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UNUSUAL COURSE OF THE CHROMATE OXIDATION OF SECODODECAHEDRENE AND ITS MONOEPOXIDE

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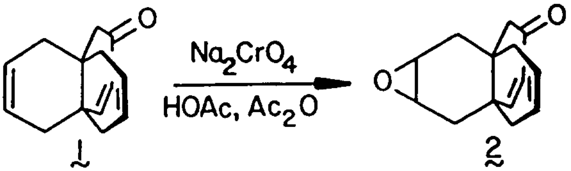
Summary: Secododecahedrene (5) and its epoxide derivative 6 are both transformed by sodium chromate and acetic acid/acetic anhydride into the C_2-symmetric product 7 via an unusually regiospecific and unprecedented oxidative process.

Although the utilization of chromium-based oxidants is widespread,[2] there remain certain associated phenomena that are little understood at the mechanistic level. Deserving of special mention are those reactions that result in the epoxidation of isolated double bonds as in 1 → 2[3] (usually an inefficient process) and in the transformation of certain allylic alcohols into epoxy ketones (e.g., 3 → 4).[4] Yields for the latter conversions are generally good.[4,5]



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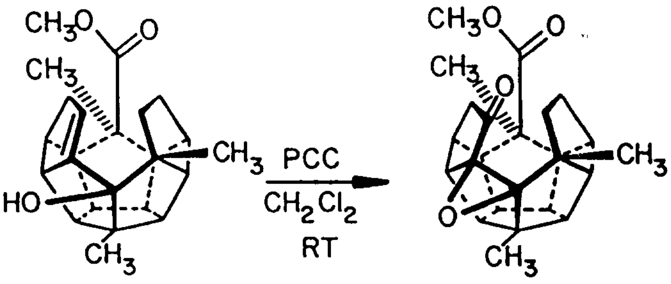

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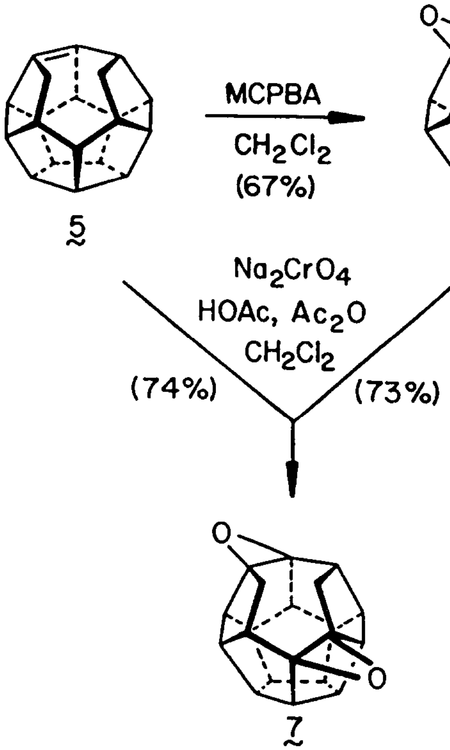
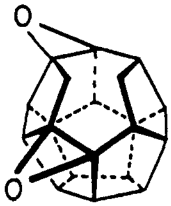
Related oxidations of saturated hydrocarbons have not received significant attention in organic synthesis, chiefly because of the large variety of reactions which often follow the initial oxidation step. For reasons to be detailed elsewhere, we had occasion to subject the secododecahedrene 5[6] to chromate oxidation. The unprecedented and strikingly clean conversion of 5 to diepoxide 7 is detailed here.



The double bond in 5 is recognized to be strained and highly reactive.[6] When a solution of 5 in dichloromethane-acetic acid-acetic anhydride (1:1:1 v/v) was stirred at room temperature with 2 mol equiv of sodium chromate for 48 h, the diepoxide 7 was formed in 74% yield. Because this result implicated epoxide 6 as a possible intermediate, its independent preparation was accomplished by standard peracid treatment.[7] When 6 was in turn exposed to the identical oxidation conditions, 7 could be isolated in an equally remarkable 73% yield.

The structural assignment to 7 is based on its NMR and high resolution mass spectral features [*m/z* (M^+) calcd for $C_{20}H_{18}O_2$ 290.1290, obsd 290.1310]. Particularly revealing is its ^{13}C spectrum, which consists of only ten lines[8] and is therefore compatible only with the presence of a C_2 symmetry axis. Additionally, the two downfield signals located at 83.87 and 81.03 ppm are characteristic of oxirane carbon atoms and demand that two such structural units be properly juxtaposed relative to the symmetry axis.

Arrival at 7 obviously requires the regiospecific removal within 6 of two adjacent tertiary hydrogens. The particular locus of attack by chromium may be rationalized in terms of our knowledge via X-ray crystallography[9,10] of the structure of secododecahedranes. The severe nonbonded interactions present along the open seam of the spherical structure causes structural distortions that are understandably borne to the greatest extent by the carbon centers most proximate to this gap. While the concurrent production of small amounts of regioisomers 8 and 9[11] cannot be entirely ruled out, no evidence was gained for their formation. Certainly there is an exceptionally strong predilection within 6 for specific oxidative attack at the two sites directly transannular to the existing oxirane ring. Since we are unaware of any precedent for a comparable chromium-induced dehydrogenation-epoxidation sequence, no comment on the mechanistic details of this unique and interesting reaction is offered here.



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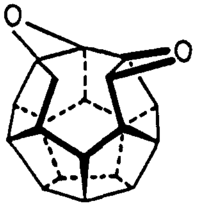

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(1) The Ohio State University Postdoctoral Fellow, 1986-1988.

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(7) For **6**: IR (CHCl$_3$, cm^{-1}) 2941, 2865, 1458, 1257, 1000, 966; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.60-2.65 (series of m, 16 H), 2.78 (d, *J* = 14.3 Hz, 1 H), 2.57 (d, *J* = 13.0 Hz, 1 H), 2.07 (dd, *J* = 13.0, 7.0 Hz, 1 H), 1.53 (ddd, *J* = 14.3, 7.9, 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 84.28, 80.53, 67.98, 67.59, 67.51, 65.04, 63.29, 62.10, 61.74, 61.48, 61.09, 60.41, 56.44, 56.12, 51.82, 51.53, 47.17, 46.44, 30.67 (1 C not observed); MS *m/z* (M$^+$) calcd 276.1514, obsd 276.1523.

(8) For **7**: IR (CHCl$_3$, cm^{-1}) 2958, 2924, 2857, 1457, 1259, 1001; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.50-2.60 (series of m, 14 H), 2.30-2.00 (m, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 83.87, 81.03, 66.95, 61.91, 60.76, 57.24, 56.18, 55.78, 41.38, 29.60.

(9) Christoph, G. G.; Engel, P.; Usha, R.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 784.

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(11) The planar symmetry present in **8** would lead to a ^{13}C NMR spectrum characterized by twelve signals. Isomer **9** would necessarily possess a characteristic oxirane proton absorption.

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