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PHOTOREARRANGEMENT OF 4-ALKYL-4-ALKOXY-2,5-CYCLOHEXADIENONES: SYNTHESIS OF 4-(ALKYLDIMETHOXYMETHYL)CYCLOPENT-2-EN-1-ONES[1]

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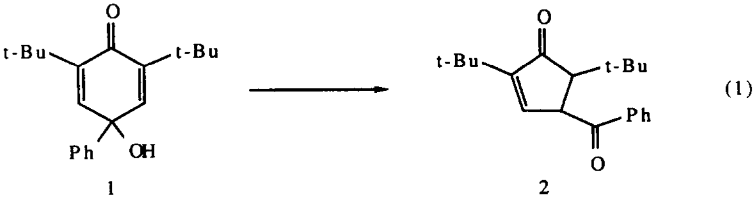
Summary: The irradiation of 4-alkyl-4-alkoxy-2,5-cyclohexadienones 3a-d at 366 nm in methanol affords 4-(alkyldimethoxymethyl)cyclopent-2-en-1-ones 5a-d.

The photochemical rearrangements of 2,5-cyclohexadienones have been of considerable importance for over two decades.[2] Bicyclo[3.1.0]hexenones and substituted phenols are usually the major photoproducts, but, on occasion, 4-substituted-2-cyclopentenones have been obtained. For example, Altwicker and Cook found that the photolysis of 2,6-di-*tert*-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadienone 1 in aqueous dioxane afforded 2 in 20% yield[3] (Eq. 1). Patel and Schuster have postulated that this phototransformation requires the presence of ionic intermediates in the product determining stage of the reaction.[4]

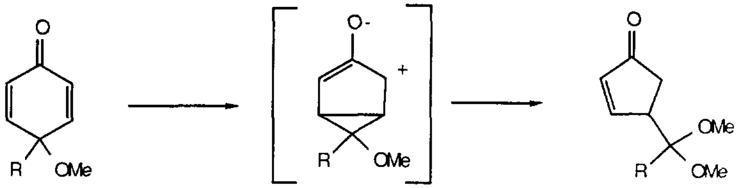


(1)

The present paper reports solvent incorporation during the photolysis of 4-alkyl-4-methoxy-2,5-cyclohexadienones 3a-d in methanol affording 4-(alkyldimethoxymethyl)cyclopent-2-en-1-ones 5a-d. The starting 4-methyl-, 4-ethyl-, 4-isopropyl-, and 4-*tert*-butyl-4-methoxy-2,5-cyclohexadienones (3a-d) were prepared in excellent yield from the 4-substituted phenol.[5] Irradiation of each of these substrates, dissolved in deaerated, spectrochemical grade methanol, at 366 nm[6] (until consumption of starting cyclohexadienone as determined by TLC analysis) provided an oil upon evaporation of solvent *in vacuo*.

Analysis (NMR, IR, MS, CH) of the product mixtures showed that cyclopentenone ketals 5a-d formed in moderate to good yields (Scheme I). Photoproduct 5a was found to be stable to further irradiation (10 hours). The decomposition of 5c on attempted chromatography prevented its isolation in pure form. Other unidentifiable products were also formed from the photolysis of 3d.

Scheme I

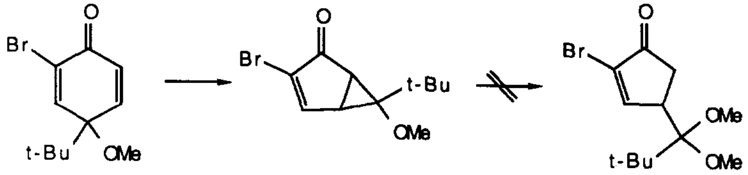


3 4 5

Substrate	Overall Yield from Phenol (%)	Product	Isolated Yield (%)
3a, R=Me	72	5a, R=Me	67
b, R=Et	87	b, R=Et	74
c, R=*i*-Pr	86	c, R=*i*-Pr	(51)[a]
d, R=*t*-Bu	72	d, R=*t*-Bu	37

[a] Determined from ^{1}H NMR spectrum of crude 5c

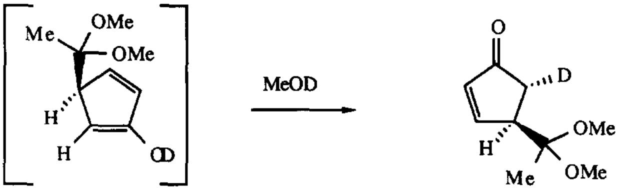
Cyclopentenone ketals 5a-d could be formed by methanol addition to a zwitterion (4a-d) or to an intermediate bicyclo[3.1.0]hex-3-en-2-one. It seems reasonable to assume that a retro-aldol reaction of a bicyclohexenone would give 2, but the photochemistry of 6 suggests that addition of methanol to a 6-alkyl-6-methoxybicyclo[3.1.0]hex-3-en-2-one may not be involved in the formation of 5a-d. Irradiation of 2-bromo-4-*tert*-butyl-4-methoxy-2,5-cyclohexadienone 6[1] in methanol at 366 nm afforded only 3-bromo-6-*tert*-butyl-6-methoxybicyclo[3.1.0]hex-3-en-2-one 7 (Eq. 2). Furthermore, Matsuura has reported the isolation of 1,3,6-tri-*tert*-butyl-6-methoxybicyclo[3.1.0]hex-3-en-2-one from the photolysis of 4-methoxy-2,4,6-tri-*tert*-butyl-2,5-cyclohexadienone in methanol.[7] Matsuura did not report the isolation of any products that



6 7 5e (2)

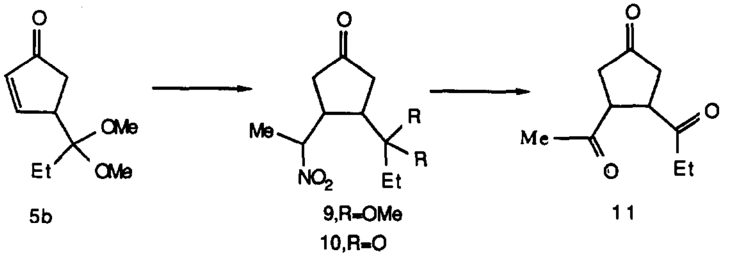
incorporated methanol.

Addition of methanol to zwitterion 4 would generate an enol intermediate equivalent to 8. It was desirable to determine if there was any stereoselectivity in the ketonization of 8. Cyclohexadienone 3a was a suitable substrate for this study since its photoproduct 5a produced a ^{1}H NMR spectrum showing each of the C-5 methylene protons at different chemical shifts (2.28, 2.46 ppm). The coupling constants of each resonance allowed the configuration of each C-5 proton relative to the C-4 proton to be determined. The NMR spectrum of the product 5a' obtained from the photolysis of 3a in methyl alcohol-d was identical to that of 5a, except in the methylene region where only a broad doublet (2.26 ppm, 1H, J = 2.5 Hz) was present. The chemical shift and coupling constant suggested a trans relationship between protons at C-4 and C-5. No other diastereomer was detected by NMR spectroscopy. Hence, deuterium is added to C-5 from the sterically less-hindered face of enol 8 opposite the ketal moiety (Eq. 3). Presumably, the formation of 5a' is a result of kinetic incorporation of the deuterium atom at C-5.^{8}



8 5a' (3)

Cyclopent-2-en-1-ones of type 5 offer a wide variety of possibilities for synthetic manipulations. For example, 5b underwent 1,1,3,3-tetramethylguanadine-catalyzed^9 Michael addition of nitroethane to afford nitro ketone 9 as a mixture of diastereomers in quantitative yield upon workup with dilute hydrochloric acid (<1%). Workup with 10% hydrochloric acid afforded nitro diketone 10 as a colorless solid (mp 98°C). Nitro diketone 10 was converted to triketone 11 (81% yield) using 20% aqueous titanous chloride^{10} (Eq. 4). These reactions may be useful in the construction of polyquinane-type ring systems.



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Acknowledgment. I thank Professor A. G. Schultz for guidance and support of this research.

References and Notes

1. For additional experimental detail, see: Taveras, Jr., A. G. B.S. Thesis, Rensselaer Polytechnic Institute, 1986.

2. For reviews of 2,5-cyclohexadienone photochemistry, see: (a) Zimmerman, H. E. *Adv. Photochem*. 1963, 1, 183. (b) Chapman, O. L. *Adv. Photochem*. 1963, 1, 323. (c) Schaffner, K. *Adv. Photochem*. 1966, 4, 81. (d) Kropp, P. *Org. Photochem*. 1967, 1, 1. (e) Chapman, O. L.; Weiss, D. S. *Org. Photochem*. 1973, 3, 197. (f) Schuster, D. I. *Acc. Chem. Res*. 1978, 11, 65. (g) Schaffner, K.; Demuth, M. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

3. Altwicker, E. R.; Cook, C. D. *J. Org. Chem*. 1964, 29, 3087.

4. Patel, D. J.; Schuster, D. I. *J. Am. Chem. Soc*. 1968, 90, 5137.

5. Corey, E. J.; Barcza, S.; Klotmann, G. *J. Am. Chem. Soc*. 1969, 91, 4782.

6. The light source was a Hanovia 450-W medium pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well. Reaction vessels containing solutions to be irradiated were attached to the immersion well and were saturated with nitrogen prior to irradiation. The Hanovia lamp in the Pyrex immersion well fitted with Corning color filters 0-25 and 7-54 was employed as the 366-nm light source.

7. Matsuura, T. *Bull. Chem. Soc. Japan* *37*, 564 (1964).

8. Zimmerman, H. E. *Acc. Chem. Res*. *20*, 263-268 (1987).

9. Pollini, G. P.; Barco, A.; DeGiuli, G. *Synthesis* 1972, 44-45.

10. McMurry, J. E.; Melton, J. *J. Org. Chem*. 1973, *38*, 4367.

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