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CYCLOADDITION OF N-PHENYLTRIAZOLINEDIONE TO OCTAMETHYLSEMIBULLVALENE AND RELATIVE EASE OF NITROGEN EXTRUSION FROM THE DERIVED AZO ADDUCTS

Y. C. Toong, Weston Thatcher Borden*, and Avram Gold

Department of Chemistry, Harvard University, Cambridge, Mass. 02138

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In connection with some studies of substituted semibullvalenes[1] we had occasion to examine the cycloaddition of N-phenyltriazolinedione (PTAD)[2] to octamethylsemibullvalene (OMSB). Criegee and Askani have found that azo esters add to OMSB[3a] and that the adducts have the structures[3b] expected from the products of a symmetry allowed[4] ${}_{\pi}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ reaction--a Diels-Alder type cycloaddition to a vinylcyclopropane.[5] Although we have confirmed that azo esters do, in fact, yield only this type of product (vide infra), we have found that PTAD adds to OMSB to give both **1**[6] [nmr[7] ($CDCl_3$): δ0.88 (s, 6H), 1.64 (q, 6H, J = 1 Hz), 1.70 (q, 6H, J = 1 Hz), 1.75 (s, 6H) and 7.39 (s, 5H)] and **2**[6] [nmr ($CDCl_3$): δ1.07 (s, 3H), 1.10 (s, 3H), 1.56 (s, 6H), 1.68 (q, 6H, J = 1 Hz), 1.78 (q, 6H, J = 1 Hz) and 7.50 (s, 5H)]. The ratio of **1** to **2** shows a small dependence on the solvent used for the reaction, varying from 7:3 in CCl_4 to 6:4 in acetonitrile to 1:1 in CH_2Cl_2 to 3:7 in THF, when the reaction is carried out at 0°.[8] At lower temperatures in CH_2Cl_2 **2** becomes the predominant product. The product ratio is kinetically rather than thermodynamically controlled; for **1** rearranges quantitatively to **2** on heating at 60° in polar solvents like methanol ($t_{1/2}$ = 6 hr).[9] In non-polar solvents the rearrangement is much slower. For instance, a sample of **1** heated at 110° in benzene was unchanged after 13 hr and only partially isomerized after 14 hr at 140°.

Since both "allowed" (**1**) and "forbidden" (**2**) adducts are formed in the reaction of PTAD with OMSB, we were led to question whether there is, in general, any stabilization of the transition

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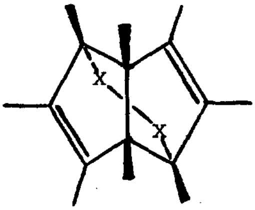
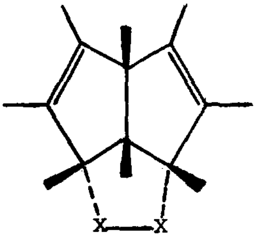
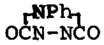
*Address correspondence to this author at the Department of Chemistry, University of Washington, Seattle, Washington, 98195.

state for a concerted ${}_{\pi}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ cycloaddition over that for a forbidden or stepwise process. In order to investigate this question we chose to examine the reverse reaction and study the relative ease of nitrogen loss from the azo compounds derived from 1 and 2. The diazatriquinacene derivative (4)[6] was readily prepared by hydrolysis of 2 in refluxing methanolic KOH for three days, followed by air oxidation of the resulting hydrazo compound (6). On irradiation or heating in solution, 4 decomposes smoothly to OMSB. The half time for the thermal reaction in pyridine is 1.5 hr at 105°--about what would be expected for a derivative of 3,3'-azo-1-propene.[10] Since concerted loss of nitrogen from 4 is a forbidden process,[4] this correspondence is not altogether surprising.[11]






$\overset{\ulcorner NPh \urcorner}{OCN\text{-}NCO}$

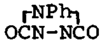
1 X-X = $\overset{\ulcorner NPh \urcorner}{OCN\text{-}NCO}$

3 X-X = N=N

5 X = NH

7 X = $NCO_2CH_2CH_3$

9 X = $NCO_2CH_2CCl_3$


$\overset{\ulcorner NPh \urcorner}{OCN\text{-}NCO}$

2 X-X = $\overset{\ulcorner NPh \urcorner}{OCN\text{-}NCO}$

4 X-X = N=N

6 X = NH

8 X = $NCO_2CH_2CH_3$

The instability of 1 with respect to rearrangement to 2 made 7 much more attractive than 1 as a precursor of 3. The adduct (7) of OMSB and diethyl azodicarboxylate was prepared; however, its hydrolysis gave not the desired hydrazo compound (5), but instead 6. It could be shown that under the hydrolysis conditions 7 rearranges to 8, although this rearrangement requires higher temperatures (150°), and a more polar medium (methanolic KOH or methanol-water-KCl) than that of 1 to 2. In order to circumvent the rearrangement of 7 to 8, we prepared an azo ester whose adduct with OMSB could be hydrolyzed to 5 under much milder conditions. Reaction of OMSB with di-2,2,2-trichloroethyl azodicarboxylate[12] gave only the "allowed" adduct (9), which was converted to 5 by heating in refluxing methanol in the presence of a zinc-copper couple. After purification, 5 was oxidized by one of several methods; but in no case were we able to isolate or even detect the diazalumibullvalene derivative (3) that is the expected oxidation product.[13] For instance, when oxygen is bubbled through a solution of 5 at -20°, the only product isolated is the endoperoxide of OMSB,[3a] which is also formed by exposure of OMSB to the reaction conditions. Treatment of **5** with mercuric oxide at -20° resulted in its slow conversion to OMSB, which itself was slowly oxidized under the reaction conditions. Our failure to isolate **3** is understandable in light of the experience of others[14] with the rapidity of allowed[4] nitrogen extrusion reactions.

Although other factors, such as ground state energies, may contribute to the difference in ease of nitrogen loss from **3** and **4**, we believe that orbital symmetry[4] is chiefly responsible. This raises the question of why both the "forbidden" and "allowed" adducts are formed in the reaction of OMSB with PTAD. The answer probably is that **1** and **2** both arise from a zwitterionic intermediate, which is also implicated in the facile rearrangement of the former to the latter. Such intermediates are formed in the additions of PTAD to olefins that can give highly stabilized carbocations.[15] Attack of an electrophile on OMSB generates a carbocation that is simultaneously ditertiaryallylic and homoallylic, and the sensitivity of OMSB to acid is indicative of the stability of this cation.[16]

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References and Notes

1. A. Gold and W. T. Borden, *J. Amer. Chem. Soc.*, **94**, 7179 (1972).

2. Prepared from the urazole by the method of J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966).

3. (a) R. Criegee and R. Askani, *Angew. Chem. Int. Edit.*, **7**, 537 (1968).
   (b) Personal communication.

4. R. B. Woodward and R. Hoffmann, *ibid.*, **8**, 781 (1969).

5. Possible examples of such a cycloaddition have been reported by J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971) and by S. R. Tanny and F. W. Fowler, *J. Org. Chem.*, **39**, 2715 (1974).

6. A satisfactory elemental analysis was obtained for this compound.

7. The nmr spectrum of **1** proved temperature dependent. At low temperatures the resonance at high field for the bridgehead methyls was considerably broadened, although even at -100° it was not resolved into two separate peaks. This may indicate flipping of the urazole ring with a low barrier to planarity in the hydrazide nitrogens.

8. Even at lower temperatures the reaction between OMSB and PTAD is so fast that we were unable to study the effect of solvent polarity on the rate.

9. Rearrangement can also be effected at room temperature by addition of a drop of trifluoroacetic acid to a $CHCl_3$ solution of **1** or by stirring such a solution over silica gel. Use of Quanta Gram PQ 5F preparative plates was found to allow the separation of **1** from **2** without isomerization.

10. B. H. Al-Sader and R. J. Crawford, *J. Can. Chem.*, **48**, 2745 (1970).

11. Only one bond is thought to cleave in the transition state for decomposition of 3,3'-azo-1-propene [R. J. Crawford and K. Takagi, *J. Amer. Chem. Soc.*, **94**, 7406 (1972)], and the correspondence between this compound and **4** in rate of nitrogen loss suggests a similar transition state for decomposition of **4**. In contrast, rate studies [M. Schneider and G. Mossinger, *Tetrahedron Lett.*, 3081 (1974) and R. J. Crawford and M. Ohno, *Can. J. Chem.*, **52**, 3134 (1974)] show that in 3,5-divinylpyrazolines, other than **4**, both vinyl groups stabilize the transition state, implying concerted nitrogen extrusion.

12. M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Amer. Chem. Soc.*, **95**, 7325 (1973) have independently prepared this azo ester and put it to a similar use.

13. R. Aksani has informed us (private communication) that he has observed similar behavior in **3**, which he prepared by a route different than ours.

14. See, for instance, N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, **91**, 5668 (1969) and references therein.

15. E. K. van Gustorf, D. V. White, B. Kim, D. Hess, and J. Leitish, *J. Org. Chem.*, 35, 1155 (1970); S. R. Turner, L. J. Guilbault, and G. B. Butler, *ibid.*, **36**, 2838 (1971); R. Huisgen, W. E. Konz, and U. Schnegg, *Angew. Chem. Int. Edit.*, **11**, 715 (1972).

16. R. Criegee, *ibid.*, **1**, 519 (1962).