The Photochemical and the Thermal Reaction of Dimethyl *trans*-Spiro[2.6]nona-4,6,8-triene-1,2-dicarboxylate[1]

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The irradiation of dimethyl *trans*-spiro[2.6]nona-4,6,8-trien-1,2-dicarboxylate (I) with a low-pressure mercury lamp afforded two tricyclic valence isomers (II and III). Upon heating, II and III were converted into dimethyl *trans*-indan-1,2-dicarboxylate (IV), which was also obtained by the thermolysis of I. In order to elucidate the reaction mechanism for the formation of IV from I, we studied the thermal reaction using a deuterium-labelled compound (V).

Dimethyl *trans*-spiro[2.6]nona-4,6,8-trien-1,2-dicarboxylate (I)[2,3] is an interesting unsaturated cyclic compound; it possesses both a cycloheptatriene and a cyclopropane ring, like the spiro system. Therefore, it seems that it would be interesting to study the thermal photochemical reactions of I to distinguish whether such a compound behaves as a spiro compound,[3-8] as a cyclopropane derivative, or as a cycloheptatriene derivative. It has already been reported by Jones and Ennis[3] and by our group[2] that I, when heated over 150 °C, easily rearranged to dimethyl *trans*-indan-1,2-dicarboxylate (IV). On the other hand, however, no photochemical study of I has ever been reported. We investigated the photoreaction of I and found that I exhibited the photochemical valence isomerization characteristic of the cycloheptatriene moiety.[9-14] In addition, the reaction mechanism of the thermolysis of I leading to IV was studied using a deuterized spiro compound (V). In this paper, we wish to report the results obtained concerning the photoreaction and the reaction mechanism of the thermolysis of I.

The irradiation of I, which has an absorption maximum at 263 nm (log ε, 3.52) and a tailing around 350 nm (log ε, ca 2.5), using a high-pressure mercury lamp, did not cause any photoreaction, but resulted in the recovery of I in a quantitative yield. The benzophenone-sensitized photoreaction of I also resulted in the recovery of I. On the other hand, when the irradiation of I was carried out in a quartz vessel using a low pressure mercury lamp, a crystalline material (II)(mp 105.5 °C), and an oily substance (III) were obtained in 23 and 22% yields respectively. When methanol, ether and *n*-hexane were used as the solvents, no solvent effect was observed. Under these irradiation conditions, no interconversion between II and III was detected; this fact indicated that II and III were the primary photoproducts.

The two products, II and III, have the same molecular formula, $C_{13}H_{14}O_4$, and the same molecular ion peak (M^+, 234) in their mass spectra. In addition, they possess almost the same spectral properties: IR ($CHCl_3$), 1720, 1440, 1340, and 1160 cm^{-1}; UV (methanol), 225 nm (log ε, 3.39). Their NMR spectra are shown in Table 1, while the coupling constants as determined by the double and triple resonance techniques are shown in Table 2. These data support the idea that II and III are isomers of I, and that they are stereoisomers with relation to each other. In addition, the chemical shifts and coupling constant of the H_c–H_h protons of II and III are similar to those of the corresponding protons of the bicyclo[3.2.0]hept-2,5-diene derivatives.[10-14] The H_a and H_b protons are assigned to the cyclopropane protons which are located in the *trans*-configuration on the basis of the chemical shifts, which are coincident with those of the cyclopropane protons of I, and the coupling constant (5.5 Hz).[15] Thus, the structure shown in Fig. 1 are proposed for II and III.

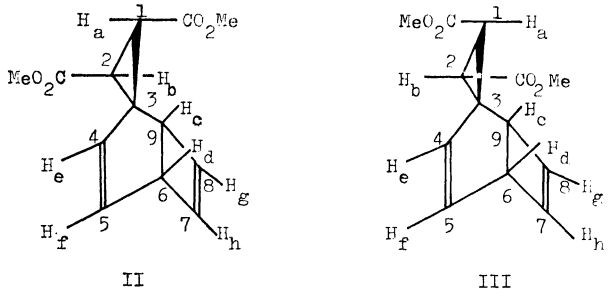


Fig. 1.

The configuration of the two ester groups of II and III could be deduced from the chemical shifts of their H_c and H_g values. The signals of the H_c of II appear at a higher field than those of the H_c of III, and the signals of the H_g of II come at a lower field than those of the H_g of III, while the chemical shifts of the other hydrogens of II and III do not differ very much from each other. By an investigation of the Dreiding models of II and III, the ester group at C_1 of II is found to be closer to H_c; also the H_g of III is closer to the ester group at C_2. Furthermore, by the repulsion between the ester group at C_1 and the cyclopropane protons, the conformation in which the sp^2 plane of the ester carbonyl group is set over to H_c is the most stable form of II; also, for the same reason, in the case of III H_g is

TABLE 1. CHEMICAL SHIFTS OF II AND III (δ ppm) (100 MHz, in $CDCl_3$)

	H_a	H_b	H_c	Ester Me	H_d	H_e	H_f	H_g	H_h
II	2.45	2.57	3.19	3.64, 3.66	3.73	5.61	5.97	6.16	6.40
III	2.43	2.54	3.36	3.67, 3.69	3.80	5.56	6.05	5.78	6.39

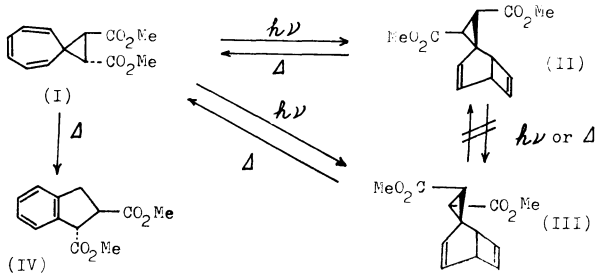
Table 2. Coupling constants of II and III (Hz)

	J_{ab}	J_{cd}	J_{df}	J_{dh}	J_{ef}	J_{gh}	J_{ce}
II	5.5	3.5	2.5	~1	5.5	3.0	~1
III	5.5	3.5	2.5	~1	5.3	3.0	1.0

covered by the sp^2 plane of the ester group at C_2. Thus, considering the anisotropic effect of the ester groups, the differences in the chemical shifts of H_c and H_g in II and III can be reasonably explained by those models.

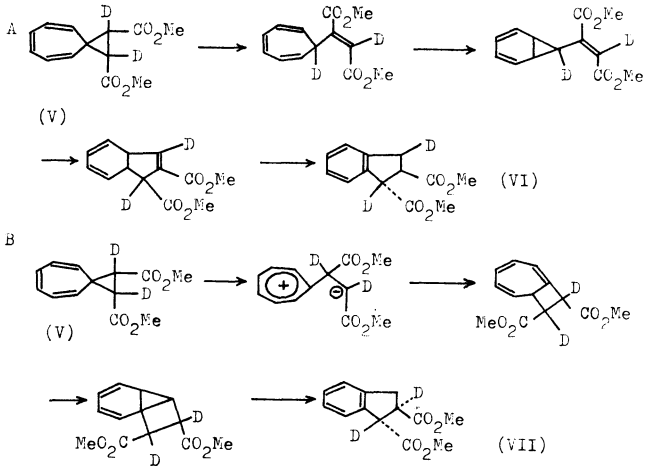
The results obtained above make it clear that the irradiation of I did not undergo a reaction involving the cyclopropane ring; instead, the cycloheptatriene ring dominated its photoreaction. The fact that this photoreaction was not sensitized by benzophenone is compatible with the fact that the photovalence isomerization of the cycloheptatriene derivatives proceeds *via* singlet excited states.[11,12] In addition, it should be noted that both ring-closure products, II and III, were formed in almost the same yield, the yields being 22 and 23% respectively. This seems to prove that the ester groups located near the reaction center do not have any effect on the photochemical ring closure of I, either stereochemically or electronically.

The photoproducts, II and III, were fairly stable to heat, and they were recovered when the thermolysis was attempted by a flow method by heating about 350 °C. Above 400 °C, however, both II and III gave the same pyrolyzate, dimethyl *trans*-indan-1,2-dicarboxylate (IV), in good yields. Since I is transformed thermally to IV under less severe pyrolyzing conditions (about 150 °C), it is most probable that II and III, upon heating, are converted first into I by the ring opening and are then rearranged to IV (Scheme I).



Scheme 1.

Previously, Mukai, Nakazawa, and Isobe suggested the possibility of two reaction paths for the rearrangement of I to IV.[2] Recently, Jones and Ennis also investigated this rearrangement; they pointed out that the rate of the rearrangement depended on the nature of the solvents, and proposed an ionic mechanism resembling the mechanism of Mukai *et al.*[3] Therefore, the following two mechanisms (A and B shown in Scheme 2) are proposed for the rearrangement of I to IV. In order to investigate the adequacy of the mechanisms, A and B, we did the same thermolysis using a dideuterized spiro compound (V), which had been synthesized by the addition reaction of dideuterized dimethyl maleate with cycloheptatrienylidene.[2,3]



Scheme 2.

As Scheme 2 exhibits, if the reaction proceeds *via* Mechanism A, dimethyl *trans*-1,3-dideuteroindan-1,2-dicarboxylate (VI) will be formed, whereas if Mechanism B occurs, 1,2-dideuteroindane derivative (VII) is formed. On the basis of the NMR spectral data, the indane derivative obtained here found to be VII, not VI. That is, in the NMR spectrum of IV, the methylene protons at the C_3-position and the two methine protons at the C_1- and C_2-positions show their signals at δ 3.1, 3.9 and 4.6 respectively, whereas the indane derivative obtained from V exhibits peaks of the methylene protons at δ 3.1, but does not show any peak ascribed to the methine protons. These results fit VII and confirm that the thermal rearrangement of I proceeds *via* Mechanism B.

Experimental[16]

Photoreaction of I. A solution of I (1.50 g) in *n*-hexane (1.5 l) was irradiated with a low-pressure mercury lamp (Rayonet 2537 Å) in a quartz vessel for 44 hr under a nitrogen atmosphere. After the removal of the resinous substances (100 mg), a yellow oily product (1.4 g) was obtained and subsequently chromatographed on alumina (50 g). A crystalline product (A)(400 mg) was eluted with petroleum ether–benzene (4 : 1); 261 mg of an oily product (B) with petroleum ether–benzene (7 : 3); 174 mg of the starting substance with benzene, and 475 mg of a tarry material with methanol. The crystalline product (A) was found to contain II (60%) and III (40%) by vpc analysis (20% Ucon 50 LB; Chromosorb W; temp. 150 °C). In the same way, the oily product (B) was found to contain II, III, and the starting material in percentages of 18, 42, and 40% respectively. The total yields of II and III were 287 mg and 270 mg (23 and 22%) respectively. Both products were purified by recrystallization from methanol and by distillation. II, mp 104.5—105.5 °C. Found: C, 66.43; H, 6.09%. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02%. IR(KBr); 1720, 1440, 1340, and 1160 cm^{-1}. Mass; M^+, 234 at 70 eV. III, oil bp 105 °C/1 mm Hg. Found: C, 66.51; H, 5.92%. Calcd for $C_{13}H_{14}O_4$; C, 66.65; H, 6.02%. IR ($CHCl_3$); 1720, 1440, 1340, and 1160 cm^{-1}. Mass; M^+, 234 at 70 eV.

Thermal Rearrangement of II and III. We attempted to pyrolyze a solution of II (34 mg) in benzene (20 ml) by passing it under a nitrogen stream (30 ml/min) through a quartz tube (9 mm × 45 cm) preheated at 350 °C which

contained quartz pieces. After the removal of the solvent, a white crystalline product was obtained. NMR and vpc studies of the obtained product showed that the crystalline product contained IV and the starting substances in 2.6 and 97.4% yield respectively.

The pyrolysis at a higher temperature (420 °C) resulted in the formation of IV and the recovery of II in 82% and 18% yields respectively. The NMR spectrum and the retention time of the vpc of IV were in accordance with those of an authentic sample of dimethyl *trans*-indan-1,2-dicarboxylate.[2]

By the same procedure at 400 °C, III gave IV in an 80% yield, accompanied by the recovery of III in a 20% yield.

Preparation and Thermal Rearrangement of Dimethyl trans-*1,2-dideuterospiro[2.6]nona-4,6,8-trien-1,2-dicarboxylate (V).* V was formed from the addition reaction of dimethyl dideuteromaleate with troponetosylhydrazone sodium salt by the methods of Jones and Ennis[3] and Mukai *et al.*[2] The thermolysis of V was carried out under the same conditions as were used by Mukai *et al.*[2] Mass; M^+, 236 at 70 eV.

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16) All mp were uncorrected. NMR spectra were measured by Varian-HA-100 spectrometer, and referred to TMS as an internal standard.