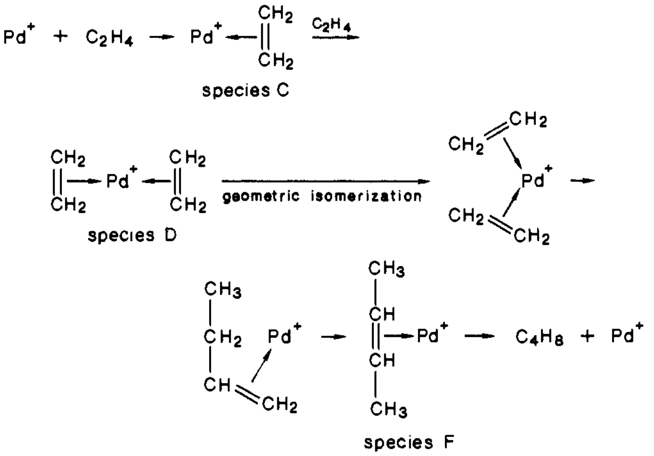
posure of the zeolite sample to ethylene and that species B, attributed to Pd^+ ions, appears immediately, indicating that reduction of Pd^{3+} and Pd^{2+} to Pd^+ cations by ethylene occurs rapidly. The Pd^+ ions so formed migrate toward the α-cage to interact with ethylene. Our ESR and ESE results suggest that initially one molecule of ethylene interacts with a Pd^+ ion, giving a π-complex identified as species C, followed by the addition of another ethylene molecule to the same Pd^+ ion, giving an intermediate identified as species D. Bonneviot et al.[18] have suggested that two molecules of ethylene are π-bonded to Ni^+ in Ni–X zeolite for dimerization. The intermediate complex D is postulated to undergo a geometric isomerization to bring the two ethylene molecules into a favorable position for the reaction to form 1-butene, which is then isomerized to *cis*- and *trans*-2-butene. Since the zeolite is shown to be highly active for 1-butene isomerization, an equilibrium composition of *n*-butenes is observed even in the early stages of product formation. The proposed reaction mechanism is shown below.



Conclusions

Ethylene dimerization occurs on both NaPd–X and CaPd–X zeolites after an induction period. The catalytic activity increases with an increase of Pd content in the zeolite due to an increase of active Pd sites. The reaction induction period is found to decrease with increase of Pd content or reaction temperature. It is also less for CaPd–X zeolite in comparison to NaPd–X zeolite due to the different Pd species locations. In CaPd–X zeolite, Pd^{2+} ions occupy site SII′ due to the strong affinity of Ca^{2+} ions for site SI′. But in NaPd–X zeolite Pd^{2+} ions occupy site SI′. A part of the Pd^{2+} ions, during O_2-pretreatment, are oxidized to Pd^{3+} ions, which migrate to site SII, a more accessible site to ethylene, in CaPd–X zeolite. However, in NaPd–X zeolite the Pd^{3+} ions migrate to site SI in the hexagonal prism of the zeolite structure. In the presence of ethylene, the Pd cations are reduced to Pd^+ ions and migrate toward the α-cage for coordination with ethylene molecules. The formation of paramagnetic species B–D is observed prior to ethylene dimerization, and it is concluded that monovalent Pd cations are the active species for the dimerization reaction. The present ESE results confirm that species C and D are due to $Pd^+–C_2H_4$ and $Pd^+–(C_2H_4)_2$ complexes, respectively. Paramagnetic $Pd^+–C_4H_8$ complexes are also detected when most of the ethylene is converted to butenes. In a proposed reaction mechanism ethylene dimerization on Pd-exchanged Na–X and Ca–X zeolites is suggested to occur via the addition of two ethylene molecules to the same Pd^+ cation. In ethylene dimerization, 1-butene is initially formed and is subsequently isomerized to *cis*- and *trans*-2-butene. These catalysts are deactivated at longer reaction times and higher temperatures most likely due to reduction of active Pd^+ ions to atomic palladium.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHM-8514108) and the Texas Advanced Technology Research Program.

Registry No. Pd, 7440-05-3; ethylene, 74-85-1; 1-butene, 106-98-9.

Nonplanarity of the Methylcyclobutyl Cation

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Abstract: α,β,α'-Trideuteriated methylcyclobutyl cation was prepared and studied in the NMR to look for isotopic perturbation of the inversion of a possibly nonplanar structure, without interference from the known rapid process that interchanges the nonequivalent methylene groups. Observation of a splitting in the ^1H NMR spectrum of the deuteriated ion with intensity ratio of 2:1 unambiguously demonstrates that the cation is nonplanar. A temperature-dependent downfield shift of the proton peaks in the deuteriated ion was also observed and may indicate a rapid equilibrium with a minor species.

Phenomena involving the ready ionization of cyclobutyl and cyclopropylcarbinyl derivatives to form cationic intermediates have been studied for many years. We have wanted to learn the structures and energies of all significant intermediates and transition states involved. Recently, the stable $C_4H_7^+$ ion formed from either cyclobutyl or cyclopropylcarbinyl precursors[1] has been shown by NMR deuterium isotopic perturbation[2] and high-level quantum mechanical calculations[3] to be a rapidly equilibrating set of three degenerate nonclassical bicyclobutonium ions and three degenerate cyclopropylcarbinyl cations, quite different in geometry, yet very close in energy and interconverting rapidly over a very flat energy surface.[3] Introduction of a methyl group to produce an analogous ion, which is formally tertiary, might be expected to alter the situation to favor classical structure and behavior. However, the experimental results indicate distinctly nonclassical behavior for methylcyclobutyl cation.

Ionization of methylcyclobutyl chloride or alcohol in $SbF_5–SO_2ClF$ solution to yield a $C_5H_9^+$ cation (**1**) was reported in 1970.[4]

[†] Postdoctoral Fellow at Yale University, 1987–1988.

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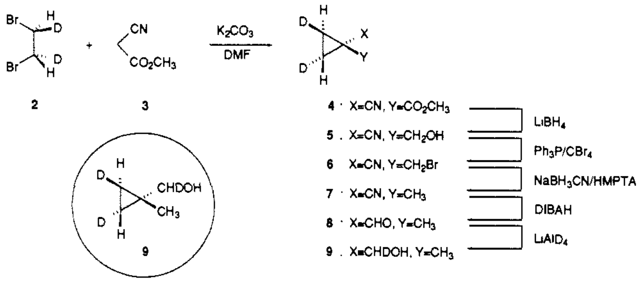
Scheme I



The ^{1}H NMR spectrum consists of two singlets at $\delta = 2.87$ (methyl group) and $\delta = 3.89$ (6 methylene hydrogens). The structure suggested for **1** was a methylcyclobutyl cation (planar) in rapid equilibrium with the corresponding 1-methylcyclopropylcarbinyl cation to account for the single methylene peak. The ^{13}C NMR spectrum of **1** has signals at $\delta = 25.4$ (CH_3), $\delta = 163.3$ (C^+), and one peak for three methylenes at $\delta = 48.6$.[5,6] In 1977, Kirchen and Sorensen[7] found that the process averaging the methylene groups can be frozen out at −158 °C; the CMR methylene signal splits into peaks at $\delta = 71.7$ (α-carbons) and $\delta = -3.0$ (β-carbon) ($\Delta G = 5.8$ kcal/mol). To account for the remarkable upfield shift of the β-methylene carbon, they suggested a sp^3-hybridized (nonplanar) methylcyclobutyl cation as the dominant species. Olah et al.[8] preferred to call it a nonclassical 1-methylbicyclobutonium structure. Application of the isotopic perturbation method using deuterium[9-11] confirmed the rapid interchange of nonequivalent methylene groups. Furthermore, calculation of the chemical shifts of a structure for the 1-methylbicyclobutonium cation using the IGLO method gave agreement with the experimental values.[12]

These results clearly demonstrate rapid interchange of nonequivalent methylene positions. The question of the planarity or nonplanarity of **1** resulting in the equivalence or nonequivalence of the averaged exo and endo hydrogens on each methylene is less unambiguously settled. The upfield shift of the β-methylene and the unusual sign of the isotopic perturbation were interpreted as favoring a bicyclobutonium structure, which was assumed to be nonplanar.[10,11] However, strictly speaking, these observations only infer a hypervalent β-methylene nonclassically bonding to the cationic center diagonally across the ring. A planar structure is not ruled out. Even if the species *is* nonplanar, it *must* be undergoing a very rapid ring inversion presumably via a planar intermediate or transition state lying no more than a few kilocalories above the ground state, since only a single methylene proton peak is seen in the NMR even at low temperature, in contrast with the result in the $C_4H_7^+$ ion where noninterconverting exo and endo peaks are seen. The very small energy difference between a possible nonplanar structure and the planar one makes it difficult to predict with certainty which is the best.

If the structure were nonplanar, the rapid ring inversion might be perturbed by appropriate deuterium substitution. A single deuterium on one methylene should produce such a perturbation. However, it also will perturb the interchange of the nonequivalent methylenes. Siehl[10] studied the monodeuteriated species and interpreted his results only in terms of perturbing the interchange of nonequivalent methylenes. It is not evident how one could specifically detect nonplanarity with this experiment. The ring inversion and the interchange of methylenes would *both* contribute to the observed isotope effect. To perturb the inversion of a (possibly) nonplanar structure *without* interference from the methylene interchange, we synthesized the 3-fold labeled α,β,α'-trideuterio-1-methylcyclobutyl cation. If the structure were planar, the interchange of methylenes should produce *no* energy change and there should be *no* isotope perturbation. If two of the deuteriums were on one side of the ring and the third on the other side in a *non*planar structure, we hoped to observe an equilibrium isotope effect on the ring inversion.

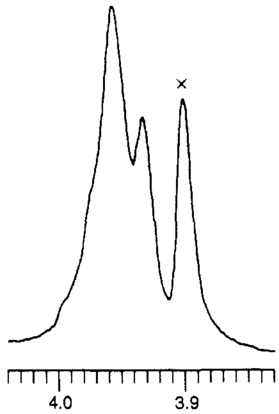


Figure 1. 250-MHz ^{1}H NMR spectrum of a mixture of **1** (×) and $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** at −80 °C.

Results and Discussion

The precursor for the trideuteriated 1-methylcyclobutyl cation, (2,3-dideuterio-1-methylcyclopropyl)deuteriomethanol (**9**), was synthesized as outlined in Scheme I. Starting from commercially available 1,2-dibromo-1,2-dideuterioethane (**2**; MSD Isotopes), the cyclopropane ring was formed by condensation with methyl cyanoacetate (64%);[13] the deuterium atoms were found to have the trans configuration. The ester function was then transformed into a methyl group via reduction with lithium borohydride (55%),[14] conversion to the bromide with triphenylphosphine/carbon tetrabromide (93%),[15] and reduction with sodium cyanoborohydride/HMPTA (47%).[16] Finally, the cyano group was reduced in two steps with diisobutylaluminum hydride [17] and lithium aluminum deuteride (26% for both steps), leading to **9** in 4% yield over six steps.

Stable solutions of a mixture of **1** and $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** in SbF_5–SO_2ClF were prepared by the molecular beam method.[18] The ^{1}H NMR spectrum (Figure 1) shows two peaks in the ratio 2:1 for the methylene protons of $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1**, shifted downfield with respect to the methylene protons of the unlabeled ion; these downfield shifts are slightly temperature dependent and vary between 0.065 (−100 °C) and 0.045 ppm (−30 °C) for the larger peak and between 0.039 (−100 °C) and 0.026 ppm (−30 °C) for the smaller peak. No shift of the methyl resonance of $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** with respect to unlabeled **1** was observed.

This result indicates isotopic perturbation of *two distinct* rapid equilbria in **1**. The first perturbed process is the inversion of nonplanar **1**. Since the two ring-deuterium atoms in the precursor **9** are trans, the ion should have two deuteriums on one side of the ring and the third on the other side; subsequent interchange of the methylene groups then leads to the formation of all six possible isomers with a trans,cis relationship of the deuterium

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atoms. Inversion interconverts the exo and endo positions and should be perturbed by an equilibrium isotope effect. A difference of the average chemical shifts of the exo and endo hydrogens would then lead to splitting of the methylene signal. Our observation of this splitting unambiguously demonstrates that **1** is nonplanar. Once one concludes that the structure is nonplanar, one must consider that the interchange of α- and β-methylenes may now also contribute to the isotope effect; however, at this point it is not possible to estimate the extent of this contribution since the equilibrium isotope constant for the methylene interchange in $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** is not known.

In addition to the isotopic splitting in the deuteriated ion, the center of the two methylene peaks of $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** is found to be shifted downfield with respect to the unlabeled ion. This is unlikely to be due to an intrinsic deuterium isotope shift, since such shifts are usually small, upfield, and temperature-independent.[19] We believe that this finding may indicate the presence of a minor species in rapid equilibrium with the major isomer, the equilibrium being perturbed by the deuterium. Isotopic perturbation, even if it is due to several processes, in a single species would be expected to produce a splitting but *not* an overall shift unless there is an unusual combination of proton shifts and equilibrium isotope effects in the nonplanar cation. The independent observation of this isotopic shift was only possible because the deuterium atoms in $[\alpha,\beta,\alpha'\text{-}^2H_3]$-**1** have a trans,cis configuration. If we had examined the all-cis isomer only, a singlet for the methylene protons of the labeled ion would have been found, and its shift from that of the unlabeled ion might have been interpreted as resulting only from the perturbation of ring inversion. A high-level quantum mechanics study of this system is under way. Preliminary results support the conclusion both that the lowest energy structure is nonplanar and that there is a minor species.

Experimental Section

Reagents and Procedures. All reactions were carried out in thoroughly dried glassware under nitrogen. Ethyl ether, THF, and DMF were distilled from lithium aluminum hydride prior to use. All other reagents were used without further purification. ^{1}H NMR spectra were recorded at 250 MHz with a Bruker WM-250 spectrometer in $CDCl_3$ as solvent and internal standard (δ = 7.27). Preparative gas chromatography was carried out with a Varian Aerograph Model 90-P.

Methyl 1-Cyano-2,3-dideuteriocyclopropanecarboxylate (4).[13] To a solution of 10.2 g (53.7 mmol) of 1,2-dibromo-1,2-dideuterioethane (**2**) and 3.8 g (38.4 mmol) of methyl cycanoacetate (**3**) in 220 mL of DMF was added 11.7 g (84.4 mmol) of potassium carbonate, and the mixture was stirred for 20 h at room temperature. The precipitated salts were filtered off and washed with DMF; the filtrate was evaporated in vacuo. Residual salt was removed by addition of 100 mL of ethyl ether and filtration; evaporation of the solvent was followed by distillation; bp$^{0.1}$ 46–48 °C, yield 3.13 g of **4** (64%, colorless liquid). ^{1}H NMR: δ 1.63 (m, 1 H, cyclopropyl H), 1.69 (m, 1 H, cyclopropyl H), 3.83 (s, 3 H, CH_3).

(1-Cyano-2,3-dideuteriocyclopropyl)methanol (5).[14] To a solution of 3.13 g (24.6 mmol) of **4** in 75 mL of THF was added 0.54 g (25.0 mmol) of lithium borohydride, and the mixture was refluxed for 1 h. Hydrolysis with 10 mL of water and acidification with 1 N HCl was followed by extraction with ethyl ether (10 × 50 mL). The combined extracts were dried over $MgSO_4$, and the solvent was evaporated; boric acid present in the crude product was removed by addition of 50 mL of methanol and evaporation in vacuo. Purification by distillation (bp$^{0.25}$ 70–72 °C) yielded 1.33 g of **5** (55%, colorless liquid). ^{1}H NMR : δ 0.98 (m, 1 H, cyclopropyl H), 1.28 (m, 1 H, cyclopropyl H), 2.05 (s, 1 H, OH), 3.64 (s, 2 H, CH_2).

1-(Bromomethyl)-2,3-dideuteriocyclopropanecarbonitrile (6).[15] To a solution of 1.33 g (13.4 mmol) of **5** and 6.67 g (20.1 mmol) of carbon tetrabromide in 15 mL of ethyl ether was added dropwise a solution of 4.22 g (16.1 mmol) of triphenylphosphine in 20 mL of ethyl ether. The reaction mixture was stirred for 30 min at room temperature, and the precipitate formed was removed by filtration through silica gel. The filtrate was dried over $MgSO_4$, and the solvent was removed in vacuo. Distillation (bp^{10} 85–90 °C) furnished 2.02 g of **6** (93%) as a slightly violet liquid. ^{1}H NMR: δ 1.10 (m, 1 H, cyclopropyl H), 1.53 (m, 1 H, cyclopropyl H), 3.40 (s, 2 H, CH_2).

2,3-Dideuterio-1-methylcyclopropanecarbonitrile (7).[16] To a solution of 2.02 g (12.5 mmol) of **6** in 60 mL of HMPTA was added 3.14 g (50.0 mmol) of sodium cyanoborohydride, and the mixture was stirred for 3 h at 100 °C. Hydrolysis with brine was followed by extraction with ethyl ether (10 × 50 mL); the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed with a 20-cm Vigreux column, and the crude product was distilled at reduced pressure; bp^{150} 75–80 °C, yield 485 mg of **7** (47%, colorless liquid). ^{1}H NMR: δ 0.76 (m, 1 H, cyclopropyl H), 1.21 (m, 1 H, cyclopropyl H), 1.38 (s, 3 H, CH_3).

2,3-Dideuterio-1-methylcyclopropanecarbaldehyde (8).[17] To a solution of 480 mg (5.8 mmol) of **7** in 15 mL of hexane was added dropwise at 0 °C 10.0 mL (10.0 mmol) of diisobutyl aluminum hydride (1.0 M solution in hexane), and the mixture was stirred for 3 h at room temperature. The reaction was quenched by addition of 5 mL of methanol at 0 °C; after 15 min the precipitate formed was dissolved with 1 N HCl. The aqueous phase was extracted with ethyl ether (5 × 25 mL) and the combined extracts were washed with brine and dried over $MgSO_4$. The solution of crude **8** was used in the next step without further purification.

(2,3-Dideuterio-1-methylcyclopropyl)deuteriomethanol (9). To the solution of the crude aldehyde **8** in ethyl ether/hexane was added at 0 °C 210 mg (5.0 mmol) of lithium aluminum deuteride. The mixture was stirred at 0 °C for 1 h and hydrolyzed with 2 mL of saturated aqueous ammonium chloride. The precipitate formed was filtered off and washed with ethyl ether; the filtrate was dried over $MgSO_4$. The solvent was removed over a 20-cm Vigreux column, and the crude product was distilled at reduced pressure; bp^{130} 85 °C, yield 132 mg of **9** (26% with respect to **7**) as a colorless liquid. Pure **9** was obtained by preparative GC using a 5-m Carbowax column at 95 °C. ^{1}H NMR: δ 0.32 (m, 1 H, cyclopropyl H), 0.38 (m, 1 H, cyclopropyl H), 1.16 (s, 3 H, CH_3), 1.39 (s, 1 H, OH), 3.37 (t, J_{HD} = 1.6 Hz, 1 H, CHDOH).

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank the Deutsche Forschungsgemeinschaft for a postdoctoral scholarship to N.K.

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