

PHOTODIMERIZATION OF 2-CHLOROTROPONE (I)

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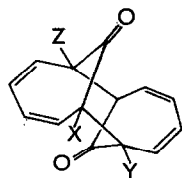
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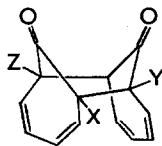
Recent studies on the photochemistry of troponoids have shown that, upon irradiation, tropono derivatives isomerize or dimerize depending on the nature of the substituents located (2,3,4). We have investigated the photoreaction of 2-chlorotropone to clarify the effect of halogen substitution and found the formation of a homobarrelenone derivative condensed with tropono, in addition to two dimers.

2-Chlorotropone (I), on irradiation in benzene in a Pyrex vessel with mercury lamp (Toshiba H-400p) for 15 hr, afforded $C_{14}H_{10}O_2Cl_2$ (II), m.p. 143° , (2%), and $C_{14}H_9O_2Cl$ (III), m.p. 156° , (22%), accompanied by 40% recovery of I (5). Product II has the following physical data: IR spectrum (KBr), 1733 (α -chloroketone) cm^{-1} ; UV spectrum (MeOH) $m\mu$ ($\log \epsilon$), 223 (3.97) and 253 (3.92); NMR spectrum (60 Mc) in $CDCl_3$, δ 5.86 (m, 8H) and 3.63 (m, 2H); Mass spectrum, m/e 247, 245 (M-Cl), 114, 112 and 77. Pyrolysis of II at 150° gave I. The similarity of these data to those of the (6+6) π type dimer of tropono (3) suggests that II is also (6+6) π type dimer of I, for which four stereoisomers (IIa-IId) are possible. Of these structures, IIa can be selected as most preferable because its observed dipole moment (3.44 D at 25° in benzene) better fits to the calculated value for IIa (3.28 D) than those for IIb, IIc and IId (0, 7.19 and 6.51 D) (5).

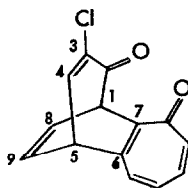
Physical data of III are as follows: IR spectrum (KBr), 1675 (C=C-C=O), 1610 and 1570 cm^{-1} (C=C and C=O of tropono); UV spectrum (MeOH) $m\mu$ ($\log \epsilon$), 233 (4.29) and 315 (3.70); NMR spectrum (60 Mc) in $CDCl_3$, δ 7.50 (d, $J = 9.4$ cps, 1H), 7.2-6.4 (m, 6H, including aromatic protons), 5.72 (splitted doublet, $J = 7.0$ and 1.8 cps, 1H) and 4.35 (splitted quartet, $J = 9.4, 6.0$ and 1.4 cps, 1H); Mass spectrum, m/e 246, 244 (M), 218, 217, 216, 215, 181, 153, 152 and 128. These data indicate the presence of an α -chlorinated α,β -unsaturated keto group and a tropono ring in III. On the basis of this evidence, structures IIIa and IIIb are proposed for III. The observed dipole moment of III (7.36 D at 25° in benzene)



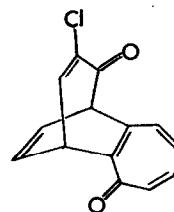
IIa X = Y = Cl, Z = H
IIb Y = Z = Cl, X = H



IIc X = Y = Cl, Z = H
IIId Y = Z = Cl, X = H



IIIa

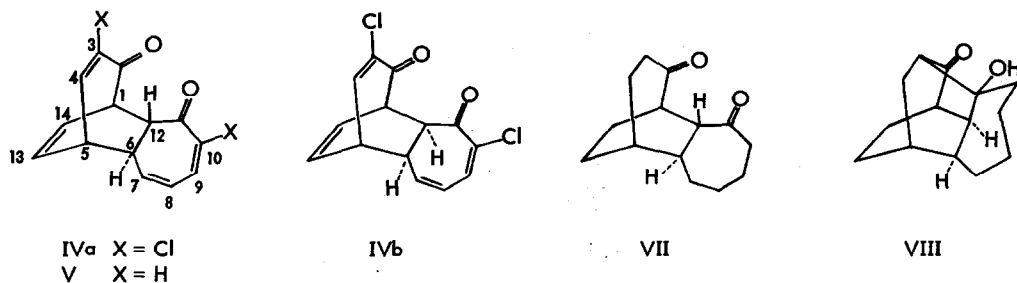


IIIb

agrees more closely with IIIa than IIIb, 7.72 D for IIIa and 4.34 D for IIIb (6). Furthermore, the C₁-proton (δ 5.72) of III is deshielded by carbonyl group of the tropone, as shown in comparison to chemical shift (δ 4.59) reported for C₁-proton of 6,7-benzobicyclo[3.2.2]-nona-3,6,8-trien-2-one (7).

Irradiation of I in 1N hydrochloric acid resulted in an increase of the yield of II (9%), accompanied by III (16%) and I (42%) (3). When I was irradiated in cyclohexane for 15 hr, a new dimer C₁₄H₁₀O₂Cl₂ (IV), m.p. 123° (decomp), (25%) was obtained in addition to II (1.5%), and III (33%) and recovery of I (25%). On the basis of the following physical and chemical evidence, dimer IV is assumed to be a (4+2) π type dimer (3,4): IR spectrum (KBr), 1681 cm⁻¹ (C=C=O); UV spectrum (MeOH) mμ (log ε), 235 (4.26) and 310 (4.09); Mass spectrum, peaks are very similar to those of III, except for m/e 284, 280 (M). NMR spectrum (100 Mc) in CDCl₃, δ 7.34 (d, J = 9.0, 1H), 7.12 (d, J = 9.0, 1H), 6.65 (q, J = 8.8, 6.7 cps, 1H), 6.51 (q, J = 10.2, 3.6 cps, 1H), 6.24-6.0 (m, 2H), 4.48 (d, J = 7.8, 1H), 3.54 (m, 1H), 3.00 (d, J = 11.2, 1H) and 2.67 (m, 1H). This NMR spectrum is very similar to that of the reported dimer (V) of tropone (3) except for signals ascribed to C₃- and C₁₀- protons, indicating that both positions are substituted by chlorine atom.

When IV was catalytically hydrogenated, after absorption of 5 equiv. of hydrogen, it afforded an octahydro-monochloro compound C₁₄H₁₉O₂Cl (VI), m.p. 130°; IR spectrum (KBr) 1701 cm⁻¹. Reductive dechlorination of VI by treating with zinc in acetic acid (8) provided (VII), m.p. 97°, which was confirmed to be identical with the octahydro compound of V (3) by mixed melting point method and by comparison of their IR spectra. Of the possible four stereoisomers for IV, the two structures having C₆- proton trans to the etheno-bridge (C₁₃=C₁₄) should be discarded, because, as reported (3), VII could be converted to ketol (VIII) by intramolecular condensation with base. Consideration of the relation of dihedral angle between the C₁- and C₁₂- protons or C₆- and C₁₂-protons with coupling constants (J_{1,12} = 0, J_{6,12} = 11.2), would

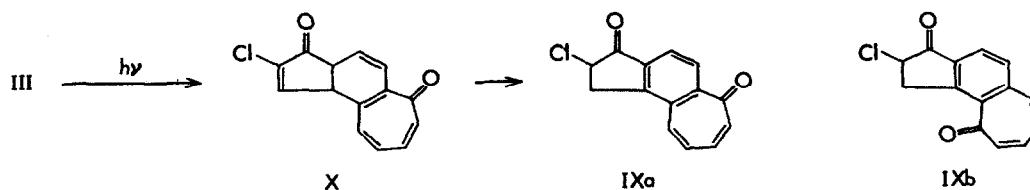


suggest that trans structure (IVa) is more preferable to cis structure (IVb).

When dimer IV was heated in benzene for 30 min, III was obtained quantitatively by evolution of hydrogen chloride, suggesting III is a secondary product. The mechanistic pathway may be considered similar to that proposed for some Grignard reaction of the troponoid system (9).

Recently Kende (7) and Goldstein (10) reported an interesting photochemical transformation of homo-barrelenone derivatives to dihydroindene derivatives. Irradiation of III, in acetonitrile in a Pyrex vessel for 3 hr using a mercury lamp (Toshiba H-400p), afforded $C_{14}H_9O_2Cl$ (IX), m.p. 200° (decomp), (10%). Product IX showed the following spectral data: IR spectrum (KBr), 1727 (five-membered C=O), 1600 and 1575 cm^{-1} (C=C and C=O of troponoid); UV spectrum (MeOH) $m\mu$ ($\log \epsilon$), 228 (4.33), 248 (4.40), 325 (3.91) 360 (3.73) and 395 (sh); NMR spectrum (60 Mc) in $CDCl_3$, δ 3.47 (q, $J = 7.0$ and 4.0 cps, 1H), 4.10 (q, $J = 17.0$ and 7.0 cps, 1H) 4.70 (q, $J = 17.0$ and 4.0 cps, 1H), 6.7-7.6 (m, 4H), 8.0 (d, $J = 7.5$ cps, 1H) and 8.45 (d, $J = 7.5$ cps, 1H); Mass spectrum, m/e 246, 244 (M), 218, 216, 181, 154, 153, 152, 126 and 76. The NMR spectrum exhibiting aliphatic ABX and aromatic AB systems and the above IR and UV spectra indicate two possible structures (IXa and IXb) for IX. Furthermore the fact that one proton of the aromatic ring appears as a doublet at such low field as δ 8.45 indicates the deshielding effect of carbonyl group of the troponoid ring, precluding structure (IXb). The primary photoproduct might be a dihydroindene derivative (X) (7,10), which was converted to the IX during the work-up procedure.

In comparing the photodimerization of I to that of troponoid, it should be noted that I underwent (6+6) π and (4+2) π type photocycloaddition without formation of (6+4) π and (6+2) π type dimers. Although the yield of dimer II increased in acidic medium rather than in aprotic solvent, IV was also formed in the same medium. On the other hand, in an aprotic solvent such as cyclohexane, dimer IV was formed as primary product, with a small amount of II. In addition, I afforded no valence isomers such as bicyclo-



[3.2.0]-hepta-3,6-diene derivatives. These phenomena may be explained by the effect of the chlorine substituent on the excited state of I. It is also interesting to note that the two chlorine atoms in II are vicinal and the (4+2) π type cycloaddition of I occurs at positions without chlorine. These facts help clarify the mechanism of photocycloaddition of the troponoid systems. Detailed discussion will be reported elsewhere in a full report.

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** Abbreviations used are d, doublet; t, triplet; q, quartet; m, multiplet.