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BIMOLECULAR CYCLOADDITIONS OF *o*-XYLYLENE: THE CYCLOREVERSION OF DEWAR *o*-XYLYLENE

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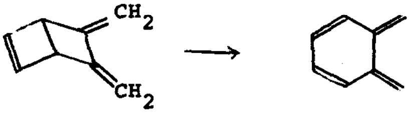
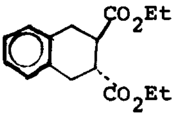
This report concerns the cycloadditions of *o*-xylylene (II), studied under exceptionally mild conditions with emphasis on stereochemistry, and the cycloreversion whereby it is formed from Dewar *o*-xylylene (I).[1] *o*-Xylylene has previously been trapped (by Diels-Alder addition) only at relatively high temperatures;[2,3] therefore little is known concerning its reactivity and nothing concerning the stereochemistry of its additions.[4] The cycloreversion of I is inherently interesting because the symmetry "allowed" conrotatory mode is prohibited by excessive angle strain.[5]

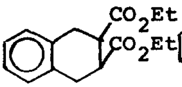


I II

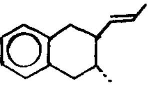
The reactions of I with diethyl fumarate and maleate were studied in tetrachloroethylene solution at 60-80°. The Diels-Alder adducts III and IV, respectively, were formed in good yield as the only detectable products (nmr). The fumarate adduct (III) has nmr (CCl$_2$=CCl$_2$)τ3.0(s,4H),5.9(q,4H, J=7Hz) 7.05(s,6H), 8.75(t,6H,J=7Hz); mass spectrum *m/e* 276 (M); the maleate



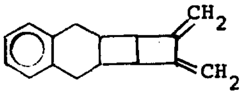
III



IV



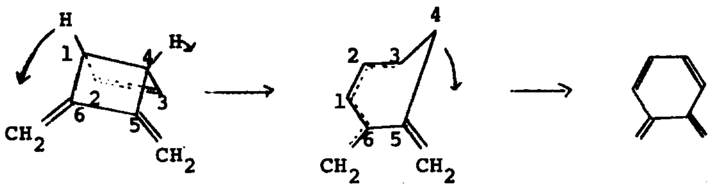
V



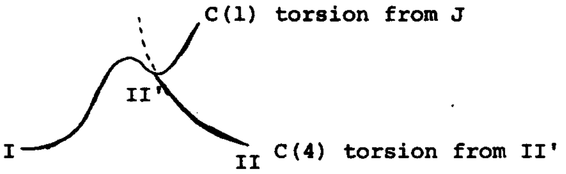
VI (exo, endo)

adduct (IV) has nmr (CCl$_2$=CCl$_2$)τ3.0(s,4H), 5.9(q,4H,J=7Hz), 6.9(s,4H), 7.06(broad s,2H), 8.75(t,6H,J=7Hz); mass spectrum *m/e* 276 (M). The cycloadditions of II with the maleate-fumarate pair are $\geq$ 98% stereospecific (nmr). The kinetics of the reaction of I with diethylfumarate in tetrachloroethylene solution were studied by nmr spectroscopy at several different fumarate concentrations and three temperatures. The reactions were followed in each case to greater than three half lives. The first order rate law $-d[I]/dt=k_1[I]$ was obeyed in all cases, with rate constants $k_1 \times 10^5$ sec^{-1}=7.614$\pm$0.003 (66.5$\pm$0.5°, 2:1 ratio of I: fumarate), 7.264$\pm$0.003 (66.5°, 1:4 ratio), 10.687$\pm$0.004 (71.8, 1:2), and 22.171$\pm$0.011 (81.5°, 1:2). The initial concentration of I was 5M in each run, and no intermediates were formed in detectable amounts. The activation parameters obtained by least squares regression analysis of the Eyring equation are $\Delta H^{\ddagger}$=17.17$\pm$0.34 kcal/mole and $\Delta S^{\ddagger}$=-27.19$\pm$0.99 eu. Thus, even with a moderately reactive dienophile the cycloaddition of I proceeds *via* II. The reaction of I with refluxing neat *t,t*-2,4-hexadiene (1:90 mole ratio) is also cleanly first order (as expected for the poorly dienophilic hexadiene) and stereoselective. The adduct V, purified by vpc, has nmr (CDCl$_3$, HA-100)τ3.00(s,4H), 4.57-4.70(m,2H); 7.0-8.2(m,6H), 8.34(d,3H,J=5.0Hz), 9.04(d,3H,J=6.0Hz). Only a single peak was resolved by vpc. Both cycloadditions emerge as typical, stereospecific Diels-Alder reactions, but the ability of II to react with 2,4-hexadiene suggests that it is a rather reactive diene. Some selectivity is evident however. Heating I and *t,t*-2,4-hexadiene (1:10 mole ratio) in tetrachloroethylene solution gives mainly the hydrocarbon dimers VI, which are obtained solely upon heating I (60-80°) in tetrachloroethylene: nmr(CCl$_4$)τ2.95(s,4H), 4.93(s,2H), 5.33(s,2H), 7.25(s,4H), 7.0-7.6 (m,2H); mass spectrum *m/e* 208 (M). Pyrolysis of I in the vapor phase (270°) gives benzocyclobutene cleanly.

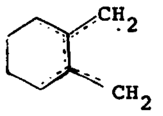
The mechanism whereby II is formed from I cannot be specified with certainty, but a tentative proposal may be offered. Though a symmetrical disrotatory cycloreversion of I should be harshly penalized by antibonding overlap, a highly unsymmetrical disrotatory mode should escape most of this penalty (an extreme form of this latter mechanism is the one in which only C(1) rotates at first). The C(1)-C(4) bond is cleaved, in such mechanisms, with assistance from the release of most of the angle strain of I, while the



I • II' III



inefficient C(4)-C(3,5) overlap keeps the antibonding penalty low. Some C(2)-C(3) overlap is sacrificed but is compensated for by a gain in C(1)-C(2,6) and C(3)-C(5) overlap. Continuation along this torsional coordinate eventually passes C(1) through the C(2,3,5,6) plane, leading to the increased angle strain of a chair form. Therefore II' is suggested as a relative energy minimum along this torsional coordinate. It is emphasized that II' is not a diradical; two non-overlapping radical fragments are impossible in such a small ring; rather, it is a twisted (torsionally excited) state of II. It is probable that II' is not a true intermediate, for torsion along a new coordinate [C(4) now moving downward] leads to II with probable monotonic decrease in angle strain and increase in pi bonding. C(1)-C(4) overlap is, by now, small, so that the conversion to II should not be seriously hampered by the antibonding nature of this interaction. The torsional relaxation of II' → II is probably no slower than diffusion controlled, and trapping such a state would seem hopeless. For example, the diradical VII, though probably



VII

more reactive than II', exhibits impressive selectivity in its cycloadditions.[7]

In summary, it has been suggested that II is formed from I in an unsymmetrical disrotatory cycloreversion involving a pseudo intermediate state. The II formed is highly reactive but not unselective. Its cycloadditions are stereospecific and therefore probably concerted.

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(2) M. P. Cava and A. A. Deana, ibid., 81, 4266 (1959).

(3) K. Sisido, Y. Udo, and H. Nozaki, J. Org. Chem., 26, 584 (1961).

(4) However, the stereochemistry of the additions of diphenyl-o-xylylene has been studied: R. Huisgen and H. Seidl, Tet. Letters, 3381 (1964).

(5) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim Germany, 1970, p. 173.

(6) A mixture of cis and trans isomeric adducts is obtained from VII and t,t-2,4-hexadiene, by contrast. These are partially resolved by vpc and have well resolved methyl nmr doublets. To be published.