Synthesis of 5-Chloro-4-ethoxy-8*H*-cyclohepta[*b*]thiophen

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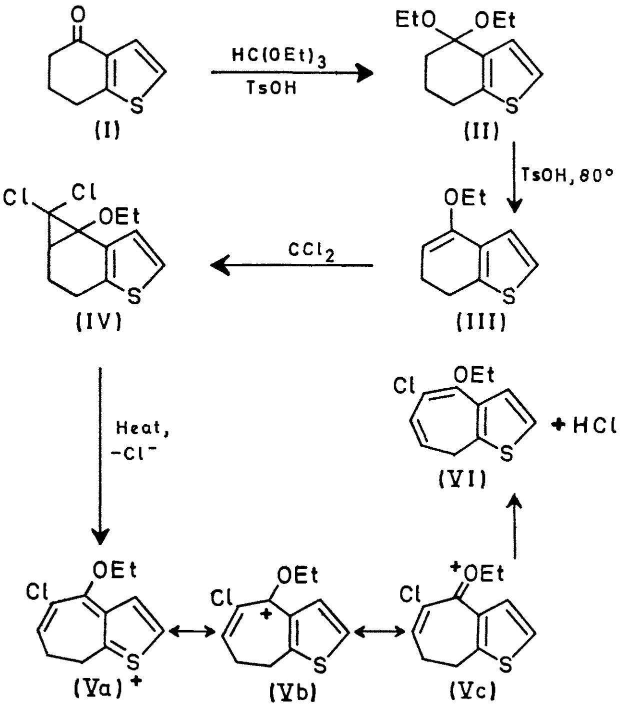
Summary 4-Ethoxy-6,7-dihydrobenzo[*b*]thiophen reacted with dichlorocarbene to afford an adduct which rearranged thermally to 5-chloro-4-ethoxy-8*H*-cyclohepta-[*b*]thiophen.



THE interesting rearrangements of 7,7-dichloro-1-ethoxynorcarane to 1-ethoxycyclohepta-1,3,5-triene[1] and of 7,7-dichloro-2-oxanorcarane to 6-chloro-2,3-dihydro-oxepin,[2] initiated the exploration of this method for the synthesis of thia-azulenes. We now report a convenient synthesis of 5-chloro-4-ethoxy-8*H*-cyclohepta[*b*]thiophen (VI).

4,4-Diethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen (II), b.p.$_{0\cdot1}$ 70—74° (m.p. 66—67°) was prepared in 85% yield by heating an ethanolic solution of 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophen (I)[3] under reflux with a two-fold molar excess of triethyl orthoformate and a catalytic amount of toluene-*p*-sulphonic acid. The diethyl acetal (II), unstable in air at room temperature, slowly eliminated ethanol to produce 4-ethoxy-6,7-dihydrobenzo[*b*]thiophen (III). The rate of this conversion of (II) into (III) was enhanced by treatment of (II) with toluene-*p*-sulphonic acid for 10 min. at 80°. Distillation (b.p.$_{0\cdot1}$ 57—59°) followed by g.l.c. analysis (175°, Apiezon-L) showed one component in the distillate [50% yield of (III)].† The enol ether (III) showed: λ_{max}† 225 (ϵ 14,700) and 288 nm (1820); i.r. absorptions (neat) 1685 (·C:C· of vinyl ether) and 1250

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† All new compounds gave satisfactory elemental analyses. U.v. spectra were measured in 95% ethanol.

cm^{-1} (:C·O·C). An n.m.r. analysis (neat)‡ showed absorptions at 7·0 (2H, aromatic), 4·5 (triplet, 1H, vinylic), 3·6 (quartet, 2H, ·OCH_2·), 2·5 (complex multiplet, 4H, ·CH_2·CH_2·), 1·2 (triplet, 3H, CH_3).

The enol ether (III) was allowed to react with dichlorocarbene (ethyl trichloroacetate–sodium methoxide[4] or chloroform–potassium t-butoxide[5] method) in pentane which afforded (IV) as a dark brown oil. Attempts to purify this adduct were unsuccessful because of its thermal instability. The crude adduct (IV) was heated under nitrogen (i) neat at 125—140° (25 min.), (ii) in quinoline at 190–200° (25 min.), (iii) in freshly distilled pyridine at 115–116° (5 hr.), or (iv) in distilled triethylamine at 89—91° (48 hr.) to afford, respectively, 40, 20, 48, and 45% yields of (VI), b.p.$_{0\cdot1}$ 89—92°. The freshly distilled product turns yellow immediately on exposure to air. An analytical sample prepared by g.l.c. purification showed the confirmatory spectral data: λ_{max} 228 (ϵ 20,900), 282 (8000), and 362 nm (690); ν_{max} (neat) 3055 (:C·H), 2965, 2860, and 1360 (CH_3), 1620 (·C:C·), 1225 and 1050 cm^{-1} (:C·O·C·); n.m.r. (neat) 7·0 (singlet, 2H, aromatic), 6·0 (doublet, 1H, :CH·C(Cl):), 5·4 (complex multiplet, 1H, vinylic), 3·8 (quartet, 2H, ·OCH_2·), 3·1 (doublet, 2H, ·CH_2·C:C·), 1·2 (triplet, 3H, CH_3).

The decomposition of (IV) to (VI) most likely occurs as shown through the intermediate carbonium ion (V), somewhat similar to the suggestion by Schweizer and Parham[2] for the decomposition of 7,7-dichloro-2-oxanorcarane. The ease of this conversion (low temperature) is accounted for by the resonance stabilization contributed by the "octet structure" (Vc).

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‡ Performed on a Varian A60A, chemical shifts in p.p.m. (δ) with Me_4Si as internal standard.

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