

PYROLYSIS OF DIMETHYLSULFOXONIUM (3-OXO-1-CYCLOHEXEN-1-YL)METHYLIDES

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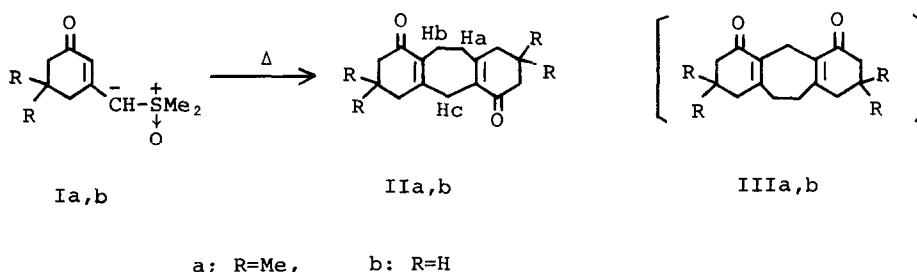
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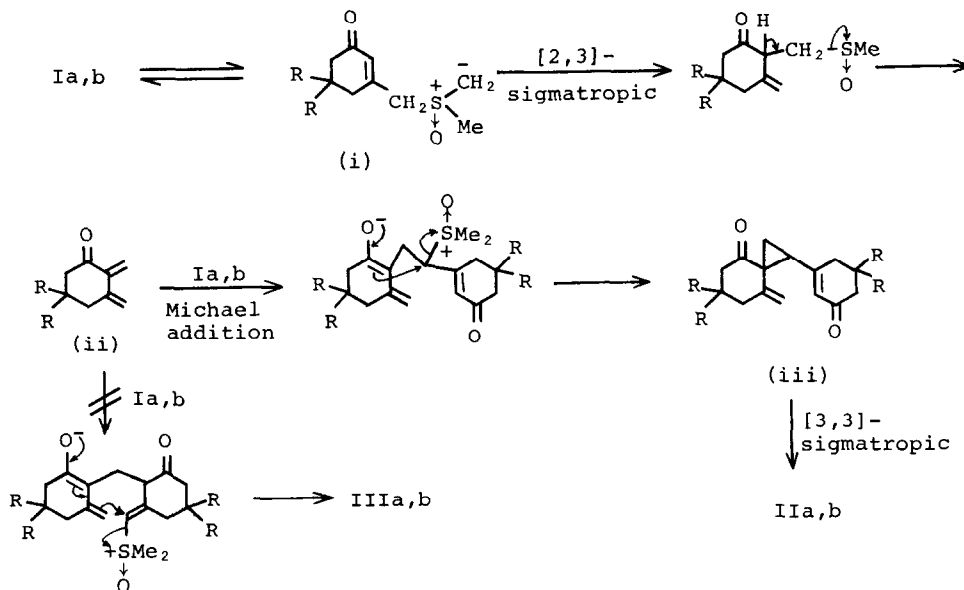
In the preceding paper,¹ we reported the synthesis of the stabilized sulfoxonium ylide, dimethylsulfoxonium (3-oxo-1-cyclohexen-1-yl)methylide (I), and its fundamental reactions such as acylation and alkylation. We now wish to report that the pyrolysis of I causes an interesting series of reactions involving the Michael addition of I leading to tropilidene derivative (II).

Heating dimethylsulfoxonium (5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)methylide [Ia, R=CH₃, mp 170-171°, $\nu_{\text{max}}^{\text{CHCl}_3}$ 1595 and 1540 cm⁻¹, $\lambda_{\text{max}}^{\text{EtOH}}$ 355 nm (log ϵ 4.67)], prepared from 3-chloro-5,5-dimethyl-2-cyclohexen-1-one by the same procedure as described previously,¹ in the absence of solvent at 170° for 5 min followed by preparative thin layer chromatography (alumina-benzene) gave 33% yield of IIa [R=CH₃, bp 155-160°/0.08 mmHg (bath temp.), m/e 286 (M⁺)]. The uv spectrum of IIa [$\lambda_{\text{max}}^{\text{EtOH}}$ 240 nm (log ϵ 4.28)] and a strong band in the ir spectrum at $\nu_{\text{max}}^{\text{CHCl}_3}$ 1655 cm⁻¹ showed the presence of the conjugated ketone. No other bands were present in the functional group region of its ir spectrum. On the basis of analytical (C₁₃H₂₆O₂) and these spectral data, two possible structures, IIa and alternative one (IIIa) are considerable for the product. The nmr spectral evidences presented below are consistent with the structure IIa rather than IIIa. The nmr spectrum (90 MHz in CDCl₃) of IIa exhibits signals at τ 6.65 (2H, b-s, Hc), 7.26-7.46 (2H, m, Hb), 7.56-7.87 (10H, m, Ha and other methylenes) and 9.03 (12H, s, 4×CH₃). These assignments were supported by decoupling technique and

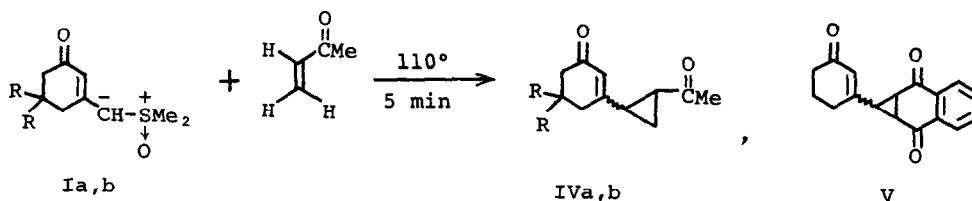
experiments using a shift reagent, $\text{Eu}(\text{DPM})_3^2$: The nmr spectrum run after the addition of $\text{Eu}(\text{DPM})_3$ (35 mg) to a solution of IIa (44 mg) in CDCl_3 (0.4 ml) exhibited clean peaks at τ 3.97 (2H, b-s, Hc), 4.68 (2H, b-t, Hb) and 6.32 (2H, m, Ha). Irradiation of Ha at τ 6.32 caused the broad triplet-like signal (Hb) at τ 4.68 to collapse to a broad singlet. Signals due to Hb and Hc were more strongly affected than Ha by addition of $\text{Eu}(\text{DPM})_3$. By a similar reaction to that employed for Ia, IIb [mp 79-79.5°, m/e 230 (M^+)] was obtained from Ib in 25% yield, which was assigned on the basis of spectral comparison with IIa.



The formation of IIa and IIb may be reasonably explained by the mechanism as shown in Chart. That is, the methylyde (I) is in equilibrium with its isomer



(i), which caused a [2,3]sigmatropic shift³ followed by elimination of methyl sulfenic acid to give the diene (ii). The diene is immediately attacked by the starting methyllide (I) (so-called the Michael addition⁴) followed by elimination of dimethylsulfoxide to yield the divinyl cyclopropyl derivative (iii), which undergoes well-established [3,3]sigmatropic rearrangement,⁵ giving II. Similar behavior to the first step, [2,3]sigmatropic shift of I, had been observed in the reaction of 3-ethoxycarbonyl-2-phenylallylde with triethylamine in anhydrous benzene, giving ethyl 3-phenyl-1,3-butadiene-2-carboxylate.⁶ The possibility of the Michael addition of I to ii was strongly supported by the fact that the methyllide (I) smoothly undergoes the Michael addition to the typical α,β -unsaturated ketones such as methyl vinyl ketone and naphthoquinone to yield the corresponding cyclopropyl derivatives [IVa, bp 120-125°/0.08 mmHg (bath temp.), $\nu_{\text{max}}^{\text{CHCl}_3}$ 1700, 1660 and 1620 cm^{-1} , 92%; IVb, bp 120-130°/0.09 mmHg (bath temp.), $\nu_{\text{max}}^{\text{CHCl}_3}$ 1700, 1660 and 1620 cm^{-1} , 62% and V, mp 174-174.5°, 47%], which were confirmed by spectral evidences. We expect to obtain the definite evidence for the above mechanism and will submit a detailed report of this study in the near future.



a; R=Me,

b: R=H

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