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# PYROLYSIS OF TETRACYCLO $[4.3.0.0.^{3,9}0^{4,7}]$NONANE-2,5-DIONE: A NOVEL INTRAMOLECULAR REARRANGEMENT OF AN ALICYLIC KETENE DERIVATIVE

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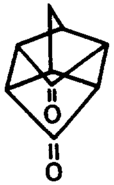
We have recently described the synthesis of the novel diketone tetracyclo $[4.3.0.0^{3,9}0^{4,7}]$ nonane-2,5-dione 1.[1] We now report that the substantial strain energy of 1 (70-75 Kcal/mole) is reflected in its thermal lability and that the products which are generated, result from extensive skeletal rearrangement. When a sample of 1 (0.68M) in benzene is heated to 125° (5hr) three products are produced (>90% overall). The most volatile material (39%) which is easily separated by glpc is readily identified by its spectral data[2] as bicyclo [3.2.1] octa-3,6-dien-2-one 2. The other two products each isomeric with 1 (32% and 18% respectively) were separated by TLC (Silica Gel, 60/40 hexane-ether), and the similiarity in their spectral data indicated that they were stereoisomers. The low $R_f$ material (18%) was isolated as a colorless solid (mp 53-55°) and showed the following spectral properties: ir(neat) 3070(w), 2910(w), 2830(w), 1750, 1580, 1130, 910 and 695 $cm^{-1}$; nmr ($CCl_4$) $\tau$ 2.70 (d, J=6Hz, 1H), 4.03 (d, J=6Hz, 1H), 4.12-4.43 (m, 2H), 7.12-7.40 (m, 3H) and 7.62 (m, 1H); UV (EtOH) $\lambda_{max}$=262nm ($\varepsilon$=7038); mass spectroscopic molecular weight 148. The low field doublets at $\tau$ 2.70 and 4.03 are characterisitic of an $\alpha,\beta$-unsaturated carbonyl compound with no $\gamma$-hydrogens, and the relatively high frequency carbonyl in the ir is indicative of an $\alpha,\beta$-unsaturated $\gamma$-lactone. The use of $Eu(fod)_3$ shift reagent and subsequent decoupling showed that the remaining two vinyl protons at $\tau$ 4.2-4.43 were coupled to each other (J=5.5Hz) which is consistent with the presence of an additional cyclopentene ring.[3] Catalytic hydrogenation of the lactone produced the acid 5 and the lactone 6 in a ratio of 1.5/1.[4] The spectral data of the major lactone (32%) isolated also as a colorless solid (mp 88.5-90.5°) was extremely similar: ir($CDCl_3$) 3070(w), 2950(w), 2840(w), 1750, 1575, 1210, 1125 and 810$cm^{-1}$; nmr ($CCl_4$) $\tau$ 2.55(d, J=6Hz, 1H), 3.90 (d, J=6Hz, 1H), 4.16 (unresolved m, 2H) and 6.90-7.69 (m, 4H); UV (EtOH) $\lambda_{max}$=262nm ($\varepsilon$=8174); mass spectroscopic molecular weight 148. This lactone also hydrogenated to a mixture of 5 and 6 in a ratio of 1.3/1.

Consideration of this data leads to an assignment of 3 and 4 to the minor and major lactone respectively. While the basic structural features of the lactones follow logically from the spectral and hydrogenation data, the stereochemical assignment is tenative and based, among other things, on relative chemical shift effects in their nmr spectra.



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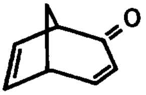

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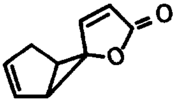

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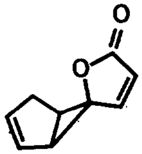

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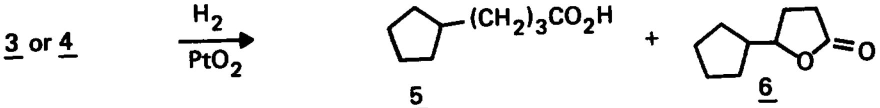
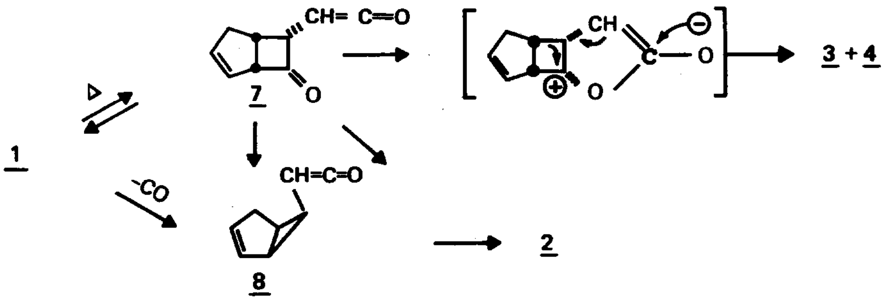


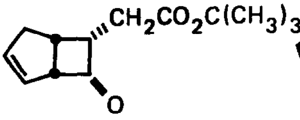
For example, the minor lactone designated as 3 shows the β proton of the unsaturated lactone ring shifted upfield (τ2.70 vs 2.55) relative to the analogous proton in the major isomer 4, a fact consistent with the expected shielding effect of the additional cyclopentene double bond. In a similar fashion, one of the allylic methylene protons in 3 is also upfield and well separated from the remainder of the protons, consistent with the expected shielding effect of the proximate double bond of the lactone ring.

A mechanistic postulate consistent with the nature of the rearranged products is presented below. The suggestion that the ketene derivative 8 produced by decarbonylation of 1 could be precursor to 2 seems reasonable based on literature precedent.[5] The keto ketene derivative 7 is the result of simple cycloelimination from 1, a well known thermal pathway of cyclobutanones. Nucleophilic attack of the cyclobutanone carbonyl of 7 on the reactive and proximate ketene electrophile and subsequent cyclobutyl-cyclopropylcarbinyl rearrangement rationalizes the formation of the lactone mixture. While this pathway seems reasonable, we can find no direct precedent in the literature, although non-concerted cycloadditions of ketenes are probably related in the initial step.[6]



When the dione 1 was heated for 2 hr (90°) in dry t-butanol two products were generated in good yield (>90%). The major product was identified as the t-butyl ester 9 by its analytical and spectral data: ir(neat) 3070, 2980, 2930, 1775, 1725, 1370, 1160, 915, and 730$cm^{-1}$; nmr($CCl_4$) τ 4.17 (m, 1H), 4.41 (m, 1H), 5.82 (m, 1H), 6.85 (m, 1H), 7.28-7.80 (m, 4H) and 8.57 (s, 9H). The mass spectrum of 9 showed no distinct parent peak but a strong fragment at m/e 207 (loss of isobutylene). The isolation of 9 provides strong evidence for the intermediacy of 7, and the failure to detect the lactones 3 and 4 in this reaction mixure suggests that it is the precursor of the lactones. The minor product was again 2 produced now in lower yield (13% vs 40% under comparable reaction conditions in benzene) which implies an additional route to 2 other than via the ketene 7. It should be noted however, that the significant reduction in the yield of 2 upon pyrolysis of 1 in t-butanol does not necessarily insure that 7 is indeed a precursor to 2. For example, the rate of disappearance of 1 shows an interesting solvent dependence. After 35 min at 93°, a sample of 1 in t-butanol was >95% consumed while a comparable sample in benzene was only 15% decomposed. A simple solvent polarity effect was ruled out when 65-70% of 1 was recovered from acetonitrile under identical conditions. An attractive explanation of this phenomenon lies in the potential reversible formation of 7.[8] Solvent addition which is competitive with the reverse reaction would explain the increased rate of disappearance of 1 in t-butanol, and at the same time would reduce the yield of any 2 produced independently of 7. This provides a possible alternative to the actual intermediacy of 7 in the formation of 2.

None of the expected t-butyl ester 10 which would be produced from competitive trapping of 8 by solvent could be detected in the pyrolysis mixture. This ester was, in fact, a major product when 8 was produced independently by irradiation of the diazoketone 11[5a,7] in t-butanol at 25°. However, irradiation of 11 (GE Sunlamp) under conditions more closely resembling the pyrolysis (refluxing t-butanol) produced a rather complex mixture which contained 2 as a major product and showed no appreciable quantity of 10 (glpc analysis) even though 10 was shown to be stable to the reaction conditions. Similar results were obtained for the thermal decomposition of 11 in refluxing t-butanol catalyzed by silver benzoate. Apparently at 80°, intermolecular solvent capture by 8 is not competitive with intramolecular rearrangement. For this reason, the failure to observe 10 under the pyrolysis conditions does not exclude the intermediacy of 8.



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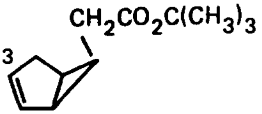

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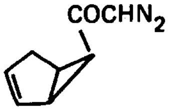

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Further mechanistic and synthetic investigations on this and related systems are proceeding.

References

1. R. D. Miller and D. L. Dolce, Tet. Lett., 3813 (1974).
2. We thank Prof. O. L. Chapman for providing the nmr spectrum of 2.
3. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, N. Y., N. Y. 1969, p. 303.
4. a. An authentic sample of 6 was prepared by treatment of vinylcyclopentane with manganic acetate; b. E. I. Heiba, R. Dessau and W. J. Koehl, Jr., J. Am. Chem. Soc., 90, 5095 (1968).
5. a. P. K. Freeman and D. G. Kuper, Chem. Ind., 424 (1965); b. O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen and H. E. Wright, J. Am. Chem. Soc., 91, 6857 (1969); c. H. Hart and G. M. Love, ibid., 93, 6266 (1971); d. Z. Goldschmidt, V. Gutman, Y. Bakal, and A. Worchel, Tet. Lett., 3759 (1973).
6. a. H. Ulrich, "Cycloaddition Reactions of Hetrocumulenes," Academic Press, N. Y., N. Y., 1967, p. 38; b. R. Huisgen, B. A. Davis, and M. Morikawa, Angew. Chem. Int. Ed., 7, 827 (1968); C. R. Huisgen and P. Otto, J. Am. Chem. Soc. 91, 5922 (1969).
7. J. Meinwald and G. H. Wahl, Jr., Chem. Ind., 425 (1965).
8. Intramolecular cycloadditions of ketenes generated thermally and photochemically to produce strained polycyclic cyclobutanones have been reported: a. P. Yates and A. G. Fallis, Tet. Lett., 2493 (1968); b. R. R. Sauers and K. W. Kelley, J. Org. Chem., 35, 3286 (1970); c. D. Becker, N. Nagler and D. Bernbaum, J. Am. Chem. Soc., 94, 4772 (1972).