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BICYCLO[1.1.0]BUTYL-2-CARBINYL CATIONS[1]

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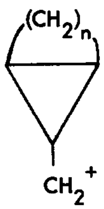
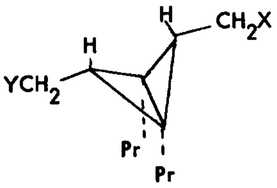
Since the discovery[2] that cyclopropylcarbinyl cation is stabilized by participation of the cyclopropane single-bond electrons, many studies[3] have been concerned with obtaining a detailed understanding of the electronic interactions, and accompanying geometric changes, in this cation. While some speculation involved the participation of only one of the cyclopropane σ bonds to form a "bicyclobutonium ion", with an expansion of the ring towards the geometry of cyclobutyl cation, more recent work has indicated that at the transition state for solvolysis the cation still has a plane of symmetry, although products may be derived from subsequent unsymmetrical rearranged cations. Our early studies on cyclopropenylcarbinyl cation[4] (Ia) indicated that at the transition state for solvolysis no appreciable expansion of the ring had yet occurred.



I a, n=0
b, n=1



II

The substituent effect studies on the cyclopropylcarbinyl cation by Schleyer[5] also suggest at least no unsymmetrical expansion. He has studied[5] the solvolysis of a number of fused-ring cyclopropylcarbinyl derivatives which produce carbonium ions of structure I, with n = 3,4,5, and 6, and Wiberg and Asche[6] have studied the case in which n = 2. Ring fusion resulted in slower solvolysis as n in I decreased from 5 to 2. However, only in the case of the bicyclobutylcarbinyl cation (Ib) and the cyclopropenylcarbinyl cation (Ia) would ring-expansion to a four-membered ring lead to greater strain relief than in the parent cyclopropylcarbinyl cation. For this reason we initiated studies on the solvolysis of bicyclo[1.1.0]butyl-2-carbinyl derivatives some time ago, and our preliminary results[7] have been cited by others[6]. In this report we wish to describe our studies on the solvolysis of the monotosylate (II, X = OTs, Y = OH) and the bistosylate (II, X = Y = OTs) of di-exo-1,3-dipropylbicyclo[1.1.0]-butanedicarbinol (II, X = Y = OH). In addition, we have prepared exo-1,3-dimethylbicyclo[1.1.0]butyl carbinol (III, X = OH) and the corresponding endo derivative (IV, X = OH) and studied the solvolyses of the corresponding tosylates.

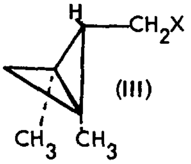
Compound II (X = Y = OH), m.p. 72-72.5°, was prepared by $LiAlH_4$ reduction of the corresponding dicarboxylic acid -- 1,3-dipropyl-2,4-dicarboxybicyclo[1.1.0]butane, m.p. 241-242° -- prepared by reaction of ethyl diazoacetate with 1,2-dipropylcyclopropene-3-carboxylic ethyl ester and subsequent hydrolysis. Treatment of (II, X = Y = OH) with tosyl chloride in cold pyridine afforded the bis-tosylate (II, X = Y = OTs), m.p. 82-83°, and an oily mono-tosylate (II, X = OTs, Y = OH) isolated from the mother liquors. Solvolyses in ethanol and in acetic acid were followed titrimetrically, and the data were treated by the Guggenheim method. Good first-order data were obtained, and they are listed in Table I.

Table I

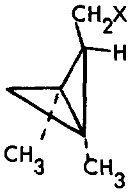
Tosylate Solvolyses

Compound	Solvent	T	$k \times 10^4$, sec^{-1}
II-monotosylate	EtOH	30°	0.67 ± .25
"	AcOH	40°	5.74 ± .04
II-bistosylate	"	40°	1.96 ± .34
"	"	70°	7.0 ± .4
"	"	70°	k_2 = .18
1,2-Dipropylcyclopropenyl-3-carbinyl tosylate	EtOH	20°	1.18 ± .17
"	"	25°	2.42 ± .09
"	"	30°	4.14 ± .20
III-tosylate	4 : 1 dioxane - H_2O (v/v)	25°	5.63 ± 0.25
IV-tosylate	"	25°	2.71 ± 0.31

The kinetic data indicate that the rates of solvolysis of these derivatives of II are even slower than for a cyclopropenylcarbinyl derivative (for comparison the dipropylcyclopropenylcarbinyl system was prepared and its kinetic behavior is listed in Table I also; the rates and ring-opened products are similar to those we have reported[4] for the diphenyl analog). Spectra of the products, and the slow rate of solvolysis of the second tosylate group in II-bistosylate, indicate that the products contain no cyclopropane ring. However, to simplify the product identification we decided to prepare and study compound III. In order to examine the possibility of a stereochemical preference, or perhaps a different type of interaction of the bicyclobutane with the carbinyl cation, we also prepared the endo isomer IV.

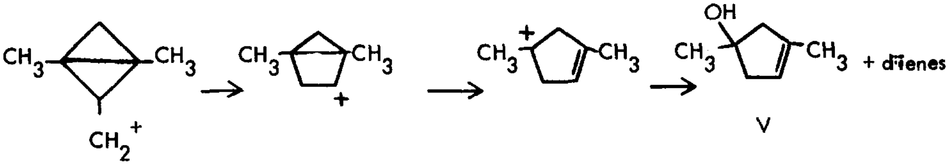


(III)



(IV)

Compound III (X = OH) was obtained by addition of diazomethane to 1,2-dimethylcyclopropene-3-carboxylic ester, low-temperature photolysis of the resulting pyrazoline, and LiAl$_4$ reduction of the product bicyclobutanecarboxylic ester. Compound IV (X = OH) was obtained by reaction of 1,2-dimethylcyclopropene-3-carbinol with CH_2I_2 and Et_2Zn.[8] This latter reaction produced 72% of IV and 28% of III, which were separated by preparative vpc. The tosylates were prepared at low temperature and solvolyzed in 80% dioxane - 20% water (by volume) at 25°. Again, good first-order plots were obtained titrimetrically, using the Guggenheim method.



V

The products from these solvolyses were 1,3-dimethylcyclopent-3-en-1-ol (V) (95%) and 1,3-dimethylcyclopentadiene (5%), in the same proportion from either III or IV. Thus the situation is like that we have discussed for the cyclopropenylcarbinyl case[4]. The products are all derived from ring expanded cations, and in the bicyclobutylcarbinyl case both cyclopropane rings are opened in the final products. However, none of the overall strain relief is yet found at the transition state for solvolysis, and thus none of these compounds solvolyzes more rapidly than simple cyclopropylcarbinyl tosylate.

References

1. For the complete experimental and analytical details, see the Columbia University Ph.D. theses of P. Wolf (1964) and H. Bozimo (1969), available from University Microfilms.
2. C. Bergstrom and S. Siegel, J. Am. Chem. Soc., **74**, 145 (1952).
3. For a review, cf. M. J. J. Dewar and A. P. Marchand, Ann. Rev. Phys. Chem., **16**, 231 (1965).
4. R. Breslow, J. Lockhart, and A. Small, J. Am. Chem. Soc., **84**, 2793 (1962).
5. P. Schleyer and G. van Dine, J. Am. Chem. Soc., **88**, 2321 (1966).
6. K. Wiberg and A. Asche, J. Am. Chem. Soc., **90**, 63 (1968).
7. P. Wolf, Ph.D. thesis, Columbia University, 1964.
8. Cf. J. Furukawa, N. Kawabata, and J. Nishimura, Tet. Lett., 3358 (1966).