

THERMAL DECOMPOSITION OF TETRACYCLO [5.3.0.0^{2,10}.0^{3,6}] DECA -4,8-DIENE. AN UNUSUAL DISPROPORTIONATION REACTION.

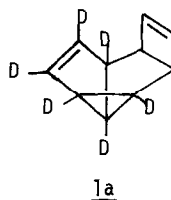
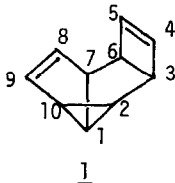
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(Received in USA 16 August 1973; received in UK for publication 3 September 1973)

In contrast to the isomerization processes which seem to predominate in the thermal and photochemical reactions of C₁₀H₁₀ hydrocarbons¹, it has been observed that the title compound (1) undergoes an unusual

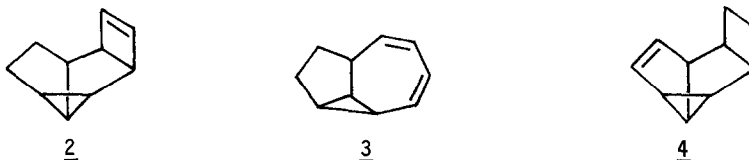


disproportionation reaction to give C₁₀H₈ and C₁₀H₁₂ products. The irradiation of 1 was reported to give an isomeric cage compound by a (2+2) cycloaddition².

1² in solution in cyclohexane had a half-life of 1 hour at 200°. The major products of the pyrolysis which accounted for 80% of the starting material³ consisted of naphthalene (43%) and two new compounds (2 and 3) whose ratio depended on the extent of the decomposition. Rate studies indicated that 2 rearranged thermally to yield 3. At 230°, only 3 could be isolated.

2 analyzed to the composition C₁₀H₁₂ (Mol. Wt. 132) and showed olefinic absorption in its infrared (3010, 1545 cm⁻¹) and ultraviolet spectra (end absorption). Its nmr spectrum⁴ (δ , 6.27-1H- br. s.; 6.02-1H-d., J=2Hz; 3.66-1H-d. of d.; 3.53-1H-d. of d.; 2.50-1H; 2.40-1H-quartet, J=7Hz; 2.00-1H; 1.82-1H; 1.53-1H; 1.30-1H; 0.92-2H) indicated the presence of (a) 2 olefinic protons, (b) a cyclopropyl ring, and (c) a significant structural relationship to 1 since the first six proton absorptions listed resembled those of 1 in chemical shifts and coupling patterns. The spectral characteristics of the olefinic bond in 2 suggested that it was located in a cyclobutane ring. This was confirmed by examining the thermal decomposition product of 2, i.e., 3. The latter also analyzed to C₁₀H₁₂, and in its ultraviolet spectrum (solvent: pentane) had an absorption maximum at 262.0 nm (ϵ_{\max} = 4700) which could be attributed to a cyclic conjugated diene.⁵ The nmr spectrum of 3 (δ , 6.23 -2H; 5.77-1H-d. of d.; 5.67-1H-d. of d.; 3.02-1H;

1.0-2.0-6H; 0.85-1H) showed the presence of four olefinic protons and further indicated that the cyclopropyl ring from 2 was intact in 3. These data require that 2 should be tetracyclic and 3 should be tricyclic and the following structures seemed appropriate:



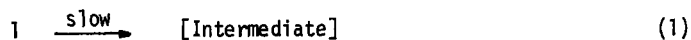
Confirmatory evidence for structure 2 was obtained by catalytic hydrogenation (Adam's catalyst; $H_2/1$ atm) of the compound to a solid $C_{10}H_{16}$ derivative which proved identical to the one derived from the photochemical 1,3-adduct of benzene to cyclobutene (4)⁶ by a similar reduction.

Further structural and mechanistic evidence for these reactions was gathered from the pyrolysis of 1a which was prepared by using deuteriobenzene instead of benzene in the photoaddition to cis-3,4-dichlorocyclobutene². The nmr spectrum of 1a consisted of four absorptions at δ , 6.20, 5.60, 3.92, and 3.81, all of equal intensity. These could be attributed to the four protons at C_3 , C_4 , C_5 and C_6 positions. It was estimated that the other positions in the molecule were at least 96% deuterated.

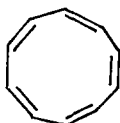
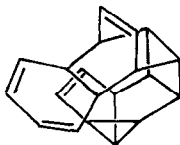
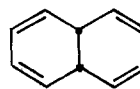
2a derived from the pyrolysis of 1a in cyclohexane solution⁷ was made up of $C_{10}H_4D_8$ 31%, $C_{10}H_5D_7$ 47%, and $C_{10}H_6D_6$ 22%⁸. The nmr spectrum of the compound showed four absorptions of equal intensity at δ , 6.25, 6.00, 3.64, and 3.52 and two other absorptions at δ , 1.81, and 1.36 of about 60% intensity each. The naphthalene derived from the same pyrolysis analyzed to $C_{10}H_4D_4$ 30.2%, $C_{10}H_3D_5$ 45.9%, and $C_{10}H_2D_6$ 22.9%. Its nmr spectrum showed that the α and β positions were equally deuterated ($\pm 5\%$).

The isotopic labelling demonstrates that the hydrogen (or deuterium) atoms lost from 1 to give naphthalene are almost exactly accounted for by the atoms picked up by a second molecule of 1 to yield 2. The latter process seems to be a straight-forward reduction of the C_8 - C_9 olefinic bond (although the stereochemistry is unknown) without any scrambling of hydrogens or reorganization of the carbon skeleton.

The predominant mode of disappearance of 1 corresponds to the overall process: $2 \text{ } \underline{1} = \text{ naphthalene} + \underline{2}$. Kinetic study indicated that in solution at 200°, the reaction followed pseudo first-order rather than a second-order dependence on the concentration of 1.⁹ It suggests that the mechanism of the disproportionation can be visualized as:



A clue to the nature of the intermediate is provided by the deuterium labelling. The naphthalene derived from this experiment is completely scrambled and the loss of two atoms of H (or D) is nearly according to a random selection process provided all of the carbon atoms are in equivalent positions¹⁰. Therefore the intermediate may be all cis-1,3,5,7,9-cyclodecapentaene (5)¹¹ which can be readily formed from 1 by breaking the three internal bridges. The transfer of two hydrogens from 5 to a

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molecule of 1 with the degree of specificity that is observed represents an intriguing process. It may involve an initial addition of 5 to 1 to give a transient species such as 6 which could subsequently split into $C_{10}H_8$ and $C_{10}H_{12}$ ¹². This would account for one of the peculiar features of the disproportionation step (2) which is the preferential reduction of the cyclopentene over the cyclobutene group in 1. The formation of 6 may, in principle, go through the sequence: 5 \rightarrow cis-9,10-dihydronaphthalene(7) \rightarrow 6 because 5 is known to give 7 predominantly¹ and the latter has been shown to have reducing properties even at 100°¹³. This alternative route may be excluded on the grounds that the disproportionation of 7 seems less site-specific¹³ than the reaction described here¹⁴.

Acknowledgment: The author thanks the Air Force Office of Scientific Research (AFSC), U.S. Air Force for Contract No. F44620-72-C-0024 under which this work was carried out. He is also grateful to Professor R. M. Moriarty of the University of Illinois, Chicago Circle for a very useful discussion.

References:

1. L. T. Scott and M. Jones, Jr., Chem. Rev., 72, 181 (1972).
2. E. L. Allred and B. R. Beck, J. Am. Chem. Soc., 95, 2393 (1973). The synthesis of 1 was achieved in essentially the same manner although the present work was completed before that communication was published. The dechlorination was achieved with 2% Li - Hg rather than the Na-anthracene used by these workers.

3. The mass imbalance was entirely due to condensed material which was not characterized. In contrast to the pyrolysis of other dihydrosemibullvalenes (R. Srinivasan, *J. Phys. Chem.*, 76, 15 (1972)), there was scarcely any fragmentation to low molecular weight products.
4. All Nmr spectra were run at 220 Mhz in CCl_4 solution with tetramethyl silane as internal reference.
5. E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, 72, 5757 (1950). Note that the structure of 3 contains a 1,3-cycloheptadiene in which a cyclopropyl ring extends the conjugation.
6. R. Srinivasan, *IBM J. Res. Dev.*, 15, 34 (1971).
7. The results of the pyrolysis of 1a in cyclohexane and in cyclohexane- d_{12} were identical in all major details that could be checked.
8. The uncertainty in these values is $\pm 4\%$. It comes from the fact that in the mass spectrum of 2, even at the lowest ionizing voltage that was used, the p-1 peak amounted to 19% of the parent peak. The composition of 2a was calculated by assuming that a hydrogen or a deuterium atom could be lost from the molecule ion with equal probability, i.e., there was no isotope effect. This introduced an uncertainty which could be as large as $\pm 4\%$.
9. A 50-fold change in concentration led to no observable change in the half-life of 1 or in the products formed from it.
10. Such a random selection would give the following composition for the naphthalene: $\text{C}_{10}\text{H}_4\text{D}_4$, 33.3%; $\text{C}_{10}\text{H}_5\text{D}_3$, 53.3%; $\text{C}_{10}\text{H}_6\text{D}_2$, 13.3%. In other computations in which all *cis* 1,3,5,7,9-cyclodecapentaene- d_6 was considered the reactant, it was found that the loss of two atoms (H or D) from the 1,4 - positions would also give naphthalene with the correct composition of deuterium but 1,2-, 1,3-, 1,5-, or 1,6- elimination would not account for the observed product composition. The proposed mechanism in which 6 is the intermediate structure corresponds to a 1,6-transfer. It suggests that partial scrambling of 5 may occur during its formation.
11. S. Masamune and R. T. Seidner, *Chem. Comm.*, 542 (1969).
12. For similar internal hydrogen migrations followed by aromatization, see K. Mackenzie, *J. Chem. Soc.(C)*, 1784 (1969).
13. W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 89, 4534 (1967).
14. The ease with which 7 has been detected by other workers¹ leads one to believe that its presence in this system would have been recognizable.