CHEMISTRY LETTERS, pp. 1203-1206, 1979. Published by the Chemical Society of Japan

PHOTOREACTIONS OF KETONES IN STRONG ACID MEDIA. A NOVEL TYPE REARRANGEMENT IN CYCLIC β-DICARBONYL SYSTEM

Tadashi SATO*, Katsuyuki NAGUMO, Kimitoshi SAITO, Toshiyuki OHYAMA⁺
and Ryohei NAKANE⁺
Department of Applied Chemistry, Waseda University, Ookubo 3,
Shinjuku, Tokyo 160
+ The Institute of Physical and Chemical Research, Wako, Saitama 351

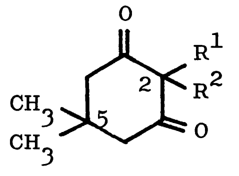
Cyclic β-dicarbonyl compounds 1a, 1b, 10a and 10b undergo isomerization involving reconstruction of the ring system by the UV-irradiation in strong acid media. It is suggested that the isomerization is aided by the formation of stabilized cation after the ring opening.

The photochemistry of ketones in strong acid media has been characterized by the unique reaction pattern induced by the controlled excitation due to the protonation of the carbonyl group. The acid-induced photoreaction of cycloheptadienone system has been studied extensively, and isomerization to bicyclo system and ring contraction have been reported as typical reaction patterns.$^{1)}$ These reactions are explained by the initial electrocyclic opening of the seven-membered ring.

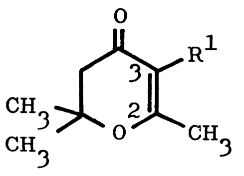
In connection with characteristic effects of metal ions on organic photoreactions, as observed in our laboratories$^{2)}$, we are interested in comparing the titanium(IV) chloride-catalyzed photoreaction of ketones with the photoreaction of protonated ketones, and found now that cyclic β-diketones underwent a novel type isomerization of the ring system by the photolysis in strong acid media.

Irradiation of 1a in FSO_3H or 98% H_2SO_4 with quartz-filtered light (high-pressure mercury lamp, Ushio UM 452 (450 W)) for 24 h and subsequent work-up with water gave 2a as a sole product in 19% yield. The solution became darkened toward the end of irradiation, and the longer irradiation did not increase the yield. Although the isolated yield of 2a was low, the NMR analysis of the acid solution after the irradiation revealed that no other signals were noticeable except those of 2a and the starting material. Similarly the methyl derivative 1b afforded 2b in 18% yield, but the compound 1c, lacking hydrogen on C2, failed to give any product under the same conditions. The presence of the gem-dimethyl substituents at C5 is necessary for the present reaction to proceed, and compounds 3a-3c were recovered unchanged under the same conditions. The structures of 2a and 2b were identified by comparing spectroscopic data with the reported values.$^{3)}$

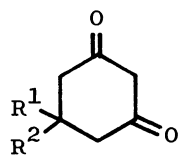
The present reaction could be schemed in the following way. The starting ketone 1a, which exists as a protonated form 1aH in acid media4), undergoes, upon irradiation, a C4-C5 bond fission to give a cation 4aH, and the cation gives the product 2a by the ring closure between carbon and oxygen atoms. The alternative path involving electrocyclic ring opening of the cyclohexadiene system 5, as advocated in cycloheptadienone system, was considered and ruled out by the following experiment in D_2SO_4. When 1a was irradiated in D_2SO_4 and worked-up with H_2O, a deuterated 2a was obtained. The NMR and mass spectroscopic analyses of the product indicated that 100% of one proton on C2-methyl group and 84% of C3-proton had been exchanged with deuterium. Since it was confirmed separately that C3-deuterium in the deuterated 2a was exchangeable with the proton in water under the work-up conditions, it was concluded that the primary product of the reaction in D_2SO_4 is a dideuterated compound 6, from which 16% of C3-D was expelled by proton during the work-up procedure. In spite of the deuteration at C3 and C2-methyl group, no indication of exchange of C5-proton with deuterium was observed at all in this



1



2



3

1, 2

a: $R^1 = R^2 = H$

b: $R^1 = CH_3,\ R^2 = H$

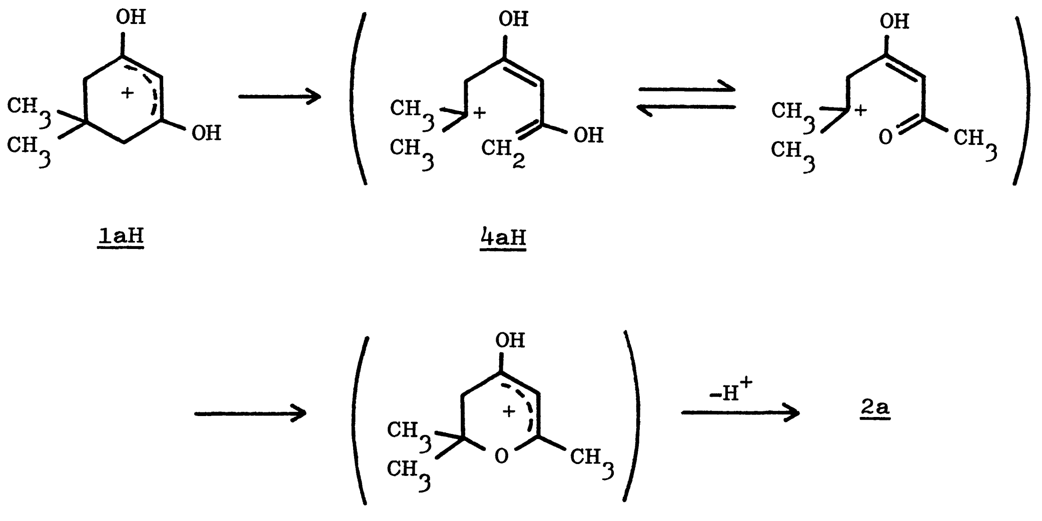
c: $R^1 = R^2 = CH_3$

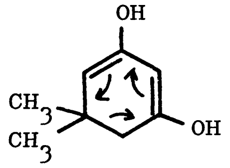
3

a: $R^1 = CH_3,\ R^2 = H$

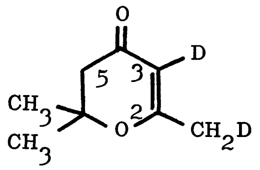
b: $R^1 = C_6H_5,\ R^2 = H$

c: $R^1 = R^2 = H$

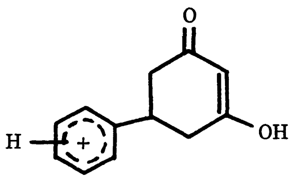




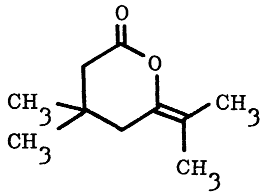
5



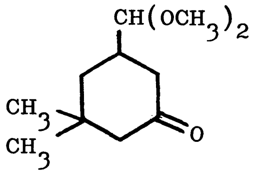
6



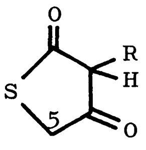
7



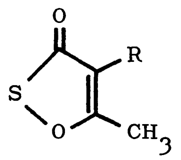
8



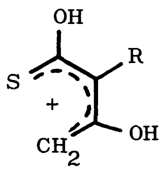
9



10



11



12

a: R = H; b: R = $COCH_3$

reaction, and the possibility of intervening 5 was thus eliminated.

The driving force for the present reaction seems to be a ring cleavage to give a cation 4aH, stabilized by two methyl groups. The failure of the phenyl derivative 3b to undergo the isomerization might be ascribable to the protonation on the phenyl ring as shown in 7.

The photoreaction of cyclic β-diketones under the unprotonated conditions might be worth mentioning here. It is reported$^{5)}$ that compound 1c, upon irradiation in benzene, undergoes C1-C2 bond cleavage followed by recyclization to give 8. This reaction proceeds irrespective of the presence or absence of the methyl group(s) on C5. In the present study we confirmed that cyclic β-diketone having no methyl group on C2, such as 1a, was intact under the irradiation in methanol. Previously we reported that the irradiation of 1a in methanol in the presence of titanium(IV) chloride gave 9 as major product.$^{6)}$ Evidently complexation with titanium(IV) chloride and protonation lead to the entirely different reaction pattern.

The same type rearrangement through 1,3-shift was also observed with sulfur-containing cyclic β-diketones. Irradiation of <u>10a</u> in FSO_3H with quartz- or Pyrex-filtered light and subsequent work-up with water afforded <u>11a</u> in 76% yield. Similarly <u>10b</u> afforded <u>11b</u> in 49% yield. The NMR analyses indicated that no other products are present in the acid solution after the irradiation in both cases.

There seems to be no precedent of the 3-oxo-3H-1,2-oxathiole ring system, and the structures of the products <u>11a</u> and <u>11b</u> were confirmed by spectroscopic data.7) The reaction could be schemed as involving S-C5 bond fission and recyclization with the formation of S-O bond. Again, the stabilization of the ring-opened system <u>12</u> through the intervention of sulfur atom might be responsible for the present isomerization to proceed.

REFERENCES

1) R. F. Childs and Y. C. Hor, Can. J. Chem., <u>55</u>, 3501 (1977), and references cited therein.
2) T. Sato, S. Yamaguchi, and H. Kaneko, Tetrahedron Letters, <u>1979</u>, 1863.
3) S. Gelin and R. Gelin, Bull. Soc. Chim. Fr., <u>1968</u>, 288; ibid., <u>1969</u>, 4091.
4) G. A. Olah and M. Calin, J. Am. Chem. Soc., <u>90</u>, 4672 (1968).
5) H. Nozaki, Z. Yamaguchi, T. Okada, R. Noyori, and M. Kawanisi, Tetrahedron, <u>23</u>, 3993 (1967).
6) T. Sato, S. Yoshiie, T. Imamura, K. Hasegawa, M. Miyahara, S. Yamamura, and O. Ito, Bull. Chem. Soc. Jpn, <u>50</u>, 2714 (1977).
7) <u>11a</u>: MS, m/e 116 (M), 88, and 43. IR, 1710-1745 and 1630 cm^{-1}. ^1H NMR, δ(ppm from TMS in CCl_4), 2.11 (d, J = 1.2 Hz, 3H), and 5.15 (q, J = 1.2 Hz, 1H). <u>11b</u>: mp 72-73.5°C. MS, m/e 158 (M), 114, 87, and 43. IR, 1745, 1650, and 1610 cm^{-1}. ^1H NMR, δ(ppm from TMS in CCl_4), 2.3 (s, 3H) and 2.5 (s, 3H). ^{13}C NMR, δ(ppm from TMS in $CDCl_3$), 189 (acetyl carbonyl), 168 (C3), 153 (C5), 118 (C4), 30 (C2-methyl), and 15 (acetyl methyl).

(Received June 25, 1979)