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PHOTOLYSIS OF [n.2.2]PROPELLANONES INVOLVING A CYCLOBUTANONE RING

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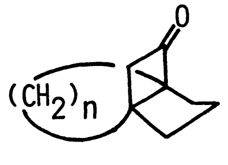
Photolysis of [n.2.2]propellanones (5) and (6) involving a cyclobutanone ring in methanol afforded the cycloelimination products 7 and 9 in good yields, especially in the case of highly strained [3.2.2]propellanone (6), via α-cleavage in the direction leading to the less favorable acyl-alkyl radical pair.

Recently, we reported the remarkable ring size effect on the formation ratio of the acetals derived from ring-expansion to oxacarbenes vs. the olefins formed by cycloelimination in the photolysis of [n.3.2]propellanones (1a-d; n=3-6) in methanol.1) In the above study, it was noted that the smallest [3.3.2]propellanone (1a) gave a small amount (25 %) of the esters 2 and 3 derived from α-cleavage in the direction opposite to the usual radical stability prediction in addition to the acetal 4, while α-cleavage of 1b-d occurred regioselectively leading to form the more stable acyl-alkyl radical pairs. In the present work, in order to clarify the relationship between the direction of α-cleavage and the degree of strain of the propellane skeletons, we investigate the photolysis of highly strained [4.2.2]- and [3.2.2]propellanones (5) and (6) involving a cyclobutanone ring in methanol.2)

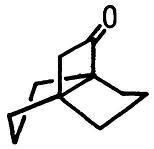
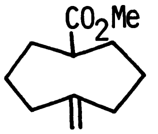
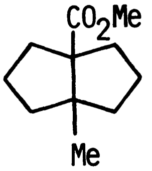
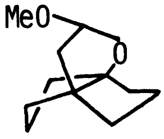
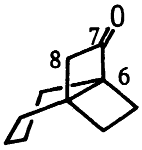
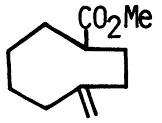
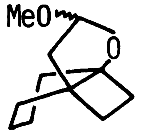
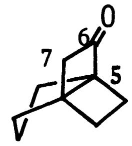
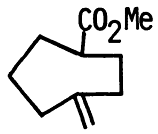
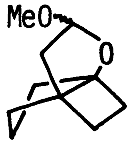


1a, 1b, 1c, 1d
n = 3, 4, 5, 6

The propellanones 5 and 6 were prepared from the corresponding propellanecarboxylic acids3) by (i) the reaction with methyl lithium, (ii) the Baeyer-Villiger oxidation of the propellanyl methyl ketones using MCPBA, (iii) the lithium aluminum hydride reduction of the propellanyl acetates, and (iv) the oxidation of the propellanols with chromium trioxide-pyridine (for 5) or N-chlorosuccinimide-dimethyl sulfide (for 6).4)

When a degassed solution of 5 in methanol (0.02 M) was irradiated in a Pyrex tube, methyl 4-methylenecyclooctanecarboxylate (7) formed by cycloelimination via α-cleavage of C_7,C_8-bond was obtained in a 41 % yield in addition to the usual acetal 8 (~1:1 mixture of epimers; 51 %) derived from the oxacarbene generated by the cleavage of C_6,C_7-bond. It is noteworthy that α-cleavage of C_7,C_8-bond of 5 leading to the less favorable acyl-alkyl radical pair takes place efficiently in a marked contrast to the case of the less strained propellanones. More interestingly, the photolysis of [3.2.2]propellanone (6) under similar conditions gave methyl 4-methylenecycloheptanecarboxylate (9) derived from cycloelimination via α-cleavage of C_6,C_7-bond predominantly in a 84 % yield, while the acetal 10 (~1:1 mixture of epimers) was given in a 6 % yield.

TABLE. Photolysis of Propellanones **1a**, **5**, and **6**.

Propellanone (SE/kJmol^{-1})^a		Products (Yield/%)^b		
	**1a**^{c} (158)	 **2** (10)	 **3** (15)	 **4** (74)
	**5** (218)	 **7** (41)		 **8** (51)
	**6** (243)	 **9** (84)		 **10** (6)

a Strain energy of the corresponding propellane skeleton estimated by the sum of the strain energies of bicyclo[3.2.0]heptane or bicyclo[2.2.0]hexane and cyclopentane or cyclohexane; A. Greenberg and J. F. Liebman, "Strained Organic Molecules," Academic Press, New York, 1978, p 66, 72.
b Determined by GLC based on the reacted propellanones.
c Refernce 1).

It is clearly observed that the photolysis of **5** and **6** affords the cycloelimination products **7** and **9** in good yields, especially in the case of highly strained [3.2.2]propellanone (**6**), via α-cleavage in the direction opposite to the usual radical stability prediction. Moreover, it is significant that the extent of the unusual α-cleavage increases with increasing the strain energy of the propellane skeleton as shown in Table. Consequently, the predominance in the unusual α-cleavage in the strained propellanones is reasonably attributed to the inherent strain which is relieved by the spontaneous cleavage of the central bond with α-cleavage.

References

1) Y. Fukuda, T. Negoro, Y. Tobe, K. Kimura, and Y. Odaira, J. Org. Chem., 44, 4557 (1979).
2) Only a few cyclobutanones fused to the rigid bicyclic systems have been reported to undergo α-cleavage in the unusual direction; R. D. Miller and V. Y. Abraitys, J. Am. Chem. Soc., 94, 663 (1972). R. D. Miller, D. L. Dolce, and V. Y. Merritt, Tetrahedron Lett., 1974, 3347.
3) Y. Sakai, S. Toyotani, M. Ohtani, M. Matsumoto, Y. Tobe, and Y. Odaira, Bull. Chem. Soc. Jpn., 54, 1474 (1981). Y. Sakai, K. Terashima, Y. Tobe, and Y. Odaira, ibid., 54, 2229 (1981).
4) All new compounds gave satisfactory analytical and spectral properties. Selected data for **5**, **6**, **7**, and **9** are as follows:
5: mp 64-65 °C; IR 1760, 1080, 1020 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.0-2.6 (m, 12H), 2.80, 3.34 (AB, J=19 Hz, 2H); UV (MeOH) 292 nm (ε 45).
6: mp 79-81 °C; IR 1760, 1060, 1040, 990 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.4-2.6 (m, 10H), 2.86, 3.30 (AB, J=19 Hz, 2H); UV (MeOH) 300 nm (ε 49).
7: IR 3060, 1730, 1640, 1160, 880 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.3-2.5 (m, 13H), 3.56 (s, 3H), 4.76 (br s, 2H).
9: IR 3060, 1730, 1640, 1155, 880 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.3-2.6 (m, 11H), 3.56 (s, 3H), 4.64 (br s, 2H).

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