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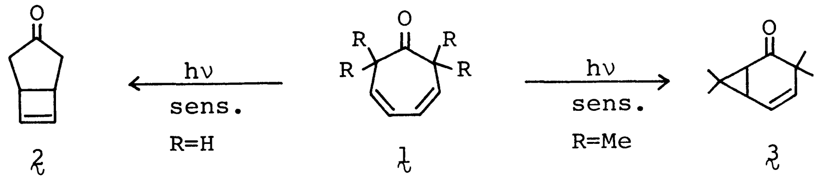
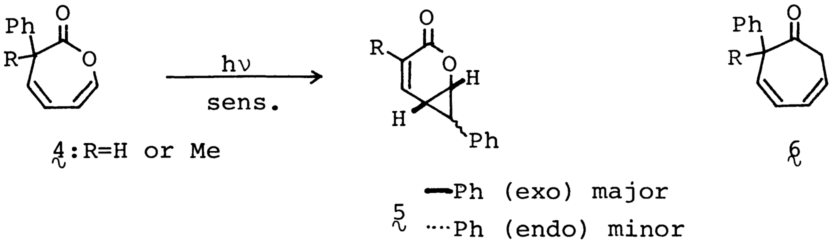
PHOTOCHEMISTRY OF 2-PHENYLATED CYCLOHEPTA-3,5-DIENONES

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

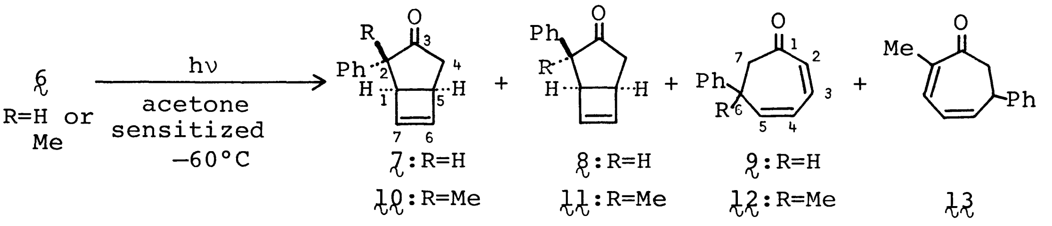
Acetone sensitized photolysis of 2-phenyl- and 2-methyl-2-phenylcyclohepta-3,5-dienones gives in about equal yield 2-substituted bicyclo[3.2.0]hept-6-en-3-ones and 6-substituted cyclohepta-2,4-dienones as the major products, while on direct irradiation both dienones undergo mainly decarbonylation to produce unstable trienes.

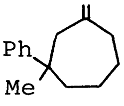
Recently attention has been focused on the photochemistry of cyclohepta-3,5-dienones. Sensitized irradiation of the parent compound **1** (R=H) led only to the cyclopentanone **2** by cyclization,[1] while the tetramethyl derivative **1** (R=Me) gave only the bicyclo[4.1.0]heptenone **3** by [1,2]-sigmatropic acyl shift (oxa-di-π-methane rearrangement).[2] Recent work in this laboratory[3] has demonstrated that the sensitized photolysis of the 3-phenylated 2(3*H*)-oxepinones **4**, the oxygen-hetero analogues of cyclohepta-3,5-dienones, led exclusively to 7-phenyl-2-oxabicyclo[4.1.0]-hept-4-en-3-ones (**5**) by 1,4-phenyl migration (formally vinylogous di-π-methane rearrangement). Hence, the photochemical behavior of the 2-phenylated cyclohepta-3,5-dienones **6** seems to be of quite interest, and we now report results in the sensitized photolysis of **6** which indicate that cyclization and [1,2]-sigmatropic acyl shift are the competitive main reaction pathways.





Irradiation of **6** (R=H)[4] in acetone[5] with a 500-W high-pressure mercury lamp through Pyrex gave two cyclization products **7** and **8** (total 35%)[6] and the rearrangement product, 6-phenylcyclohepta-2,4-dienone (**9**) (27%).[7] Similarly, the methylated derivative **6** (R=Me)[8] afforded two cyclization products **10** (30%) and **11** (6.2%), and two rearrangement

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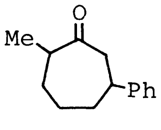
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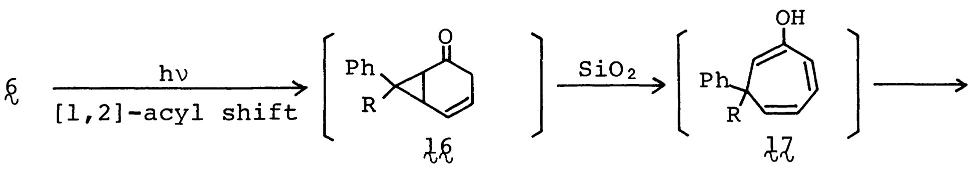
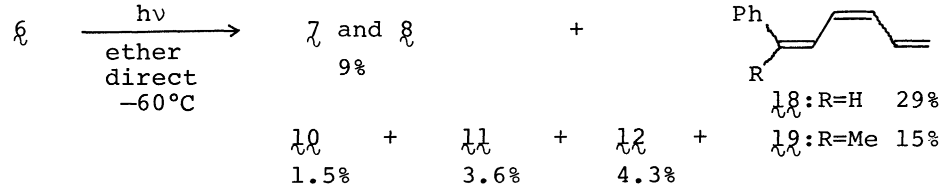
products, 6-methyl-6-phenylcyclohepta-2,4-dienone (12) (34%) and 2-methyl-6-phenylcyclohepta-2,4-dienone (13) (5.7%); there was no indication of the presence of the 1,4-phenyl shift products in both cases as observed in the 2(3H)-oxepinones 4. The structures of the cyclization products 7, 8, 10, and 11 were apparent from their spectral properties with reference to the analogous compounds.[1,3,10] The coupling constants between C-1 and C-2 protons [$J(^1/_2W)$=2.5 Hz in 7 and J=8.9 Hz in 8] and the observed NOE enhancement (18%) between the methyl protons and the C-1 proton in 11 confirm the assigned stereochemistries of the cyclization products. The structures of the rearrangement products 9, 12, 13 were assigned on the basis of the spectroscopic properties.[11] Catalytic hydrogenation (Pd-C, EtOH) of the methyl-phenyl derivatives 12 and 13 afforded the cycloheptanones 14 and 15, respectively, which were identified by comparison with the authentic samples.[12]

It should be noted that the remarkably intense absorption band at 1690 cm^{-1}, in addition to the absorption bands at 1745 and 1660 (relatively weak) cm^{-1}, was observed in the infrared spectrum of the total crude product from both compounds 6 before separation by preparative t.l.c. on silica gel, and that on treating with silica gel this 1690-cm^{-1} band gradually disappeared with increasing the intensity of the 1660-cm^{-1} band. Furthermore, no compound having the 1690-cm^{-1} band was isolated from the whole fraction of a t.l.c. plate. These results suggest that on the photolysis of 6 the compound having the 1690-cm^{-1} band was initially produced together with the cyclopentanones and transformed into the compound having the 1660-cm^{-1} band during isolation. The absorption bands at 1745 and 1660 cm^{-1} are clearly assignable to the cyclopentanones (7 and 8; 10 and 11) and the cyclohepta-2,4-dienone (9 or 12), respectively, and the frequency value of 1690 cm^{-1} may be most reasonably assignable to the six-membered ketone conjugated with a cyclopropane or double bond. Thus, the rearrangement leading to 9 or 12 would be accounted for by a reaction pathway, which postulates the [1,2]-sigmatropic acyl shift of 6 to the bicyclo[4.1.0]heptenone 16 (1690 cm^{-1} component), analogous to the tetramethyl derivative 1 (R=Me), the silica gel-catalyzed ring opening to form 17, and the subsequent ketonization.



Compound **13** would be produced directly from **6** (R=Me) through photoinduced [1,5]-sigmatropic phenyl shift.[13]

Direct irradiation (30-W low-pressure mercury lamp) of both cycloheptadienones **6** gave the decarbonylation products, 1-phenyl-1,3,5-hexatriene (**18**) and 2-phenyl-2,4,6-heptatriene (**19**), as the major products, in addition to the cyclization products, and in the case of the methylated derivative **6** (R=Me) a small amount of the rearrangement product **12** was also obtained. The trienes **18** and **19** were quite unstable and, therefore, characterized only by the spectral data taken immediately after separation by chromatography.



From these results, the immediate conclusion which can be drawn is that for the 2-phenylated cyclohepta-3,5-dienones a major singlet-derived reaction (direct) is decarbonylation, and that on sensitized photolysis (triplet) cyclization and [1,2]-sigmatropic acyl shift are competitive main processes, accompanied by [1,5]-sigmatropic phenyl shift as a minor reaction pathway in the case of the methylated derivative **6** (R=Me). Thus, the main sensitized photochemical property of 2-phenylated cyclohepta-3,5-dienones is intermediate between the parent and tetramethylated compounds **1**; a phenyl substituent α to the carbonyl group does not entirely affect the reaction course, which indicates that the 1,4-migration of a phenyl group observed in the 2(3_H_)-oxepinones **4** is not the essential photochemical process of a cyclic 1-phenyl-2,4-diene moiety.[14]

References and Notes

1) O. L. Chapman and G. W. Borden, J. Org. Chem., 26, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, J. Am. Chem. Soc., 84, 1220 (1962); D. I. Schuster, B. R. Sckolnick, and F. -T. Lee, ibid., 90, 1300 (1968); D. I. Schuster and D. J. Blythin, J. Org. Chem., 35, 3190 (1970).

2) L. A. Paquette, R. F. Eisember, and O. Cox, J. Am. Chem. Soc., 90, 5153 (1968); D. I. Schuster and C. W. Kim, ibid., 96, 7437 (1974); J. Eriksen, K. Krogh-Jespersen, M. A. Ratner, and D. I. Schuster, ibid., 97, 5596 (1975).

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

4) Prepared by the reaction of tropone with phenyllithium. ν_{max} (CCl_4) 1715 cm^{-1}; λ_{max} (EtOH) ∿201 (ε 32000), 239 (sh) (ε 12800), and ∿305 nm (sh) (ε 2400).

5) The reaction was also sensitized with β-acetonaphthone. However, isolation of the products was difficult because of the close Rf values of the products and β-acetonaphthone on a silica gel t.l.c. plate. In the case of the transformation of **4** to **5**, it has been found that acetone also acts as a sensitizer. K. Sato, H. Hagiwara, M. Sato, H. Uda, and N. Harada, unpublished result.

6) Compounds **7** and **8** were separable and isolated by preparative t.l.c. on silica gel in almost pure state. However, these are easily inter-convertible on chromatographic separation.

7) All new compounds in this communication gave satisfactory elemental analyses.

8) Prepared from 2-phenylcycloheptanone[9] through nine steps. Details will be reported elsewhere. ν_{max} (CCl_4) 1715 cm^{-1}; λ_{max} (EtOH) ∿202 (ε 16000), 245 (sh) (ε 5000), and 290 nm (sh) (ε 650).

9) C. D. Gutsche and H. E. Johnson, "Organic Syntheses", Coll. Vol. IV, p. 780 (1963).

10) 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).

11) For **9**: IR (CCl_4) 1660, 1630, and 1600 cm^{-1}; UV (EtOH) λ_{max} ∿200 (ε 23000) and 293 nm (ε 5900); ^{1}HNMR (CCl_4) δ 2.71 (1H, dd, *J*=15.3 and 3.0 Hz), 2.95 (1H, dd, *J*= 15.3 and 11.8 Hz), 3.62–3.87 (1H, m), 6.02 (1H, ddd, *J*=11.0, 7.1, and 2.0 Hz), 6.07 (1H, d, *J*=11.8 Hz), 6.42 (1H, dd, *J*=11.0 and 4.2 Hz), 6.51 (1H, dd, *J*=11.8 and 7.1 Hz), and 7.08–7.40 (5H, m); ^{13}CNMR ($CDCl_3$) δ 40.04 (C-6), 49.50 (C-7), 126.88 (C-4), 131.65 (C-2), 137.23 (C-5), 145.12 (C-3), 199.12 (C-1), and aromatic carbons.
For **12**: IR (CCl_4) 1660, 1630, and 1600 cm^{-1}; UV (EtOH) λ_{max} ∿202 (ε 16000) and 295 nm (ε 5800); ^{1}HNMR ($CDCl_3$) δ 1.50 (3H, s), 2.96 and 3.17 (1H each, AB type q, *J*= 14.7 Hz), 5.95 (1H, d, *J*=12.0 Hz), 6.11 (1H, dd, *J*=11.0 and 7.3 Hz), 6.46 (1H, d, *J*=11.0 Hz), 6.47 (1H, dd, *J*=12.0 and 7.3 Hz), and 7.10–7.34 (5H, m); ^{13}CNMR ($CDCl_3$) δ 28,75 (Me), 40.34 (C-6), 54.84 (C-7), 123.82 (C-2), 131.89 (C-4), 136.20 (C-5), 149.85 (C-3), 198.33 (C-1), and aromatic carbons.
For **13**: IR (CCl_4) 1655 and 1600 cm^{-1}; UV (EtOH) λ_{max} ∿204 (ε 19000) and 300 nm (ε 6000); ^{1}HNMR ($CDCl_3$) δ 1.98 (3H, s), 2.90 (1H, dd, *J*=14.9 and 3.5 Hz), 3.10 (1H, dd, *J*=14.9 and 11.4 Hz), 3.62–3.88 (1H, m), 6.02 (1H, ddd, *J*=11.2, 7.4, and 2.0 Hz), 6.33 (1H, dd, *J*=11.2 and 4.4 Hz), 6.59 (1H, d, *J*=7.4 Hz), and 7.07–7.42 (5H, m).

12) Compound **14** was prepared from 2-phenylcycloheptanone through seven steps. Details will be reported elsewhere. Compound **15** was prepared by α-methylation of cyclohept-2-enone, followed by the conjugate addition of lithium diphenylcuprate.

13) Cf. Photoinduced 1,5-phenyl migration, G. W. Griffin and E. J. O'Connell, J. Am. Chem. Soc., **84**, 4148 (1962); H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis, and S. Bram, ibid., **84**, 4149 (1962); H. E. Zimmerman, H. G. C. Dürr, R. S. Givens, and R. G. Lewis, ibid., **89**, 1863 (1967).

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