Tetrahedron Letters No.28, pp. 2661-2666, 1967. Pergamon Press Ltd. Printed in Great Britain.

THERMAL DOUBLE SIGMATROPIC REARRANGEMENT OF 9,9-DIPHENYLBICYCLO[5.2.0]NONA-3,5-DIENE-2,8-DIONE

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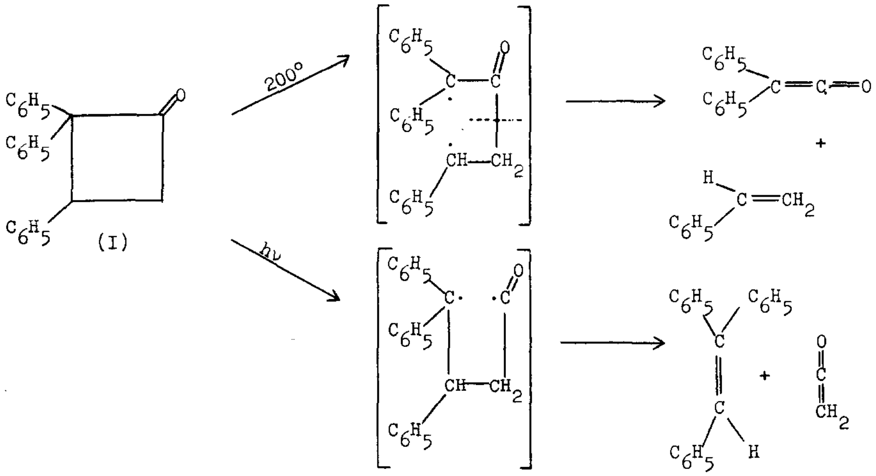
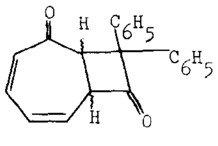
(Received 26 April 1967)

Demonstration of a large secondary deuterium isotope effect upon the orientation of diphenylketene addition to 1-deuteriocyclohexene has led Katz and Dessau to propose that σ - bond formation is not symmetrical in the four-center transition state (1). Microscopic reversibility demands that thermal retrogression of such diphenylketene adducts should proceed by unsymmetrical cleavage of the σ - bonds being broken, and in special cases products derived from selective scission of the weaker σ - bond should be observable. This principle may well control, for example, the thermal fragmentation of 2,2,3-triphenylcyclobutanone (I) into styrene and diphenylketene (2a), in contrast to its photochemical cleavage to triphenylethylene and (presumably) ketene (2b).

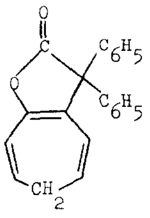


We shall show that the hitherto unexplained thermal rearrangement of 9,9-diphenylbicyclo [5.2.0]nona-3,5-diene-2,8-dione (II) presents a novel variant of this type of transformation. The diketone II, m.p. 108-109°, has been identified as the sole product of the reaction of diphenylketene with tropone at room temperature (3). Its structure was established by analysis, mass spectrum, carbonyl maxima at 1655 and 1799 cm^{-1}, an ultraviolet maximum ($\lambda_{max}^{C_2H_5OH}$ 290 mμ log ε 3.34) consistent with a partially planar 2,4-cycloheptadienone grouping, and by 100 MHz. decoupling studies. Jütz and co-workers report that diketone II undergoes irreversible conversion to a new substance at 160° in the presence of quinoline, but is recovered unchanged when heated without the base. The new product is *isomeric* with diketone II and can be independently prepared by heating tropone with diphenylketene-quinoline (4) to 160° for three hours. Despite some spectroscopic and chemical study of this isomer no structure could be deduced from the available data.

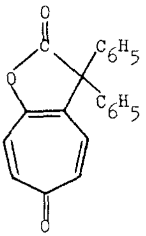
In our hands the diketone II was found to undergo the reported isomerization at 140-190° in inert solvents *in the presence or absence of quinoline*. The resulting isomer, melting at 157° as reported, had lost the 1655 cm^{-1} band of its precursor but retained not only the 1799 cm^{-1} band but also the ultraviolet maximum ($\lambda_{max}^{C_2H_5OH}$ 290 mμ log ε 3.53) of diketone II. These apparently conflicting data were interpreted by noting that (a) enol γ-lactones often absorb near 1799 cm^{-1} and (b) simple substituted 1,3,5-cycloheptatrienes often show maxima near 290 mμ.(5) Our hypothesis of a cycloheptatriene enol γ-lactone structure was strongly supported by the 60 MHz. n.m.r. spectrum [Fig. 1] of the isomer. The spectrum is amenable to first-order analysis as an $A_2BB'CC'$ pattern with the parameters cited and is uniquely compatible with structure III for the lactone.



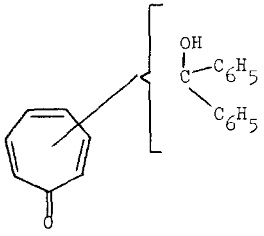
II



III

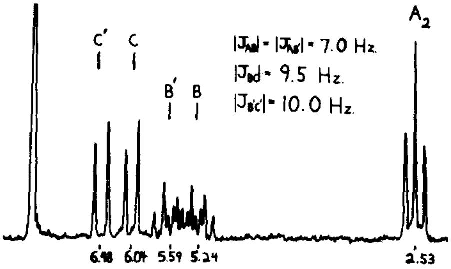


IV



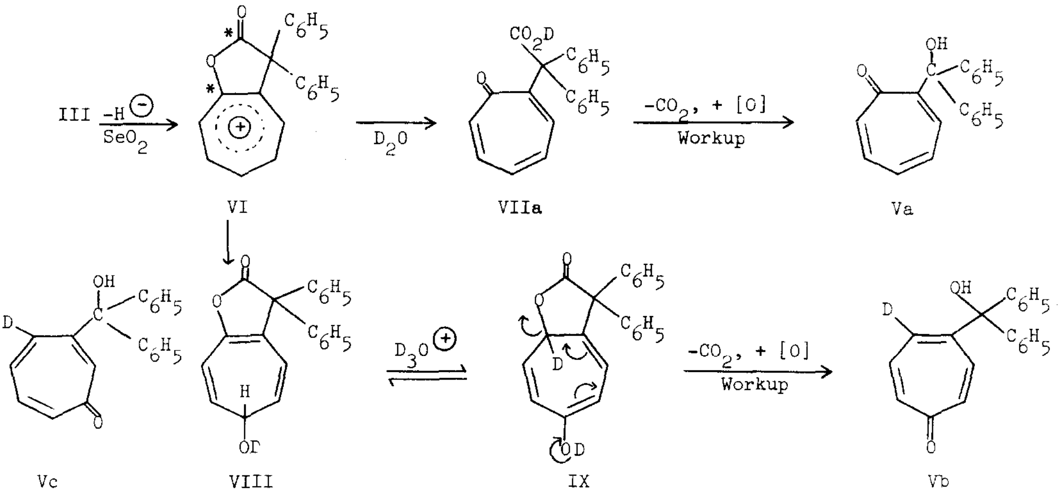
V

FIG. 1 60 MHZ N.M.R. SPECTRUM OF LACTONE III IN $CDCl_3$

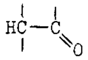


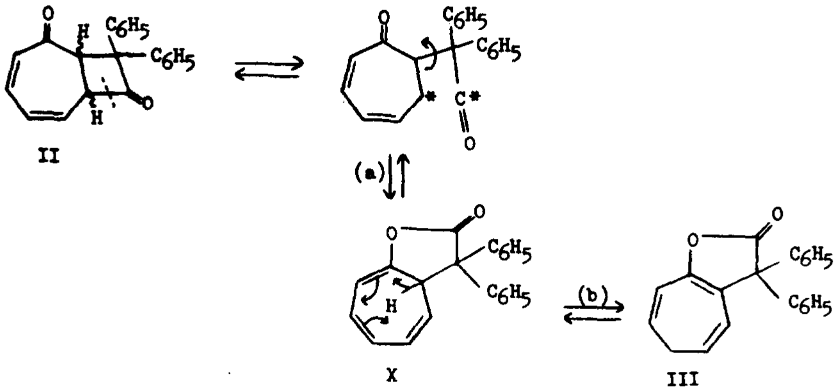
Selenium Dioxide Oxidation of III. To confirm structure III, the selenium dioxide oxidation (6) of the 157° compound to the tropone lactone IV was attempted. In aqueous acetic acid at 80° the oxidation gave a $C_{20}H_{16}O_2$ crystalline tropone, m.p. 155-156°, which lacked carbonyl absorption below 6 μ, but exhibited the characteristic tropone vibration at 6.4 μ. Its mass spectrum showed a parent peak at $\frac{m}{e}$ = 288 and prominent fragments at $\frac{m}{e}$ = 105 ($C_7H_5O^{\oplus}$), 77 ($C_6H_5^{\oplus}$) 165 ($C_{13}H_9^{\oplus}$) and 183 ($C_{13}H_{11}O^{\oplus}$). The typical tropone ultraviolet spectrum ($\lambda_{max}^{CH_3OH}$ 310 mμ, log ε 3.86) *unchanged by alkali*, the absence of n.m.r. signals above 3 τ, and presence of a lone hydroxyl group (by i.r. and n.m.r.) suggested gross structure V, an α-hydroxybenzhydryl tropone.

Three isomeric tropones of structure V exist. Although the n.m.r. spectrum was not sufficiently resolvable to allow analysis, a probable structure assignment could be made by the criterion of deuterium incorporation. If the tropylium ion VI, produced as the initial intermediate of the selenium dioxide oxidation of III, were to undergo solvolysis on the lactone ring at the starred positions, there would result a tropone carboxylic acid VIIa which on decarboxylation and oxidation would produce the isomer Va. On the other hand, solvolysis of cation VI at any unsubstituted carbon on the tropylium ring would form a cycloheptatrienol, e.g., VIII, which by acid-catalyzed prototropic shift would give an enol, e.g., IX, and subsequently by elimination of the lactone function an acid VIIb isomeric with VIIa and ultimately an isomeric α-hydroxybenzhydryl tropone, Vb. An operational distinction between the mechanism leading to Va and those leading to Vb or Vc should lie in deuterium incorporation, for whereas the formation of Va permits no incorporation of carbon-bound deuterium that of Vb (and correspondingly Vc) almost certainly would involve some deuteration either during formation of enol IX or by its partial ketonization prior to generation of acid VIIb.



In the event, selenium dioxide oxidation of III at 80° in D_2O-CD_3COOD produced no detectable (< 1%) carbon-bound deuterium in the product (7); this result favors structure Va over alternatives Vb and Vc for the oxidation product.

Kinetics and Mechanism of the Thermal Rearrangement. That the isomerization of diketone II to lactone III does not proceed by dissociation of II to diphenylketene and tropone followed by recombination to lactone X was proven by use of aniline as cosolvent. Rearrangement of II in mesitylene containing 10 volume percent aniline does not change the yield of III. Since diphenylketene should be efficiently intercepted by aniline at these concentrations its intermediacy in the rearrangement is decisively excluded. The most direct intramolecular mechanism appears to involve two steps:(a) scission of the  $\overset{|}{\underset{|}{\mathrm{HC}}}-\overset{|}{\mathrm{C}}\overset{}{\underset{\mathrm{O}}{\searrow}}$ cyclobutanone bond followed by rotation of the $(C_6H_5)_2CCO$ residue 180° with reclosure to a lactone X, and (b) subsequent thermal 1,5-hydrogen transfer (8) to the final product, III.



Disappearance of II follows first-order kinetics in several solvents and is insensitive to solvent dielectric constant and the presence of added quinoline. In di-n-butyl ether ($\varepsilon = 3.1$) and in n-valeronitrile ($\varepsilon = 17.4$) at 142° the rate constants 1.2 ± 0.2 and $1.3 \pm 0.2 \times 10^{-5}$ $\sec^{-1}$ respectively are in agreement within experimental error. An attempt to identify the rate-determining step by searching for a kinetic deuterium isotope effect foundered upon our inability to label substrate II in acidic or basic media. Distinction between step (a) and step (b) above as rate-determining was therefore based on the following indirect evidence.

Infrared analysis of heated solutions of II or of III show that the equilibrium constant must favor III by at least a factor of 100. Thus III must be at least 4 kcal./mole more stable than II and in view of an estimated 15-20 kcal. strain (9) in II the relative stability of product III is probably even larger than 4 kcal. If step (a) above were rate-determining, then under no circumstances should intermediate X be observable. If, however, the hydrogen transfer step (b) were rate-determining then X could in principle be detected provided that it is not more than 3 kcal. higher in energy than II. Since this proviso is almost certainly operative we have monitored the n.m.r. spectrum of II in o-dichlorobenzene through the first half-life of reaction at 150°. No trace of any signal other than those already assigned to II or III was detected during this experiment. We conclude that (a) the rate-determining step is probably the formation of lactone X, the hydrogen transfer being relatively rapid, and (b) that cleavage of the cyclobutanone ring probably involves a transition state largely of homolytic character. Whether the net 1,7-migration of the acyl group from carbon to oxygen occurs directly or by a "conducted tour" along the conjugated system remains an intriguing but unsolved question. (10) (11)

References

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2. (a) H. Staudinger, H. W. Klever and P. Kober, *Annalen,* **374**, 1 (1910); (b) A. S. Kende and H. Brandman, unpublished observations.

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5. E.g., W. Parham, R. W. Soeder and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1755 (1962).

6. G. Sunagawa, N. Soma and H. Nakao, Japan, Pat. 13482 (1960); *Chem. Abst.*, **55**, 15376h (1961).

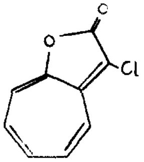
7. Mass spectrometric analyses were performed by T. Mead and D. Desiderio, Amer. Cyanamid Co., Stamford, Conn. We acknowledge the services of W. Fulmor, L. Brancone and their associates for the n.m.r. and analytical data reported.

8. E.g., A. P. ter Borg, H. Kloosterziel and N. Van Meurs, *Proc. Chem. Soc.*, **1962**, 359; E. Weth and A. Dreiding, *Proc. Chem. Soc.*, **1964**, 59.

9. R. A. Krall and J. D. Roberts, *Am. Chem. Soc.*, *Div. Petrol. Chem.*, *Symposium 3*, No. 4B, 63-8 (1958).

10. All compounds isolated gave satisfactory CH analyses.

11. The direct formation of heptafulvene XI by reaction of dichloroketene with tropone at 25° in the presence for a tertiary amine has recently been observed (Prof. J. Ciabattoni, private comm.)



XI