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REVERSAL OF REGIOSPECIFICITY IN GROUND-STATE VS. EXCITED-STATE CYCLOADDITIONS

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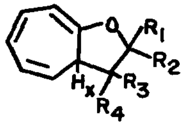
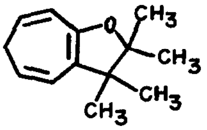
Some time ago we reported that tropone (1) undergoes facile 8 + 2 photochemical cycloaddition to many electron-rich alkenes to give 2-oxa-2,3,4,4a-tetrahydroazulenes.[1] More recently, we have observed that this process occurs[2] with the ketene acetals 1,1-diethoxyethene and 1,1-dimethoxyethene to afford adducts 2a and 2b in modest yield (~ 40%); [(2a, nmr ($CDCl_3$, 220 MHz):

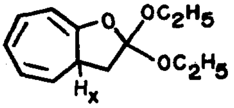




2a, $R_1 = R_2 = H$, $R_3 = R_4 = OC_2H_5$ 2b, $R_1 = R_2 = H$, $R_3 = R_4 = OCH_3$ 3

τ 3.46 (2d, J = 11, J' = 6.0), 3.74 (1H, 2d, J = 10.8, J' = 6.0), 3.85 (1H, m), 4.38 (1H, *l*, J = 6.6), 4.64 (1H, 2d, J = 9.5, J' = 5.0) 5.99 (2H, AB, J = 9.7, $\Delta\nu$ = 0.46 ppm), 640 (4H, 2Q, J ~ 7), 7.58 (1H, m), 8.77 (6H, 2 , J ~ 7); m/e 222 (P, 14), 116 (100).] The orientation follows from the appearance of the methylene group α to oxygen as an AB pattern not further split by H_x, (just as was the case with the previously reported 2c ($R_1 = R_2 = R_3 = R_4 = CH_3$). Compounds 2a and 2b survive gas chromatographic purification at 170°, in contrast to the behavior of 2c which undergoes 1,5 sigmatropic shift of hydrogen to afford 3[1].

In contrast to the photochemical process, thermal reaction of 1 with 1,1-diethoxyethene gave the 8 + 2 adduct 4[3] (60%) and the 4 + 2 (Diels-Alder) adduct 5[3] (22%). The orientation of 3 was evident from the appearance of the signal due to the methylene hydrogens in the 220 MHz nmr spectrum of 4 as the AM part of an AMX pattern; τ 7.37 (2d, J = 11.5, J' = 10.0) and 7.81 (2d, J = 11.5, J' 6). The signal due to H_x was an unresolved blur (τ 7.1). Chemical confirmation of this assignment was provided by the formation, on acid hydrolysis of ortho ester 4, of keto ester 6, identified by its analytical and spectral data [(ir (film) 1710 and 1727 cm^{-1}; nmr ($CDCl_3$, 220 MHz): τ 3.72 (2H, m), 415 (1H, d of d of d, J= 8.8, J' = 4.5, J" = 4), 4.47 (1H, 2d, J = 10, J' = 4.5), 5.88 (2H, a, J = 7), 6.49 (1H, m, br), 6.72 (1H, 2d, J = 19, J' = 7.4), 6.97 (24, m), 7.36 (1H, 2d, J= 16.5, J' = 5), and 8.70 (3H, t, J = 7); m/e 194 (p, 11), 165 (23), 148 (100).] The normal Diels-Alder product, 5, is assigned the orientation shown on the basis of the fact that



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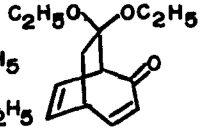

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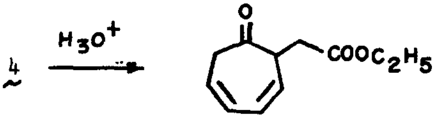

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the nmr signal for the bridgehead hydrogen α to carbonyl appears as only a doublet (τ 6.23, J = 6).

The complete reversal of regiospecificity observed here on going from thermal to photochemical conditions is interesting and rare. Examples are known of 4 + 2 thermal vs 2 + 2 photochemical addition with a given pair of reactants[4]. A second example of the phenomenon observed here is with the pair of reactants 2-cyclohexenone and 1,1-diethoxyethene. The major photochemical cycloadduct is 7, analogous to the results of Corey, et. al.,[3] using 1,1-dimethyoxyethene[5]. We find that thermal reaction (140°, 50 hrs) gives ~ 15% of isomer 8, identified by its spectral parameters and by its acid-catalyzed hydrolysis to a product with properties expected for a β-diketone

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2. Rayonet reactor with 3600 A° lamps, benzene solvent, reaction temperature of 5-10°.
3. Complete spectral details on this compound will be reported in our full paper on these and related reactions.
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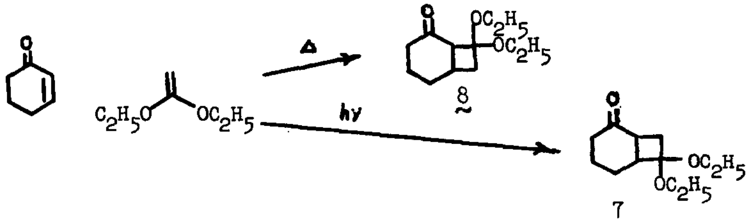

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