

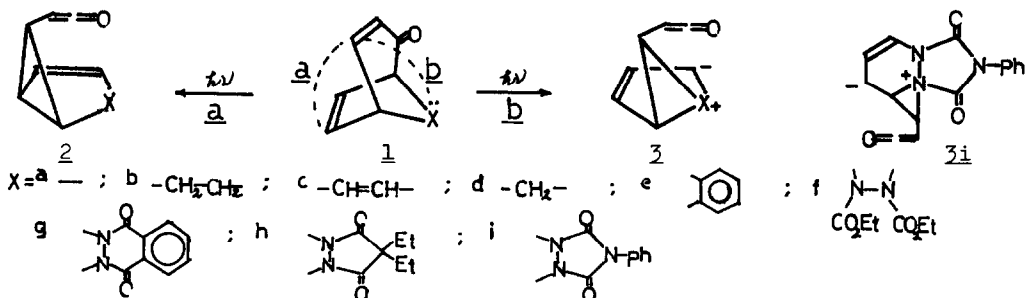
MECHANISM OF THE PHOTO-REARRANGEMENT OF ARYL-6,7-DIOXABICYCLO[3.2.2]-  
NONA-3,8-DIEN-2-ONE INTO TRICYCLIC LACTONE

T. Tezuka, R. Miyamoto, M. Nagayama and T. Mukai

Department of Chemistry, Faculty of Science, Tohoku University  
Sendai, Japan

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It has been shown that the enone- $\pi$  interaction (shown by a) is inherent to the excited state of homoconjugated cyclic dienones (1a~h), which brings about the photo-Cope rearrangement probably through their singlet states, giving rise to the formation of the ketenes (2a~h)(1,2,3). Recently, however, Sasaki and co-workers have reported that in the dienone (1i) the enone-lone pair electrons interaction (shown by b) competed with the enone- $\pi$  interaction giving rise to the formation of 3 (or 3i) along with 2 (or 2i)(4). Some time ago we reported a novel photo-rearrangement of 4a and 4b into 5a and 5b, respectively (5). In view of the increasing interest in the interaction of enone- $\pi$  v.s. enone-lone pair electrons in the homoconjugated system containing hetero atoms, we studied the mechanism of the rearrangement of 4 to 5 by carrying out a low temperature photolysis, and found that the rearrangement was induced by the enone- $\pi$  interaction in 4. This report concerns our studies on this point.



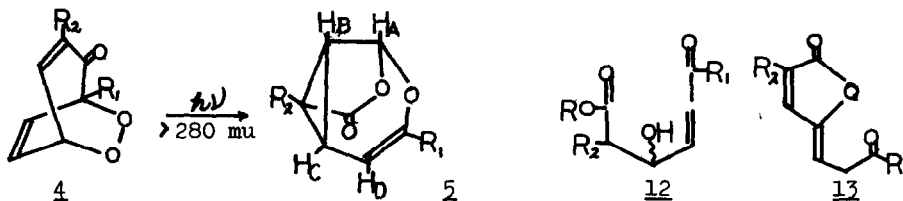
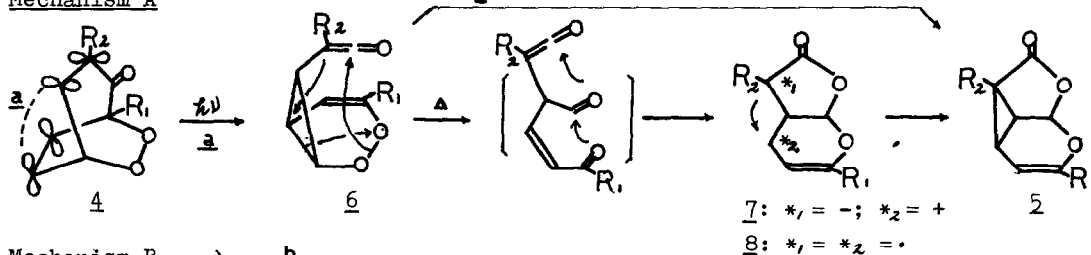
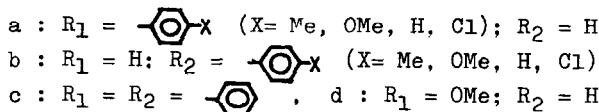
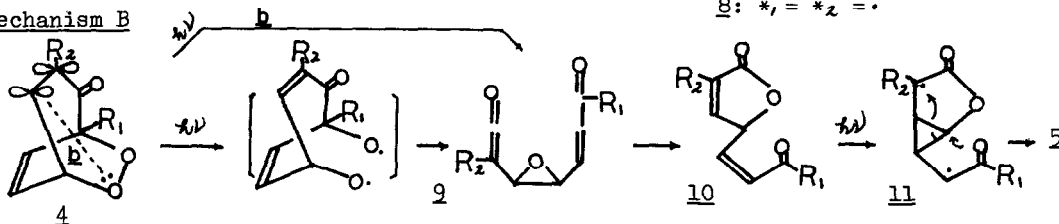
As previously postulated (5), there are two mechanistic paths A and B to account for the rearrangement of 4 to 5. In mechanism A, the reaction starts

with the enone- $\pi$  interaction (a), which gives the ketene intermediate (6). Then, 6 rearranges thermally to 5 either by a concerted  $\pi^2_s + \sigma^2_s + \sigma^2_s$  manner as shown by the arrows, or by the stepwise way via 7 or 8. On the other hand, in mechanism B the reaction begins with the enone-lone pair electrons interaction (b) or by the cleavage of the O-O bond, by which ketene (9) is produced (6). The ketene (9) is transformed thermally to 10 which is then photochemically converted to 5 via 11. We suggested in the previous paper that the enone- $\pi$  interaction may play an important role in the rearrangement of 4 to 5. In order to establish the mechanistic path definitely, the following studies were undertaken.

A suitable model compound (4c) for this study was prepared. Diphenyl derivative (4c), m.p. 137° C was obtained by the action of singlet oxygen with 2,7-diphenyltropone (7), which has the following spectral properties:  $\lambda_{\text{max}}^{\text{EtOH}}$  290 ( $\epsilon=9384$ ), 350 (tailing,  $\epsilon=4500$ );  $\nu_{\text{CO}}$  1680  $\text{cm}^{-1}$ . Photolysis of 4c under the same conditions as in the case of 4a (or 4b), afforded in 35% yield tricyclic lactone 5c, m.p. 154° C;  $\nu_{\text{CO}}$  1780  $\text{cm}^{-1}$ ; nmr ( $\delta_{60}^{\text{CDCl}_3}$  Mc), 6.57 ( $H_A$ ; d.d.,  $J_{A,B}=5.0$  Hz), 5.99 ( $H_D$ ; d.,  $J_{D,C}=4.4$  Hz), 3.07 ( $H_B$ ; d.d.,  $J_{B,C}=8.0$  Hz), 2.31 ( $H_C$ ; d.d.). By comparing its spectral properties with those of 4a and 4b (5) the structure 5c was confirmed.

After irradiation of 4c as a KBr disc at -196° C with a high pressure Mercury lamp through a Pyrex filter for 45 min, the infrared spectrum was measured, which showed a ketene band at 2100  $\text{cm}^{-1}$  with disappearance of the band at 1680  $\text{cm}^{-1}$  of 4c. On warming to the room temperature, the 2100  $\text{cm}^{-1}$  band disappeared completely to give a new band at 1780  $\text{cm}^{-1}$  corresponding to the lactone 5c. The same result was obtained with the low temperature photolysis of 4c in nujol null. These facts point to that a ketene was formed by the photochemical process, which then thermally rearranged to 5c. The mechanism best fitted to this observation is A, in which the intermediate ketene (6) is transformed thermally into 5.

If the intermediate ketene is 9c instead of 6c, a solvent addition product such as 12c would be formed by the photolysis of 4c in alcoholic solvents. Forbes, et al. have obtained the solvent addition product (12d) from 9d (6).

Mechanism AMechanism B

Contrary to this, the ketene (6) may probably not form the solvent addition product. Due to the oxide group in 6, the intramolecular addition reaction of the oxide oxygen to the ketene may be overwhelming to the solvent addition reaction. With these in mind, photolysis of 4c in ethanol or methanol was carried out. The sole product obtained was 5c. No solvent addition products were detected. The same results were obtained for the photolysis of 4a and 4b (X=Me) in ethanol solvent. These facts support the conclusion obtained from the low temperature photolysis that the ketene initially formed by the photo-reaction was 6c.

As previously reported (5), the fact that the photolysis of 10d afforded isomeric lactone (13d) arising by the hydrogen shift in good yield suggests that even if 10 is formed from 4, it isomerizes photochemically to the lactone 13, rather than it rearranges to 5. From all the facts cited, the mechanism A was assigned for the rearrangement of 4 to 5.

In the mechanism A there are two or three pathways to derive 5 from the

ketene 6. The observed substituent effects reported in our previous paper (5) may support the stepwise path from 6 to 5 via the zwitterionic intermediate (7) rather than via the biradical (8). Furthermore, the concerted  $\pi^2_s + a^2_s + a^2_s$  addition path as shown by the arrows may be ruled out. It has been shown that in the rearrangement of 4a to 5a in which  $R_1$  and  $R_2$  are aryl and hydrogen respectively, the electron donating substituent at  $R_1$  increased the yield of 5a, whereas the electron attracting substituent at  $R_1$  decreased the yield of 5a. In the case of 4b to 5b, the situation became just the reverse (5). These facts may best be interpreted as that the rearrangement of 6 to 5 proceeds through the ionic intermediate (7). When 7 is stabilized (or destabilized) by either substituent  $R_1$  or  $R_2$ , the yield of 5 increases (or decreases).

The multiplicity of the rearrangement was examined. The formation of 5c from 4c was neither quenched nor sensitized, suggesting that the singlet state was responsible for the rearrangement of 4 to 6 (2). It is important to note that despite the presence of the photolabile dioxide group and the fact that the lone pair electrons of the dioxide are capable of interacting with the enone part in 4, the enone- $\pi$  interaction in the excited state of 4 still makes a significant contribution to the photo-reaction of 4.

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