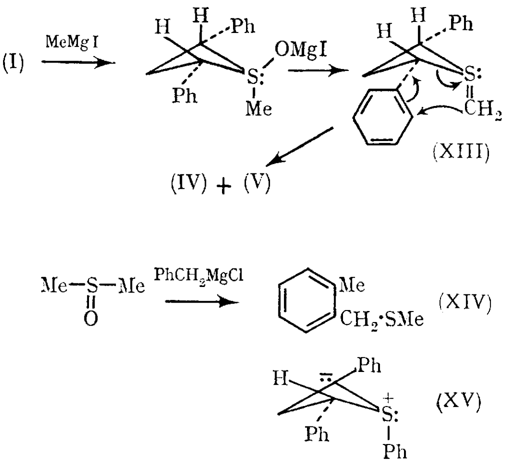

Chart 2

Recently, Anderson and Wills,[10] on the basis of n.m.r. spectra alone, tentatively assigned the structures 1,4,4-trimethyl-3-phenylpyrrolidine and 2,3,4,5-tetrahydro-2,4,4-trimethyl-1*H*-2-benzazepine to two of the minor products formed by the reaction of 1,1,3,3-tetramethyl-2-phenylazetidinium iodide with phenyl-lithium. Thus, analogous rearrangements occur with azetidinium salts.

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