Tetrahedron Letters No. 50, pp 4811 - 4814, 1971. Pergamon Press. Printed in Great Britain.

PHOTOREARRANGEMENT OF A 4-BENZOYLCYCLOPENTENONE

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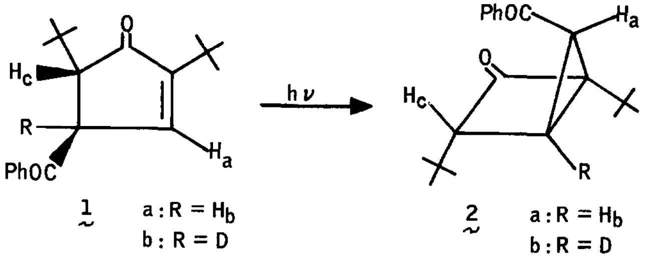
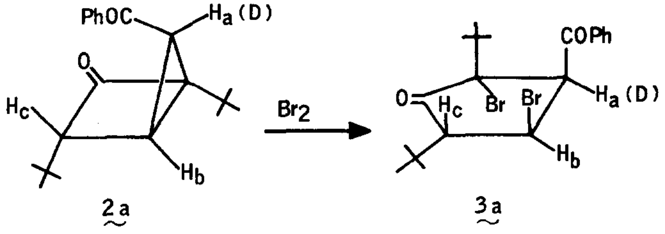
(Received in USA 18 October 1971; received in UK for publication 15 November 1971)

The photochemistry of 4-alkyl-4-hydroxy-2,5-cyclohexadienones has been extensively studied.[1] In general, these compounds rearrange to 4-acylcyclopentenones and upon further irradiation give bicyclo[2.1.0]pentanones. However, only one example of the photolysis of a 4-aryl-4-hydroxy-2,5-cyclohexadienone has been reported. Irradiation of 2,6-di-t-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadienone gave, as the only identified product, low yields of trans-2,5-di-t-butyl-4-benzoylcyclopent-2-enone 1a.[2] We have reinvestigated this reaction in order to compare it with the 4-alkyl substituted cases. This communication describes one aspect of that study, the stereospecific photorearrangement of the trans-4-benzoylcyclopentenone 1a.

Irradiation of 1a in methanol gave a quantitative yield of the bicyclo[2.1.0]pentanone 2a: mp 117.5-118°.[3] The nmr spectrum showed peaks at δ 8.10-7.35 (m, 5, aromatic), 3.47 (d, 1, J = 7.0 Hz), 3.10 (d, 1, J = 7.0 Hz), 2.15 (s, 1), 1.07 (s, 9), 0.98 ppm (s, 9). In order to assign the stereochemistry in 2a at C_3 and C_5, it was necessary to definitely assign the aliphatic proton signals.



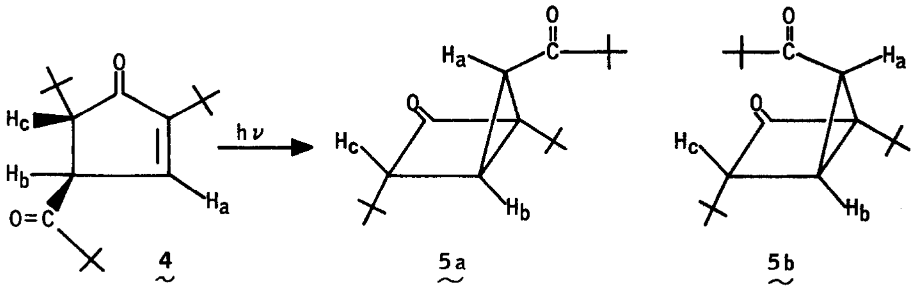
Bromination of 2a gave the dibromide 3a:[3] nmr ($CDCl_3$) δ 8.15-7.40 (m, 5, aromatic), 5.03 (dd, 1, J_{ab} = 6.0 Hz, J_{bc} = 10.3 Hz), 4.81 (d, 1, J = 6.0 Hz), 3.22 (d, 1, J = 10.3 Hz), 1.22 (s, 9) and 1.13 (s, 9).[4] Spin decoupling of the *ortho*-phenyl protons sharpened the doublet at δ 4.81 indicating that H_a = δ 4.81. Treatment of 2a with NaOMe/D_2O gave mono-deuterated 2a (D)[5] with nmr proton singlets at δ 3.10 and δ 2.15. Bromination of 2a (D) gave 3a (D)[5], with aliphatic proton signals at δ 5.03 (d, 1, J = 10.3 Hz) and δ 3.22 (d, 1, J = 10.3 Hz).



Thus deuterium exchange in 2a must have occurred at H_a. The nmr proton signals of 2a can be assigned as H_a = δ 3.47, H_b = δ 3.10, and H_c = δ 2.15. The cyclopropane vicinal proton coupling J_{ab} = 7.0 Hz is indicative of *cis*-coupling.[6a,b] Therefore, the H_a proton must be *anti* to the cyclobutanone ring. The zero coupling of H_b and H_c is indicative of *trans* stereochemistry[6b] and therefore H_c must be *syn* to the cyclopropane ring. This assignment is consistent with the relatively high field position of H_c (δ 2.15), which is probably due to shielding by the cyclopropane ring.[7]

The mechanism of the reaction 1a → 2a was established by irradiation of the mono-deuterated cyclopentenone 1b.[5] Photorearrangement of 1b gave 2b.[5] The nmr spectrum of 2b, aliphatic protons: δ 3.47 (s, 1) and δ 2.16 (s, 1), established the position of the deuterium as H_b = D. Thus the rearrangement must involve cyclopropane bond formation between C_2 and C_4 with benzoyl group migration to C_3.

Previously Matsuura and Ogura[8] have reported a similar type rearrangement of the *trans*-4-pivaloylcyclopentenone 4 to 5a proceeding *via* the same mechanism.[9] However, based on the present work, we would suggest that the stereochemistry at C_5 should be as in 5b.



4 **5a** **5b**

Irradiation of **4** in methanol gave **5** in a quantitative yield: nmr ($CDCl_3$) δ 3.15 (d, 1, J = 7.0 Hz), 2.95 (d, 1, 7.0 Hz), 2.07 (s, 1), 1.22 (s, 9), 1.02 (s, 9) and 0.99 (s. 9).[10] Treatment of **5** with NaOMe/D_2O gave monodueterated **5**[5] with nmr proton singlet signals at δ 2.94 and δ 2.07. Therefore, the aliphatic proton signals in **5** can be assigned as H_a = δ 3.15, H_b = δ 2.95,[11] and H_c = δ 2.07. The cyclopropane vicinal proton coupling J_{ab} = 7.0 Hz is indicative of *cis*-coupling[6a,b] and thus the H_a must be *anti* to the cyclobutanone ring as in **5b**.

One interesting aspect of these reactions is that both **1a** and **4** rearrange to bicyclo-[2.1.0]pentanones of identical stereochemistry. This stereospecificity suggests that these rearrangements may be concerted processes and as such would be photochemically allowed concerted [σ 2a + π 2a] additions.[12] Indeed, if the [σ 2a + π 2a] cycloaddition rules are applied to the rearrangements, the correct products are predicted.

Acknowledgment. We wish to thank Mr. H. J. Tarski for excellent technical assistance and Dr. W. H. Starnes, Jr. for his constructive comments.

Footnotes

1. T. Matsuura and K. Ogura, *Bull. Chem. Soc. Japan*, **43**, 3187 (1970); G. F. Burkinshaw, B. R. Davis, P. D. Woodgate, *J. Chem. Soc. (C)*,. 1607 (1970).
2. E. R. Altwicker and C. D. Cook, *J. Org. Chem.*, **29**, 3087 (1964).
3. All spectral properties are consistent with this structure.
4. The stereochemistry shown is tentatively based on nmr data.
5. Identical to the undeuterated compound.

6\. a. W. G. Dauben and W. T. Wipke, J. Org. Chem., 32, 2976 (1967); M. P. Schneider and R. J. Crawford, Can. J. Chem., 48, 629 (1970).

b. A. Padwa and S. Clough, J. Amer. Chem. Soc., 92, 5803 (1970); K. B. Wiberg and D. E. Barth, J. Amer. Chem. Soc., 91, 5124 (1965).

7\. E. L. Allred and R. L. Smith, J. Amer. Chem. Soc., 91, 6766 (1969).

8\. T. Matsuura and K. Ogura, J. Amer. Chem. Soc., 89, 3850 (1967).

9\. T. Matsuura and K. Ogura, Chem. Commun., 1247 (1967).

10\. Identical in all respects to that obtained by Matsuura. See ref. 8.

11\. In agreement with previous assignment. See ref. 9.

12\. R. B. Woodward and R. Hoffman, Angew. Chem. Intern. Ed. Engl., 8, 781 (1969).