CHEMISTRY LETTERS, pp. 175-178, 1977. Published by the Chemical Society of Japan

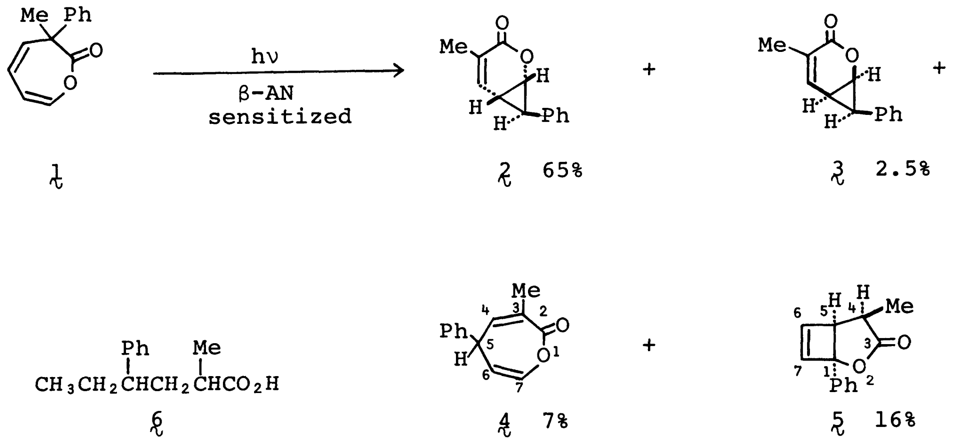
REVERSE DI-π-METHANE REARRANGEMENT.
MINOR PRODUCTS OF PHOTOLYSIS OF 3-METHYL-3-PHENYL-2(3H)-OXEPINONE

Kazuhiro SATO, Hisahiro HAGIWARA, and Hisashi UDA
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira-2, Sendai 980

The structures of two minor products from the sensitized photolysis of 3-methyl-3-phenyl-2(3H)-oxepinone have been confirmed to be 3-methyl-5-phenyl-2(5H)-oxepinone and 4-methyl-1-phenyl-2-oxabicyclo[3.2.0]hept-6-en-3-one, respectively. Both of them are shown to be produced, on direct photolysis, from the major photoproduct, 4-methyl-7-phenyl-2-oxabicyclo[4.1.0]hept-4-en-3-one, through the formal reverse di-π-methane rearrangement.

We recently reported that the β-acetonaphthone (β-AN) sensitized photolysis of 3-methyl-3-phenyl-2(3H)-oxepinone (**1**) gave, through a novel rearrangement involving photoinduced 1,4-phenyl migration, 4-methyl-7-phenyl-2-oxabicyclo[4.1.0]hept-4-en-3-ones (**2**) and (**3**).[1] We now wish to report the structures of two minor products in this reaction, arising from the photochemical rearrangement of **2**, which are the first examples of the formal reverse di-π-methane rearrangement.[2]

In the scale-up sensitized photolysis of **1**,[3] we found the presence of two minor products, in addition to **2** and **3**, in the crude photolysate, which were detected at the slightly upper and lower positions of the β-AN spot (partially overlapped) on a silica gel tlc plate. Repeated tlc and the removal of β-AN by recrystallization from a mixture of benzene and hexane gave the pure products **4** and **5** in ca. 7 and 16% yields, respectively.[4] Spectral data of **4** were in accord with the assigned structure, 3-methyl-5-phenyl-2(5H)-oxepinone: ir (CHCl$_3$) 1715 (br.) cm^{-1}; uv (EtOH) λ_{max} 202 nm (ε 19000); ^{1}Hnmr (100 MHz, CDCl$_3$, TMS) δ 1.97 (3H, finely splitted s, >-Me), 4.31 (1H,



1

2 65%

3 2.5%

$CH_3CH_2\underset{}{C}HCH_2CHCO_2H$ (Ph on C-3, Me on C-5)

6

4 7%

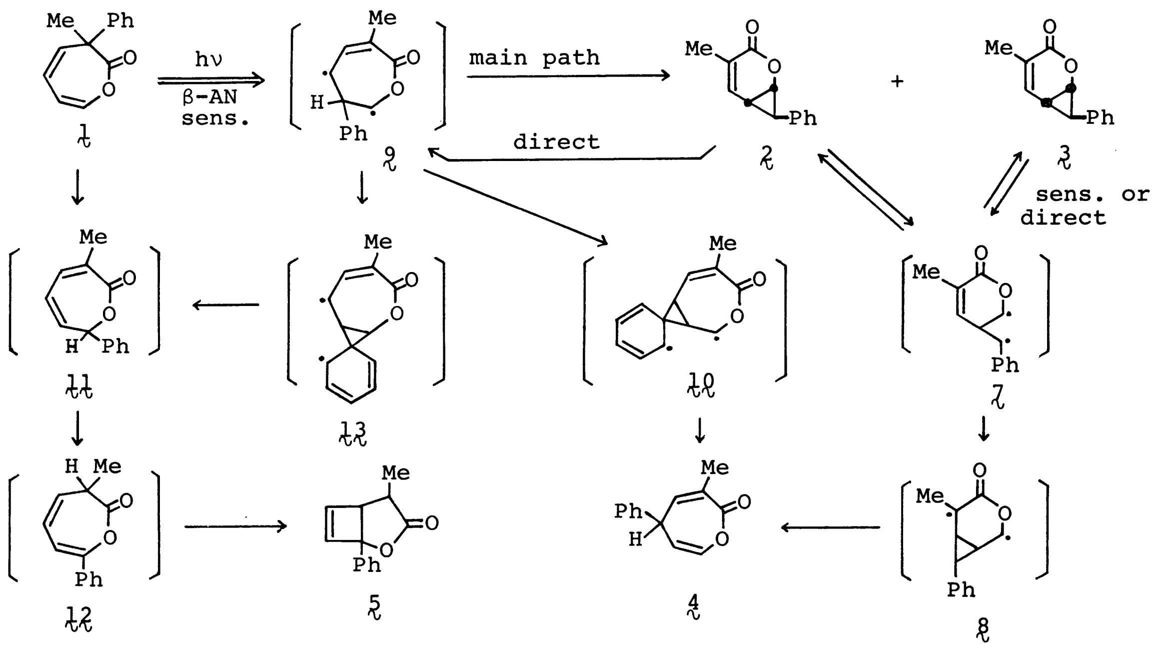
5 16%

m, H-5), 5.50 (1H, t, J_{56} = J_{67} = 6.4 Hz, H-6), 6.38 (1H, dd, J_{57} = 2 Hz, H-7), 6.47 (1H, finely splitted d, J_{45} = 5.5 Hz, H-4), and 7.08–7.46 (5H, m, phenyl); ^{13}Cnmr ($CDCl_3$, TMS) δ 20.74 (Me), 41.37 (C-5), 119.58 (C-6), 127.28 (aromatic C-2), 127.89 (aromatic C-4), 128.44 (C-3), 129.04 (aromatic C-3), 139.48 (C-4), 141.60 (aromatic C-1), 146.64 (C-7), and 165.57 (C-2). On catalytic reduction (PtO_2–MeOH) the product **4** underwent complete hydrogenolysis of the enol-lactone linkage giving rise to a saturated carboxylic acid in 75% yield, which was found to be a mixture of the diastereomers of 2-methyl-4-phenylcaproic acid (**6**) from the spectral properties of the free acid and the methyl ester, and difinitely identified with the authentic sample.[5] The structure of **5**, 4-methyl-1-phenyl-2-oxabicyclo[3.2.0]hept-6-en-3-one, was assigned on the basis of the following evidence: ir ($CHCl_3$) 1770 and 1760 cm^{-1}; ^{1}Hnmr (100 MHz, C_6D_6, TMS) δ 0.99 (3H, d, J = 7.5 Hz, -CH<u>Me</u>), 2.31 (1H, dq, J_{45} = 9.5 Hz, H-4), 2.88 (1H, d, H-5), 5.93 and 6.10 (1H each, each d, J_{67} = 2.9 Hz, H-6 and H-7), and 7.00–7.32 (5H, m, phenyl); ^{13}Cnmr ($CDCl_3$, TMS) δ 10.98 (Me), 38.70 (C-4), 54.36 (C-5), 87.97 (C-1), 125.22 (aromatic C-2), 128.25 (aromatic C-4), 128.50 (aromatic C-3), 137.48 (aromatic C-1), 141.30 (C-6 or C-7), 143.12 (C-7 or C-6), and 178.91 (C-3), and finally confirmed by comparison with the authentic sample.[6] Configuration of the methyl group, being *endo*, was assigned from the coupling constant (9.5 Hz, *cis* coupling) between H-4 and H-5.[8] Thus, it is apparent that compound **4** would be produced formally from **1** through a 1,3-phenyl migration, while compound **5** through a 1,5-phenyl migration, a subsequent 1,5-hydrogen shift, and photocyclization of the resulting 2(3*H*)-isomer (**12**).[9]

In order to clarify the pathways for the formation of these photoproducts **2**–**5**, we have examined the photolyses of **2**–**5** under the identical conditions (ether, room temperature, a 500-W high-pressure mercury lamp through a Pyrex filter) and observed the following results:

	Compound	β-AN	Time (min)		Products
Run 1	**2**	1 equiv	300	⟶	**2** + **3** + **4** 13% 7.4% 61%
Run 2	**3**	"	"	⟶	**2** + **3** + **4** 10% 37% 20%
Run 3	**4**	"	"	⟶	**4** + complex mixture >77% recovery
Run 4	**5**	"	"	⟶	**5** 100% recovery
Run 5	**2**	0	100	⟶	**4** + **5** 60% 7.7%
Run 6	**1**	1 equiv	95	$\xrightarrow[-60°]{\text{in MeOH}}$	**2** + **3** + **4** 65% 3.2% 24%
Run 7	**1**	"	300	$\xrightarrow{\text{in hexane}}$	**2** + **3** + **4** + **5** 30% 3.5% 24% 30%

From these results, the following conclusions can be drawn. It is apparent that compound **4** was formed, on both sensitized and direct (more efficiently) photolyses, from compound **2** (or **3**), not directly from **1** *via* a 1,3-phenyl migration. Clearly, the process from **2** to **4** is structurally the conversion of a vinylcyclopropane system into



a 1,4-diene system, and thus, is most reasonably accounted for by the formal reverse di-π-methane rearrangement through the diradical intermediate 7 leading to 8 or 9, which has been proposed as the plausible intermediate leading to 2 and 3 from 1, leading to 10.[10] The latter process (2→9→10→4), however, seems unlikely under the sensitized condition (Run 1), since it would be also expected to produce compound 5 (see below).

The precursor of compound 5 is probably 3-methyl-7-phenyl-2(3H)-oxepinone (12) which would arise from the 1,5-hydrogen shift of the 2(7H)-isomer (11)[12] as described earlier. For the formation of 11, in contrast to no isolation of 5 in the sensitized photolysis of 2 or 3 (Run 1 and 2), the actual formation of 5 from 1 suggests that the direct 1,5-phenyl migration in 1 would be one of the possible reaction pathways. However, the fact that 5 was produced from 2 by direct irradiation indicates that there would be an alternative pathway to provide 11. The formation of 11 from 2 is explained by assuming the diradical 9 and the subsequent phenyl bridging leading to 13 and cleavage to give 11. This process is also the formal reverse di-π-methane rearrangement.[13]

On the photolysis of 1, the reaction pathways of the common intermediate 9 would be greatly affected by the solvent used; methanol (protic solvent) may prevent markedly the pathway leading to 13, whereas hexane (aprotic nonpolar solvent) does not (Run 6 and 7).[14]

References and Notes

1) K. Sato, H. Hagiwara, H. Uda, M. Sato, and N. Harada, J. Am. Chem. Soc., 98, 8281(1976).
2) For the excellent reviews of di-π-methane and oxa-di-π-methane rearrangements see S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, Chem. Rev., 73, 531 (1973); K. N. Houk, ibid., 76, 1 (1976).
3) A solution of 1 (1.0 g) and β-AN (0.85 g, 1 equiv) in ether (500 ml) was irradiated

for 270 min with a 500-W high-pressure mercury arc lamp through a Pyrex filter at room temperature.

4) These compounds gave satisfactory elemental analyses.

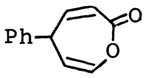
5) Prepared by sequential treatment of α-phenylbutyraldehyde with the dianion of propionic acid at −45°C to give a hydroxy carboxylic acid, esterification with diazomethane, dehydration with thionyl chloride–pyridine at 90°C to a mixture of unsaturated esters, and catalytic hydrogenation on platinum oxide.

6) Prepared by photocycloaddition of 3-methyl-5-phenyl-2(3*H*)-furanone[7] to acetylene.

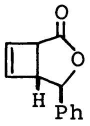
7) F. Ramirez and M. R. Rubin, J. Am. Chem. Soc., **77**, 3768 (1955).

8) (a) O. L. Chapman and E. D. Hoganson, J. Am. Chem. Soc., **86**, 498 (1964); L. A. Paquette, ibid., **86**, 500 (1964); H.-D. Becker and K. Gustafsson, Tetrahedron Lett., 1705 (1976); (b) H. Kosugi, S. Sekiguchi, R. Sekita, and H. Uda, Bull. Chem. Soc. Jpn., **49**, 520 (1976).

9) Similarly, compounds **i** (detected by nmr, inseparable from β-AN) and **ii** (7%) were obtained as the minor products from the sensitized photolysis of 3-phenyl-2(3*H*)-oxepinone.[1] Direct photolysis of the major photoproduct (corresponding to **2**) of the above oxepinone under the same condition as Run 5 also gave both **i** (58%) and **ii** (trace, detected by tlc). Compound **ii** was identified with the authentic sample prepared by photocycloaddition of 5-phenyl-2(5*H*)-furanone to acetylene.



i



ii

10) Photochemical rearrangement of benzonorcaradienes to benzobicyclo[3.2.0]heptadienes has been accounted for by sequential 1,5- and 1,3-shifts.[11] But this process is also explicable in terms of the formal reverse di-π-methane rearrangement.

11) E. Ciganek, J. Am. Chem. Soc., **89**, 1458 (1967); R. K. Murray, Jr. and H. Hart, Tetrahedron Lett., 4995 (1968).

12) Compound **ii**[9] would be formed by the photocyclization of 7-phenyl-2(7*H*)-oxepinone, which provides the evidence for the intervention of 3-methyl-7-phenyl-2(7*H*)-oxepinone (**11**) in the course of the formation of **5**.

13) Such a stereoselective photocyclization as from **12** to **5** has been observed in the photocyclization of substituted 1,3-dihydro-2*H*-azepin-2-ones.[8a]

14) This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 147028). We are grateful to Professor Y. Senda and Mr. J. Ishiyama, Department of Applied Science, Faculty of Engineering, Tohoku University, for measurement of the ^{13}Cnmr spectra.

(Received December 20, 1976)