The Barrier to Rotation in Cyclopropylmethyl Cations

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Received December 16, 1971

The barrier to rotation of a cyclopropyl ring around the planar carbon of a cyclopropylmethyl cation has been estimated from rates of solvolysis to be 14 kcal/mol. This value is obtained by a comparison of the rates of solvolysis of molecules which contain conformationally rigid cyclopropane rings. The results obtained compare favorably with estimates made by other methods.

La barrière de rotation du cycle cyclopropyle autour du carbone plan du cation cyclopropyl méthyle a été évaluée à 14 kcal/mol, à partir des vitesses de solvolyse. Cette valeur a été obtenue en comparant les vitesses de solvolyse des molécules contenant des cycles cyclopropane de conformation rigide. Les résultats obtenus sont tout à fait comparables à ceux calculés à partir des autres méthodes.

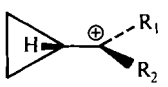
Canadian Journal of Chemistry, **50**, 2432 (1972)

The mechanism of solvolysis of cyclopropylmethyl compounds has been the object of numerous investigations (1). It has been observed that their rates of solvolysis are generally much higher than those of model compounds. The solvolysis products often exhibit a high degree of skeletal rearrangement, as well as a degenerate cyclopropylmethyl–cyclopropylmethyl rearrangement (2, 3).

One of the first definitive pieces of information regarding the structure of cyclopropylmethyl cations was presented simultaneously by Pittman and Olah (4), and Deno *et al.* (5). The n.m.r. spectra observed by these workers, for the 2-cyclopropyl-2-propyl cation in SbF_5–SO_2–SOClF, can be explained by assuming that the cyclopropyl cation exists in the bisected conformation, **1**, $R_1 = R_2 = CH_3$

Support for **1** as the structure of the cyclopropylmethyl cation has been derived from the interpretation of the u.v. spectra of several cyclopropyl ketones and esters (6). Electron diffraction data (7) are also consistent with **1** as the structure of the cyclopropylmethyl cation.

Evidence that **1** is an intermediate formed on solvolysis of substituted cyclopropylmethyl compounds has been presented by several authors (1, 8). Schleyer and van Dine (1) showed that the effects of methyl substituents on the rate of solvolysis were consistent with **1** as an intermediate while both Vogel and Roberts (8) and Richey and Richey (9) showed that ionization of optically active 1-cyclopropyl-1-ethyl compounds led to racemization, an observation consistent only with **1**, $R_1 = CH_3$, $R_2 = H$, as intermediate. Brown and Cleveland (10) showed that the intermediate formed on solvolysis of *p*-cyclopropyl-*t*-cumyl chloride (**3**), $R_1 = R_2 = H$ adopts conformation **1**. Introduction of two methyl groups ortho to the cyclopropyl substituent forces the cyclopropyl group to rotate away from the bisected conformation and a decrease in the rate of solvolysis was observed. In a similar study Sharpe and Martin (11) found that the pK_{R^+} of **4** was similarly affected by



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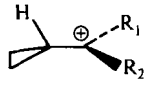

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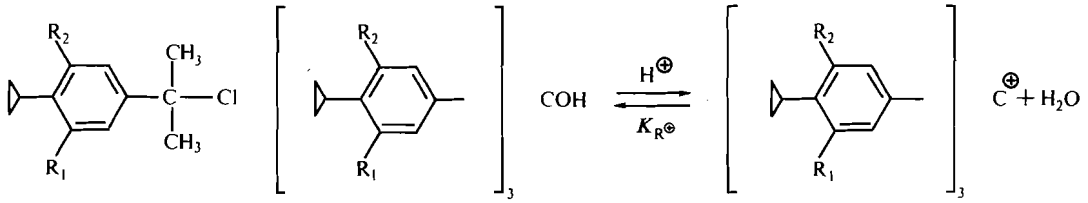

3 **4** **5**

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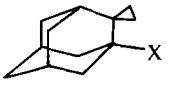
ortho methyl groups. However, the chemical shift difference for the cyclopropyl ring protons in **4** and **5**, $R_1 = R_2 = CH_3$, indicates that charge is still delocalized into the cyclopropyl ring, even though the preferred conformation **1** is not accessible. The slower rate of solvolysis of spiro[cyclopropane-1,2-adamantyl] derivatives (12) **6** than model compounds is significant. In



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X = Cl or CH_3—C$_6$H$_4$—SO_3—

these compounds the solvolysis intermediate is restricted to conformation **2**. Thus, there appears to be a large net destabilization of cyclopropylmethyl cations when the cyclopropyl group is rotated from the bisected conformation of **1** to that in **2**.

We wish to report experimental results which indicate the magnitude of the torsional barrier for rotation of the cyclopropyl group about the plane of the cationic carbon in secondary cyclopropylmethyl cations. We have obtained such data from a measurement of the rates of solvolysis of *N*-methyl-4-(*cis*- and *trans*-2-bicyclo-[3.1.0]hexanoxy)pyridinium iodides (**7***a* and **8***a*) and *N*-methyl-4-(spiro[2.4]heptan-4-oxy) pyridinium iodide (**9***a*) in 80% aqueous ethanol.

Results and Discussion

cis-2-Bicyclo[3.1.0]hexanol (**7***b*) was prepared by the method of Dauben and Berezin (13). *trans*-2-Bicyclo[3.1.0]hexanol (**8***b*), was obtained by the aluminum isopropoxide equilibration of **7***b*. 4-Spiro[2.4]heptanol (**9***b*), was prepared according to the method of Closson and Kwiatkowski (14). The mixture of **7***b* and **8***b* obtained by equilibration with aluminum isopropoxide could not be separated on a preparative scale using various techniques. The mixture of isomeric compounds also proved inseparable at the various stages in the preparation of the *N*-methyl-4-alkoxypyridinium iodides. However, since **7***a* could be obtained as a single isomer, the solvolysis of a mixture of **7***a* and **8***a* of known composition gave the data required for the solvolysis of **8***a*.

TABLE 1. The rates of solvolysis of *N*-methyl-4-alkoxy pyridinium iodides in 80% aqueous ethanol

Substrate	Temperature (°C)	$10^4 k_{obs}$ (s^{-1})
7*a*	86.4	2.20 ±0.05
8*a*	86.4	1.70 ±0.05
9*a*	39.6	0.498±0.003
"	49.3	2.06 ±0.01
"	59.3	6.41 ±0.01
"	86.4	148

The rates of solvolysis of **7***a* and **8***a* were measured in 80% aqueous ethanol at 86.4°. The rate constant for **9***a* at 86.4° was obtained by extrapolation of the values obtained at lower temperatures. The progress of the reaction was monitored by an acidimetric titration using the ampoule technique. The rate of liberation of acid followed first order kinetics for more than three half-lives in all cases.

The rate constants at 86.4° and the relative rates are presented in Table 1. The value listed for **8***a* was calculated using eq. 1, where k_{obs} is the rate constant observed for the solvolysis of a mixture of 49.5% of **7***a* and 50.5% of **8***a*, X_{8a} being the mole fraction of **8***a* and k_{7a} the independently measured rate constant for solvolysis of **7***a*. Equation 1 is only an approximation and

$$[1] \qquad k_{8a} = \frac{k_{obs} - (1 - X_{8a})k_{7a}}{X_{8a}}$$

is strictly obeyed only in the initial stages of the reaction. However, in the case where the rate constants are similar, as with **7***a* and **8***a*, the deviation from first order behavior is much less than the experimental error.

Vogel and Roberts (8) showed that the intermediate cation formed on solvolysis of *N*-methyl-4-(1-cyclopropyl-ethyl)pyridinium iodide in the rate determining step must have a plane of symmetry. They concluded that **1**, $R_1 = H$, $R_2 = CH_3$, is a reasonable representation of the structure of this intermediate. The mechanism of solvolysis of derivatives of **7**, **8**, and **9**, have been discussed previously (14–18). Compounds **7***a*, **8***a*, and **9***a* all undergo solvolysis reactions that involve the formation of a cyclopropylmethyl cation in the rate determining step. The cationic intermediate formed in the

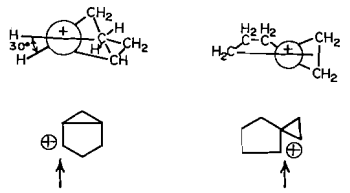

FIG. 1. Structures of the cations obtained by solvolysis of **7***a*, **8***a*, and **9***a*.

rate determining step of the solvolysis of **9***a* has been shown to be symmetrical (15) having the structure shown in Fig. 1. While the solvolysis of **7** and **8** was originally postulated to occur with the homoallylic ions as intermediates (16, 17) it has recently been established (19) that the intermediate formed in the rate determining step in the solvolysis of cyclopropylmethyl compounds retains the structure of the substrate. In the case of **7***a* and **8***a* this intermediate is best represented by a structure which is planar at the cationic carbon, C-2, with the neighboring cyclopropyl group rotated approximately 30° from **1**, as illustrated in Fig. 1. The slight differences in the rates for **7***a* and **8***a* reflect the difference in ground state stabilities, **7***a* being slightly less stable (18). The solvolysis products from either **7***a* or **8***a* consist of the alcohols and corresponding ethyl ethers derived from **7**, **8**, and 3-cyclohexenol (18). The products of the solvolysis of **9***a* were found to be identical to those previously reported (14, 15). These products are consistent with the formation of a cationic intermediate.

Schleyer and van Dine (1) have found that substitution at the α- and β-positions of the cyclopropane ring produces a five-fold and eight- to eleven-fold increase in rate, respectively; over that of the unsubstituted compound. Thus, substitution at the β-position of the cyclopropyl ring is twice as effective as substitution at the α-position. In the absence of any additional gross complications **7***a* and **8***a* would be expected to solvolyze twice as fast as **9***a*. The rate constants in Table 1 reveal that this is not the case.

If it is assumed that the major difference in the rates of solvolysis of **8***a* and **9***a* is caused by the fact that the cyclopropyl ring in **8***a* cannot assume the preferred bisected conformation **1**, an approximation to the torsional barrier for rotation of the cyclopropyl group in **1**, R_1—H, R_2—CH_3, can be calculated. Using eq. 2, the difference in the free energies of activation for **8***a* and **9***a* is found to be approximately 3.5 kcal/mol at 86.4° (3.48 kcal/mol for **7***a* and 3.66 kcal/mol for **8***a*). If it is assumed that the difference in energy between the *cis*- and *trans*-conformers of the 1-cyclopropyl-1-ethyl cation is small compared to the barrier of rotation between the conformers, then the barrier will appear to have two-fold symmetry. The energy, $V(\theta)$, required to rotate a group from the minimum potential energy through an angle, θ, is given by eq. 3 (20), where V_o is the barrier to rotation through $\pi/2$.

$$[2] \qquad \Delta\Delta G^{\ddagger} = RT \ln (k_{8a}/2k_{9a})$$

$$[3] \qquad V(\theta) = V_o/2(1 - \cos 2\theta)$$

The difference in free energy of activation for **8***a* and **9***a* is equal to the energy required to rotate the cyclopropyl group by 30° away from the bisected conformation. In this way the torsional barrier, V_0, can be calculated to be 14 kcal/mol.

There are several assumptions inherent in this calculation. Firstly, the assumption is made that the barrier to rotation of **1**, $R_1 = H$, $R_2 = CH_3$, will have the same angular dependence on energy as the intermediate formed on solvolysis of **7***a* and **8***a*. Secondly, the usual assumption is made that during the rotation of the cyclopropane ring, the entropy changes, as well as $\Delta\Delta S^{\ddagger}$, are zero.

Finally it is assumed that rotation of the cyclopropane ring does not alter the α and β substituent effects determined by Schleyer and van Dine (1).

The value of 14 kcal/mol calculated in this study is in good agreement with the value of 13.7 kcal/mol calculated by Kabakoff and Namanworth (22) for **1**, $R_1 = H$, $R_2 = CH_3$, using n.m.r. measurements, as well as other values from *ab initio* calculations (21) (17.5 kcal/mol) and from the solvolysis of **6** (23, 24) (10 kcal/mol).

Our result for the rotational barrier is obtained by using an average value for $\Delta\Delta G^{\ddagger}$. If the rotational barrier is calculated from the data of solvolysis of **7***a* and **8***a* values of 13.9 and 14.6 kcal/mol are obtained respectively. This small difference of 0.7 kcal/mol indicates that our third assumption is reasonable.

We would like to conclude from these results, that the major factor which causes the barrier to rotation in cyclopropylmethyl ions must also be a major factor contributing to the stability of cyclopropylmethyl cations. This factor may be "vertical" stabilization as defined by Traylor and co-workers (25), but charge delocalization, as in the allyl cations, can not be great. This view is supported by the hundred-fold greater effectiveness of a methyl group at the C-1 position of a cyclopropane ring in stabilizing the transition state than methyl groups at positions C-2 and -3 (2). Further, the products from solvolysis of **7***a* and **8***a* are derived mainly from solvent capture at C-2, even though considerable strain release would be achieved by solvent capture at C-5, giving 3-cyclohexenyl derivatives (26).

Further support of this conclusion is derived from the contrasting effects of methyl groups on the rotational barriers estimated for allylic and cyclopropylmethyl cations described by Schleyer and co-workers (23). These authors also concluded that the cyclopropylmethyl cation is stabilized in a different manner than the allyl cation.

Experimental

Melting and boiling points are uncorrected. Elemental micro-analyses were carried out by A. B. Gygli of Toronto.

cis-2-Bicyclo [3.1.0]hexanol (7b)

Compound **7***b* was prepared by the procedure of Dauben and Berezin (13) in 60% yield; b.p. 62–65° (9 mm); n_D^{25} 1.4790 (lit. b.p. 78–79.5° (20 mm), n_D^{25} 1.4742 (13); b.p. 76° (17 mm), n_D^{25} 1.4788 (26)).

4-(cis-Bicyclo [3.1.0.]hexyl-2-oxy)pyridine

This compound was prepared according to the method of Schmid and Wolkoff (27) in 76.5% yield. The liquid was sublimed onto a cold finger rather than being distilled. I.r. ν_{max} (CCl_4); 3090, 3050, (cyclopropyl C—H stretch); 2950–2980, 1590, 1560, (pyridyl ring vib.) 1495, 1420, 1366, 1330, 1275, 1210, (pyridyl C—O stretch), 1015 cm^{-1}. N.m.r. ($CDCl_3$); 1.6–1.8, quart., $J_1 = 5$, $J_2 = 1$ Hz, (2H), 2,6-pyridyl protons; 3.0–3.2, quart., (2H), $J_1 = 5$, $J_2 = 1$ Hz, 3,5-pyridyl protons; 4.9–5.2, mult., (1H), methine proton; 7.2–8.9, mult., (6H), cycloalkyl protons; 9.2–9.8, mult., (2H), cyclopropyl methylene protons.

N-Methyl-4-(cis-bicyclo[3.1.0]hexyl-2-oxy)pyridinium Iodide (7a)

Iodide **7***a* was prepared from 4-(*cis*-bicyclo[3.1.0]hexyl-2-oxy)pyridine by the method of Schmid and Wolkoff (27) in 96.5% yield. The solid was recrystallized from methylene chloride and ether as white needles, m.p. 118–119.5°. I.r. ν_{max} ($CHCl_3$); 2930, 1645, 1570, (pyridyl ring vib.), 1340, 1295, 975 cm^{-1}. N.m.r. ($CDCl_3$); 0.7–1.0, doub., $J = 7$ Hz, (2H), 2,6-pyridyl protons; 2.4–2.6, doub., $J = 7$ Hz, (2H), 3,5-pyridyl protons; 4.4–4.8, mult., (1H), methine proton; 5.5, sing., (3H), *N*-methyl protons; 7.5–8.8, mult., (6H), cycloalkyl protons; 9.2–9.6, mult., (2H), cyclopropyl methylene protons.

Anal. Calcd. for $C_{12}H_{16}ONI$: C, 45.58; H, 5.16; N, 4.46; I, 40.23. Found: C, 45.49; H, 5.21; N, 4.43; I, 40.03.

trans-2-Bicyclo [3.1.0]hexanol (8b)

Hexanol **8***b* was prepared by isomerizing **7***b* by the method of Eliel and Ro (28). The fractions obtained by distillation, b.p. 61–65° (11.5 mm) varied in ratio of **7***b* to **8***b* and weighed 4.36 g (44% recovery).

2-Carbomethoxycyclopentanone

Following the method of Pinkney (29), 342.1 g of methyl adipate (1.97 mol) gave 212 g (79% yield) of a clear liquid after distillation under vacuum, b.p. 95–96° (11 mm) (lit. (29) b.p. 83–88° (5 mm); yield, 81%).

4-Spiro [2.4]heptanone

The heptanone was prepared by the method of Mayer (30, 31) from 56 g of 2-carbomethoxycyclopentanone (0.394 mol) in an overall yield of 32%; b.p. 44–46° (10 mm) (lit. (30, 31) b.p. 54–55° (14 mm)).

4-Spiro [2.4]heptanol

The heptanol was prepared by lithium aluminum hydride reduction of 4-spiro[2.4]heptanone in 76% yield; b.p. 59.5–60° (9 mm) (lit. b.p. 68–69° (13–14 mm) (32).

4-Spiro [2.4]heptan-4-oxy)pyridine

The compound was prepared according to the method of Schmid and Wolkoff (27) in 81.5% yield, b.p. 80° (0.075 mm). I.r. ν_{max} (neat); 3010, 2955–2860, 1590, 1565, (pyridyl C=C vib.), 1495, 1280, 1210, (pyridyl C—O stretch), 1080, (alkyl C—O stretch) cm^{-1}. N.m.r. (CCl_4); 1.7–1.8, quart., $J_1 = 5$, $J_2 = 2$ Hz, (2H), 2,6-pyridyl protons; 3.3–3.4, quart., $J_1 = 5$, $J_2 = 2$ Hz, 3,5-pyridyl protons; 5.8–5.9, doub., (1H), methine proton; 7.6–8.8, mult., (6H), cycloalkyl protons; 8.9–9.6, mult., (4H), cyclopropyl protons.

Anal. Calcd. for $C_{12}H_{17}ON$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.32; H, 8.11; N, 7.41.

N-Methyl-4-(spiro[2.4]heptan-4-oxy)pyridinium Iodide

The iodide was prepared by the method of Schmid and Wolkoff (27) from 4-(spiro[2.4]heptan-4-oxy)pyridine in 97% yield, m.p. 86–88.5°. I.r. ν_{max} ($CHCl_3$); 2930, 1645, 1590, 1510, (pyridyl ring vib.), 1485, 1330, 1305, 1290 (pyridyl C—O stretch), 1080 (alkyl C—O stretch), 1015, 945 cm^{-1}. N.m.r. ($CDCl_3$); 0.6–0.9, doublet; $J = 7$ Hz, (2H), 2,6-pyridyl protons; 2.5–2.7, doublet $J = 7$ Hz, (2H), 3,5-pyridyl protons; 5.4–5.6, multiplet, methine proton; 5.5 singlet, *N*-methyl protons (3H); 7.4–8.7; multiplet, (6H), cycloalkyl protons; 9.0–9.5, multiplet (4H), cyclopropyl protons.

Kinetics

All kinetic runs were carried out in thermostated oil baths, with temperature controlled to maximum deviation of ±0.05°. The rate constants were determined using the general procedure of sealing portions of the reacting solutions in glass ampoules, removing ampoules at chosen intervals from the bath, freezing, and titrating. All samples were titrated automatically to a predetermined p*H* using a Coleman Model 31 p*H* meter and Companion Automatic Titrator. The end point for the titration was determined from a titration curve of *N*-methyl-4-pyridone hydroiodide.

The rate constants were calculated from the volume of base required for neutralization, V_t, in the usual manner (33).

Products

The ratios of products obtained by the solvolysis of **7***a*, **8***a*, and **9***a* were determined using several v.p.c. columns. The ethers and alcohols from **7***a* and **8***a* were isolated as two mixtures and examined by n.m.r. spectroscopy. It was possible to determine the ratio of the three products from the integrated ratios of the three methine resonances as well as from the chromatograms. The n.m.r. product ratio agreed well with that determined by v.p.c.

The products of the solvolysis of **9***a* were isolated by v.p.c. and the structure of each was established by comparing its infrared and n.m.r. spectra with published data (14, 15).

Continued financial support by the National Research Council of Canada is gratefully acknowledged.

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