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THE PREPARATION AND SOLVOLYSIS OF 2-CHLOROTRICYCLO[3.3.0.0^{3,7}]OCTANE[1]

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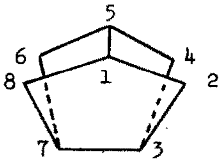
Our interest in the hydrocarbon tricyclo[3.3.0.0^{3,7}]octane (1) has been stimulated by its bisnor relationship to adamantane (zero carbon bridges between C-1-C-5 and C-3-C-7 rather than one carbon bridges), its symmetry (D_{2d}) and the fact that it contains the most twisted norbornane skeleton of record. It was felt that a study of the chemistry associated with the generation of radical and carbonium ion centers at C-1 and C-2 should serve to characterize this unique hydrocarbon.



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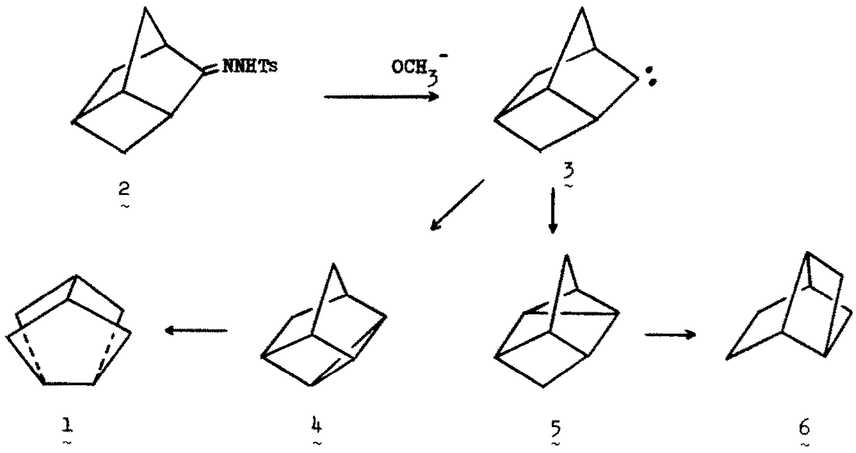
Previously we reported a route to 1 via 2-carbenatricyclo[3.2.1.0^{3,6}]octane (3), which was generated by carbenoid decomposition of tosylhydrazone 2 and which underwent insertion reactions typical of an isopropylcarbene intermediate[3] to produce a mixture of tetracyclic hydrocarbons 4 and 5.[4] Hydrogenation of 4 over platinum resulted in reductive bond fission producing 1, while similar treatment of 5 gave tricyclo[3.3.0.0^{2,7}]octane (6).[4] We have now developed a more economical preparation of 1, using the fact that the rate of reductive bond fission of the transannular bicyclo[2.1.0]pentane bond of 4 is more rapid than that for the bicyclo[3.1.0]hexane bonds of 5. Thus controlled hydrogenation of a mixture of 4 and 5 over platinum yielded a mixture of 1 and 5, which when treated with 0.08 M sulfuric acid in glacial acetic acid gave acetate, principally 2-tricyclo[3.2.1.0^{3,6}]octyl acetate (7-OAc), and 1. Chromatography over silica gel gave a facile separation of acetate 7-OAc and symmetrical tricyclic hydrocarbon 1.

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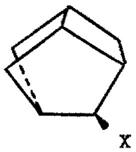
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Photochemical chlorination of tricyclo[3.3.0.0^{3,7}]octane was carried out in benzene at -5°. Vapor phase chromatographic analysis indicated the presence of only one monochloride, which was subsequently isolated by distillation in 68% yield. The nmr spectrum (220 MHz), τ 6.03 (t, 1H, J = 2.3 Hz), 7.39 (doublet of multiplets, 1H, J = 10, ca. 2 Hz), 7.64 (m, 3H), 7.75 (sextet, 1H, J = 2.8 Hz), 8.46 (m, 2H), 8.64 (m, 3H); the infrared spectrum, no absorption in the region 1550 - 1750 cm^{-1}; and the mass spectrum, m/e 142 and 144; are consistent with the assignment of structure as 2-chlorotricyclo[3.3.0.0^{3,7}]octane (8). Thus, substitution occurs exclusively at the bridge positions (C-2, 4, 6, 8), rather than the bridgehead positions (C-1, 3, 5, 7), which is similar to the free radical chlorination pattern found for norbornane (CH_2Cl_2, exo-C-2: endo-C-2:C-7 = 70:25:2)[5], and contrasts with that reported for adamantane (Cl_2 in benzene, C-1:C-2 = 1.17:1.00).[6] No evidence for β-fission of the 2-tricyclo[3.3.0.0^{3,7}]octyl radical, leading to the bicyclo[3.3.0]oct-6-en-3-yl radical, as observed by Sauers[7] in the thermal decomposition of 8-$CO_3C_4H_9$, was uncovered.

Solvolysis of 8-Cl was carried out at 85.4 ± 0.1° in 80% aqueous ethanol. Rearrangement of 8-Cl to 7-Cl competes with the solvolysis of 8-Cl, which leads to 7-OH and 7-OEt.[8] Using the method of Young, Winstein and Goering, the rate constants for the isomerization of 8-Cl to 7-Cl and for the solvolyses of 8-Cl and 7-Cl were determined (Table I).

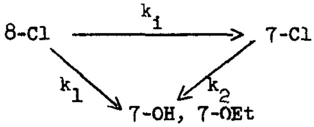

Table I. Rates of Solvolysis and Rearrangement of Chlorides in 80% Ethanol

Chloride	Temp	Rate Constant hr^{-1}		Ref
8-Cl	85.4 ± 0.1°	k_1	0.20	
8-Cl	85.4	k_i	0.16	
7-Cl	85.4	k_2	5.1×10^{-4}	
exo-2-norbornyl	85.0 ± 0.1		0.14	10

The solvolysis of 8-Cl proceeds at essentially the same rate as that for exo-2-norbornyl chloride, and since models reveal that the geometry of the 2-tricyclo[$3.3.0.0^{3,7}$]octyl position resembles the 7-norbornyl position much more closely than the 2-norbornyl position, a rate enhancement of ca. 10^8 is indicated.[11] The large degree of strain present in the [$3.3.0.0^{3,7}$] system is revealed by the facile Wagner-Meerwein rearrangements which take place during solvolysis and rearrangement, a cyclopentyl to cyclobutylmethyl conversion. Making the assumptions that the same intermediate is formed in the solvolyses of 8-Cl and 7-Cl and that return to 7-Cl is favored over return to 8-Cl by a factor of 100 or greater, the standard free energy of the cyclobutyl form (7-Cl) is at least 7 kcal/mole less than that for the cyclopentyl form (8-Cl). This contrasts with the situation which prevails for ionization of 7-norbornyl substrates, where the cyclopentyl form (2.2.1) is more stable than the cyclobutyl form (3.2.0) by about 14 kcal/mole.[12] Thus, to the degree that the transition state for solvolysis of 8-Cl resembles the tricyclo[$3.2.1.0^{3,6}$]octane system, the enhanced rate may be rationalized by the greater stability of the [$3.2.1.0^{3,6}$] skeleton and the reduced angle strain at C_α for the developing carbonium ion center.

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2. Postdoctoral research participant in the RPCT program supported by the National Science Foundation (GY-5408).
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