

Propellanes 8. Some Bent Cyclopropyl Cations--Are They Partially-Opened?¹

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Solvolyses of simple cyclopropyl systems have been extensively studied.³ The "partially-opened" cyclopropyl cation, with charge shared by all 3 carbons of the cyclopropane ring, was suggested by Schöllkopf, *et al.*,⁴ to explain the solvolysis of, among others, several *exo*-7-norcaryl derivatives. Some data⁵ have since appeared in support of this postulate, and the accompanying theoretical⁶ expectation of non-planarity in such an ion; results for some tertiary systems,^{5e,f,h} including direct observation,⁵ⁱ seem especially important. However, a somewhat confused picture persists for some secondary cyclopropyl systems, including the possible role of frontside S_N2 displacements.⁷ We now report kinetic and product studies on constrained cyclopropyl systems^{5a,b,d,h,i,7,8} which bolster the "partially-opened" ion concept.

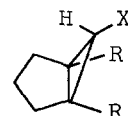
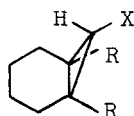
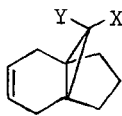
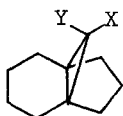
The compounds utilized were either known (1-2,^{8a} 3,^{9b} 4-6^{9a}), or made by triflation of 7-OH^{9a} (7) and 8-OH^{9a} (8). The observed buffered acetylation rates are collected in Table I. The products from 1 and 2 have been reported;⁸¹ they arise mainly from ring opening. Contrariwise, the products from 3, 4, 7 and 8 are solely (within pmr detection limits) those of ring and stereochemical retention--namely 9 (>90% pmr yield, 75% isolated), 10 (>90% pmr yield, 76% isolated), 11 (44% isolated yield¹⁰) and 12 (77% pmr yield), respectively. This marks the first secondary cyclopropyl systems which give only complete retention upon solvolysis.¹²

The acetylation rate of 5 was estimated by dividing the rate for 7 by the 13/14 rate ratio,^{12b} wherefrom it was concluded that 3 ionizes *ca.* 10^{6.6} times faster than its epimer (5) at 125°. For comparison, the 16/18 rate ratio [obtained by multiplying the 13/17 rate ratio^{5g} by the 15/14 ratio^{12b} (the 18/17 ratio is 1^{12b})] should be *ca.* 10^{4.8} (HOAc, 200°). What can cause such a large (10^{6.6}) rate change between epimers 3 and 5 (and similarly 4 and 6)? Certainly not steric or strain factors.^{5d,9b} The only possibility is electronic effects--namely one epimer (3) enjoys an enhanced ionization rate due to $\sigma_{1,e}$ -bond participation leading to a delocalized ("partially-opened") cyclopropyl cation (really a monohomocyclopropenium ion^{51,13}); the ionization of 5 may or may not receive σ assistance (see below). The inductive effect of the double bond¹⁴ in 2 and 4 also supports the generation of partially-opened ions;¹⁵ the

double bonds don't participate in the positive fashion observed for that of 25.^{5c}

Although the kinetics for 1-4 appear to be first order (only a small ionic strength effect upon varying [⁻OAc]), one might worry about solvent displacement. While the solvolyses may involve ion pairs only, we cannot understand the large epimeric rate differences in terms of frontside S_N2-like processes in both epimers (i.e., 3 and 7 or 4 and 8). However, Yamaguchi, *et al.*,⁷ have proposed frontside S_N2 displacements to explain the stereoretentive conversions of 19 to 20 and 21 to 22 (acetone, Et₄NOAc, rt). We therefore treated triflate 8 with Et₄NBr (95% aq. acetone, 100°, 7h) and *n*Bu₄NOAc (acetone, 80°, 1/4h); no reaction was observed in either case. Furthermore, bromides 4 and 6 were each totally inert to the aforementioned conditions. Since these substrates are stereochemically similar to 21, we conclude that the reported reactions of 19 and 21 are not frontside S_N2 displacements, but rather solvolyses.

As mentioned, the products from 3 and 4 provide evidence for non-classical, bent ion intermediates, in accord with theory. The products from 7 and 8 implicate bent cation intermediates, too, but their non-classicity is questionable. The evidence accumulated by Schleyer^{12b} and Creary^{5e} indicate virtually no σ -participation for the ionization of 17. Thus, in contrast to the partially-opened ions derived from 23 and 24^{8h} (on the basis of the nmr of 25⁵ⁱ), the ions derived from 7 and 8 may be essentially classical, bent cyclopropyl cations (e.g., 27).¹⁶



- 1, X=Y=Br
3, X=Br, Y=H
5, X=H, Y=Br
7, X=H, Y=OTf
9, X=OAc, Y=H
11, X=H, Y=OAc

- 2, X=Y=Br
4, X=Br, Y=H
5, X=H, Y=Br
8, X=H, Y=OTf
10, X=OAc, Y=H
12, X=H, Y=OAc

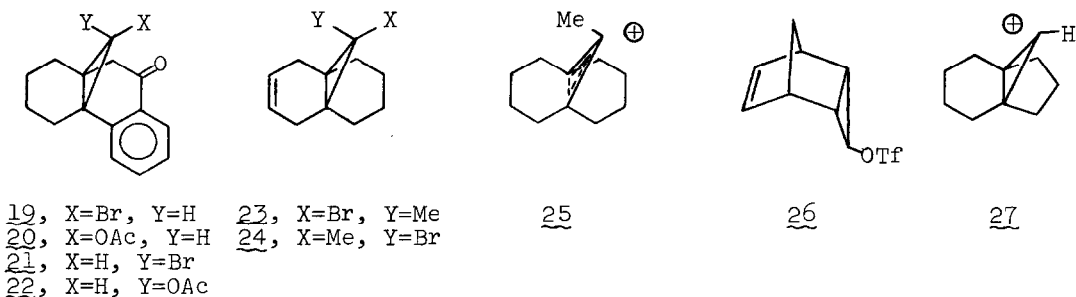
- 13, X=OTf, R=H
14, X=Br, R=H
15, X=Br, R=Me
16, X=OTf, R=Me

- 17, X=OTf, R=H
18, X=OTf, R=Me

Table I. Buffered^a Acetolysis Rates^b at 125 ± 1°.

Cpd. ^c	$k_t \times 10^6$ (sec ⁻¹)	k_{rel}	k_{rel}	k_{rel}	k_{rel}
<u>1</u>	1800	25.9			
<u>2</u>	69.4	(1.0)			
<u>3</u>	118		20.1		3.9 x 10 ⁶
<u>4</u>	5.86		(1.0)		
<u>5</u>	no solvolysis (calcd ^d : 3 x 10 ⁻⁵)				(1.0)
<u>6</u>	no solvolysis				
<u>7</u>	47.5			5.5	
<u>8</u>	8.70			(1.0)	

(a) for [NaOAc] = 0.012M; (b) the errors in k_t are ≤10%; (c) [Cpd.] varied from 0.004 to 0.012M; (d) see text for details.



References and Footnotes

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15. Ledlie^{a, b, d} has drawn similar conclusions from inductive effects on the solvolyses of some cyclopropyl bromides induced by excess Ag ion. But since these measure a composite of processes involving Ag-olefin complexes,^{8e} conclusions regarding partially-opened ions must be tenuous.
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