Non-symmetrical Isothianaphthenes

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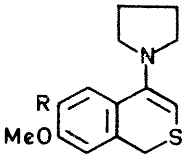
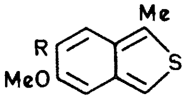
Summary On pyrolysis of isothiachromanone enamines, quadrivalent sulphur compounds were obtained, the structures of which were established *via* formation of the N-phenylmaleimide adducts.

WE report a novel rearrangement which leads to the synthesis of isothianaphthenes.[1] Mechanistically the reaction is of interest because of the possible intermediacy of thiiranium ions.[2]

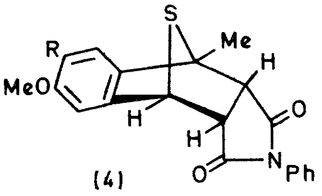
A number of anomalous results in the total synthesis of 7-thiasteroids, synthesized from the isothiachromanones (1),† invited to a closer investigation of the chemistry of the starting ketones. Although recently the photochemical conversion of both the ketone[3] and the corresponding sulphonium ylide[4] were reported, no polar reactions seem to have been investigated. We considered that the anomalous results were probably due to a competing reaction between a carbonium-ion intermediate and the sulphur lone pairs,[5] and have studied several reactions in order to examine this interaction. Enamine (2a) was prepared according to the procedure of White and Weingarten.[6] It could be purified *via* repeated sublimation at 80—120°/2 × 10^{-5} mm Hg and had m.p. 85—87°. When (2a) was heated at 160°/2 × 10^{-5} mm Hg for 40 min., a white solid was deposited on the walls of the reaction vessel. It was purified *via* sublimation, m.p. 91—94°; yield 19% based on the enamine. The spectral data indicate the formation of a non-symmetrical "quadrivalent sulphur" compound, the structure of which was established by preparing the *N*-phenylmaleimide adduct (4a), m.p. 254—256°, the n.m.r. parameters of which indicated that it was an *exo*-adduct. The reaction sequence was also carried out with isothiachromanone (1b), the enamine (2b), m.p. 108—111°, upon heating afforded isothianaphthene (3b), m.p. 110—113°, which was again characterized as its maleimide adduct (4b), m.p. 207—209°.



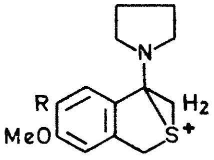
(2)



(3)



(4)



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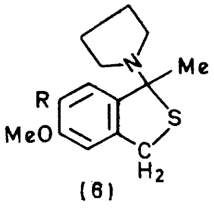

(6)

a, R = H; b, R = OMe

Although the exact mechanism of this rearrangement is not certain, the necessary transfer of two hydrogen atoms indicates a disproportionation process. The probable occurrence of a thiiranium ion (5) as an intermediate is noteworthy. It may be considered as arising *via* protonation of the enamine and participation of sulphur in the stabilization of the resulting imminium form. Transfer of a hydride ion, presumably from a second molecule of enamine (2)‡ leads to (6) which, after loss of pyrrolidine, gives (3). The possibility of other mechanisms remains open, especially since a number of electrophilic additions to enamine (2) did lead to normal α-substituted isothiachromanones, no rearrangement products being detected.

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† Synthesized *via* addition of $HSCH_2{\cdot}CO_2H$ to the corresponding benzyl chloride and subsequent $SnCl_4$ cyclization.

‡ Enamine (2) could easily undergo oxidation to an aromatic sulphonium compound. However, investigation of the sublimation residue gave no evidence of this.

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