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A NEW PHOTOCHEMICAL REARRANGEMENT OF 2,4-CYCLOHEXADIENONES

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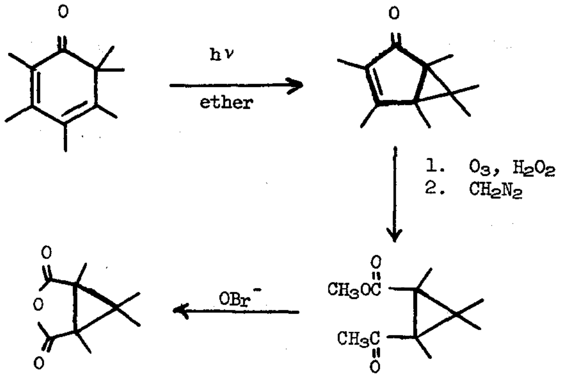
The three known types of photochemical transformations of 2,4-cyclohexadienones were elucidated in the classic work of Barton and Quinkert[1,2]: (a) ring fission between C_1 and C_6 to a diene-ketene; (b) expulsion of an acetoxyl group from the 6-position and aromatization of the dienone; and (c) rearrangement of an acetoxyl group from the 6- to the 5-position, again with aromatization. We wish to record here a fourth alternative, rearrangement to a bicyclo[3,1,0]hexane derivative.

A 1% ether solution (anhydrous or saturated with water) of hexamethyl-2,4-cyclohexadienone (I)[3] was irradiated in Pyrex, N_2 atmosphere, with a Hanovia S 200 watt lamp for several hours. Reaction was allowed to proceed until there was no further change in the ultraviolet absorption spectrum of the mixture, the observed spectral change being a decrease in the dienone absorption at 330 mμ and appearance of a new maximum in this solvent at 268 mμ. Evaporation to dryness gave a semicrystalline oil which was purified by v.p.c., using a 20% silicone SE-30 column at 170-

180°. The principal product amounted to over 80% of the whole.* Pure



I

II

III

IV

material melted at 47-50° and analyzed for an isomer of I. It showed infrared bands in CCl_4 solution at 1690 and 1640 cm^{-1} (*cf.* umbellulone[4], 1695 and 1620 cm^{-1}) and ultraviolet maxima in 95% ethanol at 235 mμ (6270), 274 mμ (3240) and 320 mμ (605).** The n.m.r. spectrum showed five singlets at 8.12, 8.45, 8.78, 8.90, and 9.08_{τ}, with area ratios 1:1:1:2:1. On the basis of these data and degradations described below, the photoproduct appears to be 1,3,4,5,6,6-hexamethylbicyclo[3,1,0]hex-3-ene-2-one (II).

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*Four minor products, one of which came to about 10%, have not yet been investigated.

***Cf.* umbellulone[4], 220 mμ (5900), 265 mμ (3290) and 308 mμ (200). The shapes of the curves were nearly identical, but the spectrum of II was bathochromically shifted by an amount reasonable for the additional α-methyl substitution.

Crude photoproduct (500 mg.) was ozonized in CH_2Cl_2 solution at dry ice temperature and the ozonide decomposed with boiling dilute alkali and hydrogen peroxide. Acidification (pH 4) and ether extraction gave an acid which was immediately converted by diazomethane to an oily ester, subsequently purified by v.p.c. (>80% one peak). The ester had infrared bands at 1720 cm^{-1} (ester) and 1705 cm^{-1} (cyclopropyl ketone) and singlets at 6.34τ (methyl ester), 7.90τ (methyl ketone), 8.73, 8.80 and 8.90τ with relative areas 1:1:2:1:1. This compound is formulated as the *cis*-Ketoester III.

III (215 mg.) in dioxane was treated with sodium hypobromite[5]. The resulting oil was purified by v.p.c. and gave a white solid (overall from photoproduct, about 70%) m.p. 144-145° which analyzed correctly for tetramethylcyclopropane-1,2-dicarboxylic anhydride (IV)*. It showed bands at 1875, 1825, and 1775 cm^{-1}. (order of increasing intensity) and two singlets in the n.m.r. at 8.65 and 8.82τ (CCl_4 solution) with relative intensities 3:1.**, ***

The photoproduct II is reasonably stable toward the irradiating conditions; overirradiation resulted in only a slight decrease in yield of II.

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* The anhydride appears to be formed directly in the hypobromite reaction; treatment of the crude product from this reaction with diazomethane gave predominantly anhydride, rather than ester.

** A spectrum of three singlets might have been expected for IV; apparently two of these (not unreasonably) appear at the same or very nearly the same magnetic field. It is thought that the single methyl at higher field is the one cis to the anhydride ring.

*** New compounds II, III and IV gave satisfactory microanalyses.

The mechanism by which II is formed from I can be formulated in a variety of ways, which will not be speculated upon here. The net result is cleavage between C_1 and C_8 with 'bond-crossing' addition to C_5 and C_4 respectively.

Work is continuing on the scope and mechanism of this rearrangement, and on the chemistry of the photoproduct.

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