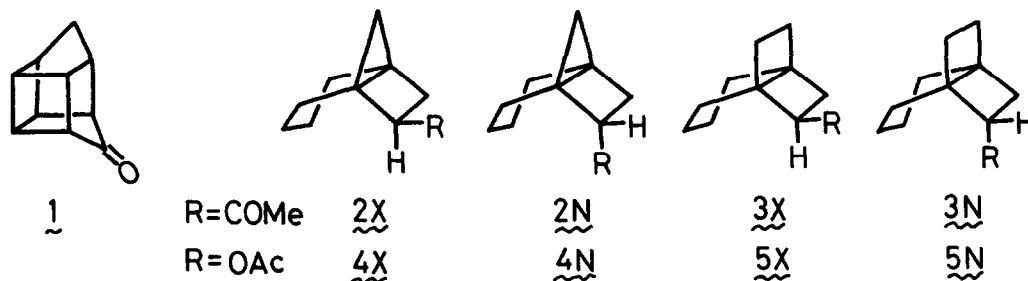


THE BAEYER-VILLIGER OXIDATION VIA CARBOCATION. OXIDATION OF 7-ACETYL[4.2.1]- AND 7-ACETYL[4.2.2]PROPELLANES

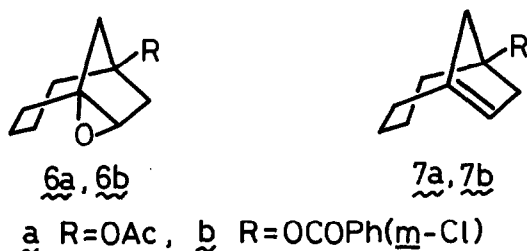
Yoshito Tobe,* Masaru Ohtani, Kiyomi Kakiuchi, and Yoshinobu Odaira
 Department of Applied Fine Chemistry, Faculty of Engineering
 Osaka University, Suita, Osaka 565, Japan

Summary: The Baeyer-Villiger oxidation of exo-7-acetyl[4.2.1]- and exo-7-acetyl[4.2.2]propellanes (2X) and (3X) mainly proceeds via unusual carbocation intermediates to afford the rearranged products.

It has been well documented that the rate-determining step in the Baeyer-Villiger oxidation is the acid-catalyzed decomposition of the intermediate ketone-peroxy acid adduct and that the migration occurs in a concerted manner without involving a carbocation intermediate.¹ Interestingly, in the oxidation of strained cage ketone such as 1,3-bishomocubanone (1), the occurrence of the migration via a carbocation intermediate was recently observed by Yonemitsu et al., irrespective of the minor pathway.² The above anomalous reactivity is attributable to the pronounced ionization ability of this ring system due to σ participation of the strained central bond of bicyclo[2.2.0]hexane ring system to the cation center. In this communication, we wish to demonstrate that the Baeyer-Villiger oxidation of exo-7-acetyl[4.2.1]propellane (2X)³ and its [4.2.2] homologue 3X³, having bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane ring systems, mainly proceeds via carbocation intermediates.

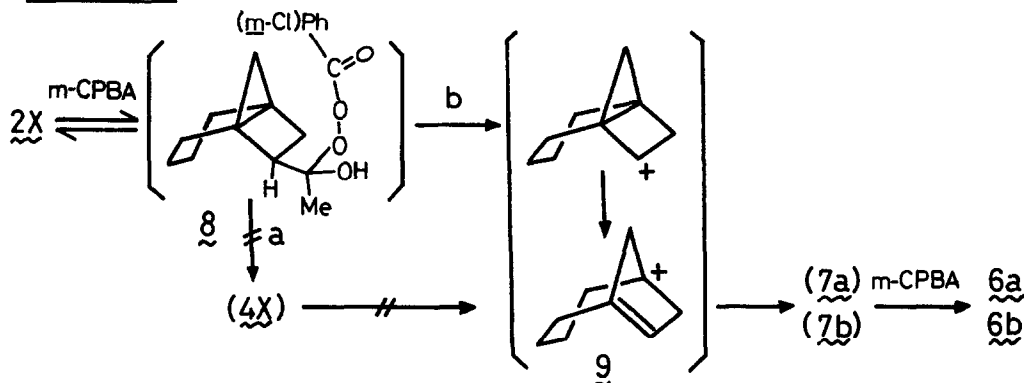


In marked contrast to the case of the endo isomer 2N,⁶ oxidation of exo-[4.2.1]propellanyl ketone 2X with 2.2 equiv. of m-chloroperbenzoic acid (m-CPBA) in CH_2Cl_2 at room temperature afforded the epoxy acetate 6a and the epoxy m-chlorobenzoate 6b in 57 and 27 % yields, respectively,^{7,8} while the formation of the unrearranged acetate 4X was not observed throughout the reaction.

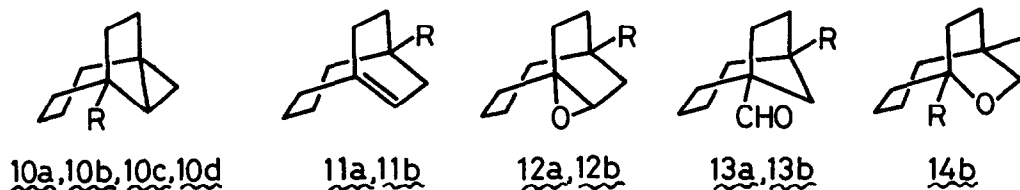


The structures of $\underline{6a}$ and $\underline{6b}$ followed from the spectral data⁸ and, moreover, that of $\underline{6a}$ was confirmed by the identity with an authentic sample prepared by epoxidation of the bridgehead olefin $\underline{7a}$ ⁹ with *m*-CPBA. It is, therefore, reasonable to consider that $\underline{6a}$ and $\underline{6b}$ are the further oxidation products of $\underline{7a}$ and $\underline{7b}$, though the latters were not detected. Consequently, the above results indicate that the oxidation of $\underline{2X}$ exclusively proceeds through a carbocation intermediate $\underline{9}$ (path b), formed from a heterolytic cleavage in a tetrahedral intermediate $\underline{8}$, to give the allylcarbinyll type olefins $\underline{7a}$ and $\underline{7b}$ without involving a normal concerted migration (path a) (Scheme I).¹⁰

Scheme I (Compounds in parentheses are not observed.)



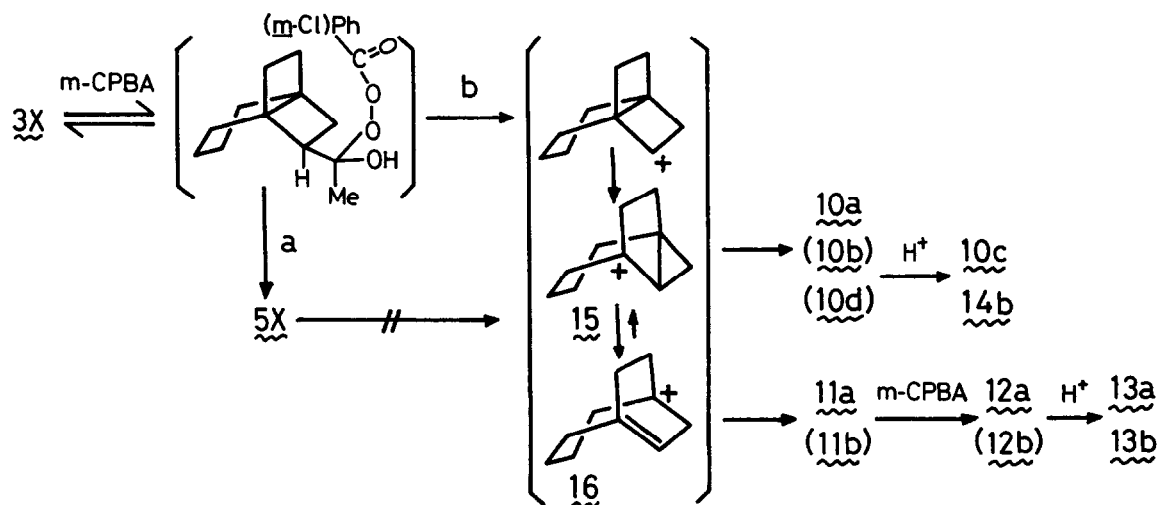
While, in the case of *exo*-[4.2.2]propellanyl ketone $\underline{3X}$, although similar oxidation (*m*-CPBA, CH_2Cl_2) gave the rearrangement products $\underline{10a}$ (5 %), $\underline{10c}$ ¹¹ (38 %), $\underline{11a}$ (2 %), $\underline{12a}$ (2 %), $\underline{13a}$ (2 %), $\underline{13b}$ (5 %), and $\underline{14b}$ ¹¹ (5 %)



$\underline{a} \text{ } R=\text{OAc}, \underline{b} \text{ } R=\text{OCOPh}(\underline{m}\text{-Cl}), \underline{c} \text{ } R=\text{OH}, \underline{d} \text{ } R=\text{O}_2\text{COPh}(\underline{m}\text{-Cl})$

predominantly which are derived from the cyclopropylcarbinyl and allylcarbinyl type cation intermediates 15 and 16, small amount (25 %) of the unrearranged acetate 5X was obtained.⁷ 10a, 10c, and 11a were identified with their authentic samples⁵ and the structures of 5X, 12a, 13a, 13b, and 14b were elucidated on the basis of the spectral properties.⁸ Moreover, that of 12a or 13a was established by oxidation of 11a with *m*-CPBA or treatment of 12a with silica gel or heat (GLC).¹³ Significantly, it is confirmed by the separate experiment that 5X is stable under the oxidation conditions, thus excluding the possibility of the further reaction of 5X.¹⁰ The reaction pathways, therefore, may be summarized as shown in Scheme II.

Scheme II (Compounds in parentheses are not observed.)



The difference in the reactivity of 2X and 3X is interpreted in terms of the difference in the ionization ability of endo-bicyclo[2.1.0]pent-2-yl and endo-bicyclo[2.2.0]hex-2-yl ring systems.¹⁴ Finally, it is concluded that, in the Baeyer-Villiger oxidation of highly strained system, the unusual carbocation pathway might predominate over the usual concerted migration because of the remarkable ionization ability due to the participation of the strained σ bond to the cation center.

References and Notes

- 1) a) R. Curci and J. O. Edwards, "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 241-242. b) H. O. House, "Modern Synthetic Reactions", Benjamin, New York, N. Y., 1972, pp 321-329. c) V. A. Stoute, M. A. Winnik, and I. G. Csizmadia, J. Am. Chem. Soc., **96**, 6388 (1974).
- 2) a) K. Hirao, H. Miura, H. Hoshino, and O. Yonemitsu, Tetrahedron Lett., **1976**, 3895. b) H. Miura, K. Hirao, and O. Yonemitsu, Tetrahedron, **34**, 1805 (1978). See also c) J. Mainwald, M. C. Seidel, and B. C. Cadoff, J. Am.

- Chem. Soc., 80, 6303 (1958). d) S. A. Monti and C. K. Ward, *Tetrahedron Lett.*, 1971, 697.
- 3) The ketones 2X, 2N, 3X, and 3N were prepared from the corresponding methyl esters^{4,5} by alkaline hydrolysis followed by methylation with methyl lithium.⁸
 - 4) P. G. Gassman and E. A. Armour, *J. Am. Chem. Soc.*, 95, 6129 (1973).
 - 5) Y. Sakai, S. Toyotani, M. Ohtani, M. Matsumoto, Y. Tobe, and Y. Odaira, *Bull. Chem. Soc. Jpn.*, 54, 1474 (1981).
 - 6) Oxidation of the endo ketones 2N and 3N with *m*-CPBA gave the corresponding endo propellanyl acetates 4N and 5N as the sole products quantitatively.
 - 7) Yields are isolated yields after chromatography on silica gel.
 - 8) All new compounds gave satisfactory spectral and analytical properties. Selected data are as follows:
 - 6a: ¹H NMR (CDCl₃) δ 1.0-2.6 (m, 15H), 2.92 (d, J=4 Hz, 1H); ¹³C NMR (CDCl₃) δ 169.5 (s), 90.2 (s), 64.0 (s), 61.3 (d), 41.6 (t), 38.9 (t), 38.4 (t), 29.4 (t), 24.5 (t), 22.6 (t), 21.4 (q).
 - 6b: mp 79-80 °C; ¹H NMR (CDCl₃) δ 1.0-2.8 (m, 12H), 2.95 (d, J=4 Hz, 1H), 7.2-8.0 (m, 4H); ¹³C NMR (CDCl₃) δ 164.0 (s), 134.4 (s), 132.7 (s+d), 129.5 (2d), 127.6 (d), 91.3 (s), 64.3 (s), 61.5 (d), 41.8 (t), 39.1 (t), 37.7 (t), 29.6 (t), 24.7 (t), 22.9 (t).
 - 12a: mp 54-5 °C; ¹H NMR (CCl₄) δ 0.8-1.2 (m, 1H), 1.5-2.2 (m, 15H), 2.4-2.6 (m, 1H), 2.81 (dd, J=4, 7 Hz, 1H); ¹³C NMR (CDCl₃) δ 170.2 (s), 85.8 (s), 58.5 (d), 56.7 (s), 39.2 (t), 34.8 (2t), 30.2 (t), 26.7 (t), 25.9 (t), 24.9 (t), 22.5 (q).
 - 13a: ¹H NMR (CDCl₃) δ 1.3-2.5 (m, 17H), 9.44 (s, 1H); ¹³C NMR (CDCl₃) δ 202.6 (d), 170.0 (s), 90.6 (s), 54.6 (s), 41.8 (t), 38.9 (t), 38.5 (t), 34.0 (t), 31.2 (t), 24.3 (t), 23.8 (t), 21.9 (q).
 - 13b: ¹H NMR (CDCl₃) δ 1.2-2.6 (m, 14H), 7.2-7.9 (m, 4H), 9.35 (s, 1H); ¹³C NMR (CDCl₃) δ 202.8 (d), 164.4 (s), 134.5 (s), 133.1 (s), 132.7 (d), 129.8 (2d), 127.7 (d), 91.6 (s), 54.4 (s), 41.4 (t), 38.6 (t), 38.4 (t), 33.6 (t), 31.0 (t), 23.9 (t), 23.5 (t).
 - 14b: mp 81-3 °C; ¹H NMR (CDCl₃) δ 0.84 (d, J=5 Hz, 1H), 1.0-2.8 (m, 13H), 3.49 (t, J=5 Hz, 1H), 7.2-8.1 (m, 4H); ¹³C NMR (CDCl₃) δ 163.0 (s), 134.5 (s), 132.9 (s+d), 129.8 (d), 129.6 (d), 127.9 (d), 110.3 (s), 56.9 (d), 39.6 (t), 35.2 (t), 29.1 (t), 28.3 (t), 26.7 (t), 26.1 (t), 25.0 (t), 14.5 (s).
 - 9) The synthesis of 7a will be reported elsewhere.
 - 10) In view of the stability of the higher homologue of 4X (i.e., 5X) under the reaction conditions, it may be reasonable to exclude the possibility that 7a and 7b are formed by the acid-catalyzed rearrangement of 4X which is derived by a concerted migration. cf. R. N. McDonald and G. E. Davis, *J. Org. Chem.*, 34, 1916 (1969); W. G. Dauben and L. N. Reitman, *ibid.*, 40, 835 (1975).
 - 11) Since the alcohol 10c, which was not found at the end of the reaction, was obtained together with almost equivalent of *m*-chlorobenzoic acid after column chromatography, 10c may be formed as a result of hydrolysis of the benzoate 10b during chromatography. Moreover, it is assumed that the hemiketal ester 14b might be derived by the Criegee rearrangement¹² of the perbenzoate 10d under the reaction conditions.
 - 12) L. A. Singer in reference 1a, pp 296-299.
 - 13) For a similar acid-catalyzed rearrangement of a bridgehead olefin epoxide with concomitant ring contraction: J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, 92, 956 (1970).
 - 14) a) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Am. Chem. Soc.*, 92, 564 (1970). b) R. N. McDonald and G. E. Davis, *ibid.*, 94, 5078 (1972).

(Received in Japan 13 May 1983)