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PHOTOCHEMISTRY OF A 2,3-BENZO-2,4-CYCLOOCTADIENONE; ISOLATION OF THE 4-TRANS ISOMER

Harold Hart* and Mikio Suzuki

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824, U.S.A.

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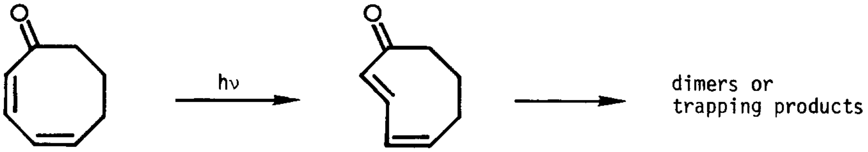
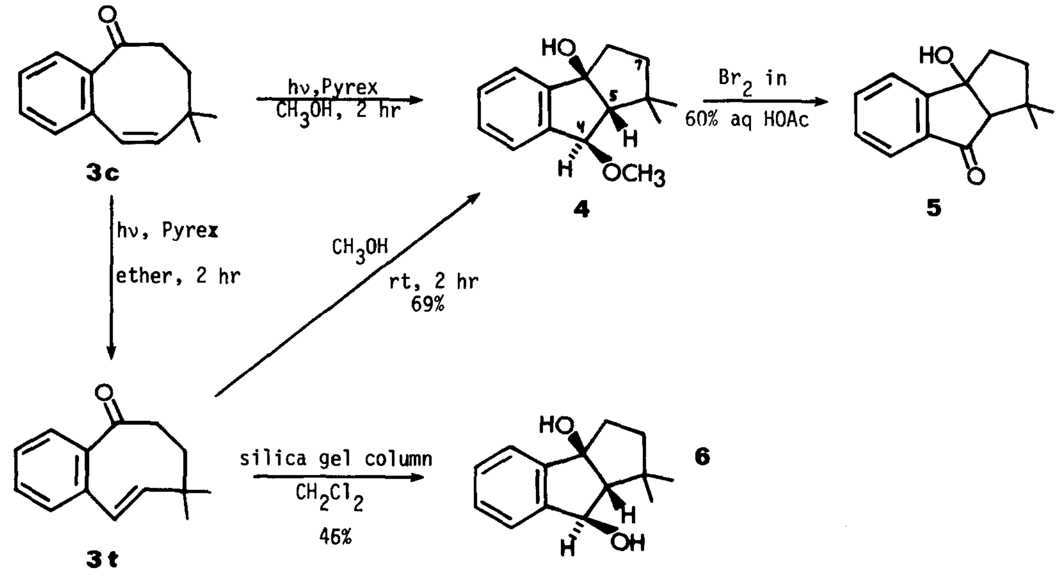
Evidence that the highly reactive *trans*,*cis*-2,4-cyclooctadienone **2** is an intermediate in the photoreactions of the *cis*,*cis* isomer has been presented.[1] The trans ketone **2** was stable at



1 **2**

-78° but too reactive to be isolated. We have found that when the 2,3 double bond of dienones such a **1** is incorporated in a benzene ring, irradiation causes isomerization of the 4,5 double bond to the trans configuration. The product is stable at room temperature, but is nevertheless considerably more reactive than *trans*-4-cyclooctenone.[2] Our results have some bearing on the photochemistry of the corresponding seven-membered ring analogs.[3]

Irradiation of **3c** [4,5] in methanol through Pyrex gave a methanol adduct to which we assign structure **4** (86%). The compound had no carbonyl group (ir) but a strong O-H bond at 3425 cm^{-1};

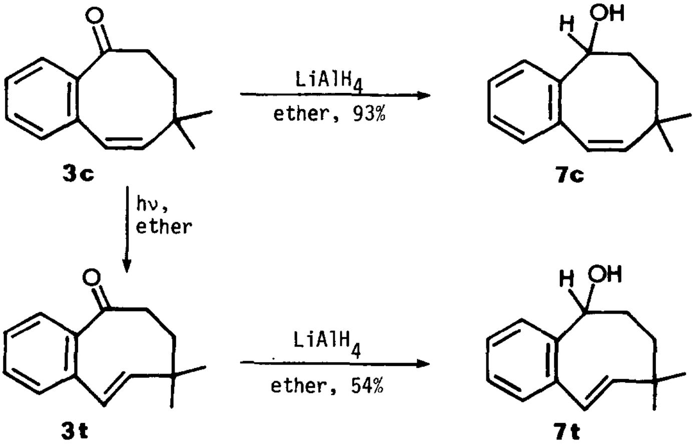


therefore it was not formed simply by adding methanol to the C=C of **3c**. The nmr spectrum was consistent with the structure;[8] the coupling constant between the two methine hydrogens is 2.5 Hz. The mass spectrum showed, in addition to the parent peak at m/e 232 (4%), a small $M-H_2O$ peak (7%) but a large $M-CH_3OH$ peak (83%). Hydrolytic oxidation of **4** gave the keto alcohol **5** ($\nu_{C=O}$ 1704, ν_{O-H} 3458 cm^{-1}).

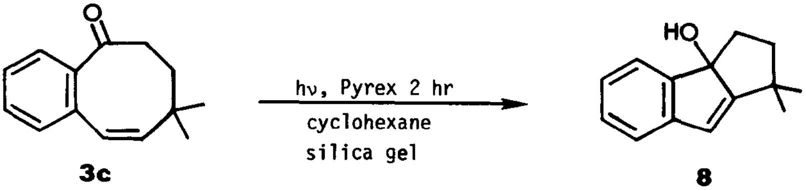
Irradiation of **3c** in ether (Pyrex, 2 hr) resulted in a number of changes in the nmr spectrum which suggested that a mixture of **3t** (87%) and **3c** (13%) was formed. In particular, the singlet at δ1.02 due to the gem dimethyl group in **3c** decreased in intensity, and two singlets appeared, 3H each, at δ1.18 and 1.23 assigned to the methyl groups in **3t**; clearly, **3t** is chiral whereas **3c** is not. The vinyl protons in **3c** appear as doublets at δ5.50 and 6.32, J = 13 Hz, whereas those in **3t** are at δ5.62 and 6.67, J = 15 Hz. Treatment of this ether solution with methanol at room temperature for 2 hr gave **4** (69%). In contrast, we found _trans_-4-cyclooctenone [2] to be inert toward methanol under these conditions.

When ether solutions of **3t** were passed through a silica gel column with CH_2Cl_2 as eluent, the crystalline diol **6** was isolated (46%) as colorless needles, mp 150-151°.[7] Only one isomer was formed in the stereospecific (and presumably concerted) addition of either methanol or water to 3t.

Reduction of 3c with $LiAlH_4$ gave alcohol 7c as an oil. In contrast, irradiation of 3c in ether followed by $LiAlH_4$ reduction gave the crystalline trans alcohol 7t, mp 85-87°.[7] Reduction did not occur in a transannular manner, since 7t still had two vinyl protons (δ5.72, 6.28, d, *J* = 16 Hz).[9] However, since 3t is chiral, one might have obtained two diastereomers of 7t; only one was found.



Finally, irradiation of 3c adsorbed on silica gel and suspended in cyclohexane gave the crystalline allylic alcohol 8,[7] mp 120-121° (vinyl proton as a singlet, δ5.95).



The established formation of 3t on irradiation of 3c tends to support our previous suggestion[3] that similar intermediates are involved in the photodimerization of the seven-membered analogs.

Acknowledgement. We are indebted to the National Institutes of Health (GM-15997) for financial support.

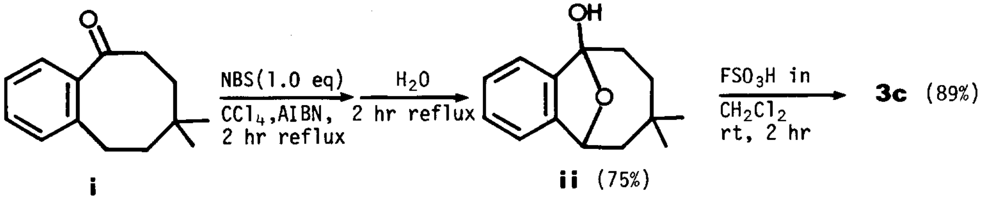
References and Notes

1. G.L. Lange and E. Neidert, Can. J. Chem., **51**, 2207, 2215 (1973), and previous references cited therein.

2. J.K. Crandall, C.F. Mayer, J.P. Arrington and R.J. Watkins, J. Org. Chem., **39**, 248 (1974), and previous references cited therein.

3. H. Hart and M. Suzuki, Tetrahedron Lett., in press.

4. Synthesized from the known[6] 6,6-dimethyl-2,3-benzo-2-cyclooctenone according to the following sequence:

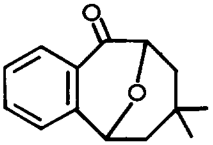


i

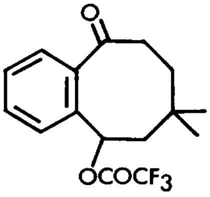
ii (75%)

+5% rec. i.

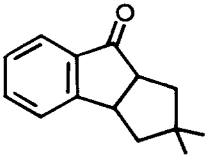
The conditions shown are critical. If excess (1.1 eq) NBS is used in the first step the yield of ii drops to 54% and some (17%) iii is formed; with 4 eq of NBS, iii becomes the principal product (72%). Attempts to dehydrobrominate the product of NBS bromination with collidine led to another series of products which could not be converted to **3c**; only the hydrolytic route was successful in eventually giving **3c**. If weaker acids are used in the last step other products are obtained. For example, with trifluoroacetic acid (rt, 12 hr) the product was iv (44%), and with refluxing 35% HCl (19 hr) the products were **3c** (19%) and v (32%).



iii



iv



v

5. The methyl groups at C6 were included to mimic the work[3] on seven-membered ring analogs. They do not influence the results significantly (unpublished results with Wolfgang Li).

6. R. Huisgen, I. Ugi, E. Rauenbusch, V. Vossius and H. Oertel, Chem. Ber., **90**, 1946 (1957).

7. All new compounds gave satisfactory elemental analyses and had spectra consistent with the assigned structures.

8. δ0.77 and 1.77 (s, 3H each, gem-dimethyl), δ2.00 (d, J = 2.5 Hz, C5 methine), δ3.15 (s, 3H, methoxyl), δ3.23 (s, 1H, OH, exchanged with D_2O), δ4.30 (d, J = 2.5 Hz, C4 methine), δ0.95-2.23 (m, 4H, methylenes), δ7.00-7.25 (m, 4H, arom). Using **3c**-d_2 (deuterium α to the carbonyl group), we obtained **4**-d_2 in which the methylene pattern simplified to two doublets at δ1.10 and 1.58, 1H each, J = 12 Hz, for the C7 methylene group.

9. The vinyl protons in **7c** appeared at 5.33 and 5.98 (d, J = 12 Hz).