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PHOTOCHEMICAL REARRANGEMENT OF 3-PHENYLATED 2(3H)-OXEPINONES IN ACIDIC MEDIA. FORMATION OF 5-STYRYL-2(5H)-FURANONES

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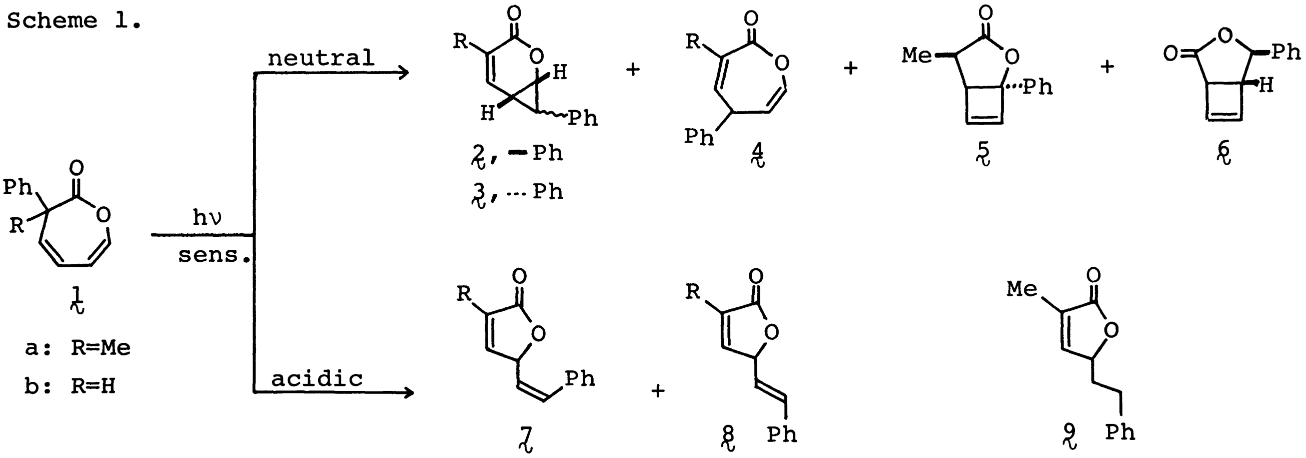
The sensitized photolysis of 3-phenylated 2(3H)-oxepinones in methylene chloride containing acids gives 5-styryl-2(5H)-furanones as the major products. The 1,5-phenyl migrated products, 7-phenyl-2(7H)-oxepinones, are proposed as the most plausible initial photoproducts.

Recent work in this laboratory[1] has demonstrated that the 2-acetonaphthone sensitized photolysis of 3-phenylated 2(3H)-oxepinones 1 in neutral media led to 7-phenyl-2-oxabicyclo[4.1.0]hept-4-en-3-ones 2 as the major products, along with the minor products 3–6, and a vinylogous di-π-methane rearrangement (1,4-phenyl shift) has been postulated for the main photolytic reaction pathway of 1. We now wish to report the preferential formation of 5-styryl-2(5H)-furanones 7 and 8 from the photolysis of 1 in acidic media, which would be strongly suggestive to produce 7-phenyl-2(7H)-oxepinones 12, the 1,5-phenyl migrated products, as the initial photoproducts of 1.

During the course of the further study on the photochemical behavior of 1a, we found that, when the photolysis of 1a was conducted in methylene chloride (long time stored) using acetophenone as a sensitizer, 3-methyl-5-cis- and trans-styryl-2(5H)-furanones (7a) and (8a) were obtained in 39 and 26% yields, respectively (Scheme 1); there was no indication for the formation of 2a. The structures of 7a and 8a were apparent from the analytical and spectral[2] properties, and the coupling constants of the styryl olefinic protons, 11 Hz in 7a and 16 Hz in 8a, clearly support the

Scheme 1.



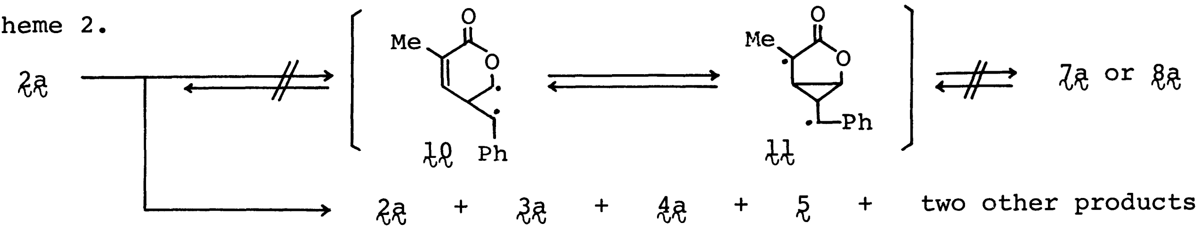
assignments of the *cis*- for **7a** and the *trans*-geometry for **8a**. Catalytic hydrogenation (Pd-C, EtOH) of both **7a** and **8a** afforded the same dihydro derivative **9**, which was identified with the authentic sample.[3] The isolation of both *cis* and *trans* isomers **7a** and **8a** would be resulted from photoequilibrium under the conditions.

In order to clarify the reaction pathway leading to the furanones **7a** and **8a**, a number of experiments were carried out, and the results are summarized in Table 1. It should be noted that the formation of **7a** and **8a** was not reproducible. Thus, when freshly distilled methylene chloride was used, **7a** and **8a** were no longer produced; **2a** was obtained as the major product (run 2). Furthermore, the results from runs 1–3 clearly indicate that the formation of **7a** and **8a** depends neither on solvents nor on the E_T values of sensitizers (2-acetonaphthone = 59, acetophenone = 74, and acetone = 80 Kcal/mole, respectively). These findings suggested that hydrogen chloride in stored methylene chloride appeared to affect the reaction pathway. In fact, the photolysis of **1a** in acidic media, except in methanol and acetone, afforded **7a** and **8a** in moderate to good yields; particularly the yield amounted to 85% by the use of acetophenone–methylene chloride–conc hydrochloric acid (run 5). In contrast to this, compound **2a** arose as the major product by photolysis in methanol or acetone (runs 8 and 10), which is probably due to the strong solvation of proton with these solvents, the reaction pathway leading to **7a** and **8a** being prevented.

Similarly, the photolysis of **1b** under the identical conditions as run 5 also gave styryl-furanones **7b** and **8b** as the major products in 36 and 22% yields, respectively.[4,5]

The reverse di-π-methane rearrangement of compound **2a** through the diradical intermediates **10** and **11** seems to be one of the possible reaction pathways leading to **7a** and **8a** (Scheme 2). This possibility, however, was ruled out from a separate experiment. The photolysis of **2a** under the same conditions as run 5 gave **2a**–**4a**, **5**, and two other products,[6] similar to the results in neutral media.[1b,7] The photolysis of **7a** or **8a** afforded only the equilibrating mixture.

Scheme 2.



From these facts, it was concluded that compounds **2** or **7** (or **8**) arose alternatively from **1** depending on the absence or presence of acid. However, it may be unlikely to assume that **7** or **8** is produced from **1** through an acid-promoted direct pathway shown as ---> in Scheme 3, since it is difficult to explain reasonably both phenyl shift and translactonization.

The fact, that the phenyl group migrates to the terminal carbon atom, C-7, during the photolysis, strongly suggests that a 1,5-phenyl shift is the essential photochemical reaction pathway of **1** shown as ====> in the scheme, and hence, 7-phenyl-2(7*H*)-oxepinones **12** may be the most probable initial photoproducts of **1**. The subsequent translactonization of **12** to **7** or **8** would be reasonable. Compounds **12** have been already proposed as the intermediates in the formation of **5** *via* **13**, or of **6**

Table 1. Photolysis of 1a under various conditions.[a]

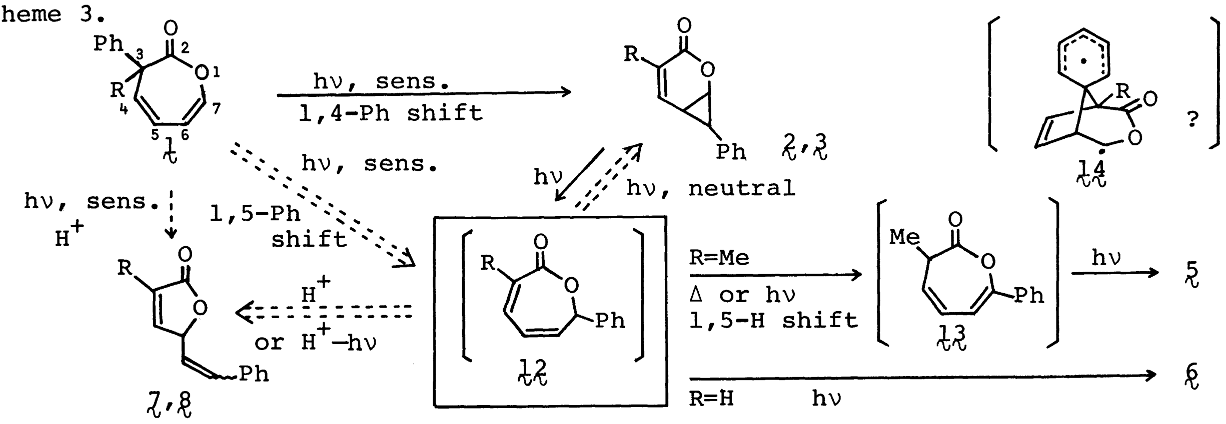
run	sensitizer[b]	solvent	additive	time, h	major product, yield % 7a and 8a[c]	 2a
neutral						
1	2-acetonaphthone	ether CH_2Cl_2[d] MeOH	——	(fast)	nil	65[e,f]
2[g]	acetophenone	CH_2Cl_2[d]	——	1.5	nil	47[h]
3	acetone	acetone	——	(slow)[i]	nil	48[e]
acidic[g]						
4	acetophenone	CH_2Cl_2[d]	HCl[j]	1.25	52[h]	12[h]
5	"	"	conc HCl[k]	1.5	85[h]	nil
6	"	"	HBr–AcOH[l]	"	77[h]	trace
7	"	hexane	conc HCl[k]	"	30[h]	nil
8	"	MeOH	" [m]	"	nil	<36[h]
9	2-acetonaphthone	CH_2Cl_2[d]	conc HCl[k]	"	25[h]	49[h]
10	acetone	acetone	" [m]	"	nil	48[h]

a) All runs were carried out in a Pyrex reaction tube at room temperature under nitrogen and irradiated externally with a 500 W high-pressure mercury lamp. Compound 1a was completely unchanged upon direct irradiation. b) 1 Equivalent except acetone. c) Total yield of the isomers. d) Freshly distilled. e) Isolated yield. f) For the reactions in ether, MeOH, and hexane, see ref. 1b. g) 50 mg of 1a in 50 ml of each solvent. h) Roughly estimated from the nmr spectrum of the crude product. i) The result after irradiation of a solution (250 ml) of 200 mg of 1a for 3 h was shown. j) Methylene chloride saturated with anhydrous hydrogen chloride (1 ml, 1 day after saturation, ca. 2 equiv) was added. k) The solvent was shaken well with 3 drops (ca. 2 equiv) of conc hydrochloric acid. l) A commercially available 30% solution (5 drops, 89 mg, ca. 2 equiv) was added. m) 3 Drops (ca. 2 equiv).

from the photolysis of 2a or 2b.[1b] However, the pathway via 12 would provide the more straightforward explanation for the actual formation of 5 or 6 from 1 than that through 2.

Furthermore, it is noteworthy that compound 12 are also the acceptable

Scheme 3.



intermediates leading to compounds **2**, which are formally the di-π-methane rearrangement products of **12**. Thus, the previous proposal of a novel bridged diradical intermediates **14** (a formally vinylogous di-π-methane rearrangement) for the formation of **2** would appear to be problematic. In conclusion, 3-phenyl-2(3H)-oxepinones **1** would undergo, upon sensitized photolysis, initially a 1,5-phenyl shift to give 7-phenyl-2(7H)-oxepinones **12**, the subsequent reaction of which is greatly affected by a medium used, giving preferentially furanones **7** or **8** in a methylene chloride—acid system, whereas 2-oxabicyclo[4.1.0]hept-4-en-3-ones **2** in neutral or protophilic solvent systems. Evidence supporting this reaction pathway will be reported in the following paper.

References and Notes

1) (a) K. Sato, H. Hagiwara, H. Uda, M. Sato, and N. Harada, J. Am. Chem. Soc., 98, 8281 (1976); (b) K. Sato, H. Hagiwara, and H. Uda, Chem. Lett., 175 (1977).

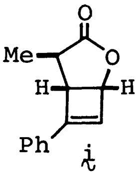
2) For **7a**: IR ($CHCl_3$) 1765 and 1755 cm^{-1}; NMR ($CDCl_3$) δ 1.95 (3H, t, J=1.5 Hz), 5.37 (1H, dd, J=11.0 and 9.0 Hz), 5.70 (1H, dm, J=9.0 Hz, changed to d-like upon irradiation at 1.95), 6.82 (1H, d, J=11.0 Hz), 6.99 (1H, quint, J=1.5 Hz, changed to d upon irradiation at 1.95), and 7.10—7.60 (5H, m).
For **8a**: IR ($CHCl_3$) 1765 and 1755 cm^{-1}; NMR ($CDCl_3$) δ 1.95 (3H, t, J=1.5 Hz), 5.43 (1H, dm, J=7.0 Hz, changed to d-like upon irradiation at 1.95), 5.95 (1H, dd, J=16.0 and 7.0 Hz), 6.72 (1H, d, J=16.0 Hz), 7.01 (1H, quint, J=1.5 Hz, changed to d upon irradiation at 1.95), and 7.10—7.60 (5H, m).
^{13}CNMR spectra are also accord with the assigned structures.

3) Prepared from the reaction of the dianion of (phenylthio)acetic acid with 4-phenyl-1-butene oxide. See K. Iwai, H. Kosugi, H. Uda, and M. Kawai, Bull. Chem. Soc. Jpn., 50, 242 (1977).

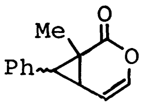
4) The analytical and spectral data are fully accord with the assigned structures.

5) Photolysis of **1b** without addition of conc hydrochloric acid gave the products **2b**, **3b**, **4b**, and **6** similar to the case of **1a**.

6) One of these compounds was assigned to be the structure **i**, and confirmed to be produced from **5** by acid-catalyzed isomerization. Another one could not be obtained in pure state. From the analysis of the nmr spectrum, the structure **ii** was tentatively assigned.



i



ii (exo and endo)

7) Compounds **1a** and **2a** in acidic media were shown to be stable in the dark.

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