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A NEW THERMAL REARRANGEMENT OF BICYCLO[3.2.0]HEPTADIENONE SYSTEM[1]

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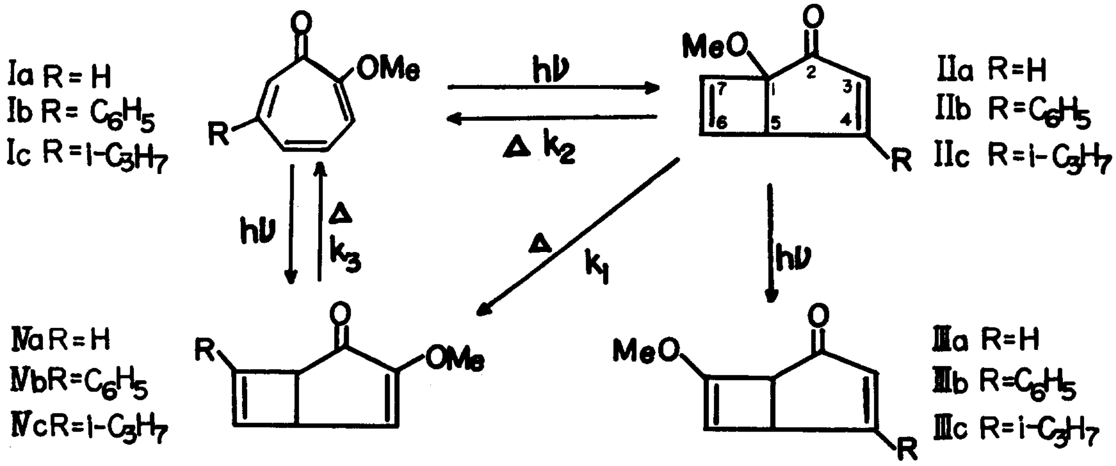
It has been reported that irradiation of tropolone methyl ether (Ia) and its alkyl derivatives provided first their valence isomers, the 1-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-ones (II), which in turn, on futher irradiation, isomerized to the 7-methoxyl derivatives (III).[2] In this case, other valence isomers, the 3-methoxyl derivatives (IV), have not been isolated,[3] although their formation was suggested from theoretical considerations.[4] On the other hand, it is also known that, on pyrolysis around 400°C, II reorganizes to the corresponding tropolone methyl ethers (I).[2] However, we find that if the pyrolysis is carried out at lower temperature, around 200°C, the 1-methoxyl derivatives (IIa, IIb and IIc) undergo mainly another type of rearrangement to give 3-methoxyl derivatives (IVa, IVb and IVc). This thermal reaction is a rearrangement in contrast to the reported photoinduced one (II → III) and is a useful synthetic method for 3-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadienones. We wish to report here an outline of the result obtained and the reaction mechanism elucidated.



When IIa,[2] IIb[5] or IIc[6] was heated in a sealed tube under the conditions shown in Table I, IVa, IVb or IVc was obtained accompanied with the corresponding tropolone methyl ether (Ia, Ib or Ic) respectively. The products IV and I were separated by preparative thin layer chromathography on silica gel using benzene-ether (5:1) as developing solvent. The structure of the products IV was demonstrated to be 3-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadiene-2-ones from the elemental analyses,[7] nmr spectra (Table II) and the following physical data: IVa, b.p.$_1$ 85-90°C (bath temp.), λ_{max}^{EtOH} 226 and 265 mμ (log ε 3.72 and 3.85), ν^{oil} 1706 cm^{-1} (cyclopentenone); IVb, m.p. 128°, λ_{max}^{MeOH} 250 mμ (log ε 4.50), ν^{KBr} 1705 cm^{-1}; and IVc, b.p.$_1$ 120-130° (bath temp.), λ_{max}^{EtOH} 240 and 265 mμ (log ε 3.78 and 3.78), ν^{oil} 1705 cm^{-1}.

Table I.

Compound (II)	Conditions	Product (yield %)	
		I	IV
(a) R=H	in $CHCl_3$, 189°C, 60 min.	31.2	56.0
(b) R=C_6H_5 m.p. 63°C	in MeOH, 189°C, 150 min.	14.5	72.0
(c) R=i-C_3H_7 b.p.$_1$ 79-80°	in $CHCl_3$, 191°C, 60 min.	14.7	68.0

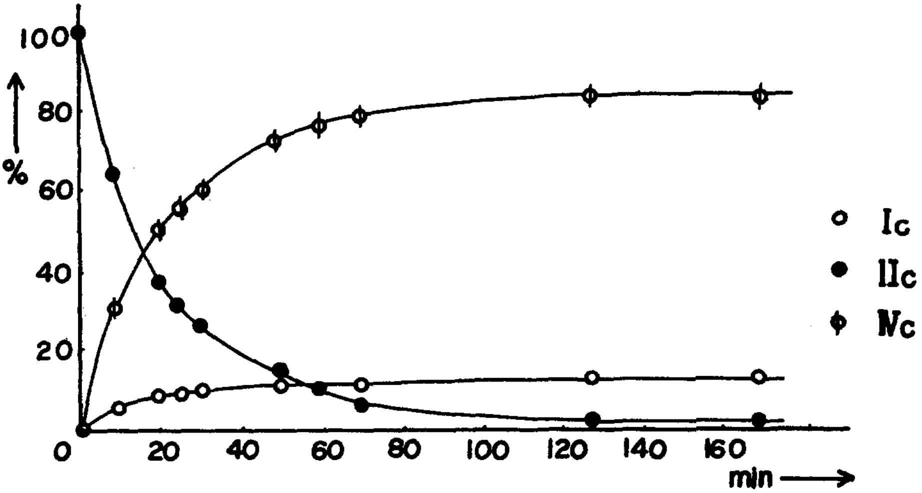


Fig I. Depletion of IIc and formation of IVc and Ic during heating of IIc at 187°C.

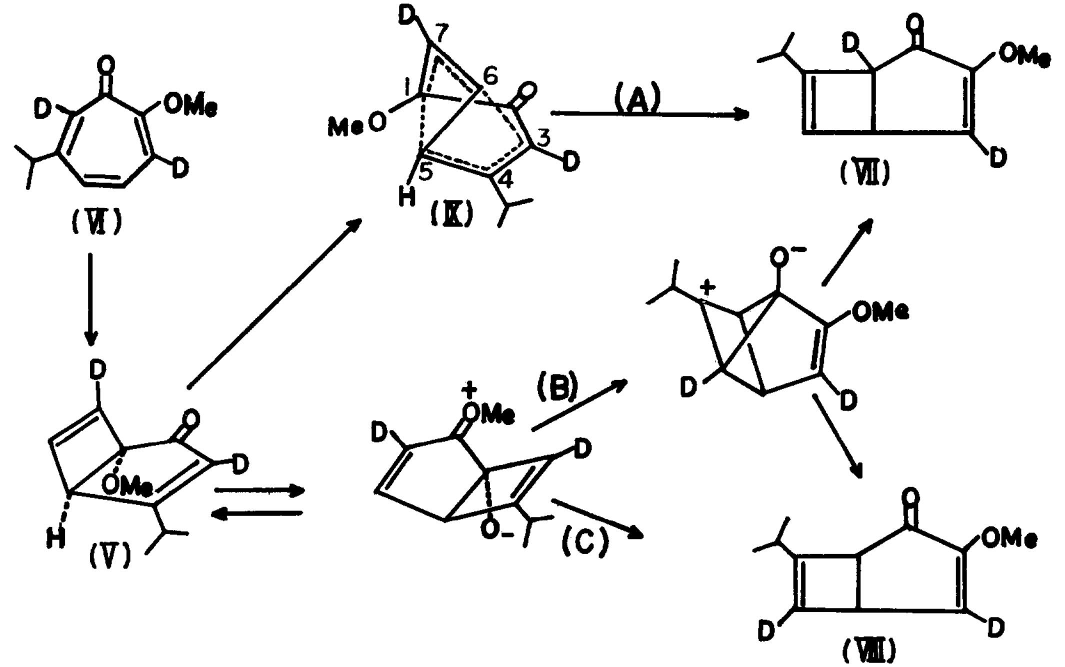
Table II. NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7
IIb	6.53(OCH_3)		3.53	2.20 ~ 2.60(ph)	5.78(t) J_{56}, J_{57}1.0	3.16(q) J_{67}2.4	3.56(q)
IIc	6.62(OCH_3)		4.18(d) J 1.8*	8.80(d) CH_3 of i-C_3H_7	6.17(d) (broad)	3.19(q) J_{56}1.2 J_{67}3.0	3.64(q) J_{57}1.0
IVa	6.16 (complex)		6.32 (OCH_3)	3.57(d) J_{45}3.2	6.55 (complex)	3.40(q) J_{56}1.0	3.68(q) J_{17}1.8 J_{67}3.0
IVb	6.13(q) J_{15}3.6 J_{16}1.0		6.38 (OCH_3)	3.58(d) J_{45}3.6	6.32 (complex)	3.36(q) J_{56}1.2	2.30~ 2.80(ph)
IVc	6.49 (complex)		6.33 (OCH_3)	3.57(d) (broad) J_{45}3.4	6.49 (complex)	3.85(d) (broad) J 1.4*	9.03(d) 8.91(d) CH_3 of i-C_3H_7
V	6.62(OCH_3)		D	8.80(d) CH_3 of i-C_3H_7	6.17(d) J_{56}1.2	3.19(d)	D
VI		6.18 (OCH_3)	D	3.11(d) J_{45}11.5	3.42(d)	8.80(d) CH_3 of i-C_3H_7	D
VII	D		6.33 (OCH_3)	D	6.49 (broad)	3.85(q) J_{56}1.0 J 1.4*	9.03(d) 8.91(d) CH_3 of i-C_3H_7

a. All spectra were measured on a Varian 60 A in $CDCl_3$ containing TMS as internal reference. Chemical shifts are given as τ-values and coupling constants (cps) are assumed to be approximately equal to the splittings; d=doublet, t=triplet, q=quartet, J^*=coupling constant between isopropyl methine proton and ring proton. D indicates deuterium situated in the shown position.

As a typical experiment, neat IIc was heated in a sealed tube at 187°C and the reaction rate was measured by calculation of the proton areas of the methoxyl signal of IIc, IVc and Ic in their nmr spectra. During the reaction, the decrease of IIc and increases of IVc and Ic are shown in Fig. I. Because of the stability of IVc at this temperature, the second step giving Ic from IVc (k_3) is insingnificant. Since the ratio of k_1/k_2 was almost constant (5.7) independently of the reaction time, the steps IIc⟶IVc and IIc⟶Ic are competitive reactions. Both steps were found to be unimolecular and the values of $k_1=3.01\times10^{-2}$ min^{-1} and $k_2=5.27\times10^{-3}$ min^{-1} were obtained.[8]

Consequently, their three possible pathways (A, B or C) can be considered for the rearrangement of II ⟶ IV, of which the Cope type rearrangement (path A) is most favorable. However, others (path B or C) can not be discarded completely, because of the following facts. In addition to the irreversibility of the rearrangement(IV $\not\rightleftarrows$ II), the thermal stability of the 7-methoxyl derivative (III) suggests that C_1-methoxyl group plays an important role in inducing the rearrangement. Furthermore, the fact that IIb or IIc afforded product IVb or IVc in better yield than IIa (see Table I) indicates that the substituent at C_4 position may assist the rearrangement.



To determine the real reaction pathway, the thermal rearrangement of the 3,7-dideuterio derivative V was carried out under the same conditions. The compound V was synthesized by the irradiation of 3,7-dideuterio-2-methoxy-6-isopropyl-tropone (VI), which was obtained from the corresponding 3,7-dibromotropone[9] by catalytic reduction with deuterium.[10] The product from V was found to contain only the 1,4-dideuterio derivative VII, not the 4,6-dideuterio derivative VIII or a mixture VII and VIII. This result establishes that the reaction proceeds through path A.

The structures of V, VI and VII were confirmed by their nmr (see Table II) and mass spectra (molecular ion, 180).

The difference in the thermal rearrangement of the 1-methoxyl derivatives II and compounds III or IV having no substituent at the C_1 position may be ascribed to a similar effect of the alkyl group at the cyclobutene series,[11] which controls conrotatory ring opening. That is, the steric repulsion between C_1-methoxyl group and C_5-hydrogen may bring about twisting of the cyclobutene ring and stretching of the C_1-C_5 bond in the transition state (IX).[12]

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