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ON THE CHLORINATION OF DICYCLOPENTADIENE-1,8-DIONE

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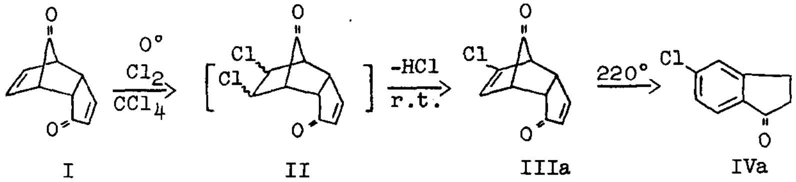
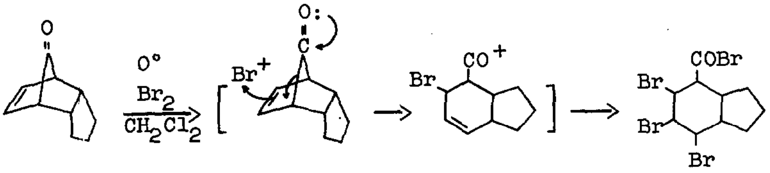
It has recently been reported[1] that the title compound (I) undergoes addition of one mole of chlorine, at 0° in carbon tetrachloride solution, to give a labile adduct which, on standing at room temperature, spontaneously loses hydrogen chloride to give a product (III), $C_{10}H_7ClO$. On the bases of infrared spectra and a pyrolytic degradation product (IV), III was assigned the structure 5-chlorodicyclopentadiene-1,8-dione (IIIa). IV was identified as 5-chloroindan-1-one (IVa) by melting point and infrared spectral properties.

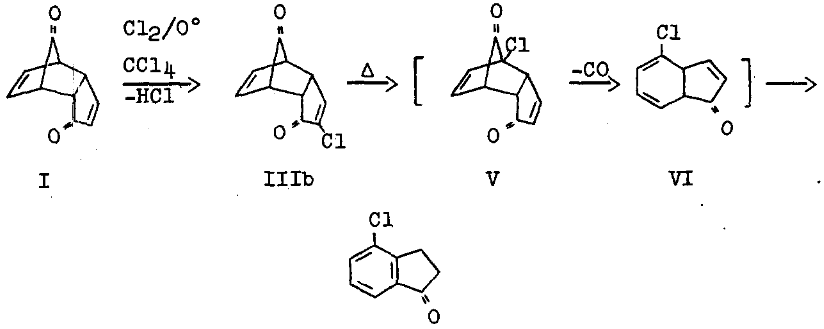


While preferential attack by halogen upon the strained, non-conjugated 5,6-double bond, vs. the enone system, of I, seems consistent with experience,[2] the ensuing loss of the elements of hydrogen chloride from the (presumably) intermediate II does not; for example, both endo-cis- and trans-2,3-dichloronorbornane are only slowly dehydrohalogenated by

20% potassium hydroxide in refluxing methanol.[3] Further doubt was cast upon the sequence depicted above by the observation of one of us, that addition of bromine to the related 2,3-dihydrodicyclopentadien-8-one proceeded only with fragmentation:[4]



We have re-examined the chlorination of I and wish to present evidence for the following sequence:



IVb

The dione I[1,5] was dissolved in CCl_4, and the solution cooled to 0° and mixed with the calculated (one equivalent) amount of a saturated solution of chlorine in CCl_4. The mixture was allowed to stand for 24 hours at about 0°, by which time some of the product had begun to crystallize spontaneously; the mixture was worked up by removing HCl and solvent <u>in vacuo</u>, then recrystallizing the residue from hexane: 72%, m.p. 118-119° (119-119.5° after a second recrystallization).

The m.p. and infrared spectrum [$\nu_{C=O}^{KBr}$ 1790 (s), 1775 (s), 1715 (s); $\nu_{C=O}^{CCl_4}$ 1805 (s), 1780 (m), 1730 (s) cm.$^{-1}$] were in acceptable agreement with constants reported for III.

Structure IIIb was assigned to the product on the bases of ultraviolet and proton magnetic resonance spectra. Thus for III, λ_{max}^{EtOH} = 238 mμ, log ϵ = 3.80, versus 221 (3.86) for I, the observed bathochromic shift of 17 mμ being consistent with substitution of -Cl for -H at the α-position of an α,β-unsaturated ketone.[6] The proton magnetic resonance spectrum of I (60 Mc) consisted of complex multiplets at 6.3-7.2 τ (4H) and 3.6-4.0 τ (3H) and a quartet centered at 2.6 τ (1H) with J_1 = 5.5 cps and J_2 = 2.7 cps. The spectrum of III was similar, but the multiplet at ca. 3.7 τ had an area corresponding to two hydrogens and was somewhat simpler, and the low field signal was now a doublet, J = 2.8 cps. The resonance at lowest field may be assigned with confidence to the β-proton of an α,β-unsaturated ketone,[7] and the diminished multiplicity demonstrates that one of the adjacent protons is missing in III. Since the surviving J is too small for coupling between cis-olefinic hydrogens,[8] the α-position must have been substituted.

Pyrolysis of III at 220°[1] gave IV contaminated by starting material and small amounts of unidentified impurities; chromatography of the volatile pyrolysate on neutral activity III Woelm alumina gave a ketone fraction melting at 84-86°, identified as 4-chlorindan-1-one (IVb) by comparison with an authentic sample, m.p. 90-91°.[9] The two samples possessed identical infrared spectra, and furnished oximes[10] with undepressed mixture m.p. (159-161°) and superimposable infrared spectra. The oxime of IVa is reported to melt at 148°.[11] Conversion of IIIb to IVb is better effected by heating in a sealed tube at 121° (boiling tetrachloroethylene) for six hours; the yield is nearly quantitative.

Chlorination of I presumably proceeds by addition-elimination, and although the elimination is very ready, compared to the analogous reaction of cholestenone,[6] it is not inordinately so. The unreactivity of the isolated double bond is more remarkable, and can only be attributed to the influence of the 8-keto function. A similar inversion in the customary order of nucleophilicity of two double bonds, one isolated and the other in conjugation with a carbonyl group, has been observed by Woodward, _et al_.[12] In their case, inverted reactivity was observed only when lactone formation altered the conformation of the molecule, bringing a second carbonyl group near, and above the plane of, the isolated double bond, much as in the case at hand.

The rearrangement, IIIb —> V, is of a type now well-recognized,[13] and the double bond migration requires no comment. There is, however, no direct evidence for either V or VI; the conversion of IIIb to IVb takes place at 100° in a sealed tube with a half-time of 10-12 hours, and infrared spectra of the mixture at intermediate conversions show only bands assignable to product and starting material.

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[7] Cf. spectra 51, 271 and 275 in *NMR Spectra Catalog*, N. S. Bhacca, L. F. Johnson and J. N. Shoolery (Varian Associates, Palo Alto, Calif., 1962).

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[10] New compound: the analytical sample had m.p. 160.5-161.8, and the empirical formula of C_9H_8ONCl was confirmed by mass spectrometry, through the courtesy of Prof. A.L. Burlingame.

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