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

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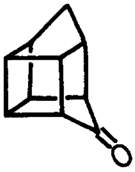
Summary: The Baeyer-Villiger oxidation of exo-7-acetyl[4.2.1]- and exo-7-acetyl[4.2.2]propellanes (2X) and (3X) mainly proceeds via unusual carbocation intermediates to afford the rearranged products.

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 3X[3], having bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane ring systems, mainly proceeds via carbocation intermediates.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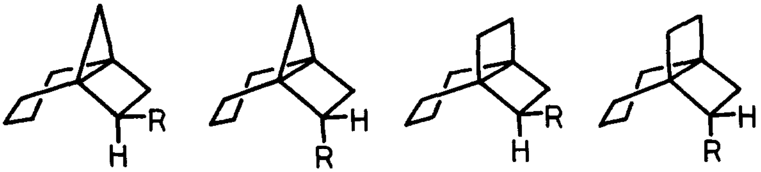
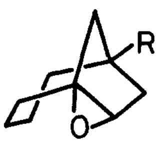
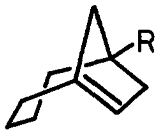


R=COMe 2X 2N 3X 3N
R=OAc 4X 4N 5X 5N

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.



6a, 6b

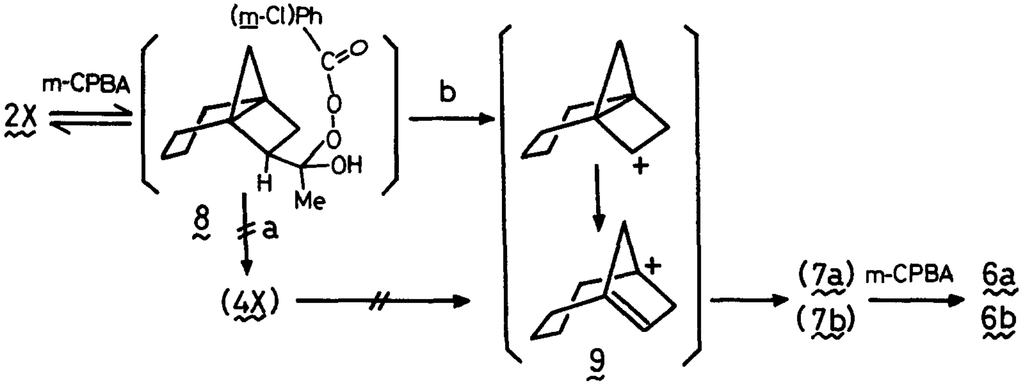


7a, 7b

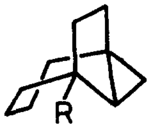
a R=OAc, b R=OCOPh(*m*-Cl)

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

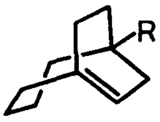
Scheme I (Compounds in parentheses are not observed.)



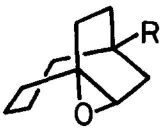
While, in the case of *exo*-[4.2.2]propellanyl ketone 3X, although similar oxidation (m-CPBA, CH_2Cl_2) gave the rearrangement products 10a (5 %), 10c[11] (38 %), 11a (2 %), 12a (2 %), 13a (2 %), 13b (5 %), and 14b[11] (5 %)



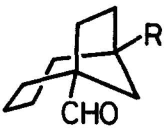
10a, 10b, 10c, 10d



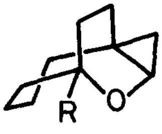
11a, 11b



12a, 12b



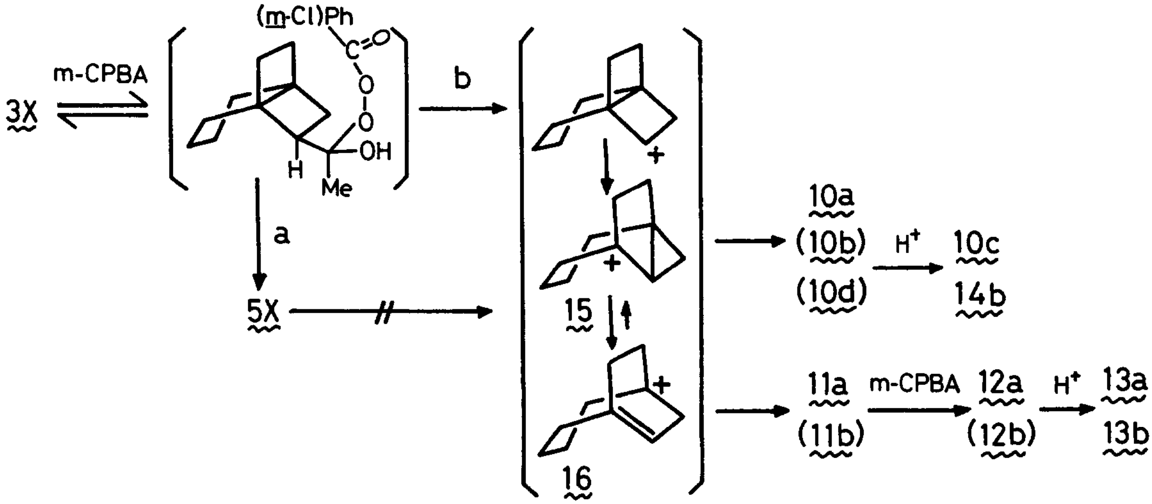
13a, 13b



14b

a R=OAc, b R=OCOPh(*m*-Cl), c R=OH, d R=O_2COPh(*m*-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 samples[5] 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: ^{1}H NMR ($CDCl_3$) δ 1.0-2.6 (m, 15H), 2.92 (d, J=4 Hz, 1H); ^{13}C NMR ($CDCl_3$) 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; ^{1}H NMR ($CDCl_3$) δ 1.0-2.8 (m, 12H), 2.95 (d, J=4 Hz, 1H), 7.2-8.0 (m, 4H); ^{13}C NMR ($CDCl_3$) 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; ^{1}H NMR (CCl_4) 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); ^{13}C NMR ($CDCl_3$) 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: ^{1}H NMR ($CDCl_3$) δ 1.3-2.5 (m, 17H), 9.44 (s, 1H); ^{13}C NMR ($CDCl_3$) 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: ^{1}H NMR ($CDCl_3$) δ 1.2-2.6 (m, 14H), 7.2-7.9 (m, 4H), 9.35 (s, 1H); ^{13}C NMR ($CDCl_3$) 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; ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 rearrangement[12] 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).

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