Tetrahedron Letters,Vol.27,No.21,pp 2331-2334,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PHOTOCHEMISTRY OF 1-CARBOMETHOXY-6-METHYLTRICYCLO[4.3.1.$0^{4,6}$]DEC-2-EN-10-ONE. PREPARATION OF A 1,3-CYCLOOCTADIENE

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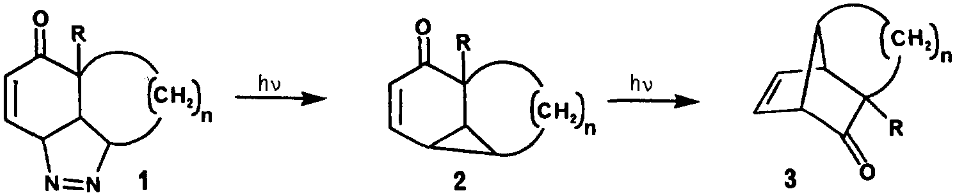
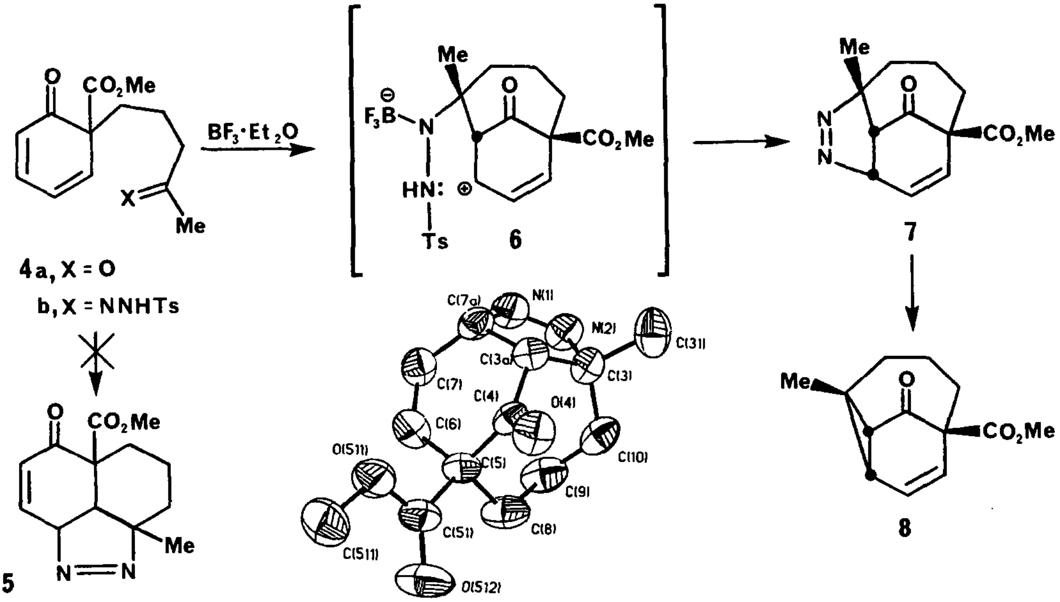
Summary: The preparation and photorearrangements of pyrazoline 7 and vinylcyclopropane 8 are described.

Pyrazolines 1 (n = 2,4) undergo photochemical conversion to vinylcyclopropanes 2, from which vinylcyclopropane-cyclopentene rearrangements provide tricyclic enones 3.[1,2] We considered an extention of the scope of this process to include cases in which n = 3, and now report novel observations encountered in this study.



2,4-Cyclohexadien-1-one 4a was prepared by methods already described in detail[3] and was converted to tosylhydrazone 4b in 85% yield on treatment with p-tosyl hydrazide (1.1 equiv) in anhydrous ether. In contrast to the reactivity of tosylhydrazones observed in the earlier study,[1] 4b failed to undergo eliminative cyclization to pyrazoline 5 under a variety of experimental conditions.[4] Instead, treatment of 4b with $BF_3 \cdot Et_2O$ (1.4 equiv)[5] in methylene chloride (2 h at 0°C, then 3 h at 25°C) gave pyrazoline 7 in 43% yield after chromatography on alumina (hexane:ethyl acetate, 3:1) and crystallization from pentane-ether (mp 102-103.5°C).

An unambiguous selection of structure from stereoisomers of 5 and 7 could not be made on the basis of spectroscopic and analytical data alone. Single crystal X-ray analysis provided a unique structural assignment; a thermal ellipsoid plot of the molecular structure of 7 is shown below.

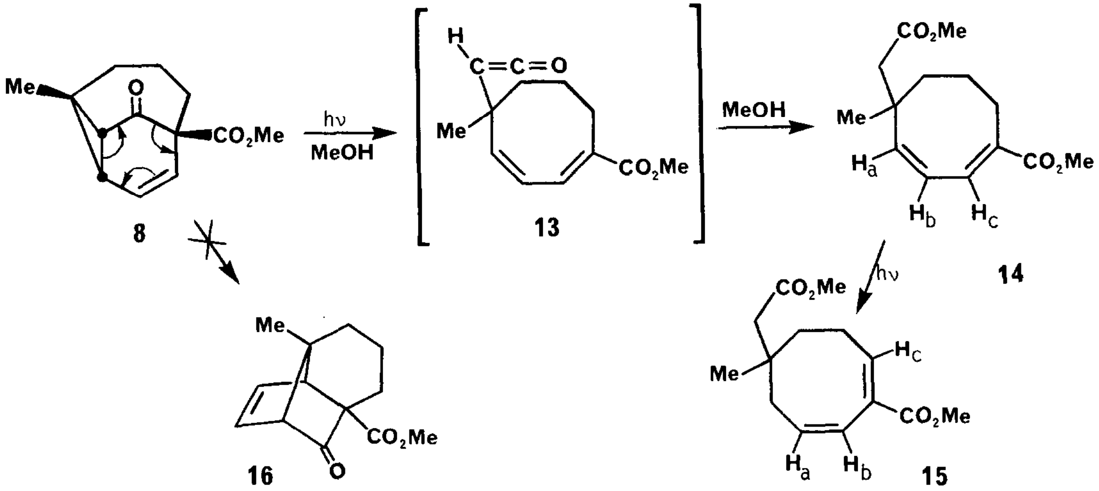


The formation of 7 may be a result of coordination of BF_3 with the internal nitrogen atom of the hydrazone group followed by cyclization at C(2) of the cyclohexadienone ring to give the allylic carbocation 6.[6] Collapse of 6 with elimination of HTs and BF_3 would give 7. Reaction at C(5) of the cyclohexadienone ring (to ultimately give 5) would be relatively disfavored because of the intermediacy of a C(1)-carbonyl destabilized carbocation.

Pyrazoline 7, on thermolysis in refluxing toluene solution, afforded 1-carbomethoxy-6-methyltricyclo[4.3.1.$0^{4,6}$]dec-2-en-10-one (8) in 90% isolated yield after chromatography on alumina.[8] This same vinylcyclopropane, 8, also was obtained (quantitative yield) from Pyrex-filtered irradiation of 7 in methanol solution (0.01 M, 1 h).

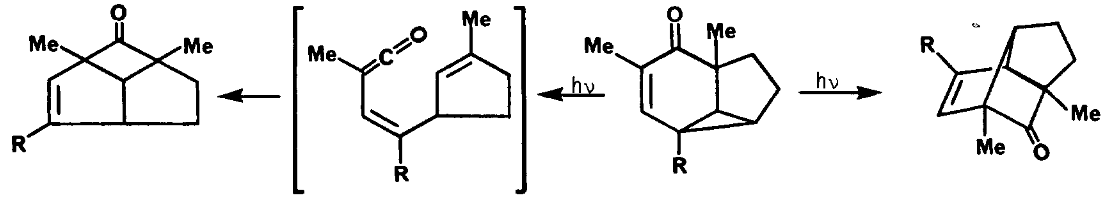
Irradiation of vinylcyclopropane 8 in methanol with Pyrex-filtered light for 1 h produced a 1:2:1 mixture of 8, 14, and 15, respectively. Extended irradiation of this mixture resulted in complete conversion to 15; 15 was isolated (99% yield) by chromatography on alumina.

The ^{1}H NMR spectrum (200 MHz) of 15 displays a singlet at δ 1.02 for the angular methyl group and overlapping multiplets in the region of δ 1.05-2.42 for the methylene protons. The two methoxy groups appear as singlets at 3.67 and 3.75. H_a appears as a multiplet centered at 5.88, while H_b appears as a doublet centered at 6.34 ($J_{a,b}$ = 10 Hz). H_c resonates at 7.01 as a triplet (J = 7 Hz). The angular methyl group in 14 also appears as a singlet at δ 1.02, but the methylene protons in 14 resonate as multiplets in the region 1.10-2.60, while the two methoxy groups appear as singlets at 3.66 and 3.73. H_a appears as a doublet at 5.56 ($J_{a,b}$ = 12 Hz), H_b appears as a doublet of doublets at 6.30, and H_c appears as a doublet at 7.19 ($J_{b,c}$ = 5 Hz).



We believe that the rearrangement of 8 to 14 occurs by a photochemical cycloreversion[9] to give diene ketene 13 (not observed), which reacts with methanol to give diester 14. The photoisomerization of 14 to 15 is formally a 1,5-hydrogen shift from C(8) to C(4); however, details of the mechanism of this rearrangement are unknown at present.

It is noteworthy that 8 does not undergo a photochemical vinylcyclopropane rearrangement to give tricycle 16. In the earlier study,[1] 17a and 17b were reported to photorearrange to 18a and 18b, while the methyl-substituted analogue 17c gave cyclobutanone 20c. We suggested that a possible intermediate in the conversion of 17c into 20c is diene ketene 19c. While we have no additional evidence for the intermediacy of 19c,[10] our observations with 8 add some support to a further consideration of the cycloreversion mechanism in the photochemistry of 17c. Also of interest is the question of the possible role of the angular methyl substituent in directing photorearrangement of 8 to 14 rather than 16. Finally, we propose that this operationally simple three-step conversion of a readily available 2,4-cyclohexadien-1-one, 4a, to a highly functionalized cyclooctadiene, 15, may be of use in terpenoid and related natural products synthesis.

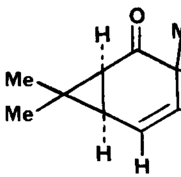


20 **19** **17a,R=*t*-Bu;b,Me$_3$Si;c,Me** **18**

Acknowledgment. This work was supported by the National Institutes of Health (GM 33061). The purchase of the Nicolet R3m X-ray Diffractometer by Rensselaer Polytechnic Institute is gratefully acknowledged. Address inquiries regarding the X-ray analysis to Dr. R. K. Kullnig.

References and Notes

1. Schultz, A. G.; Dittami, J. P.; Eng, K. K. Tetrahedron Letters 1984, 25, 1255.
2. Schultz, A. G.; Puig, S. J. Org. Chem. 1985, 50, 915.
3. (a) Schultz, A. G.; Dittami, J. P.; Lavieri, F. P.; Salowey, C.; Sundararaman, P.; Szymula, M. B. J. Org. Chem. 1984, 49, 4429. (b) Schultz, A. G.; Lavieri, F. P.; Snead, T. E. J. Org. Chem. 1985, 50, 3086.
4. Eng, K. K. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1985.
5. Padwa, A.; Ku, H. J. Org. Chem. 1980, 45, 3756.
6. An analogous mechanistic rationale was presented by Padwa and coworkers (reference 5) in their study of the cyclization reactions of olefinic tosylhydrazones.
7. Compounds 4a, 7, 8, 12, and 15 gave correct elemental analyses.
8. The assignment of structure for 8 is supported by ^{1}H NMR data reported for 9 (Bellamy, A. J.; Crilly, W. J. Chem. Soc., Perkin II 1972, 395) and 10 (Hayakawa, K.; Schmid, H.; Frater, Gy. Helv. Chim. Acta 1977, 60, 561, 1942). Occasionally, a small amount of 1-carbomethoxy-6-methylbicyclo[4.3.1]deca-2,4-dien-10-one (12) was obtained from thermolysis reactions of 7. The formation of 12 presumably occurs by the heterolytic cleavage (acid-catalyzed?) of pyrazoline 7 to give the zwitterionic intermediate 11, from which a 1,2-acyl shift together with an expulsion of N$_2$ gives 12.



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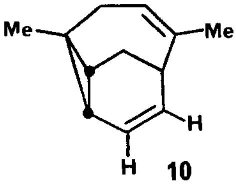

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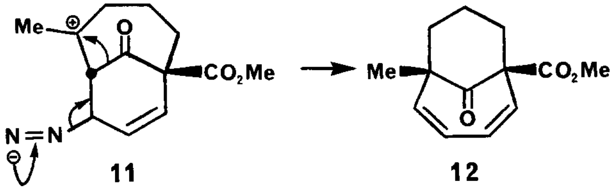

11 **12**

9. (a) Schultz, A. G.; Dittami, J. P.; Myong, S. O.; Sha, C.-K. J. Am. Chem. Soc. 1983, 105, 3273. (b) Schultz, A. G.; Myong, S. O. J. Org. Chem. 1983, 48, 2432.
10. Irradiation of 17c in methanol solution did not result in the formation of detectable quantities of the diene ester expected from the addition of methanol to diene ketene 19. For the inability to trap photochemically generated olefinic ketenes by intermolecular nucleophilic addition reactions, see Hart, H.; Love, G. M. J. Am. Chem. Soc. 1971, 93, 6266.

(Received in USA 26 February 1986)