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A NOVEL SYNTHESIS AND PHOTOISOMERIZATION OF A 4-VINYL-2,5-CYCLOHEXADIENONE

Harold Hart* and Makoto Nitta

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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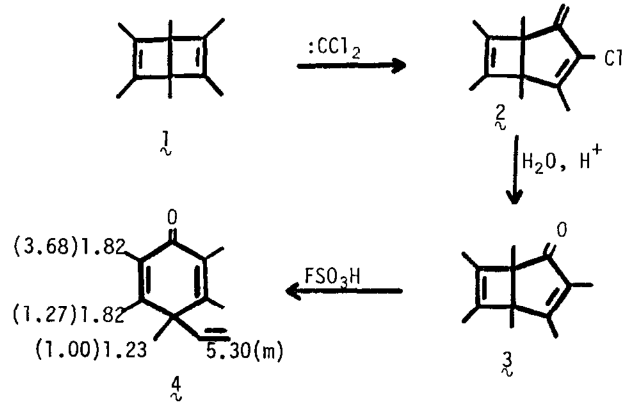
Although the photochemistry of 2,5-cyclohexadienones has been elegantly and thoroughly investigated,[1] no example with a 4-vinyl substituent has been studied. We report here on the synthesis and irradiation of 2,3,4,5,6-pentamethyl-4-vinyl-2,5-cyclohexadienone (4); the synthesis of 4 involved a novel acid-catalyzed rearrangement of an unsaturated ketone, and photoisomerization of the cross-conjugated cyclohexadienone resulted in an unusual skeletal rearrangement.

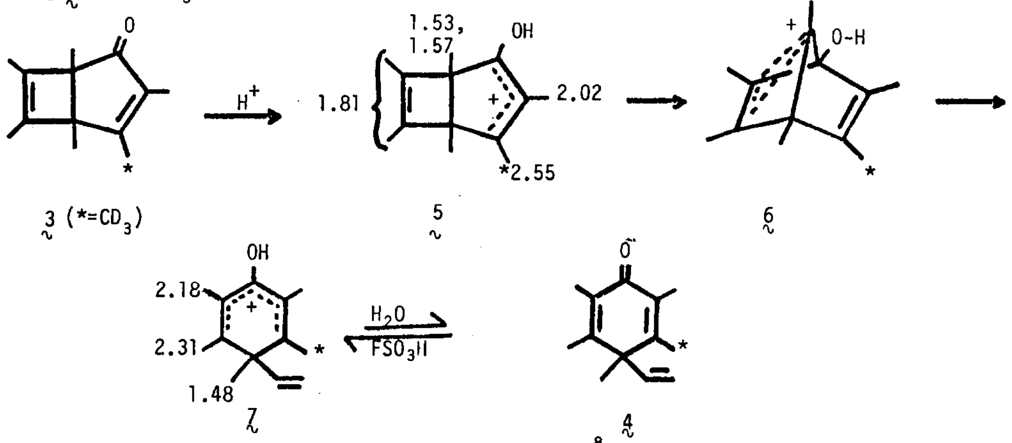
Synthesis of 4

The starting dienone 4 was prepared in three steps from hexamethyldewarbenzene according to the sequence of molecular rearrangements shown. The first two steps were described in the preceding communication.[2] In the final step, a stirred solution of 3 (800 mg) in methylene chloride (1 ml) was treated at -78° with 2 ml of FSO_3H, allowed to warm to room temperature, kept there for 2 hr and quenched (100 ml of saturated $NaHCO_3$, 0°). Workup and chromatography (Alcoa F-1, benzene eluent) gave 517 mg (65%) of an isomer[3], mp 32-33° (pentane), to which we assign structure 4. The ir ($\nu_{C=O}$ 1660 cm^{-1}) and uv [λ_{max}^{MeOH} 247 nm (ϵ13,140)] spectra are



typical[5] of a 2,5-cyclohexadienone. The pmr spectrum (CCl_4) consisted of singlets at δ1.23 (3H) and 1.82 (12H) and a multiplet at δ5.30 (3H, vinyl protons). Europium shift reagent split the signal at δ1.82 into two sharp 6-proton singlets; relative slopes are shown in parentheses on the structure.[6] Treatment of 4 (176 mg) in DMSO-d_6 (2 ml) with potassium t-butoxide (124 mg) at room temperature for 3 days gave (75%) 4-d_6 with the pmr peak at δ1.82 reduced in area to 6H; shift reagent showed that the exchanged methyl groups were at C3 and C5. Rearrangement of 3 with a CD_3 group at C4[7] gave 4 with a CD_3 group at C3 (C5), shown by nmr.

A possible mechanism for the rearrangement of 3 to 4 is shown. Ion 5 was observed by treating 3 with FSO_3H at -78°; when such solutions were quenched without being warmed to room

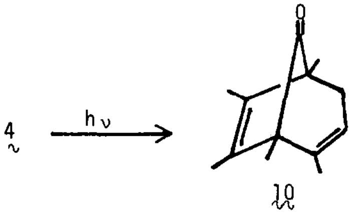


temperature, the rearrangement of 3 to 4 did not occur.[8] However at room temperature 5 rearranged rapidly to 7, whose partial pmr spectrum is shown on the structure; the same ion was obtained by adding 4 to FSO_3H at room temperature. Although a 1,2-shift to the OH-bearing carbon must have occurred, the precise structure of the intermediate depicted as 6 and the manner by which it rearranges to 7 are not yet known.

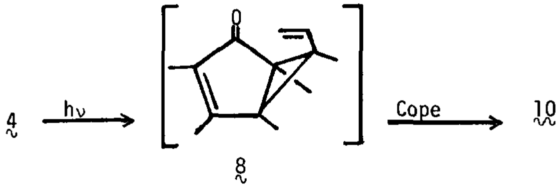
Photoisomerization of 4

Irradiation of 4 (57 mg) in methanol (15 ml) with a Hanovia 450 W lamp through a Corex filter, monitored by vpc (5% SE-30 on Chromosorb W, 150°), was essentially complete in 5 hr. Evaporation of the solvent and purification by vpc gave 50 mg (88%) of the photoproduct and 5 mg (9%) of recovered 4. Examination of the crude photoproduct by pmr showed that the vpc collection process caused no change in the structure of the product.

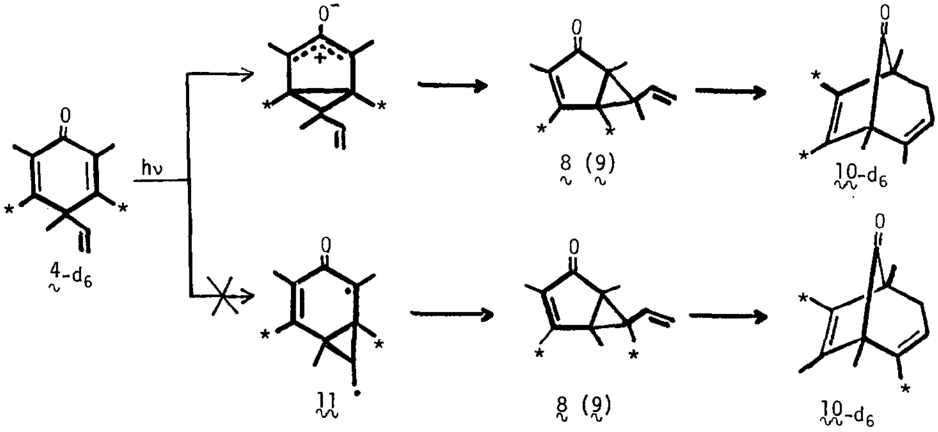
We assign the product structure 10 from its spectral data and method of synthesis. Elemental analysis and a mass spectrum showed that 10 was an isomer of 4.[9] The carbonyl absorption ($\nu_{C=O}$ 1753 cm^{-1}) and uv spectrum [λ_{max}^{MeOH} 280 nm (ε24), end absorption at 220 nm (7140)] clearly eliminated either anticipated structure 8 or 9. The pmr spectrum (CCl_4) showed one vinyl proton at δ5.13 (m), two aliphatic methyls at δ1.03, three allylic methyls at δ1.67 (m) and two additional allylic protons at δ2.17 (m), all consistent with the assigned structure 10.



One plausible path from 4 to 10 is *via* the endo-vinyl compound 8 which, being a *cis*-divinylcyclopropane may spontaneously undergo a Cope rearrangement to 10. Since the yield of 10 was nearly quantitative, one would have to argue that if this is the only route to 10, 4



must isomerize preferentially to 8 rather than to the corresponding *exo*-vinyl compound 9.[10] Alternatively 4 may photoisomerize to both 8 and 9 which may (a) interconvert or (b) rearrange to 10 by a non-Cope (thermal or photochemical) path. Neither 8 nor 9 was detected in room temperature irradiations of 4; possible intermediates between 4 and 10 and further mechanistic details are being sought experimentally.



One could also consider a di-π-methane vinyl-migration route (observed with 4,4-diphenyl-2-cyclohexenone[11]) from **4** to **10**. A labeling experiment was done to test this possibility. Irradiation of **4**-d_6 gave **10**-d_6 with the multiplet at δ1.67 (allylic methyls) reduced in area to 3 protons. The peak was still a multiplet, and nmr irradiation[12] of the vinyl proton caused collapse of this multiplet mainly to a doublet (due to long-range coupling of the C2 methyl with one of the methylene protons); irradiation at the δ1.67 methyl signal caused collapse of the vinyl multiplet to a triplet (coupling with the adjacent methylene). These results are only consistent with the unlabeled allylic methyl group being adjacent to the vinyl proton. Consequently one can confidently rule out the vinyl migration mechanism via a di-π-methane intermediate such as **11**.

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REFERENCES AND FOOTNOTES

1. For reviews, see P. J. Kropp in "Organic Photochemistry" edited by O. Chapman, Marcel Dekker, Inc., New York, **1**, 1 (1967); H. E. Zimmerman, Angew. Chem., Intl. Ed. Engl., **8**, 1 (1969).
2. H. Hart and M. Nitta, Tetrahedron Lett., preceding paper.
3. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.45. Found[4]: C, 82.18; H, 9.62. Mass spectrum: m/e (rel intensity) 190 (76), 147 (100).
4. Spang Microanalytical Laboratory, Ann Arbor, Michigan.
5. A. J. Waring, "Alicyclic Chemistry," edited by H. Hart and G. J. Karabatsos, Academic Press, New York, **1**, 184-190 (1966).
6. D. R. Kelsey, J. Amer. Chem. Soc., **94**, 1764 (1972).
7. Prepared by treating **3** with $NaOCH_3/CH_3OD$.
8. Treatment of **3** with trifluoracetic acid at room temperature (3 hr) or reflux (2 hr) also gives recovered **3** after quenching.
9. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.45. Found:[4] C, 81.91; H, 9.27. Mass spectrum: m/e (rel intensity) 190 (50), 147 (100).
10. This result would be expected on steric grounds if a vinyl group is larger than a methyl group; see T. R. Rodgers and H. Hart, Tetrahedron Lett., 4845 (1969).
11. H. E. Zimmerman and J. W. Wilson, J. Amer. Chem. Soc., **86**, 4036 (1964); H. E. Zimmerman and K. G. Hancock, ibid., **90**, 3749 (1968); H. E. Zimmerman and W. R. Elser, ibid., **91**, 887 (1969).
12. These experiments were done on a Varian HA-100 instrument.