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SYNTHESIS OF THE TAGETONES USING THE MICHAEL ADDUCT OF A MASKED ISOVALERYL CARBANION WITH 3-METHYL-1,3-BUTADIENYL PHENYL SULPHOXIDE

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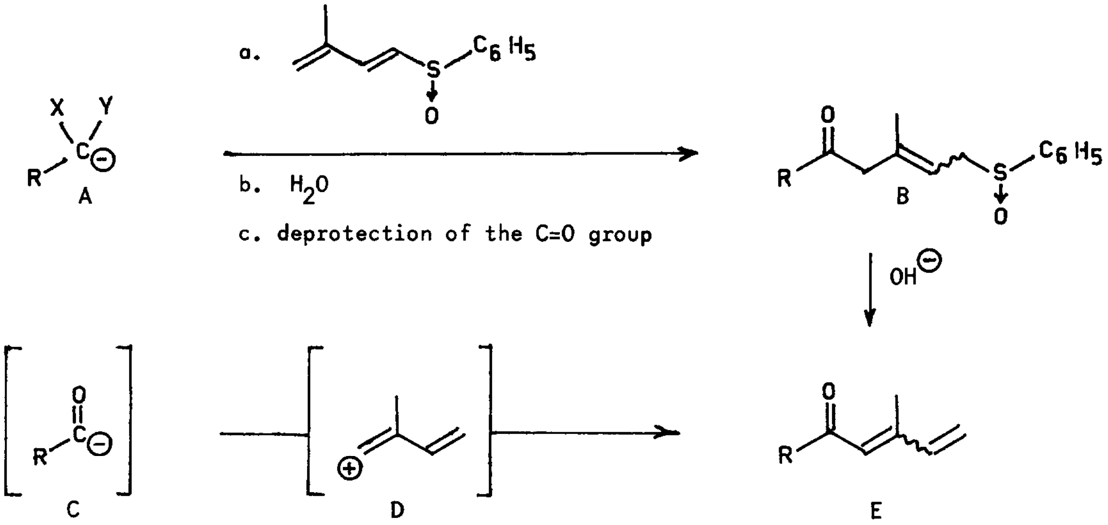
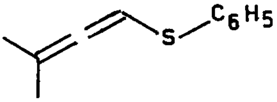
We wish to report two synthetic operations: (1) the Michael addition of a masked acyl carbanion to 3-methyl-1,3-butadienyl phenyl sulphoxide and after deprotection of the carbonyl group, (2) a mild elimination of phenylsulphenate anion to afford a conjugated dienone.



Thus, through these two operations, the dienylic sulphoxide may be viewed as an isoprenic carbonium ion (D) equivalent. This overall reaction is formally the reverse of an existing synthesis of conjugated dienones by Lewis acid catalysed acylation of isoprene followed by dehydrochlorination [1].

The allenic sulphide 1 was readily prepared (72%) from 3-chloro-3-methyl-1-butyne and benzenethiol with aqueous sodium hydroxide in the presence of a phase transfer agent [2]. When treated in sym.tetrachloroethane at 65°C for 2 hr [3], the allenic sulphide 1 was smoothly isomerised into E 3-methyl-1,3-butadienyl phenyl sulphide 2 [4] (92 %). Then a careful oxidation with a peracid or with sodium metaperiodate afforded the isoprenic sulphoxide 3 (70 %) [5].



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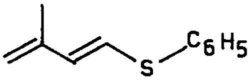

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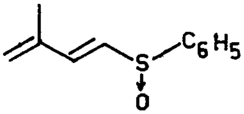

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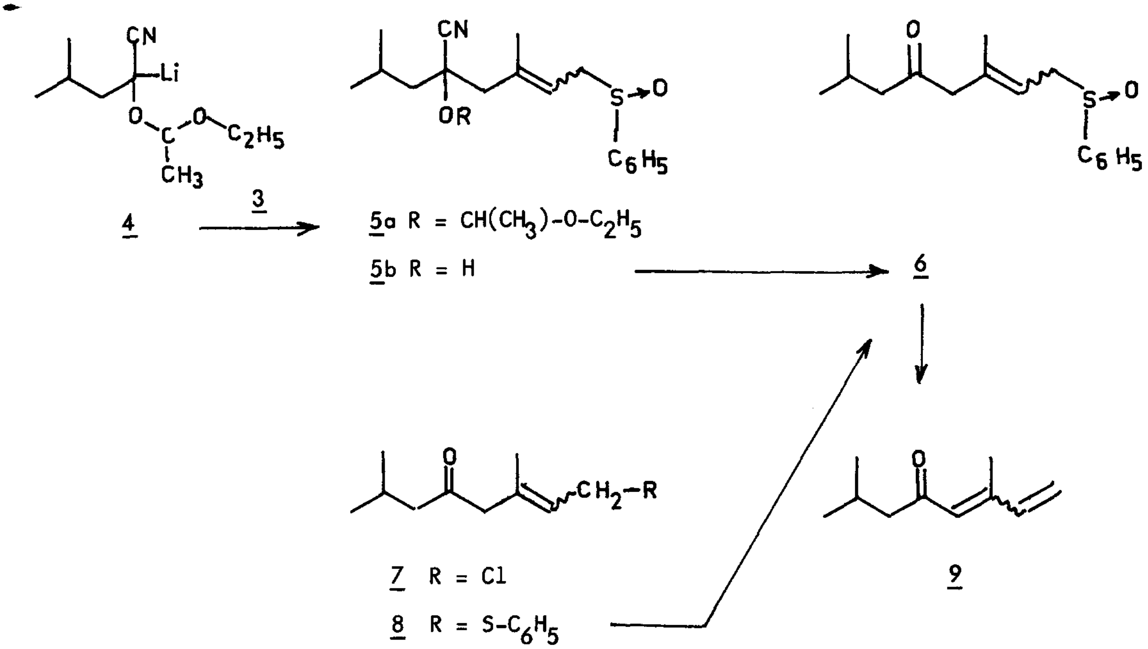
Whereas Michael additions of some metal enolates from dialkyl malonates, β-keto-esters and ketones with simple vinyl sulphoxides are known [6], the ability of dienylic sulphoxides to undergo such a reaction with carbanions remained to be examined.

When treated with a solution of the lithio derivative of the protected cyanhydrin 4 [7] in tetrahydrofuran (2 hr at - 78°C, then warmed to room temperature), the isoprenic sulphoxide 3 gave the adduct 5a as a mixture of isomers. The corresponding cyanohydrin 5b was obtained by acidic hydrolysis [7a], and after shaking of its ethereal solution with aqueous 0,5 N sodium hydroxide for 5 - 10 min., gave a mixture of oxo-sulphoxide 6 and E- and Z-tagetones 9. However, by treatment with 0,5 N sodium hydroxide for 1 hr, the E- and Z-tagetones (55 : 45) were obtained (50 % overall yield from the isoprenic sulphoxide 3).

In order to verify the structure [8] of the compound 6, the oxo-chloride 7 was prepared from isoprene and isovaleryl chloride [1], and then treated with sodium thiophenoxide in ethanol. The pure oxo-sulphide 8 [8] was thus obtained (86 % from isovaleryl chloride) and was oxidised with 1 equiv. of m.chloro-perbenzoic acid and afforded the oxo-sulphoxide 6 (70 %). Shaking an ethereal solution of compound 6 with aqueous 0,5 N sodium hydroxide for 15 min. yielded the E- and Z-tagetones (60 : 40) (78 %) [9].



The extension of this procedure to the synthesis of a variety of terpenoid dienones from other dienylic sulphur compounds is under active investigation.

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