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A SYNTHETIC ENTRY INTO TETRACYCLO $(4.2.0.0^{2,4}.0^{3,8})$ OCTANE SYSTEM

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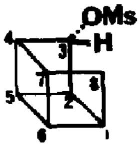
Summary: Novel ceric ion oxidation of homocubanone provides a facile entry into tetracyclo$(4.2.0.0^{2,4}.0^{3,8})$octane and tricyclo $(3.3.0.0^{2,7})$octane ring systems.

An interesting rearrangement of the tetracyclo$(4.2.0.0^{2,5}.0^{4,7})$octan-3-ol (secocubyl) mesylate 1 to the novel tetracyclo$(4.2.0.0^{2,4}.0^{3,8})$octan-5-acetate 2 during acetolysis has been described by Dauben and Reitman[1]. In the accompanying communication, we have delineated[2] a general carbonium ion rearrangement of the secocubyl cation and further shown[3] that the tetracyclic acetate 2



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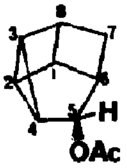

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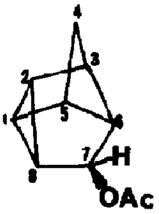

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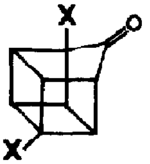
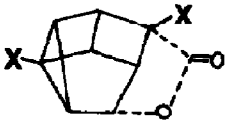
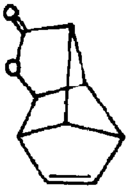
should be reformulated as bishomoprismane acetate 3. Thus, a direct synthetic entry to the interesting tetracyclic frame 2 remains unknown[4]. We describe here a simple synthesis of the tetracyclo$(4.2.0.0^{2,4}.0^{3,8})$octane system via ceric ion oxidation of homocubanone 4 and 1,4-dibromohomocubanone 7. Reaction of 4 with ceric ammonium nitrate (CAN) in aq. CH_3CN (0-5°, 30 min) yielded two novel lactonic products along with some polar intractable material. Structures 5 and 6 for the two products were deduced from the following



4. X = H
7. X = Br



5. X = H
8. X = Br



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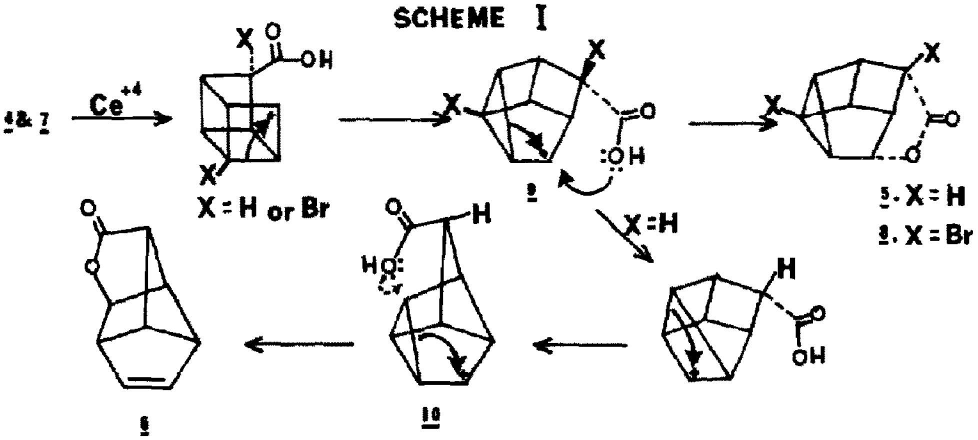
spectral data: 5 (16% yield), mp.45°, M^+ 148, IR(KBr): 1770 cm^{-1}(γ-lactone); ^1H NMR ($CDCl_3$, 100 MHz): δ 5.76(1H,d st, J=8Hz,HC-OC=O), 3.38(2H,m,ring CH's), 3.04(1H,m,ring CH), 2.74(2H,m,ring CH's), 2.16(2H,m,cyclopropane CH's); ^{13}C NMR($CDCl_3$, 25MHz): δ 177.3(s), 88.6(d), 47.3(d),39.9(d),37.6(d),34.2(d),29.6(d) 29.4(d), 19.1(d); 6 (6% yield), low melting waxy solid, M^+ 148, IR(KBr): 1780 cm^{-1}(γ-lactone); ^{1}H NMR ($CDCl_3$, 100MHz): δ 6.38(1H,m,olefinic), 5.94(1H,m, olefinic), 4.36(1H,s,$\underline{H}C$-$O\overset{|}{C}$=O), 2.6-3.4(5H,m,ring CH's); ^{13}C NMR ($CDCl_3$,25MHz): δ 175.4(s), 137.5(d), 133.1(d), 83.1(d), 56.7(d), 49.6(d), 48.7(d), 46.0(d), 41.2(d). When 1,4-dibromohomocubanone 7 was subjected to ceric ion oxidation, the tetracyclic lactone 8, mp.128-29°, IR(KBr): 1760 cm^{-1}(γ-lactone); ^{1}H NMR ($CDCl_3$,100MHz): δ 5.68(1H,d,J=8Hz), 3.0-3.8(4H,m), 2.88(1H,t,J=4Hz); ^{13}C NMR ($CDCl_3$,25MHz): δ 172.6, 88.5, 54.4, 50.4, 44.9, 44.3, 38.2, 36.4, 28.3; was formed (15%) regiospecifically along with other highly polar products. In addition to the above spectral data ^{1}H NMR spin-decoupling and LIS studies provided further supportive evidence for structures 5, 6 and 8.

SCHEME I



The mechanism for the formation of lactones 5 and 8 is depicted in Scheme I. The rearrangement of the secocubyl cation to the tetracyclo(3.3.0.$0^{2,8}.0^{3,6}$)octyl cation 10 is intercepted in the present case by the dangling C_5-endo-carboxylic acid group in 9. However, a competing escape route from the ion 9 leads to the formation of unsaturated lactone 6. The formation of tetracyclo(4.2.0.$0^{2,4}.0^{3,8}$)octane based lactones 5 and 8 in the present study constitutes the first authentic entry to this novel and compact ring system.

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References and Notes:

1. W.G. Dauben and L.N. Reitman, J. Org. Chem., 40, 835 (1975).
2. G. Mehta and S.C. Suri, Tetrahedron Letts., accompanying communication.
3. C.W. Jefford, J.C. Rossier, J.A. Zuber, S.C. Suri and G. Mehta, manuscript under preparation.
4. A polymethyl derivative bearing the skeleton of 2 has been mentioned as a byproduct in a photochemical study, H. Hart and M. Kuzuya, Tetrahedron Letts., 1913 (1974).

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