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THERMAL ISOMERIZATION OF AN ADDUCT OF TROPONE AND 8-OXOHEPTAFULVENE. A FIRST EXAMPLE OF ANTARAFACIAL [1,7] SIGMATROPIC REARRANGEMENT IN A RIGID SYSTEM

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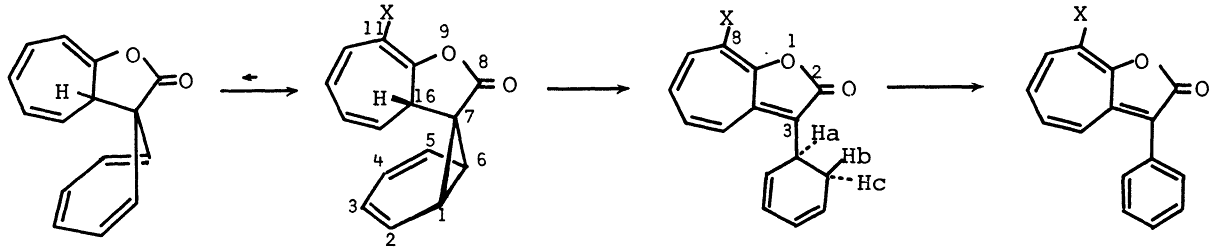
Thermal isomerization of (2 + 8)cycloadducts of tropones and 8-oxoheptafulvene afforded 3-(cyclohexa-2,4-dienyl)-1-oxaazulan-2-ones by antarafacial [1,7] sigmatropic rearrangement which is a first example in a rigid system. An activation energy (21.4 kcal. mol^{-1}) and an entropy of activation (-25.8 e.u.) were obtained for the reaction.

We have reported that 8-oxoheptafulvene reacts with tropone and its derivatives to give (2 + 8)cycloadduct (I) having norcaradiene and cycloheptatriene moieties, besides heptafulvalene and 1-oxaazulan-2-one derivatives.[1,2] The structure of the compound (I) was finally determined by X-ray crystallography.[3]

We have now observed a novel thermal isomerization of I to give oxaazulanone derivative by antarafacial [1,7] sigmatropic rearrangement, the results will be reported in this communication.

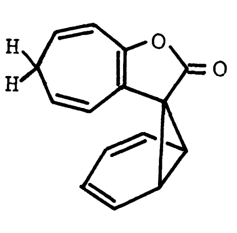
A variable temperature NMR study of the compound (I) from -50°C to 130°C exhibited that the chemical shift of the H-1 and H-6 protons shifted to lower field by 0.4 ppm from δ 2.95 ppm, which indicated a mixture of valence isomers, norcaradiene (I) and cycloheptatriene (II), was present although norcaradiene structure was predominant. However, another expected isomerization product (III) by [1,5] hydrogen shift could not be detected.[4]

When the compound (I) was heated in various solvents ($CDCl_3$, xylene, or DMSO) above 130°C (effectively at 150~180°C) under nitrogen atmosphere, irreversible isomerization occurred, and reddish prisms (IV), 89~90°C, were obtained in a good yield. The compound (IV) was found to be 3-(cyclohexa-2,4-dienyl)-1-oxaazulan-2-one from the following spectroscopic data; UV λ_{max}^{EtOH} 224 nm (log ε, 4.32), 257 (4.32), 365^{sh}(4.08), 379 (4.20), 397 (4.17), 440^{sh}(3.26), 467^{sh}(2.99), and 502 (2.69); IR (KBr), 1730 cm^{-1}; NMR (DMSO-d_6), δ 2.80 ppm (m, 2H), 4.96 (m, 1H), 5.53 (d,m, J = 10.5 Hz, 2H), 5.90 (d,m, J = 10.5 Hz, 2H), and 6.7~7.6 (m, 5H).

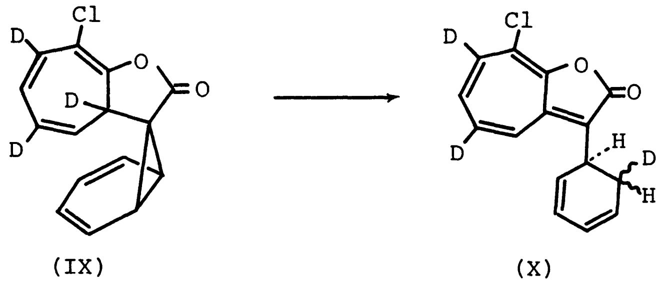


(II) (I) X = H (IV) X = H (V) X = H

(VI) X = Cl (VII) X = Cl (VIII) X = Cl



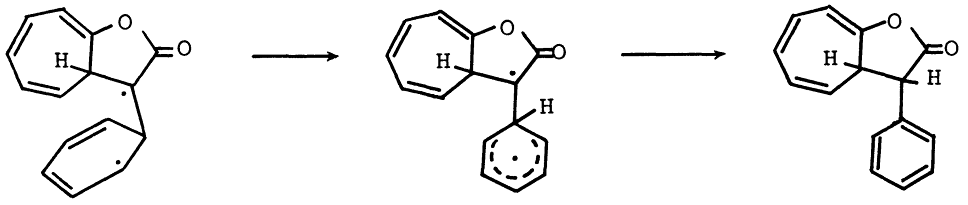
(III)



(IX) (X)

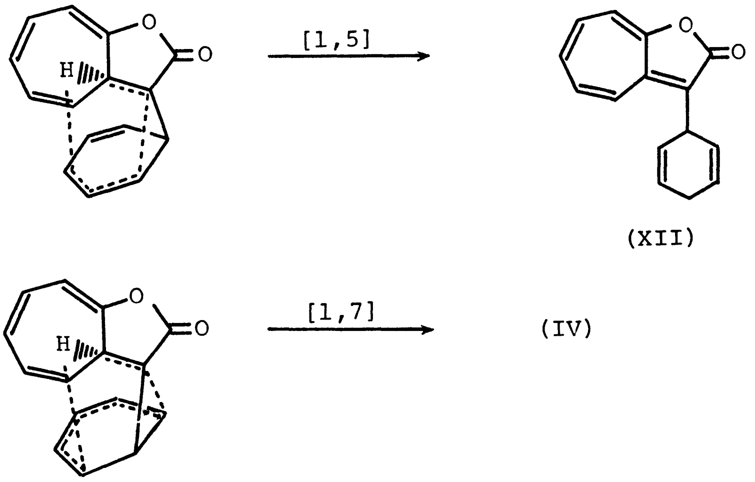
Treatment of IV with o-chloranil or heating of I at 180°C under oxygen atmosphere afforded 3-phenyl-1-oxaazulan-2-one (V)$^{5)}$ in good yields.$^{6)}$ By the similar manner, 11-chloro derivative (VI)$^{1)}$ afforded 8-chloro derivative of IV (VII), orange crystals, mp 151~152 °C, and 8-chloro-3-phenyl-1-oxaazulan-2-one (VIII), mp 182~183 °C.

The thermolysis in xylene or DMSO of an adduct (IX) of 2-chloro-3,5,7-trideuteriotropone$^{7)}$ and 8-oxoheptafulvene afforded a deuterated compound(X). The deuterium atoms were found to locate at 5,7 and 6' positions by the analysis of NMR spectrum, although the stereochemistry of the deuterium at 6' position could not be clarifird.$^{8)}$ The thermolysis of an equimolar amounts of I and IX in refluxing xylene gave IV and X, and any cross over products of deuterium atom could not be obtained. Furthermore, the heating of IX in DMSO containing water gave only trideuterated compound (X). These facts indicate that the rearrangement is intramolecular and must be concerted reaction because if the rearrangement is initiated by ionic or radical reaction, the scrambling must be observed in the above cross reaction or the aromatization of norcaradiene moiety would occur to give 3-phenyl derivative (e.g. XI) rather than IV.[9)] Furthermore, the compound (I) is found to be very stable to weak acids and weak bases at room temperature.



(XI)

According to the Woodward-Hoffmann rule,[10)] suprafacial [1,5] and antarafacial [1,7] sigmatropic rearrangements of H-16 are allowed for I depending upon which bond of the cyclopropane ring cleavage, to give 3-(cyclohexa-2,5-dienyl)-1-oxa-azulan-2-one (XII) and IV respectively as depicted below. Our result is a first example of antarafacial [1,7] sigmatropic rearrangement in a rigid system, although many examples of the rearrangement in mobile system have been reported.[11)]



(XII)

(IV)

X-ray crystallography[3)] of I shows that the distance (2.67 Å) between H-16 and C-2 is shorter than the distances (2.83 Å and 2.94 Å) between H-16 and C-3, and H-16 and C-13 respectively, this may be the reason that the facile [1,7] shift occurs in this system.

The above results seem to suggest that a hydrogen migration to the position of the shortest distance preferentially occurs in the case of competitive concerted rearrangements allowed in a rigid system, if the stereochemical requirements are satisfied.

The kinetics of this reaction have been studied by NMR measurment in $CDCl_3$, which indicated that the reaction is of the first order and the data of activation energy (Ea) = 21.4 $kcal.mol^{-1}$, enthalpy of activation ($\Delta H^{\ddagger}$) = 20.6 $kcal.mol^{-1}$, and entropy of activation ($\Delta S^{\ddagger}$) = -25.8 e.u. were obtained. These data are comparable to those (Ea = 14~21.6 $kcal.mol^{-1}$ and $\Delta S^{\ddagger}$ = -25.2~-13.6 e.u.) obtained for [1,7] sigmatropic rearrangements in the mobile system.[11)] Furthermore, Ea value (21.4 $kcal.mol^{-1}$) is lower than those (26.4~32 $kcal.mol^{-1}$) for [1,5] sigmatropic rearrangements in cycloheptatriene system.[12)] Therefore, it seems to be reasonable that [1,5]shift of I to III did not occur.

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