Synthesis of Olefins from Sterically Hindered Alcohols by Pyrolysis of Thiocarbonate *O*-Esters

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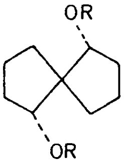
Summary Sterically hindered alcohols *e.g.* (I; R = H) were acylated with *O*-4-methylphenyl chlorothioformate in high yield and the resulting thiocarbonates were converted into olefins by pyrolysis.

ALCOHOLS can be converted into the corresponding olefins in various ways. If ionic intermediates have to be avoided because skeletal rearrangements of fragmentations may occur, pyrolysis of acetates or of *S*-methylxanthates (Chugaev reaction) is appropriate. For the conversion of *trans,trans*-spiro[4,4]nonane-1,6-diol (I; R = H) into the temperature-sensitive spiro[4,4]nona-1,6-diene (II) both methods failed in our hands. In contrast, treatment of the same diol with *O*-4-methylphenyl chlorothioformate† in pyridine for 4 h at room temperature gives the thiocarbonate *O*-ester [I; R = $C(S){\cdot}O{\cdot}C_6H_4Me$] (80%).‡ According to the literature[2] the greater ease of xanthate pyrolysis compared to acetate pyrolysis is a consequence of the conversion of the –O–C=S system into the O=C–S– system in the transition state. The other sulphur atom in the *S*-methylxanthates plays no essential role, and should therefore be replaceable by oxygen. In accord with expectation the thiocarbonate *O*-ester of diol (I) decomposes smoothly at temperatures $\geqslant$ 135° into diene (II), *p*-cresol and COS. By performing this reaction in an evacuated apparatus, consisting of a pyrolysis tube connected to an U-shaped tube cooled to −70°, pure 1,6-spiro[4,4]nonadiene, b.p. 40—41°/16 Torr, can be prepared in 68% yield.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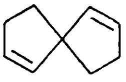
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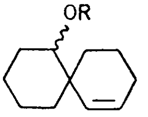
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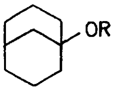
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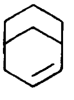
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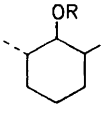
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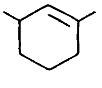
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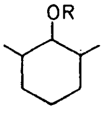
(IX)

TABLE

Alcohol	M.p. of thiocarbonate ester [R = $MeC_6H_4{\cdot}O{\cdot}C(S)$-]	Decomp. temperature	Olefin (yield, %)
(I)	131—132°	>135°	(II)[3] (68)
(III)	oil	>160°	(IV) (60)
(V)	73—74°	>200°	(VI)[4] (80)
(VII)	52—55°	>130°	(VIII) (52)
(IX)	58—59°	>210°	(VIII) (30)

Other thiocarbonates in the Table have been prepared and pyrolysed with similar yields. The case of *cis,cis*-2,6-dimethylcyclohexanol [IX; R = $C(S){\cdot}O{\cdot}C_6H_4Me$] shows that the reaction can also take place when the normally assumed[2] cyclic *syn*-elimination mechanism is not possible. Thus 1-bicyclo[3,3,1]nonanol [V; R = $C(S){\cdot}O{\cdot}C_6H_4Me$] is converted smoothly into 2-bicyclo[3,3,1]nonene (VI) m.p. 95—96°, which was identical with a specimen prepared from *endo*-2-bicyclo[3,3,1]nonanol by the above procedure. The conversion of (V) into (VI) is therefore accompanied by a hydride shift. The *O*-4-methylphenyl thiocarbonate of (+)-borneol (m.p. 69—70°) gives at 220° a 2 : 1 mixture of

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† Prepared from thiophosgene in chloroform and *p*-cresol in aqueous sodium hydroxide,[1] b.p. 52—53° at 0·1 Torr.

‡ All new compounds gave satisfactory analytical data.

camphene and bornene, as does the *S*-methylxanthate of (+)-borneol.[5] This suggests that *O*-aryl thiocarbonates of alcohols can decompose by an ionic mechanism. This, however, does not rule out the possibility of a cyclic *syn*-elimination when this is more favourable. In all cases where the ionic mechanism is suggested by the products, the reactions are characterised by substantially higher decomposition temperatures.

(*Received*, 25*th August* 1972; *Com.* 1494.)

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