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A TWISTED TRANSITION STATE IN THE THERMAL ISOMERIZATION OF BICYCLO[3.2.0]HEPTA-3,6-DIEN-2-ONES LEADING TO TROPONES (1)

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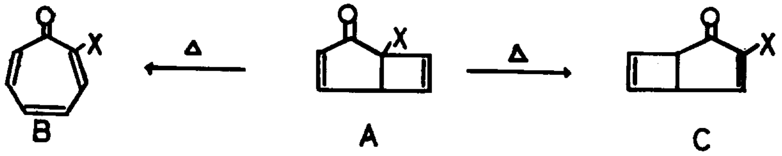
In general, the thermal isomerization of bicyclo[3.2.0]hepta-3,6-dien-2-one derivatives (A) leading to tropone derivatives (B) requires high temperatures around 400° (2), because the disrotatory opening of the cyclobutene ring included is a thermally forbidden process (3,4). However, it has been reported that 1-methoxybicyclo[3.2.0]heptadienone (IA), upon heating around 180°, has been isomerized to the 3-methoxy derivative (IC) accompanied by the 2-methoxytropone (IB) (5). That the thermal isomerization of IA to IC is an example of the antarafacial-antarafacial Cope rearrangement was supported by kinetic studies (1) as well as by the molecular orbital symmetry theory (4).



I	X=OCH_3	V	X=$NHC_6H_4CO_2CH_3$(p)
II	X=NHC_6H_5	VI	X=$NHC_6H_4COCH_3$ (p)
III	X=NHC_6H_4Cl(p)	VII	X=$NHCOCH_3$
IV	X=NHC_6H_4Br(p)	VIII	X=$NHCOC_6H_5$

Recently, we have studied the thermal reaction of 1-aminobicyclo[3.2.0]-hepta-3,6-dien-2-one derivatives which are isoelectronic with the 1-methoxy derivative (IA), and found out the striking fact that 1-arylamino derivatives IIA~VIA (6) are readily transformed into the corresponding 2-arylaminotropones (IIB~VIB) upon heating at temperatures lower than 100°, whereas 1-acylamino derivatives VIIA and VIIIA (6) treated around 170°, rearranged to 3-acylamino-bicyclo[3.2.0]heptadienones (VIIC and VIIIC), m.p. 81-82° and 107-109° (7), in good yields respectively. We wish to discuss in this paper mainly the former isomerization of compounds from type A to type B.

Although a few examples in which the thermal ring opening of the bicyclo[3.2.0]heptadiene system occurs at relatively low temperatures has been reported (8, 9, 10); their reaction mechanism is still in ambiguity (3). In order to clarify the reaction path for such thermal reactions of 1-arylamino derivatives IIA∼VIA, a study of the effect produced by the substitution in the para position of the aryl group and the solvent effect were investigated. Figure 1 shows Hammett's plots of rate factors valuable for the thermal reaction of IIA, IIIA, IVA, VA and VIA. The rate of the ring opening was measured by UV spectroscopy at 80.1° in a benzene ($\rho = -1.78$). On the other hand, the rate of the isomerization of IIA was also measured at 68.0° and 80.1° in several solvents. Figure 2 exhibits relationships between the rate and the dielectric constant of the solvents used. Although the rate of ring opening in methanol is about fifteen times faster than that in benzene, a linear relationship was obtained in aprotic solvent. From these experiments it could be postulated that the thermal ring opening of 1-arylamino derivatives IIA∼VIA proceeds probably via ionic intermediates such as IID. As an example the transformation of IIA to IIB is depicted in the following scheme. However, 1-anilinobicyclo[3.2.0]hept-3-en-2-one

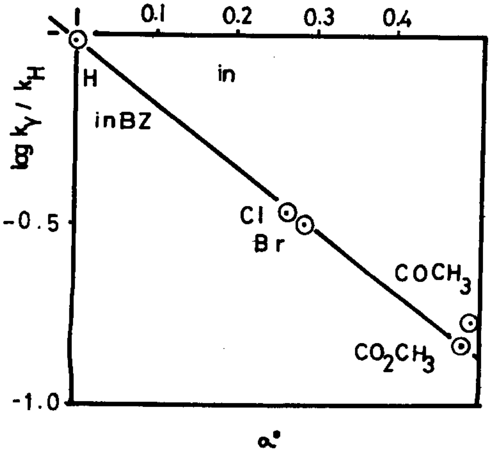


Fig. 1. Hammett's plots for the thermal isomerization of IIA∼ VIA.

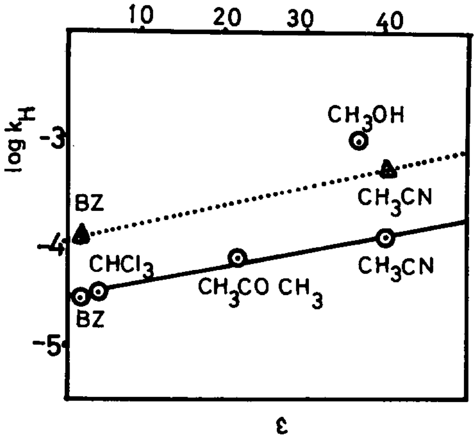
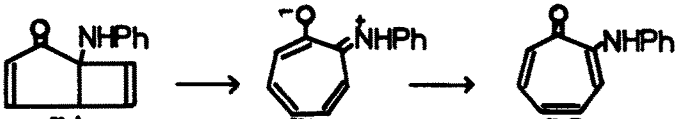


Fig. 2. Solvent effect on the thermal isomerization of IIA.
⊙: at 68.0°. △: at 80.1°.



IX

(IX), m.p. 105-106° (7), which was prepared by hydrogenation of IIA, on heating at 150° for 3 hr resulted in a complete recovery of IX without the ring opening.

Table 1 gives the rate of the thermal reaction of IIA to IIB which was measured in a benzene solution. The Arrhenius plot of the data shown in Table 1 provides a straight line, from which activation parameters shown in Table 2 were calculated.

<u>Table 1</u>. The first order rate constant of IIA IIB

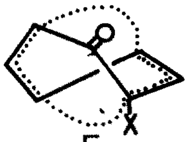
Temp (c°)	k x 10^5(sec^{-1})
68.0	3.23
80.1	12.1
82.0	13.3
102.0	88.8

Table 2. Activation parameters.

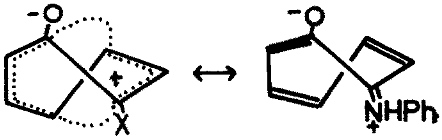
	IIA→IIB	IA→IB*
Ea (Kcal/mol)	24.7	33.5
ΔS^* (e.u.)	- 8.9	- 9.2
	(at 80.1°)	(at 170°)

* See ref. 1.

The Ea value for the isomerization of 1-anilino derivative IIA is smaller than that for 1-methoxy derivative IA, but the ΔS^* value is almost the same for both compounds. For the thermal isomerization of IA to IB and IC, a twisted structure (E) has been proposed as the common trasition state (1,4). Since our experiments suggest that the transition state for IIA → IIB may have an ionic character and have the same grade of rigidity as E, we wish to propose a new twisted transtion state (F) for the isomerization. This transtition state (F) is unique in being composed from an allyl cation and a butadiene unit; its formation is thermally allowed based on orbital symmetry considerations as well as the transition state (E)(4).



E
↓
C



F
↓
B

IID

It should be noted that a variety of substituents located at the C-1 position of the bicyclo[3.2.0]heptadienone system have an influence on the mode of the thermal isomerization. On heating at moderately high temperatures, 1-methoxybicyclo compound IA afforded IB and IC competitively, whereas 1-arylamino compounds IIA ~ VIA gave IIB ~ VIB, and 1-acylamino compounds VIIA and VIIIA afforded VIIC and VIIIC. The substituent effect which may stabilize the ionic transition state (F) is in the following order; NHAr > OCH_3 > NHCOR. The twisted IID may be considered as one canonical structure of the transition state F (X= NHPh). Thus the above results can be explained by assuming that the reaction-mode is affected by relative stability of the transition states (E) and (F).

We are continuing kinetic studies on the Cope rearrangement of 1-acylamino-bicyclo[3.2.0]heptadienones, in order to clarify the ambiguities included in this paper.

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REFERENCES AND FOOTNOTES

1. Organic Thermal Reaction XI. Preceding paper; T. Miyashi, M. Nitta and T. Mukai, J. Am. Chem. Soc., to be submitted.
2. a) W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, J. Am. Chem. Soc., **83**, 1768 (1961); **85**, 2616 (1963). b) T. Mukai and T. Miyashi, Tetrahedron, **23**, 1613 (1967). c) T. Mukai and T. Shishido, J. Org. Chem., **32**, 2744 (1967).
3. G. B. Gill, Quart. Rev. (London). **22**, 338 (1968).
4. R. B. Woodward and R. Hoffmann, Angew. Chem., **81**, 797 (1969).
5. T. Miyashi, M. Nitta and T. Mukai, Tetrahedron Letters, **1967**, 3433.
6. All these compounds were synthesized by irradiation of the corresponding tropone derivatives. T. Mukai and M. Kimura, ibid., **1970**, 717.
7. Microanalyses for all new compounds were obtained and their structures are supported by spectral data.
8. L. A. Paquette and J. H. Barrett, J. Am. Chem. Soc., **88**, 1718 (1966).
9. W. Theuer and J. A. Moore, Chem. Comm., **1965**, 468.
10. According to the communication from Prof. T. Nozoe, bicyclo[3.2.0]heptadienones which possess hydroxyl or amino group at the C-1 position and an electron attracting group such as CN or COOR at the C-5 position underwent the ring opening at very low temperatures leading to the corresponding tropone derivatives. T. Nozoe, T. Hirai, T. Kobayashi and J. Tsunetsugu will report the result at the IUPAC Symposium on Nonbenzenoid Aromatic Compounds which will be held in Sendai, in August, 1970.