Cyclobutane–Bicyclobutane System. 2. Protonation, Deprotonation, and Intermediate Carbanion Stereochemistry in the 1,3-HCl Elimination from 3-Chlorocyclobutanecarbonitrile

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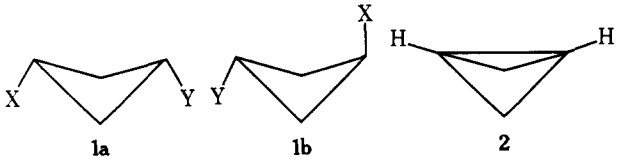
Abstract: The elimination of HCl from *trans*- and *cis*-3-chlorocyclobutanecarbonitrile (**3** and **4**, respectively) in *t*-BuOH–*t*-BuOK was studied. The reaction of the two isomers proceeds via a common carbanion or rapidly interconverting isomeric carbanions, with the trans isomer **3** having an additional effective elimination mechanism in which the potassium cation electrophilically assists in the expulsion of the leaving group. Contrary to expectations, in the presence of crown ether the product distribution from the two isomers differs markedly, indicating that the intermediate carbanions derived from the two isomers are not identical. Addition of crown ether also causes inversion of selectivity of the carbanion with respect to the elimination and reprotonation reactions. This is explained by a change in the acidity of the solvation shell as a function of the removal of the potassium cation. In *t*-BuOK–*t*-BuOH, the intermediate carbanion is protonated faster to give the less stable isomer. This is interpreted in terms of the least hindered approach principle. It is suggested that protonation and deprotonation proceed from the equatorial position in the trans isomer and from the axial position in the cis isomer.

Cyclobutane may exist in two limiting conformations. One form is planar, having D_{4h} symmetry, and the other is a bent or puckered form having D_{2d} symmetry.[2] As a result of the counterplay of two opposing forces, hydrogen eclipsing in the planar form and increased angle strain in the puckered one, the equilibrium structure of cyclobutane is bent with an angle of pucker ranging between 23 and 27°.[3] The folded structure of cyclobutanes leads to pseudoaxial and pseudoequatorial positioning of their substituents. For 1,3 derivatives, the cis diequatorial isomer **1a** is generally more stable than the trans isomer **1b**.[2]



1a **1b** **2**

The product of 1,3 elimination of HX in these systems is a derivative of bicyclo[1.1.0]butane (**2**). Bicyclobutane itself is a most unique molecule in terms of its chemical reactivity and electronic structure. For example, contrary to expectation, all the C–C bond lengths including the diagonal one are equal (1.497 ± 0.004 Å).[4] MO-SCF calculations show that the hybridization of the central bond is $sp^{24.3}$, which corresponds to 96% p character.[5] Surprisingly, the lowest energy transition in bicyclobutane, which is from the π-like central bond orbital to the corresponding π^*-like orbital, is lower in energy than the $\pi \rightarrow \pi^*$ transition in ethylene.[6]

While it is generally assumed[7] that 1,3-elimination reactions are nonconcerted, the vicinity of positions 1 and 3, the relative rigidity of the system, and the similarity of the central bond in the product to an olefinic double bond point to the title compound as a possible candidate for an E2 reaction. Upon carrying out the reaction under basic conditions, however, no evidence was found for the operation of a concerted mechanism in this system. Splitting the reaction into two steps adds to the complexity of the process, since a single transition state is replaced by two transition states and an intermediate. In return, however, the resulting stepwise mechanism lends itself as a model for the study of several interesting aspects of carbanion chemistry. This paper concentrates primarily on the various possible models for the elimination mechanism, on the stereochemical factors governing the energetics and geometry of the protonation and deprotonation reactions, and the stereochemistry of the cyclobutylcarbonitrile carbanion (retention vs. isomerization) as a function of the reaction medium.

Results

Kinetic Studies. The reactions of pure trans (**3**) and cis (**4**) isomers of 3-chlorocyclobutanecarbonitrile with *t*-BuOK in *t*-BuOH were carried out at 30.4 and 50.2 °C and followed by VPC. Starting with each isomer, isomerization of starting material was detected along with product formation. The reaction goes to completion and the product **5** is stable for several days under the reaction conditions. Substrate concentration ranged between 9.7×10^{-3} and 4.5×10^{-2} M, and base concentrations were varied from 6×10^{-3} to 2.6×10^{-2} M. The general outline of the reaction is given in Scheme I.

The four rate constants were evaluated by means of computer simulation for which eq 1–3 were used.

$$\frac{\Delta[\mathbf{3}]}{\Delta t} = -k_1[\mathbf{3}][\mathrm{B}] - k_3[\mathbf{3}][\mathrm{B}] + k_2[\mathbf{4}][\mathrm{B}] \quad (1)$$

$$\frac{\Delta[\mathbf{4}]}{\Delta t} = k_1[\mathbf{3}][\mathrm{B}] - k_2[\mathbf{4}][\mathrm{B}] - k_4[\mathbf{4}][\mathrm{B}] \quad (2)$$

$$\frac{\Delta[\mathbf{5}]}{\Delta t} = k_3[\mathbf{3}][\mathrm{B}] + k_4[\mathbf{4}][\mathrm{B}] \quad (3)$$

The estimated values for the specific rate constants obtained by the method of initial rates were iterated (using a nonlinear regression program)[8] until a best fit was obtained with the experimental points. A minimum of 10 points was used in each run. Correlation coefficients obtained for the runs were ca. 0.9990 for reactions at 30.4 °C and 0.993 at 50.2 °C. k_4, which is about an order of magnitude smaller than any of the other rate constants in the system, is not obtainable from the iteration, and hence its value was set equal to that determined by the initial rate technique. The results are presented in Table I.

The high degree of correlation in the results can be seen in Figures 1 (trans isomer) and 2 (cis isomer) in which the symbols represent the experimental points and the line the theoretical ones obtained by computer simulation. The activation parameters are presented in Table II.

Reactions in the Presence of Crown Ether. Potassium *tert*-butoxide in *t*-BuOH is known to exist in part as ion pairs and higher aggregates[9] (eq 4):

Scheme I

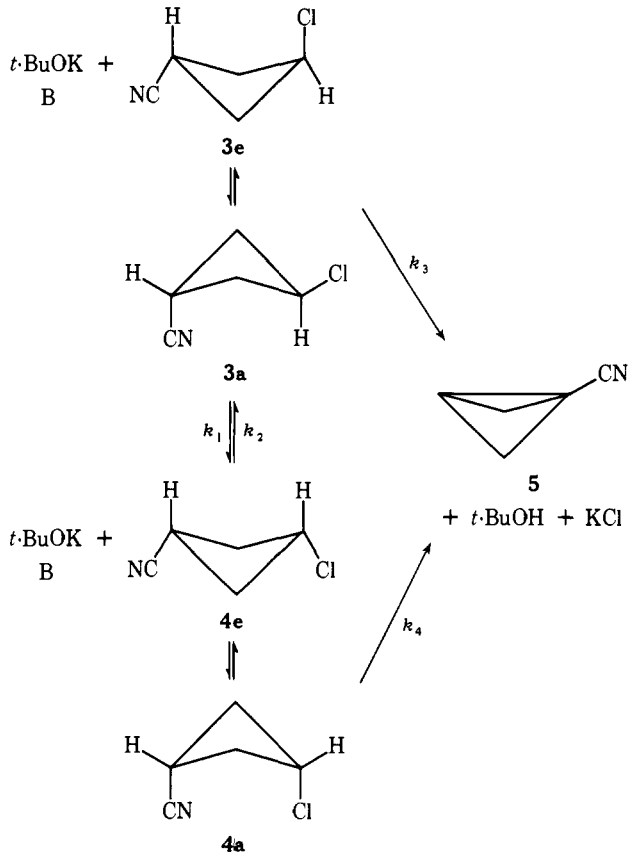


Table I. Second-Order Rate Constants for the Reaction of **3** and **4** with *t*-BuOK in *t*-BuOH at 30.4 and 50.2 °C

T, °C	10^3k_1, $M^{-1}\ s^{-1}$	10^3k_2, $M^{-1}\ s^{-1}$	10^3k_3, $M^{-1}\ s^{-1}$	10^3k_4, $M^{-1}\ s^{-1}$
30.4	42.0 ± 2.5	20.8 ± 2.0	43.2 ± 3.1	2.9 ± 0.4
50.2	242.0 ± 19	137.0 ± 14.0	208.0 ± 19	17.0 ± 2.5

Table II. Activation Parameters for the Reaction of **3** and **4** in *t*-BuOH-*t*-BuOK

reaction	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{30.4\ °C}$, kcal/mol
3 → **4**	16.6	3.6	15.5
4 → **3**	18.0	6.7	15.9
3 → **5**	14.9	−2	15.5
4 → **5**	17.5	1.1	17.2

Table III. Product Distribution as Percents of Starting Material for the Reaction of **3** and **4** in *t*-BuOH-*t*-BuOK

starting isomer	% reprotonation to starting isomer	% isomerization	% elimination
3	7.3	2.7	3.8
3	2.8	1.4	1.7
3	10.2	4.6	6.1
4	6.0	9.0	2.6
4	3.1	4.9	1.1
3[a]	2.7	~0.6	9.2
3[a]	1.0	~0.3	6.6
4[a]	2.8	~1.3	10.5
4[a]	4.0	~1.5	8.0

[a] In the presence of an equivalent amount of crown ether.

$$t\text{-BuO}^- + K^+ \rightleftharpoons t\text{-BuO}^-K^+ \rightleftharpoons (t\text{-BuO}^-K^+)_n \quad (4)$$

Zavada et al.[10] qualitatively reported that addition of crown ether to *t*-BuOK-*t*-BuOH considerably increases solution conductivity. This was confirmed quantitatively by conductivity measurements carried out in this laboratory. The conductivity of pure *t*-BuOH is 0.17 μmho, and that of 0.04 M *t*-BuOK in *t*-BuOH is 0.24 μmho. Addition of an equivalent amount of crown ether increases the conductivity to 35 μmho (additional amounts of crown ether did not affect the conductivity). If conductivity is brought about only by free ions, assuming linearity between conductivity and concentration, it can be deduced that at most one molecule out of 500 exists as a free ion under these conditions. Two pronounced effects are caused by crown ether addition to the reaction mixture. First, reaction rates are largely increased: At 50.2 °C the reaction was too fast to be measured; even at 30 °C it was possible to sample only a few points for each kinetic run. Second, unlike the reactions under base-pairing conditions, elimination greatly exceeds the isomerization rate. Second-order rate constants for the elimination reaction at 30.4 °C are 1.31 ± 0.05 and 0.84 ± 0.05 $M^{-1}\ s^{-1}$ for **3** and **4**, respectively.

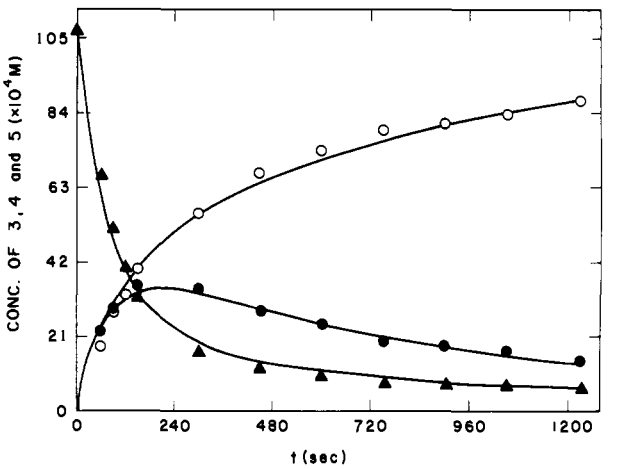


Figure 1. Reaction of **3** with *t*-BuOK-*t*-BuOH at 50.2 °C. Experimental points are presented as ▲, ●, and ○ for **3**, **4**, and **5**, respectively. Lines were calculated by the computer simulation program.

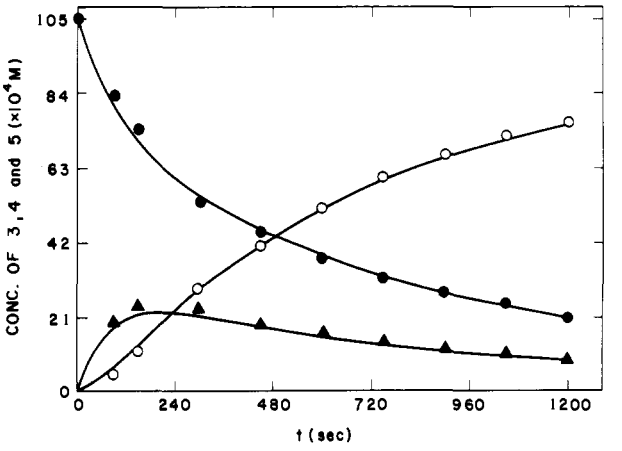
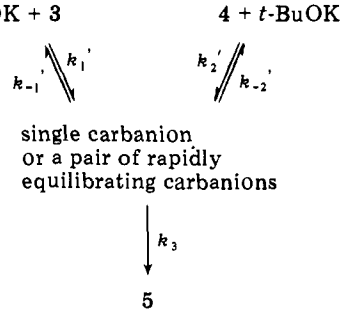


Figure 2. Reaction of **4** with *t*-BuOK-*t*-BuOH at 50.2 °C. Experimental points are presented as ▲, ●, and ○ for **3**, **4**, and **5**, respectively. Lines were calculated by the computer simulation program.

Product Distribution. By means of VPC analysis, we were able to study only the elimination and the isomerization reactions. In order to investigate the mechanism by which the intermediate might revert to starting material, we have conducted some reactions in tritiated *t*-BuOH (*t*-BuOT). The amount of ^3H incorporation into the starting material serves as a quantitative probe for analyzing this degenerate process. Product distributions for the reactions of the two isomers with and without crown ether are presented in Table III.

Scheme II



Discussion

Base-catalyzed eliminations can proceed either through a concerted mechanism (E2) or by an E1cB mechanism via a carbanionic intermediate. The preferred conformation for a concerted 1,3 elimination is that of the trans isomer **3** (*exo*-S according to Nickon and Werstiuk),[11] where the ionicity developed on C-1 in the process of the proton abstraction can approach C-3 from the rear and nucleophilically displace the chlorine atom. The facts that the trans isomer undergoes elimination faster than the cis isomer **4** and that isomerization and reprotonation to starting material are faster than elimination show that the major pathway for the elimination reaction is via the E1cB mechanism (Scheme II). In light of both the relatively short distance between positions 1 and 3 and the rigidity of the system, the observed preference for a stepwise reaction strongly supports Bordwell's contention that 1,3 eliminations are stepwise processes.[7]

Except for the single case of cyclopropyl carbanion, which will be discussed later on, it is generally assumed that nitrile-stabilized carbanions are delocalized onto the cyano group where the α carbon assumes an sp^2 configuration.[12] To the extent that this is true for this system as well, then the carbanions derived from both isomers should be identical. An assumption of a common intermediate or of two distinct intermediates (two sp^3 carbanions in this case), which are interconverting at a rate faster than that of any competing process in the system, dictates that product distribution should be the same regardless of the starting material.[13]

In Table III the experimentally determined product distributions are given. These distributions reflect the higher reactivity of the trans isomer relative to that of the cis, in that the ^{3}H-labeled **4** and product **5** arise in part from the decomposition of **3** (Scheme I) formed by the isomerization of **4**.

Such a process will obviously lower the observed concentration of **3** and at the same time increase that of **5** and of tritiated **4**. Theoretically, a more precise determination of product distribution derived from the carbanion can be achieved by carrying out measurements at lower reaction percentages. However, since the experimental error accompanying the determination of the small quantities involved would outbalance any benefit achieved by this procedure, a computer simulation technique was used for this purpose. This was done by setting k_1, k_2, and k_3 to their known values, while k_4 was set to zero. The simulation was stopped when the concentration of **3** had reached its experimental value. The amount of **5** obtained in this manner was used to correct the pertinent data of Table III. The corrected results are given in Table IV. Since the trans isomer reacts faster than the cis, there is no need for a similar correction procedure for its product distribution. Examination of the results in Table IV reveals that, for both isomers, product distribution is the same with regard to reprotonation to give **3** and **4**. The trans isomer is obtained by reprotonation of the intermediate carbanion at twice the rate of the cis, irrespective of the identity of the starting isomer. Elimination products, however, constitute about 30% of the products derived from

Table IV. Corrected Product Distribution for the Reaction of **3** and **4** in *t*-BuOH–*t*-BuOK as Percents Out of Total Reaction

starting isomer	% 3	% 4	% 5	% 5[a]
3	62	27	11	17
4	62	30	8	—

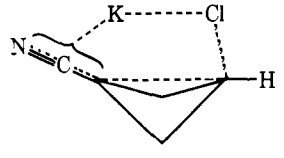
[a] Additional elimination mechanism (not counted in the 100% reaction).

3, as compared to less than 10% starting from **4**. This difference can be attributed to the existence of an additional elimination mechanism, which is specific for the trans isomer and accounts for about 70% of its total elimination route.

We have already shown that *t*-BuOK exists in *t*-BuOH largely as ion pairs. It is highly likely that the minute amount of the highly reactive "free" *t*-BuO^- is not the active form of the base since: (a) a reasonable assumption of a first order in the active form of the base will result, according to eq 5:

$$[t\text{-BuO}^-] = K^{1/2}[t\text{-BuO}^-\text{K}^+]^{1/2} \qquad (5)$$

(where K is the equilibrium constant between the two forms of the base), in a half-order in the total *t*-BuOK concentration, rather than the first order that was actually observed. (b) Deprotonation rate constants in the presence of crown ether are close to the elimination rate constants, and their upper limits in the absence of crown ether, given in Table I, are enhanced upon addition of crown ether by a factor smaller than 20, instead of about 500 as might be expected from the corresponding increase in free *t*-BuO^- concentration. It is well established that base association can appreciably determine the course of elimination. Zavada and Svoboda[10,14] and Bartsch et al.[9,15] found that ion pairing in *t*-BuOK leads to more syn elimination due to stabilizing interactions in the transition state between the metal cation and the negatively charged leaving group. In light of their findings, a reasonable mechanism for the additonal elimination route is one in which the potassium cation electrophilically assists in the expulsion of the Cl^- in the transition state (**6**) of the rate-determining step. This



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mechanism is specific for the trans isomer, since only in this isomer are the chlorine atom and the potassium cation of the *t*-BuOK on the same face of the molecule. The observation that crown ether addition to the system, under conditions where this additional mechanism cannot operate, results in a markedly diminished difference in elimination rates between the two isomers is highly supportive of the assumption of the syn K^+-assisted mechanism for the trans isomer.

Protonation and Deprotonation Reactions. Equilibrium constants between the two isomers can be evaluated from the isomerization rate ratio k_1/k_2 (Table I). This equals 1.93 and 1.77 at 30.4 and 50.2 °C, respectively, indicating that the trans isomer is destabilized by about 0.3 kcal/mol at these temperatures with respect to the cis isomer. This result is in good agreement with $\Delta G°$ values of 0.29 and 0.58 kcal/mol obtained for isomerization of 1,3-dichloro- and dibromocyclobutanes at 124.4 °C.[16] (The calculated $\Delta G°$ for **3** ⇌ **4** isomerization at 124 °C is 0.28 kcal/mol.)

As can be seen from Table I, the trans isomer is more reactive than the cis with respect to both elimination and isomerization. One reason for its higher reactivity undoubtedly stems from its higher ground-state energy. The relative height of the transition state to deprotonation has still to be considered.

Although the individual rates of the proton transfer reaction in the system were not measured separately, by the aid of eq 6 to 12 the relative rates of these processes at 30.4 °C can be evaluated for the two isomers. Assuming steady-state concentration for the carbanion, the rate constants according to Schemes I and II are related as follows:

$$k_1 = k_1'k_{-2}'/(k_{-1}' + k_{-2}' + k_3') \quad (6)$$

$$k_2 = k_2'k_{-1}'/(k_{-1}' + k_{-2}' + k_3') \quad (7)$$

$$k_3 = k_1'k_3'/(k_{-1}' + k_{-2}' + k_3') \quad (8)$$

$$k_4 = k_2'k_3'/(k_{-1}' + k_{-2}' + k_3') \quad (9)$$

Dividing eq 6 by eq 7 gives the ratio of the acidity equilibrium constants K_1' and K_2' for the two isomers:

$$\frac{k_1}{k_2} = \frac{k_1'k_{-2}'}{k_{-1}'k_2'} = \frac{K_1'}{K_2'} \quad (10)$$

Dividing eq 8 by eq 9 gives the rate ratio for the deprotonation reaction:

$$\frac{k_3}{k_4} = \frac{k_1'}{k_2'} \quad (11)$$

Dividing eq 11 by eq 10 yields the rate ratio for protonation of the carbanion to give the two isomers:

$$\frac{k_3k_2}{k_4k_1} = \frac{k_{-1}'}{k_{-2}'} \quad (12)$$

Taking the value of k_3 as 13 M^{-1} s^{-1}, which corresponds to the fraction of elimination that operates by the mechanism of Scheme II, the results of the above calculations are: (a) the trans isomer is more acidic than the cis ($K_1'/K_2' = 2$); (b) the trans isomer undergoes deprotonation faster than the cis ($k_1'/k_2' = 4.5$); and (c) protonation of the carbanion to give the trans isomer is faster than its protonation to give the cis ($k_{-1}'/k_{-2}' = 2.2$). Results obtained from product distribution experiments, which are completely independent of the kinetic ones, are reassuring in that protonation of the carbanion to give **3** is favored by a factor of about 2.2 relative to that of **4**. It is interesting to note the lack of correlation between the kinetics and the thermodynamics of these processes in that the transition state leading to the less stable isomer is of lower energy relative to that leading to the more stable one. Using the microscopic reversibility principle, it is clear that the trans isomer is more reactive not only because of its higher ground-state energy but also by virtue of its lower energy transition state for the deprotonation reaction.

Considering the two isomers as two acids for which the relative kinetic and thermodynamic acidities are known (eq 10 and 11), one can calculate Bronsted α coefficients for their ionization reactions. Bronsted coefficients usually range from 0 to 1; however, deviant Bronsted relationships in which the value of the coefficient exceeds these limits are well recognized.[17] The α value for this system is 2.17, reflecting the absence of correlation between the kinetics and the thermodynamics.

The striking preference for the formation of the less stable isomer by protonation was first pointed out by Zimmerman[18] for cyclohexane nitronates and enolates and was recognized as being steric in nature. It was assumed that the least hindered approach is from the equatorial side, since steric interactions with the two axial hydrogen atoms hampered approach of the proton donor from the "axial" side. It was later shown[19] that the origin of the steric hindrance is not the two axial hydrogens, but rather the bulky group α to the carbanion. As was shown before, the transition state for deprotonation and protonation as well is of lower energy for the trans than that for the cis isomer. In the absence of any bulky group α to the carbanion of **3** and **4**, Zimmerman's original[18] idea of 1,3-diaxial interaction as a governing factor should be adopted for the present system. The two isomers **3** and **4** exist in two rapidly interconverting conformations. (The barrier to planarity of cyclobutane itself was recently calculated to be 0.9 kcal/mol.[20]) From the similarity in $\Delta G°$ for isomerization of 1,3-dichloro- and 1-cyano-3-chlorocyclobutane (0.29 vs. 0.28 kcal/mol at 124 °C), it is evident that the steric requirements of the cyano group in this system are very close to that of Cl, and therefore conformations of the two trans isomers are probably of equal stability. For the trans isomer, the least hindered approach will be equatorial (to **3a**), since an axial approach (to **3e**) will give rise to interaction of the bulky base with the axial chlorine at position 3.

An axial approach of the base to **4e** will give rise to *t*-BuOK–H 1,3-diaxial interactions, whereas in an equatorial approach to **4a** 1,3-diaxial interaction between Cl and CN is incurred. It is not clear which of the two approaches to the cis isomer is favored, although it is clear that both are of higher energy than the equatorial approach to the trans isomer.

There is a well-recognized difference in steric requirements between dissociated ions and ion pairs.[9] The steric requirements of the ion pair, due to the presence of the cation as part of the base system, are greater than those of the "free" base. It was shown[21] that this difference in bulkiness, in the case where the base can attack the hydrogen by two different approaches (or two different hydrogens), which differ from each other by posing different steric requirements for the base attack, can be used as a probe to point to the more sterically hindered position. Addition of crown ether will in general enhance proton abstraction processes due to an increase in base reactivity. However, diminishing the base size will have a more pronounced effect on the more hindered approach. At 30.4 °C the deprotonation of the cis isomer is slower by a factor of 4.5 than that of the trans. In the presence of crown ether, the ratio of the rate constants for the elimination reactions where mainly proton abstraction is the rate-determining step is only 1.5, indicating a higher sensitivity of the cis isomer to base size. It is concluded, therefore, that the base's approach to the cis isomer is more sterically hindered than its approach to the trans isomer.

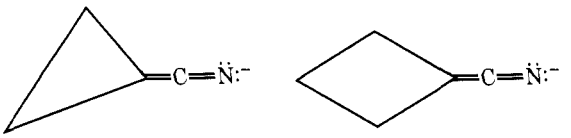
If proton abstraction from the cis isomer takes place from the equatorial position as in the trans, the two isomers should exhibit the same sensitivity toward changes in the base size. Therefore, it is reasonable to assume that while proton abstraction takes place via an equatorial approach in the trans isomer, the proton is abstracted from an axial position in the cis.

It is worthwhile to note that the ratio of elimination to overall protonation in the reaction via the common carbanionic intermediate (Scheme II) is 1:9 (Table IV). The addition of crown ether, aside from increasing the reactivity of species involved, causes an inversion in the selectivity of the carbanions. This is evidenced by the fact that in the presence of crown ether, elimination of the chloride exceeds the reprotonation rate by a factor of ca. 3. This inversion in selectivity is probably brought about by a change in the acidity of the protonating acid. The presence of the potassium cation in the carbanion solvation shell increases its acidity, since the negatively charged conjugated base (*t*-BuO$^-$) of the protonating acid (*t*-BuOH) can be stabilized by a positive potassium ion. In the absence of a potassium ion, the solvation shell is rendered less acidic, and, as a result, elimination competes more successfully with the protonation by the weaker acid.

Carbanion Stereochemistry. We have shown that the same carbanionic intermediate (or a pair of rapidly equilibrating carbanions) is obtained upon treating both isomers with *t*-BuOK in *t*-BuOH. It is striking, therefore, that addition of crown ether results mainly in retention of configuration in the reprotonated products. This means that in the absence of po-

tassium cation, the carbanions derived from both isomers are not identical, and that the protonation rate is faster than the rate by which the carbanions invert.

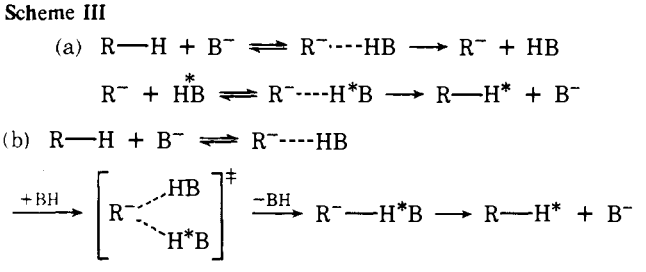
In light of Cram's work,[12b] it is assumed that in open-chain nitriles carbanions exist in the planar delocalized form and hence will lead to racemized products. The situation is markedly altered when a carbanion is confined in a small ring. As found by Walborsky,[12a] optically active 2,2-diphenylcyclopropylcarbonitrile exhibits a very high degree of retention (98.7% in *t*-BuONa-*t*-BuOH at 25 °C as compared to 50–70% in the present case). This was attributed to a strain factor that is encountered at the transition state for inversion. In order that racemization occur, the cyclopropyl anion must acquire a planar configuration at the transition state with the formation of an exocyclic double bond (delocalized form **7**).



7 **8**

This highly strained configuration affords a barrier to inversion of the cyclopropyl carbanion and, hence, retention is observed. It is difficult to weigh the net energy gain or loss due to delocalization of the negative charge onto the cyano group as opposed to formation of an exocyclic double bond in cyclopropyl (**7**) or cyclobutyl (**8**) carbanions. One can, however, estimate the height of the strain barrier by using strain energies known for the analogous all-carbon compounds. The strain energies for cyclopropane, methylenecyclopropane, cyclobutane, and methylenecyclobutane are 28.13, 41.7, 26.9, and 28.8 kcal/mol, respectively,[22] indicating that the formation of an exocyclic double bond in cyclopropane will be destabilized by 13.6 kcal/mol as compared to only 1.9 kcal/mol for cyclobutane. On the other hand, it is possible that the driving force to overcome this barrier is somewhat stronger in cyclopropane, since, if the anion retains the parent molecule geometry ($sp^{2.40}$ for an exo C–H bond in cyclopropane),[23] the overlap of the negatively charged orbital with the cyano group π orbitals is poorer than in that of the cyclobutyl anion, where the exocyclic C–H bond already has a higher p character ($sp^{2.62}$).[23] Since, however, the strain energy barrier is so low, it is highly likely that the most stable configuration of the anion is a planar one or very close to it, with a shallow barrier between the two stable configurations. It is concluded, therefore, that strain alone cannot account for the retention of configuration in the cyclobutyl carbanion. Cram, in his excellent monograph,[24] suggests three distinct retention mechanisms for symmetrical or near symmetrical carbanions. The cause for the retention in these three mechanisms is an asymmetric solvation of the carbanion due to the presence of a cation in its close vicinity. Dissociation of the ion pairs, induced by using higher dielectric solvents such as Me_2SO, leads to racemization instead of retention. It is striking that the displacement of the potassium cation from the vicinity of the cyclobutyl carbanion by means of crown ether results, contrary to expectation based on these three mechanisms, in retention of configuration.

Scheme III



The general process of proton exchange on carbon acid can occur by two possible mechanisms (Scheme III). In the first one (a), the rate-determining step is the dissociation of the hydrogen-bonded internal return complex to give "free" carbanion, which might undergo protonation on both faces of the molecule at a rate dictated by intrinsic molecular constraints. In the second mechanism (b), electrophilic substitution takes place on the hydrogen-bonded complex which will result in retention of configuration. It is thus reasonable to assume that in the presence of potassium cation, protonation occurs on the "free" carbanion as depicted in the first mechanism of Scheme III, while the presence of crown ether, which probably induced a variation in the ΔpK_a between the carbon acids and its solvation shell, gives rise to a higher contribution of the second mechanism and hence results mainly in retention.

Experimental Section

General. IR spectra were obtained with a Perkin-Elmer 621 spectrophotometer, ^1H NMR spectra were recorded on a Varian HA-100 spectrometer, and ^{13}C spectra were taken with a Varian CFT 20 spectrometer. Mass spectra were taken with a Hitachi/Perkin-Elmer RMU6 mass spectrometer, and the radioactive measurements were carried out on a Tri-Carb 2450 liquid scintillation spectrometer (Packard U.S.A.). For analytical purposes, a Packard Model 878 (FI detector) gas chromatograph was used, whereas for the preparative separations of the isomers a Varian 920 gas chromatograph (TC detector) was used. In both cases the columns were of 20% XE 60 on Chromosorb W, acid washed, 60–80 mesh. Conductivity was measured by a TH27 conductometer (El Hama, Israel).

Reactants, Preparation, and Purification. 3-Chlorocyclobutanecarbonitrile was prepared from allene and acrylonitrile by a published procedure[25] as a mixture of isomers. Pure isomers were obtained by preparative VPC separation. Each isomer was repeatedly separated until purity exceeded 99%. The identity of the isomers was established by comparing their IR spectra with that reported in the literature[26] and by ^1H NMR analysis: ^1H NMR ($CDCl_3$) for the trans isomer δ 2.5–3.1 (m, 4 H, CH_2), 3.37 (m, 1 H, CHCN), 4.6 (m, 1 H, CHCl), and for the cis isomer δ 2.5–3.1 (m, 5 H, CH_2 and CHCN), 4.3 (m, 1 H, CHCl); ^{13}C NMR ($CDCl_3$) for the trans isomer δ 19.03 (d, CCN), 38.01, 38.15 (t, CH_2), 50.39 (d, CCl) and for the cis isomer δ 16.99 (d, CCN), 38.69, 38.83 (t, CH_2), 47.43 (d, CCl).

t-BuOK (Fluka) was doubly sublimed. 18-Crown-6 (Fluka) was purified by the acetonitrile method.[27]

Kinetic Procedure. Stock solutions of the substrates containing biphenyl as an internal standard were prepared and mixed at the reaction temperatures with the appropriate aliquots of *t*-BuOK–*t*-BuOH solutions. Crown ether, when needed, was added to the base stock solution. Samples of ca. 0.1 mL were periodically removed, quenched by 0.1 mL of water, and analyzed by VPC. The composition of the quenched solution remained unchanged for at least a week.

Product Distribution. Tritiated (O-*t*) *t*-BuOH (activity, ca. 10^4 cpm per 50 mg) was prepared by refluxing 0.2 mL of tritiated water (Amersham-England) with 4 mL of *t*-BuOH over calcium hydride for 10 min. The tritiated *t*-BuOH was obtained by a fractional distillation. The general procedure for the product distribution experiment is as follows: 0.1 g (8.7×10^{-4} mol) of one of the isomers was dissolved in 1 mL of tritiated *t*-BuOH. To this, a solution of 1–10 mol % of *t*-BuOK in 1 mL of tritiated solvent was added at 26 ± 1 °C. The reaction was followed to completion by VPC, and the organic components were extracted three times using ether and water. The ethereal layer was washed with water and concentrated. The extent of tritium incorporation into the starting isomer was determined after purification by two successive separations on a preparative gas chromatograph. The specific activity drop between the two separations was 10–15%. Readings were ca. 10^2–10^4 cpm per 3–20 mg of starting isomer. In each determination several readings of 0.5 to 5 min were taken. Crown ether, when used, was added to the base solution in an equivalent amount.

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Communications to the Editor

cis-Methyldiazene

Sir:

cis-Diazene (diimide) has been implicated as an intermediate in stereospecific reductions by in situ generated diazene[1] and in nitrogenase action on nitrogen.[2] This molecule and its rather well-studied trans isomer[3,4] have been the objects of a number of theoretical studies.[5] Yet, only fragmentary and inconclusive evidence has been reported for the direct observation of the cis isomer.[6,7] We now report the isolation of the closest homologue of *cis*-diazene, *cis*-methyldiazene, and its infrared spectrum. Based on the assignment of this spectrum, we conclude that *cis*-diazene is yet to be observed.

Hutton and Steel obtained *cis*-dimethyldiazene by photolysis of solid *trans*-dimethyldiazene with near-UV light at liquid nitrogen temperature.[8] A similar experiment with *trans*-$CH_3N{=}ND$[9] has given a new substance that has properties appropriate to *cis*-$CH_3N{=}ND$. Approximately 0.5 mmol of the trans isomer were distilled onto a CsI crystal which was held at −196 °C in a conventional low-temperature infrared cell. Prior to photolysis the glassy deposit was annealed into polycrystalline material. Photolysis was carried out for 6 h with illumination from a 45-W, low-pressure mercury lamp. New infrared absorption bands appeared at 2180, 1560, and 1060 cm^{-1}. The bands due to *trans*-$CH_3N{=}ND$ had decreased in intensity and had reverted toward the structureless appearance of glassy material. After the deposit was annealed again, the new features were seen more clearly and a small amount of noncondensible gas, presumably nitrogen, was pumped from the cell. Cautious cycling of the temperature between −196 °C and values progressing through the range of −125 to −113 °C, as well as repeated evacuation of the cell (at −196 °C), caused the relatively large amount of unconverted *trans*-$CH_3N{=}ND$ to sublime from the CsI plate to the surfaces of the surrounding copper support and liquid nitrogen well. The large difference in volatility between the two isomers of methyldiazene is consistent with the boiling point difference of nearly 100 °C found for *cis*- and *trans*-dimethyldiazenes.[10]

Figure 1 gives the infrared spectrum of the residual deposit. Table I gives the vibrational assignment for *cis*-$CH_3N{=}ND$ in comparison with that of the trans isomer.[9] That many of the frequencies of the fundamentals of this molecule are nearly coincident with those of the trans isomer is reasonable and is supported by zero-order normal coordinate calculations.[11] Bands are present for methyl group stretching and bending, for N=N stretching, and for ND stretching and bending. The band due to N=N stretching is a much more intense feature of this spectrum than in that of the trans isomer. The largest frequency shift, a decrease of ~120 cm^{-1}, occurs in the ND stretching mode. Two satellite bands in the spectrum are attributed to hydrogen bonding. Several features are due to *cis*-$CH_3N{=}NH$ which was formed from the isotopic impurity present in the trans isomer.

Several other possible products of the photolysis were considered but discarded. These included CH_3D, CH_3CH_3, *trans*-$DN{=}ND$, and *trans*-$HN{=}ND$, for which published spectra were available. Furthermore, these substances should have vaporized during the temperature cycling. The hydrazone of methyldiazene-d_1, $CH_2{=}NNHD$, which is a possible rearrangement product, does not fit the observed spectrum. This molecule has no methyl group and would have a C=N

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