Tetrahedron Letters No. 18, pp 1817 - 1820, 1972. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMISTRY OF 2-PHENYLCYCLOALKANONES

Anthony A. Baum

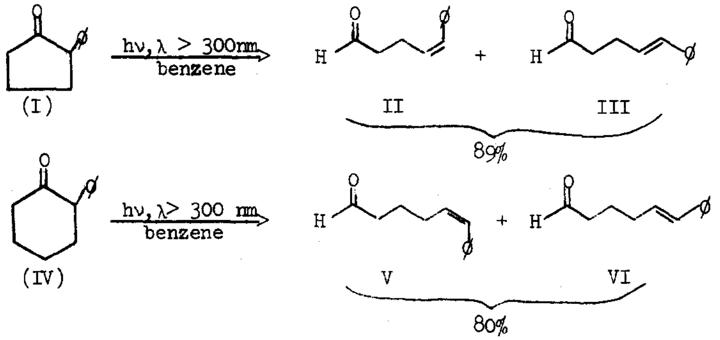
Union Carbide Research Institute
Tarrytown, N. Y. 10591

(Received in USA 16 February 1972; received in UK for publication 27 March 1972)

The benzyl ketones are electronic analogs of β,γ-unsaturated ketones to the extent that aryl and vinyl groups can be considered similar. This analogy is supported by the fact that in both systems the n,π* absorption band exhibits a hyperchromic shift the magnitude of which depends upon the relative orientations of the carbonyl group and the other π-system.[1,2] It is well known that β,γ-unsaturated ketones undergo 1,2- and 1,3- acyl migrations on sensitized and direct irradiation, respectively.[3] An earlier report suggests that unlike other cyclohexanone derivatives, 2-phenylcyclohexanone does not give unsaturated aldehydes as major products on direct photolysis in benzene solution, although the observed products were not characterized.[4] We wish to report that the 2-phenylcycloalkanones do, in fact, give high yields of alkenals on photolysis, and the structural and spectral analogy between these systems and the β,γ-unsaturated ketones does not carry over to the photochemistry.[5]

A solution of 1.20 g of 2-phenylcyclopentanone (I)[6] in 250 ml of benzene was irradiated through 4 mm of pyrex with a 450 watt medium pressure mercury lamp for 2.25 hr while being purged with nitrogen. After photolysis, careful chromatography of the resulting mixture on silicic acid afforded two products, II and III, along with 48% of the starting ketone. Products II and III were colorless oils which were shown by mass spectroscopy to be isomeric with the starting material (molecular ion at m/e 160) and were formed in 11% and 78% yield respectively.[7] Other pertinent spectral data for II were as follows: ir(CCl_4) 2810 cm^{-1}, 2720 cm^{-1}, 1720 cm^{-1}; uv λ_{max}^{hexane} 243 nm (log ε 4.04); nmr ($CDCl_3$) τ 0.40 (br s, 1 H, aldehydic proton), 2.82 (m, 5H, arom), 3.58 (br d, J=11 Hz, 1H, vinyl), 4.45 (m, 1H, vinyl), 7.49 (m, 4H, methylene). Compound III had the following spectral properties: ir (CCl_4) 2822 cm^{-1}, 2722 cm^{-1}, 1722 cm^{-1}, 960 cm^{-1}; uv λ_{max}^{hexane} 251 nm (log ε 4.20); nmr ($CDCl_3$) τ 0.40 (br s, 1 H, aldehydic proton), 2.87 (m, 5 H, arom), 3.82 (AB-part of ABX_2-multiplet, J_{AB}= 16Hz, 2H, vinyl), 7.58 (m, 4H, methylene). These spectral data allow assignment of the *cis*- and *trans*- 5-phenyl-4-pentenal structures to II and III, respectively as shown in Chart I. The ratio of II : III increased with increasing extent of conversion of the starting material, but appropriate plots of yield of II *vs* % conversion showed that the *cis* isomer was a primary photoproduct; the limiting (low conversion) percentage of *cis*-alkenal in the mixture of the two photoproducts was 8% ± 3%.

Chart I - Photochemistry of 2-phenylcyclopentanone and 2-phenylcyclohexanone

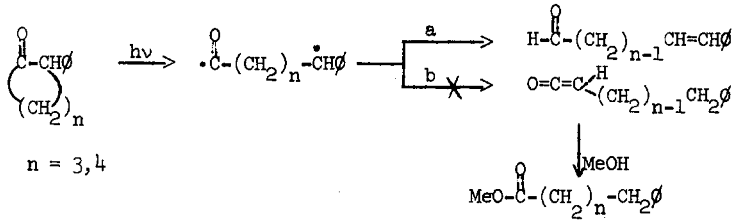


When 1.20 g of 2-phenylcyclohexanone (IV) dissolved in 250 ml of benzene was subjected to the same conditions of irradiation and work-up as described above, a mixture of two products, V and VI, was isolated in 80% yield[7] along with 51% of the unreacted starting material. The product mixture could be further separated by preparative gas chromatography, thus affording pure V and VI for spectral analysis. Each compound had a mass spectrum with a molecular ion at *m/e* 174, and was therefore an isomer of the starting material. Other spectral properties of V were as follows: ir (CCl_4) 2800 cm^{-1}, 2700 cm^{-1}, 1724 cm^{-1}; uv λ_{max}^{hexane} 242 nm (log ε 4.07); nmr ($CDCl_3$) τ 0.33 (t, J=1.5Hz, 1H, aldehydic proton), 2.78 (m, 5H, arom), 3.54 (br d, J = 11.5 Hz, 1H, vinyl), 4.46 (m, 1H, vinyl) 7.50 (m, 6H, methylene). Compound VI had the following spectral properties: ir (CCl_4) 2800 cm^{-1}, 2710 cm^{-1}, 1720 cm^{-1}, 956 cm^{-1} uv λ_{max}^{hexane} 250 nm (log ε 4.17); nmr ($CDCl_3$) τ 0.28 (t, J=1.5Hz, 1H, aldehydic proton), 2.76 (m, 5H, arom), 3.78 (AB-part of ABX_2 multiplet, J_{AB}=16 Hz, 2H, vinyl), 7.91 (m, 6H, methylene). These data confirm the *cis*- and *trans*-6-phenyl-5-hexenal structures shown in Chart I for V and VI respectively. As was the case with 2-phenylcyclopentanone, the ratio of *cis*-: *trans*- alkenal, i.e., V:VI, increased with increasing conversion of the starting material. The product mixtures formed at low conversions contained 93% ± 2% of the *trans* isomer.

When either I or IV was irradiated in methanol solution, the only significant products were the corresponding alkenals (vide supra). In neither case could any saturated methyl ester be isolated by chromatography or detected by nmr analysis.

Three significant conclusions can be drawn from the above results. First, there is nothing unusual about the qualitative aspects of the photochemistry of the 5- and 6-membered 2-phenylcycloalkanones as was previously suggested.[4] These compounds appear to cleave in the normal fashion to give the alkenal-type products expected of cyclic ketones in high yield. Second, both the overall directionality of the reaction and the fact that both cis- and trans- modifications of the product alkenals are primary photoproducts are consistent with the biradical mechanism suggested by Rickborn[8-10] and shown in Chart II for the compounds in question here. Thus, the initial cleavage is in the direction which forms the most stable biradical (acyl-benzyl as opposed to acyl-methylene), and the preponderance of the trans-isomer in the product mixture reflects the steric requirements of the phenyl group in the final internal disproportionation reaction (Chart II-path a). Finally, the direction of internal disproportionation of the 1,5- and 1,6- acyl-benzyl biradicals formed from I and IV appears to be controlled by the odd electron density at the radical centers and/or the product stabilities. Thus, path a (Chart II) in which an acyl radical abstracts hydrogen to give the styryl aldehydes completely dominates path b in which a benzyl radical abstracts hydrogen to give a ketene which, in methanol solution, would have been trapped as the methyl ester.

Chart II - Mechanism of the photocleavage of 2-phenylcyclopentanone and 2-phenylcyclohexanone.



REFERENCES

1. R. Gencarelli, H. Abajian, P. Irving, and S. MacKenzie, J. Org. Chem., **35**, 2673 (1970).

2. H. Labhart and G. Wagniere, Helv. Chim. Acta, **42**, 2219 (1959).

3. a. E. Baggiolini, K. Schaffner, and O. Jeger, Chem. Comm., 1103 (1969);

   b. D. I. Schuster, G. R. Underwood, and T. P. Knudsen, J. Amer. Chem. Soc., **93**, 4304 (1971) and references cited therein.

4. P. J. Wagner and R. W. Spoerke, J. Amer. Chem. Soc., **91**, 4437 (1969).

5. The products of direct irradiation expected by analogy with the β,γ-vinylic systems are the ring-expanded 2,3-benzocycloalkenones.

6. R. T. Arnold, J. S. Buckley, Jr., and R. M. Dodson, J. Amer. Chem. Soc., **72**, 3153 (1950).

7. Yields are based on consumed starting material.

8. B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, Chem. Ind. (London), 1951 (1964).

9. R. L. Alumbaugh, G. O. Pritchard, and B. Richborn, J. Phys. Chem., **69**, 3225 (1965).

10. C. C. Badcock, M. J. Perone, G. O. Pritchard, and B. Richborn, J. Amer. Chem. Soc., **91**, 543 (1969).