The Cycloaddition of Dichloroketen with Indene: A New Synthesis of 4,5-Benzotropolone

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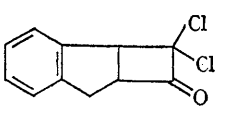
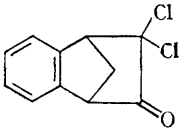
SYNTHETIC approaches to 4,5-benzotropolones and related systems are somewhat limited, the recent reports[1,2] of the 1,2-cycloaddition of dichloroketen to cyclopentadiene and subsequent hydrolysis[1] of the adduct, 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one to tropolone, prompted an investigation of the reaction of dichloroketen with indene. 1,2-Cycloaddition reactions of unsaturated compounds with indene are well known[3,4] and recently the related reaction of indene with dimethylketen has been reported.[5]

Dichloroketen was prepared *in situ* by the dehydrohalogenation of dichloroacetyl chloride with triethylamine and when generated in indene as solvent at 90°, furnished a 12% yield of an adduct $C_{11}H_8OCl_2$, b.p. 110—115°/0·5 mm., m.p. 78—79° (from hexane), (g.l.c. purity 99 + %). The mass-spectral data showed a molecular ion *m/e* 226, and fragment ions *m/e* 191 $(M-Cl)^+$, 163 $(191-CO)^+$, 149, 128 $(163-Cl)^+$ and 116 (indene)$^+$.

The adduct was considered to be the 1,2-cycloaddition product (I) rather than the 1,4-cycloaddition product (II) on the basis of the following evidence. A strong carbonyl absorption appeared in the infrared spectrum (hexane solution) at 1805 cm.$^{-1}$ consistent with an α-halogenated cyclobutanone derivative.[6] N.m.r. studies of the adduct in deuterochloroform at 100 Mc./sec. showed three multiplets at τ 2·58—2·90 (4 protons), 5·58—5·70 (2 protons), and 6·60—7·12 (2 protons). Spin-decoupling of the multiplet at τ 5·58—5·70 caused the other, two-proton, multiplet to collapse to an AB quartet (J = 16 c./sec.), indicative of geminal coupling. The spin-decoupling of the methylene protons caused the multiplet at τ 5·58—5·70 to reduce to a singlet. This assignment of the methylene protons and the recent report[7] on the C-7 bridge-methylene proton signals of benzonorbornenes, which occur at much higher field, eliminate the 1,4-cycloaddition structure (II).



(I)



(II)

Hydrolysis of the adduct with sodium acetate in aqueous acetic acid furnished 4,5-benzotropolone in 80% yield. Attempts to form an analogous adduct from indene and monochloroketen under similar conditions have failed.

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