per second and to correct for the difference in full line widths between the absorption curve at half-height and the first derivative curve between maximum and minimum leads to eq 9 which is equivalent to eq 4.

$$k = (17.6 \times 10^6)(a_A{}^H - a_B{}^H)/4\sqrt{3}(\Delta \text{ width}) \quad (9)$$

Materials. 2-Acetoxycyclobutanone,[31] 2-hydroxycyclopentanone,[32] 2-hydroxy-6-methylcyclohexanone,[33] 2-acetoxy-4-methylcyclohexanone,[34] 2-bromo-6,6-dimethylcyclohexanone,[35] 2-acetoxy-4,4-dimethylcyclohexanone,[36] 2-acetoxy-3,5-dimethylcyclohexanone,[37] 2-hydroxy-3,5,5-trimethylcyclohexanone,[38] 2-acetoxy-3,3,5,5-tetramethylcyclohexanone,[39] 2-hydroxycycloheptanone,[40] 2,2-dimethylcycloheptanone,[41] and 2-hydroxymenthone[42] were prepared according to the literature.

2-Hydroxy-6,6-dimethylcyclohexanone was prepared from the bromo ketone. The bromo ketone (100 mg) was dissolved in ethanol (2 ml) and a solution of potassium carbonate (50 mg) in water (1 ml) was added. The solution was heated to reflux for

0.5 hr at which time the reaction (monitored by tlc) appeared complete. The solution was cooled and extracted with five 2-ml portions of methylene chloride. The combined extracts were washed once with water, evaporated free of solvent, and dried by azeotropic distillation with benzene. The crude material was purified by glpc on a 5-ft column of 20% SF-96 on firebrick at 180°. The retention time of the product was 11.5 min while under identical conditions the starting material had a retention time of 6.5 min. The product was a colorless liquid: n^{25}D 1.4305; mass spectrum, parent peak at m/e 140. *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.6; H, 8.57. Found: C, 68.5; H, 8.56. The ketone gave a phenylhydrazone (methanol-water) of mp 137–139° dec whose mass spectrum gave a parent peak at m/e 208. *Anal.* Calcd for $C_{14}H_{20}N_2O$: N, 13.45. Found: N, 13.5.

2-Acetoxy-7,7-dimethylcycloheptanone was prepared. 2,2-Dimethylcycloheptanone (1 g) was dissolved in glacial acetic acid (300 ml) and to the mixture was added boron trifluoride diethyl etherate (6 ml) and lead tetraacetate (1.90 g). The mixture was stirred at room temperature for 4 hr, at 50° for 4 hr, and at 80° for 4 hr. The mixture was cooled and the excess of acetic acid was removed at an aspirator. When the volume was reduced to 10 ml, the distillation was stopped, the solution was diluted with water (200 ml) and extracted with four 100-ml portions of benzene. The combined extracts were washed once with saturated sodium bicarbonate solution (20 ml) and once with water (10 ml) and the benzene was removed by distillation. The light brown oil (1 g) was distilled, bp 100° (2 mm). Final purification was effected by glpc on a 5-ft column of 20% SF 96 on firebrick. The retention time of the product was 11.0 min, while that of the starting material under identical conditions was 5.5 min. *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 70.2; H, 9.6. Found: C, 70.2; H, 9.5. The ketone yielded a phenylhydrazone, mp 144–145°. *Anal.* Calcd for $C_{17}H_{24}N_2O_2$: C, 70.9; H, 8.33. Found, C, 71.2; H, 8.2.

Acknowledgment. The spectra of the disproportionation products of 2-hydroxymenthone in basic solution were recorded and analyzed by Mr. P. R. Whittle.

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Secondary Deuterium Isotope Effects. β-Kinetic Effects in SN2 Reactions of N,N-Dimethylaniline and Dimethylphenylphosphine with Methyl p-Toluenesulfonate and Comparison with Observed and Calculated Vibrational Frequencies of Deuterated and Undeuterated Dimethylaniline and Trimethylanilinium Ion[1]

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Abstract: The rates of reaction, in nitrobenzene at 51.29°, of methyl p-toluenesulfonate with N,N-dimethylaniline and N,N-dimethyl-d_6-aniline to form trimethylphenylammonium and methyldimethyl-d_6-phenylammonium p-toluenesulfonates, respectively, and with dimethylphenylphosphine and dimethyl-d_6-phenylphosphine to form the corresponding phosphonium salts, were determined conductiometrically. The secondary isotope effects observed are small and inverse: 1.133 ± 0.008 for the amines, and 1.050 ± 0.002 for the phosphines. The result for the amines is discussed in relation to the equilibrium isotope effect calculated using information obtained from the observed infrared spectra of the reactants and products. Though uncertainties in the assignment of spectral bands exist, it appears that there is very little shift in CH(CD) stretching force constants. The inverse effect is, therefore, very probably due to increased force constants for lower frequency vibrations, such as for bending. This interpretation is consistent with a steric explanation for the isotope effects. Inductive effects are expected to produce changes in the stretching force constants.

The origin of secondary deuterium isotope effects[3] is understood, in terms of the general theory of isotope effects,[4] to be changes in vibrational force constants[5] (along with possible changes in mass and mo-

ments of inertia) on going from reactants to transition state or products.[6] Correlation of observed isotope effects with vibrational frequency changes has led to a better understanding of certain kinetic[7] and equilibrium[8] isotope effects.
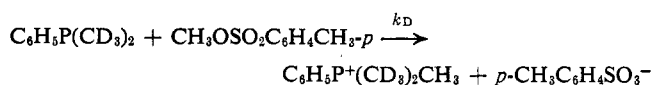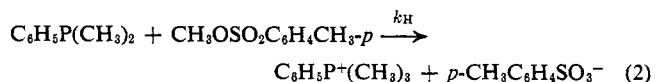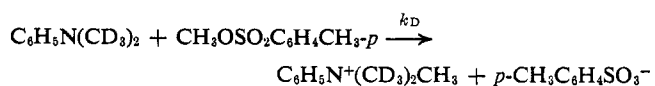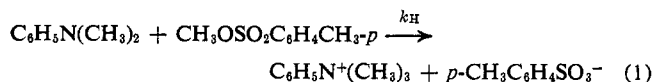
A problem of special interest is the origin of secondary β-deuterium kinetic isotope effects in solvolytic reactions,[9,10] which recent spectroscopic observations and calculations on *t*-butyl chloride and *t*-butyl cation[11] indicate to be caused largely by changes in CH(CD) stretching force constants. The isotope effect calculated for the equilibrium is essentially the same (at two temperatures) as the observed kinetic isotope effects in solvolysis of *t*-butyl chloride, suggesting the transition state is ion pair like.[11] This transition state structure can be understood in terms of a recent theory of solvolytic reaction mechanisms.[12] The small observed carbon-14 kinetic isotope effect for solvolysis of *t*-butyl chloride[13] can be understood as resulting from tighter binding of the methyl groups to the central carbon atom in the cation than in *t*-butyl chloride,[12] an effect expected upon breaking the CCl bond, but whether the deuterium and carbon-14 isotope effects result from hyperconjugation[9] or an inductive effect of the positive charge upon CC and CH force constants (along with some steric effect) is very difficult to answer, since the only difference between the two explanations would appear to be the fine details of the electron distribution in the cation relative to *t*-butyl chloride.

While it is generally acknowledged that the cause of secondary isotope effects is force constant changes,[4] various "causes" are encountered in the literature: hyperconjugative,[9] inductive,[6a] and steric[14] effects. These effects should not be thought of as direct causes of the isotope effect; they are electronic effects which, if different in reactants than in transition state or products, cause the force constant changes which are the true origin of the isotope effect. In other words, hyperconjugative, inductive, or steric effects will cause no isotope effect unless they happen to change force constants which determine the motion of H and D atoms.

It seems wise to preserve this unique feature of isotope effects which makes them so useful in solving chemical problems that they *can* be explained entirely by vibrational, rotational, and translational effects, since the electronic effects of H and D are essentially identical, *i.e.*, the motions of H and D in chemically identical environments have identical force constants[5,6] which result from identical electronic energy surfaces. How-

ever, in order to understand the causes of isotope effects, one must then understand the causes of force constant changes, which requires a vibrational analysis of different molecules to determine force constants and examination of the way in which force constants change with molecular structure.[11] Analysis is difficult, because only small changes in force constants usually occur on going from reactants to transition state or products.

We have, therefore, studied two SN2 displacement reactions (eq 1 and 2), determining β-deuterium isotope

$$C_6H_5N(CH_3)_2 + CH_3OSO_2C_6H_4CH_3\text{-}p \xrightarrow{k_H}$$
$$C_6H_5N^+(CH_3)_3 + p\text{-}CH_3C_6H_4SO_3^- \quad (1)$$

$$C_6H_5N(CD_3)_2 + CH_3OSO_2C_6H_4CH_3\text{-}p \xrightarrow{k_D}$$
$$C_6H_5N^+(CD_3)_2CH_3 + p\text{-}CH_3C_6H_4SO_3^-$$

$$C_6H_5P(CH_3)_2 + CH_3OSO_2C_6H_4CH_3\text{-}p \xrightarrow{k_H}$$
$$C_6H_5P^+(CH_3)_3 + p\text{-}CH_3C_6H_4SO_3^- \quad (2)$$

$$C_6H_5P(CD_3)_2 + CH_3OSO_2C_6H_4CH_3\text{-}p \xrightarrow{k_D}$$
$$C_6H_5P^+(CD_3)_2CH_3 + p\text{-}CH_3C_6H_4SO_3^-$$

effects and examining the infrared spectra of the amines and ammonium ions of eq 1. These are cases where an inductive effect should exist (just as in carbonium ion forming reactions) but no hyperconjugative effect (unless into d orbitals of phosphorus in the phosphonium ion); in addition, a steric effect could arise since the methyl groups are more crowded in the ions than in the bases. The steric effect alone would be expected to be inverse (increased force constants on going to the more crowded ions should favor D) and considerably smaller for eq 2 than for eq 1 since the PC bonds are considerably longer than the NC bonds. We have found $k_D/k_H = 1.133 \pm 0.008$ and 1.050 ± 0.002, for reactions 1 and 2, respectively, in nitrobenzene at 51.29°, suggesting that the steric effect is the major cause of these isotope effects. Spectroscopic study indicates that the isotope effect for the *equilibrium* between reactants and products in eq 1 is not caused by changes in CH(CD) stretching force constants. Steric effects may be expected to affect bending more than stretching. Since the kinetic secondary isotope effects should be caused by the same factors which cause the equilibrium isotope effects, we conclude that the former are caused by changes in bending force constants (for bending CH(CD) bonds) on going from reactants to transition state.

It has been reported[15] that substitution of deuterium into one methylene group of triethylamine produces a rate acceleration of 7% in the SN2 reaction with methyl *p*-bromobenzenesulfonate. A rather large isotope effect, $k_H/k_D = 1.6$, which presumably must arise, at least in part, from release of steric strain, has been reported for E1 solvolysis of a steroidal derivative, R–N⁺(CH₃)₃ *vs.* R–N⁺(CD₃)₃, in 98.6% ethanol at 70°.[16] Equilibrium isotope effects for the protonation of aromatic amines with one CH₃ or CD₃ group attached to the nitrogen atom are $K_D/K_H = 1.14$, 1.11 at 33° in aqueous sulfuric acid.[17] Compared with our best estimate of the equilibrium isotope effect for eq 1, *ca.* 1.3

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for *two* CD_3 groups, it must probably be concluded either that the inductive effect is a very important factor, or that the protons in the ammonium ions[17] are so strongly solvated that they have steric effects almost as large as methyl groups; we presently favor the latter explanation. Additionally, the recent finding that steric considerations[14] account for observed isotope effects in reactions where hyperconjugation is formally not allowed, but predict less than 10% of the observed isotope effect in compounds where hyperconjugation is allowed,[18] indicates that direct electronic interaction is important in causing certain isotope effects.[18] Though the potential functions used for calculating steric interactions[18,14] are probably not accurate enough to make the latter conclusion quantitative, it does seem likely that the steric effect alone will not always account for the force constant changes that produce secondary isotope effects.

Experimental Section

All melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. Microanalyses were performed by Micro-Analysis, Inc., Wilmington, Del. Nmr spectra were run on Varian spectrometers HA-60, A-60, and A-60A. Samples were neat, in sealed capillaries. Reported shifts are downfield from an *external* standard of tetramethylsilane. Literature values using an *internal* standard, therefore, are not directly comparable to these shifts. Vapor phase chromatography was done on a Perkin-Elmer flame ionization gas chromatograph, Model 226, using a 15 ft × 0.125 in. column of poly(propylene glycol) UCON-Oil LB-550-X, on Chromosorb W. The drybox used, a Kewaunee Controlled Atmosphere Laboratory, was filled at all times with prepurified nitrogen.

Nitrobenzene (Matheson Coleman and Bell) was dried over P_2O_5 for at least 1 week prior to fractional distillation under nitrogen on a 3-ft Todd column packed with glass helices. The fractions, collected at a reflux ratio of 5:1, bp 84.8–85.1° (10 mm), $n^{25}D$ 1.5496–1.5509 (lit.[19] bp 85.4° (10 mm), $n^{20}D$ 1.5523), were stored in the drybox.

Methyl tosylate (methyl *p*-toluenesulfonate, Matheson Coleman and Bell), to which 5 ml of benzene had been added per 100 ml of reagent, was distilled on a 40 × 2.5 cm spinning-band column at a reflux ratio of 5:1. The fractions boiling at 129.0° (2.20 mm) (lit.[20] bp 161° (10 mm)), $n^{25}D$ 1.5173, were stored in the dark in the drybox. The nmr spectrum gave the expected signals for pure methyl tosylate.[1]

N,N-Dimethylaniline (Matheson Coleman and Bell), free from monomethylaniline, mp 1.5–2.5° (100 ml), was refluxed with acetic anhydride (46 ml) for 3 hr before distilling through a helix-packed column under nitrogen.[21] The fraction boiling at 74.5–75.5° (10 mm) was collected over potassium hydroxide, from which the colorless amine was fractionally distilled under nitrogen[22] and stored in the dark in the drybox, bp 74.0° (10 mm), $n^{25}D$ 1.5562 (lit.[23] bp 73.1° (10 mm), $n^{25}D$ 1.5562).

Trimethylphenylammonium iodide was prepared by refluxing aniline and methyl iodide for 24 hr, a white solid precipitate being formed. Concentrated aqueous sodium hydroxide was added and the solution refluxed for an additional 24 hr. The basic solution, which solidified upon cooling, was filtered and the solid recrystallized from ethanol. Three recrystallizations from methanol–ether gave white crystals, yield 74%, mp 214–215° (sublimes), 205–206° (sealed tube). Trimethylphenylammonium iodide (Matheson Coleman and Bell, mp 229–230°), upon recrystallization from

methanol–ether gave mp 213–215° subl, 204–207° (sealed tube) (lit.[22] mp 228°).

Trimethyl-d_9-phenylammonium iodide was prepared by placing methanol (44 ml), finely ground sodium carbonate (15 g, 0.14 mole), and freshly distilled, colorless aniline (4.3 ml, 0.047 mole) in a 100-ml flask containing a Teflon-coated stirring bar, freezing the solution, attaching the flask to a vacuum line, and distilling methyl-d_3 iodide (Columbia Organic Chemical Co., Columbia, S. C., 99% pure by mass spectrometry, 12.2 ml, 0.19 mole) from an ampoule into the frozen solution. The flask was removed, fitted with a Dry Ice–acetone condenser, and allowed to warm to room temperature. The solution was refluxed for 4 hr, the condenser removed, and the flask stoppered. Stirring was continued overnight at room temperature. The white precipitate was filtered and the filtrate concentrated on a steam bath, affording additional solid. Ether was used to precipitate the salt remaining in the methanol, crude yield 75%, mp 213–218° subl. The nmr spectrum of the salt in D_2O exhibited an extraneous peak, which we were unable to identify; the salt was used in the preparation of N,N-dimethyl-d_6-aniline without further purification.

Undeuterated salt, prepared by this method, had mp 214–217° subl.

N,N-Dimethyl-d_6-aniline was prepared by the method of Cope.[24] Tetrahydrofuran (115 ml), dried by refluxing over sodium for 24 hr and stored, until used, over lithium aluminum hydride, was placed in a flask fitted with a condenser to which was attached a paraffin-oil bubbler. Dry nitrogen was slowly passed through the system and lithium aluminum hydride (1.2–1.3 g, 0.03 mole) was added to the ether. The suspension, stirred with a glass-coated magnetic bar, was refluxed for 2 hr, at which time trimethyl-d_9-phenylammonium iodide (6 g, 0.023 mole) was added. Gas evolution was noted during the first 15 min only. The reaction mixture was refluxed and stirred for 119 hr, after which it was cooled in an ice bath and water (1.1 ml) and a 20% NaOH solution (0.9 ml) were slowly added. Dilution with 16 ml of benzene and 50 ml of ether, followed by filtration, gave a bright yellow solution. The gelatinous precipitate was extracted with 50-ml portions of ether (three), and the washings were added to the solution. The solution was distilled to remove most of the ether. The yellow, oily residue remaining was distilled using a microapparatus to give a colorless liquid, bp 74.0° (10 mm), $n^{25}D$ 1.5532. A mass spectrum, at 5 ev, showed peaks at m/e 126 and 127, indicating N,N-dimethyl-d_5-aniline (2.7% of the total peak heights) and N,N-dimethyl-d_6-aniline (99.5 deuterium atom %). The nmr spectrum gave no signals other than those from the phenyl protons. A gas chromatogram gave two peaks, one of which was benzene (0.3% maximum). The deuterated amine was stored in nitrogen-filled sealed capillaries.

Undeuterated N,N-dimethylaniline, prepared in the same way, gave the same gas chromatographic behavior with the exception that there appeared to be somewhat more benzene present. In turn, this undeuterated material gave infrared and nmr spectra identical with the purified commercial N,N-dimethylaniline, with the exception that benzene occurred in the gas chromatogram and nmr integration. The infrared and nmr spectra were otherwise completely consistent with expectation for pure N,N-dimethylaniline.

Dimethylphenylphosphine (M & T Chemicals, Inc., Rahway, N. J.) was kept in the drybox. The nmr spectrum of the liquid had a phenyl multiplet centered at 7.08 ppm and a sharp doublet at 0.80 ppm (J_{PH} = 3.0 cps). It was used without further purification.

Dimethyl-d_6-phenylphosphine was prepared, using extreme care to exclude oxygen and using only ether which had been passed through an alumina column and stored over calcium hydride,[25] by allowing magnesium turnings (4.0 g, 0.165 g-atom) to react with methyl-d_3 iodide (9.6 ml, 0.148 mole) in 70 ml of ether; the solution was gently refluxed 0.5 hr after all the methyl-d_3 iodide had been added, followed by addition of dichlorophenylphosphine (Aldrich, Milwaukee, Wis., 8.1 ml, 0.06 mole, in 30 ml of ether) slowly to the Grignard reagent after the latter had been cooled in a Dry Ice–benzene bath.[26] The reaction was completed by refluxing for 30–45 min and then cooled again to 5°. A saturated ammonium chloride solution through which nitrogen had been bubbled for at least 8 hr was cautiously added. The work-up was carried out in the dry-

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box. The ether solution was decanted and the solid was washed thoroughly with fresh ether (total ca. 70 ml). After having dried over anhydrous sodium sulfate for 24 hr, the combined ether portions were placed on a vacuum line and degassed. The ether was distilled at room temperature into an ice-cooled flask. The residue (6-8 ml) was distilled from hot water into a Dry Ice cooled graduated centrifuge tube fitted with a vacuum stopcock. An nmr spectrum of the produvt revealed impurities which we believe were phenylphosphine and methyl-d_3-phenylphosphine, presumably formed by incomplete alkylation, hydrolysis giving phosphonous and phosphinous acids which could disproportionate to give the corresponding phosphines.[1,26] Repeated fractionation by bulb-to-bulb distillation on the vacuum line[1] gave pure dimethyl-d_6-phenylphosphine used for kinetics, 99.1 deuterium atom % (nmr), yield, very low. The phosphine was stored in nitrogen-filled, sealed capillaries.

Undeuterated dimethylphenylphosphine prepared in the same way gave pure material without extensive bulb-to-bulb distillation, nmr identical with the commercial material (above).

Trimethylphenylammonium tosylate was prepared by addition of N,N-dimethylaniline (7.43 g, 0.061 mole) and methyl tosylate (12.12 g, 0.065 mole) to 80 ml of dry, thiophene-free benzene. The solution was stirred while refluxing for 30 min, left at room temperature ca. 12 hr, and filtered. The white crystals were washed with 5 ml of fresh benzene and recrystallized (three times) to a constant mp 160-161° (lit.[27] mp 160-161°).

Anal. Calcd for $C_{16}H_{21}NO_3S$: C, 62.52; H, 6.88; S, 10.43. Found: C, 62.69; H, 7.23; S, 10.46.

There was no melting point depression when this salt was mixed with the white precipitate (mp 160-161°) isolated from a preliminary amine kinetic run in nitrobenzene.

The nmr spectrum of the salt in D_2O gave singlets at 2.40 ppm (ring methyl) and 3.63 ppm (nitrogen methyls), and a multiplet for the phenyl protons, with the ratio of protons 1.00:3.04:2.90, respectively.

Trimethylphenylphosphonium tosylate was prepared by distillation, on the vacuum line, of dimethylphenylphosphine into a frozen flask of dry, thiophene-free benzene. Methyl tosylate (benzene solution) was slowly added from a dropping funnel with magnetic stirring, while refluxing ca. 3 hr. The cloudy solution was refluxed an additional 21 hr. The solution was filtered (in air), and the white solid was rinsed with ether and recrystallized to constant mp 158.0-158.5°.

Anal. Calcd for $C_{16}H_{21}O_3PS$: C, 59.24; H, 6.53; P, 9.55; S, 9.88. Found: C, 58.96; H, 6.37; P, 9.40; S, 10.17.

The nmr spectrum in D_2O showed a singlet at 2.46 ppm (ring methyl), a doublet (J_{P^+-C-H} = 14.5 cps) with center at 2.25 ppm, and a complex for the phenyl protons, with integration in the ratio of 1.00:2.80:2.91, respectively.

Calibration Curves. Curves of concentration vs. conductivity for the salts which are products of reactions 1 and 2 were constructed from conductivity measurements on solutions of known concentration under precisely the same conditions used for kinetic measurements. The concentration of methyl tosylate used in the calibration solutions was the same as that used in all kinetic runs, to within ±0.02%. The conductivity cells, both of the same design,[1] using shiny platinum electrodes, were cleaned with acetone, distilled water, and absolute ethanol after use, dried with a stream of prepurified nitrogen for at least 1 hr, and stored in a desiccator. All conductivity measurements were made with a Wayne-Kerr Universal Bridge, Model B221, to within ±0.2%, on solutions immersed in an oil bath, temperature controlled at 51.29 ± 0.005° and calibrated with a National Bureau of Standards Certified thermometer. Conductivity readings of solutions remaining in a cell for 12-24 hr remained constant. The conductivity of the solvent, nitrobenzene 8.033$_2$ × 10^{-1} M in methyl tosylate, was less than 0.2% of any other conductivity measured, and no correction was made for its contribution.

Kinetic Procedure. All work with the amine was carried out in the drybox. The same stock solution of methyl tosylate (4.016$_6$ M) was used to make up each dilution (8.033$_2$ × 10^{-1} M) for a run. The conductivity of the methyl tosylate solution was always less than 1 μmho; therefore, the readings taken during a run were not corrected for this. Between 50 and 60 μl of the amine were injected into the cell, the reaction mixture shaken vigorously, and the system equilibrated in the oil bath at 51.29 ± 0.005° for at least 20

min. On the average, 34 readings per run were made. The reaction was followed to >85% completion, using an electric timer which could be read to 0.01 min.

Since the phosphine reaction was very rapid, the procedure was somewhat modified. A serum cap was wired over the neck of the cell before it was removed from the drybox, filled only with the methyl tosylate solution (8.033$_2$ × 10^{-1} M). While it was equilibrating in the bath, approximately 20 μl of the phosphine was drawn into a microliter syringe and the needle inserted into a clean cork. The syringe was quickly withdrawn from the drybox and the phosphine rapidly injected through the serum cap on the cell. The stopcock was reclosed, the cell lifted from the bath, vigorously shaken, and reimmersed. This procedure took less than 1 min. Readings were started immediately, and on the average, 40 observations per run were made. Kinetic measurements on the protiated and deuterated species were done in pairs, the second run following the first by no more than 30 min. Reaction was followed to >90% completion.

Product Isolations.[1] It was possible to isolate, by evaporation of solvent, crystallization, and precipitation, 87.5 and 82.5% yields of reasonably pure ammonium and phosphonium salts, respectively, directly from kinetic solutions after complete reaction.

Infrared Spectra of Amine Reactants and Products. Infrared absorption spectra were recorded over the 700-3000-cm^{-1} range using a Perkin-Elmer infrared spectrometer, Model 521. Spectra were first run at a scan speed of 50 (min) and then the regions of interest were rescanned at a rate ten times slower, with a peak expansion (ordinate) of 5. Many overlapping and ill-defined bands became discernible in this way. The 1604-cm^{-1} band of polystyrene was used to calibrate the instrument. The error in a peak is ±3 cm^{-1}. Frequencies were read from the frequency counter rather than from the spectra.

The reactants, N,N-dimethylaniline and N,N-dimethyl-d_6-aniline, were studied both neat and in carbon tetrachloride, using sodium chloride cells of 0.05- and 0.200-mm thickness, respectively. The spectra were identical within experimental error. The product salts, trimethylphenylammonium tosylate and methyldimethyl-d_6-phenylammonium tosylate, were studied as saturated solutions in chloroform-d and in chloroform and chloroform-d, respectively, using sodium chloride cells of 0.200-mm thickness.

Results

Calibration Curves. The three major assumptions made in construction of our calibration curves are justified as follows.[1] (1) The cell constants remained constant throughout the investigations, as shown by frequent checks with standard salt solutions. (2) The calibrations were done under conditions which satisfactorily reproduced kinetic conditions, as shown by excellent (pseudo first order) kinetic curves out to high per cent reaction, and the fact that the presence of small amounts of reactant amine or phosphine could not be expected to change the conductivity nor could the ca. 0.8% change in methyl tosylate concentration during the course of a kinetic run, based on analogies.[1,28] (3) The calibration curves constructed with solutions of undeuterated salts are applicable, within experimental error, to solutions of the corresponding deuterated salts, as shown by the small change in limiting conductivity observed even for tetramethylammonium ion vs. tetraethylammonium ion in nitrobenzene at 25°,[29] ca. 6%, for a rather large change in mass as well as shape.

The resulting calibration curves do not deviate a great deal from linearity. The data are not reported here, since we made no precise measurement of the cell constants.[1]

Calculation of Rate Constants. The observed conductances for a kinetic run were converted to concentrations by using the calibration curve and fitted to eq 3

(27) V. M. Rodionov and D. A. Shaposhnikov, *Akad. Nauk SSSR Inst. Organ. Khim. Sintezy Organ. Soedin. Sb.*, 1, 101 (1950); *Chem. Abstr.*, 47, 8005g (1953).

(28) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, 67, 1722 (1963).
(29) C. A. Kraus, *J. Chem. Educ.*, 35, 324 (1958).

$$Y = A_0\{1 - \exp[-k(t + b)]\} \qquad (3)$$

where Y is the salt concentration at time t, and the following three parameters were determined so as to give the best least-squares fit of observed Y values to eq 3: A_0, the final (infinity) concentration of salt; k, the pseudo-first-order rate constant; and b, the time error. The calculation was made with a generalized least-squares computer program.[1,30] Second-order rate constants were obtained by dividing k by the methyl tosylate concentration, corrected for solvent expansion at 51°[31] (7.862×10^{-1} M in almost all cases).

After a good deal of preliminary work,[1] precise rate constants were obtained, as shown in Tables I and II. Calculations eliminating various fractions of the early points in each run gave rate constants essentially identical with those obtained using all data points; therefore, we believe our results are both precise and accurate as indicated by their reproducibility, in spite of the fact that certain experimental errors are expected to be possibly as large as the reported precision in rate constants. In the phosphine reactions, it was extremely difficult to achieve the kind of reproducibility required, and, as mentioned in the Experimental Section, much more precise isotope effects were obtained by carrying out deuterated and undeuterated runs in pairs, rapidly after one another, obtaining an isotope effect from each pair, and then averaging the isotope effects (Table II).

Table I. Reaction of N,N-Dimethyl-d_6-aniline and N,N-Dimethylaniline with Methyl Tosylate in Nitrobenzene at 51.29 + 0.005°
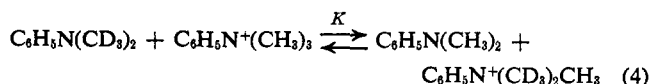
| | $10^5 k_2$, l. mole^{-1} sec^{-1} | | |
	Deuterated	Undeuterated	k_D/k_H
	5.7355	5.0746	
	5.6991	5.0277	
	5.7483	5.0646	
Av	5.727 ± 0.025	5.056 ± 0.025	1.133 ± 0.008

Table II. Reaction of Dimethyl-d_6-phenylphosphine and Dimethylphenylphosphine with Methyl Tosylate in Nitrobenzene at 51.29 ± 0.005°

| | $10^3 k_2$, l. mole^{-1} sec^{-1} | | |
	Deuterated	Undeuterated	k_D/k_H
	2.8784	2.7462	1.0481
	2.8266	2.6851	1.0527
	2.7595	2.6300	1.0493
Av	2.821 ± 0.059	2.687 ± 0.058	1.050 ± 0.002

Equilibrium Isotope Effect Calculations. Since the reactions studied (eq 1 and 2) are thought to be concerted displacements (SN2), the force constant changes for the β-hydrogen atoms on going from reactants to transition state are very probably of the same type and direction as the force constant changes on going from reactants to products. The effects producing these force constant changes, steric and electronic, should be associated with the expected crowding brought about by the incoming methyl group and with the developing positive charge; the transition-state structure, with

somewhat less crowding and less charge development, should, therefore, produce an isotope effect intermediate between 1.0 and the value of the equilibrium isotope effect. The equilibrium isotope effect, the ratio of equilibrium constants K_D/K_H for the reactions of eq 1, can be seen to be equal to the equilibrium constant K of eq 4. A vibrational analysis of the four species appearing in eq 4 would give a theoretical equilibrium isotope effect.[4] We have attempted such calculations by two methods: using the complete theory[4] with assumed force constants derived from analogous molecules, and using the observed infrared spectra to calculate the zero-point energy contribution to K (which should be the major contribution for large molecules).

$$C_6H_5N(CD_3)_2 + C_6H_5N^+(CH_3)_3 \overset{K}{\rightleftharpoons} C_6H_5N(CH_3)_2 + $$
$$C_6H_5N^+(CD_3)_2CH_3 \qquad (4)$$

The ideal method of analyzing this problem would be to assign force constants to each species which precisely reproduced its observed infrared fundamentals.[11] However, in order to obtain satisfactory results it is necessary to include off-diagonal (interaction) force constants, even when using a valence force field, and these are not easy to arrive at by analogy. Such calculations will probably require that we analyze spectra of other isotopically substituted forms (especially $C_6H_5N^+(CD_3)_3$) and use low-temperature spectra as an aid in assignment of bands, the more so because our current knowledge (see below) indicates that the major cause of the isotope effect K is changes in low-frequency vibrations, which interact a good deal more than the C–H(D) stretching vibrations.

Computer calculations, using approximate valence force constants, were made with a program developed by Wolfsberg[32] which is based on a program written by Schachtschneider.[32] The program was modified for use with the IBM 7040 computer, requiring reduction of the maximum molecular size from 29 to 14 atoms.[1] The "cutoff" procedure[32] was used, cutting off all of the phenyl group except the first carbon atom (C_p), which was assigned a mass of 12 or 77. For the dimethylanilines, the geometry was assumed to be planar,[33] with the methyl groups staggered (one CH bond of each in the NC$_3$ plane), and with 120° CNC angles, tetrahedral methyl groups. For the ammonium ions, the geometry was assumed to be tetrahedral around N and C.[1] Table III gives the bond lengths and angles employed, and Table IV gives calculated isotope effects for four hypothetical sets of force constants. The isotope effects were calculated using the Redlich–Teller product rule to calculate the mass moment of inertia (MMI[32]) contribution; the two internal rotations (of zero frequency with our force field) of the two isotopically substituted methyl groups were included along with the true vibrations, since their isotopic contribution could be calculated from the geometrically calculated MMI term divided by the ratio of products of nonzero frequencies. It was found that the contributions from these two internal rotations are almost equal for reactants and prod-

(30) M. H. Lietzke, "A Generalized Least Squares Program for the IBM 7090 Computer," ORNL-3259, Office of Technical Services, U. S. Department of Commerce, Washington, D. C. A FORTRAN IV deck was kindly supplied by Dr. Lietzke.

(31) H. C. Brown and A. Cahn, *J. Am. Chem. Soc.*, **77**, 1723 (1955).

(32) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964); J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 2618, 4105 (1966).

(33) J. C. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectry.*, **20**, 193 (1966), show that it is not quite planar for aniline.

ucts, and so nearly cancel. These calculations ignore interaction between the internal rotors and between internal rotors and molecular rotations; though interaction must certainly occur in reality, the *isotopic* effect is expected to be very nearly equal to that calculated with the assumption of independence.

Table III. Assumed Bond Lengths and Angles[a] for N,N-Dimethylaniline and Trimethylphenylammonium Ion Used in Wolfsberg Program for Calculating Isotope Effects

Angle postn	Angle
A. N,N-Dimethylaniline	
All C–N–C	120°
H–C–H	109°28'
N–C–H	109°28'
B. Trimethylphenylammonium Ion	
All C–N⁺–C	109°28'
H–C–H	109°28'

Bond	Length, A
A. N,N-Dimethylaniline	
All C–N	1.47
C–H	1.06
B. Trimethylphenylammonium Ion	
All N⁺–C	1.45
C–H	1.06

[a] Bond lengths and angles were chosen from those found for similar molecules published by L. E. Sutton, "Tables of Interatomic Distances and Configurations," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965, pp S16, M199, M200 and M101s, M149s.

Table IV. Force Constants[a] Used in Computer–Calculated Secondary Isotope Effects for the Amine–Ammonium Equilibrium at 51.29°

Internal coordinate vector used	Set 1	Set 2	Set 3	Set 4
A. N,N-Dimethylaniline				
N–C$_m$[b] stretch	3.970[c]		4.300	
N–C$_p$ stretch	3.970		3.891	
C–H stretch	5.000		4.851	
H–C–H bend	0.451		0.480	
N–C–H bend	0.310	Same	0.320	Same
C$_m$–N–C$_m$ bend	0.382		0.382	
C$_m$–N–C$_p$ bend	0.382		0.382	
Methyl out-of-plane wag	0.240		0.240	
Methyl in-plane wag	0.230		0.230	
B. Trimethylphenylammonium ion				
N⁺–C$_m$ stretch	5.500	5.500	4.500	4.500
N⁺–C$_p$ stretch	5.500	5.500	4.000	4.000
C–H stretch	5.000	5.000	4.851	4.851
H–C–H bend	0.473	0.560	0.500	0.630
N⁺–C–H bend	0.310	0.310	0.320	0.320
C$_m$–N⁺–C$_m$ bend	0.408	0.408	0.420	0.420
C$_m$–N⁺–C$_p$ bend	0.408	0.408	0.420	0.420
K_D/K_H[d]	1.099	1.545	1.086	1.774

[a] Force constants were selected from those found in R. K. Sheline, *J. Chem. Phys.*, **18**, 602 (1950), and E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations—The Theory of Infrared and Raman Vibrational Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp 175–176, and were adjusted according to the differences between the observed and calculated frequencies. [b] C$_m$ = methyl carbon. [c] All force constants are in mdyne A^{-1}. [d] C$_p$ = 77.

Since the spectra (see below) indicate very little change in CH stretching force constants on going from reactant to product, the bending force constants associated with the CH bonds were varied. It can be seen that reasonable choices for these force constants lead to isotope effects which are inverse and of the order of magnitude of the experimental kinetic isotope effects, as expected. Since the experimental infrared fundamentals did not appear to be reproduced without interaction force constants, we used the computer-calculated fundamentals as an aid in assigning observed fundamentals.

In addition to the calculations, model compounds, whose spectra had been analyzed, were chosen as guides: dimethylamine[34] and *t*-butyl chloride,[11] for amine and ammonium ion, respectively. While assignment of several of the spectral bands was unambiguous, there were many which were not easily identified. Using the models, and analyzing their spectra for isotopic relationships, *e.g.*, the ratios of methyl rocking frequencies for the protiated molecule to those for the deuterated molecule, three more or less reasonable sets of assignments were made and are given in Tables V and VI. It will be recalled that only those fundamentals which are shifted in frequency upon deuteration need be assigned, since fundamentals which are not shifted have no zero-point energy difference between deuterated and undeuterated molecules and hence produce no isotope effect.[4]

Using the zero-point energies of the observed fundamentals for the methyl stretching, bending, and rocking modes, three different equilibrium isotope effects for the amine–ammonium system were calculated (see Table VII). All three of the vibrational assignments made give an inverse effect. If we assume that both the MMI factor and the contribution from the vibrational partition functions (excluding zero-point energies) are close to unity, the equilibrium isotope effects calculated from assignments A, B, and C are 1.163, 1.311, and 1.050, respectively. The assumptions are unlikely to lead to more than a few per cent error, since the molecules are large (in relation to the mass change upon isotopic substitution), and the frequencies assigned are all ⩾740 cm^{-1}.

Assignment C gives an equilibrium isotope effect which is smaller than the observed kinetic effect. While this is not an impossible phenomenon, it is probably unrealistic in this case. The same may be said of the effect calculated from assignment A, where the kinetic effect is greater than 80% of the equilibrium effect. The inverse equilibrium isotope effect of 1.311, calculated with assignment B, seems to be the most reasonable.

The spectra of protiated and deuterated phosphines and phosphonium salts were examined briefly, but, in view of difficulty in assignments and the small kinetic isotope effect, no definite assignments were made.

Discussion

A comparison of the CH stretching frequencies of the two methyl groups in N,N-dimethylaniline with those of two methyl groups in the product salt reveals a net increase of 25 cm^{-1} ($\Sigma\omega_H{}^R$ = 17,334 cm^{-1}, $^2/_3\Sigma\omega_H{}^P$ = 17,359 cm^{-1}). The CD stretching frequencies also increase on going from reactant to product, but by a substantially greater amount, that is, 70 cm^{-1} ($\Sigma\omega_D{}^R$ =

(34) A. Finch, I. J. Hyams, and D. Steele, *J. Mol. Spectry.*, **16**, 103 (1965).

Table V. Observed Methyl Group Frequencies[a] for N,N-Dimethylaniline (1) and N,N-Dimethyl-d_6-aniline (2)

1, cm^{-1}	Approx description	2, cm^{-1}
	Assignment A	
2981 w[b]	Methyl stretches	2273 vw
2945 w	(6)	2238 s
2895 vw		2190 vs
2870 w		2120 s
2842 vw		2108 s
2801 m		2054 vs
1483 vw, sh	Methyl deformations	1089 w
1451 vw, sh[c]	(6)	1064 m[e]
1443 m[d]		
1225 m	Methyl rocks	1210 vs
1125 vw, sh[d]	(4)	900 m[d]
940 s		764[f]
	Assignment B Stretching Modes as in Assignment A	
1483	Methyl deformations	1089
1451	(6)	1064
1443[d]		1056 m[d,g]
1343[d,g]		983[d]
1225	Methyl rocks	1210
1055 m[g]	(2)	900
	Assignment C Stretching Modes as in Assignment A	
1483	Methyl deformations	1089
1451	(6)	1064[e]
1443[d]		983[d]
1343[d,g]		
1225	Methyl rocks	1210
1125[d]	(4)	900[d]
940		764[f]

[a] Frequencies observed in both CCl$_4$ and neat; values differed by no more than 2 cm^{-1}. [b] Abbreviations used are w = weak, m = medium, s = strong, sh = shoulder. [c] Counted three times. [d] Counted two times. [e] Counted five times. [e] Calculated using a ratio of 1.23, based on a similar mode in t-butyl chloride model. [g] Band appears in spectra of both protiated and deuterated reactant, but may be a superposition of two bands in the protiated species.

12,983 cm^{-1}, $\Sigma\omega_D{}^P$ = 13,053 cm^{-1}). This rather unusual phenomenon (increasing the force constants on going from reactant to transition state, or product, generally increases the CH frequencies *more* than the CD frequencies, therefore producing an inverse isotope effect) is responsible for the net decrease observed (see Table VII), giving rise to a normal isotope effect.

A conceivable explanation for this effect is coupling of the methyl CH stretching frequencies (commonly found to be independent from other frequencies) with other modes in the molecule. If coupling of the stretching vibrations occurred more extensively in the reactant amines than in the product salts, and were greater for the CD stretches than for the CD stretches, then the observed difference in stretching zero-point energy of the reactants might be greater than the difference for the products.

A comparison of the eigenvectors (from our computer calculation) for the CH stretching modes with those for the CD stretching modes (in the amines) clearly indicates more coupling with lower vibrations for the deuterated molecule than for the protiated. For instance, there is a

Table VI. Observed Methyl Group Frequencies[a,b] for Trimethylphenylammonium Tosylate (1) and Methyldimethyl-d_6-phenylammonium Tosylate (2)

1, cm^{-1}	Approx description	⸻ 2, cm^{-1} ⸻	
	Assignment A		
2966 w[c]	Methyl stretches	2966 m	2277 vs
2923 w[d]	(9)	2923 m	2238 vvw
2872 vw		2872 w	2215 vw
2822 vw[d]			2128 vw
			2115 vvw
			2080 vvw
1461 m[d]	Methyl defor-	1463 w,sh	1053[e]
1416 w[e]	mations (9)	1414 vw[c]	
1213 s[f]	Methyl rocks	1225 s	985 vw[f]
1189 m[e]	(6)	1187 m	
	Assignment B Stretching Modes as in Assignment A		
1461[c]	Methyl defor-	1463	1053 w[f]
1416[f]	mations (9)	1414	985[c]
1379 vw[d,g]		1377 vvw[g]	
1030 vs[c,h]	Methyl rocks	1030 s[h]	810 s
928 m	(3)		740[i]
	Assignment C Stretching Modes as in Assignment A		
1461[c]	Methyl deforma-	1463	1053[e]
1416[f]	tions (9)	1414	
1379[d,g]		1377[g]	
1213[f]	Methyl rocks	1208 vw[g]	985[f]
1189[c]	(6)	1187	

[a] Frequencies observed in DCCl$_3$ for the protiated species and in both DCCl$_3$ and HCCl$_3$ for the deuterated species. [b] Abbreviations used are the same as those in Table V. [c] Counted two times. [d] Counted three times. [e] Counted six times. [f] Counted four times. [g] Possibly due to uncompensated solvent band. [h] May be a skeletal ring vibration. [i] Calculated using a ratio of 1.25, based on a similar mode in the t-butyl chloride model.

Table VII. Zero-Point Energy Contributions to the Isotope Effect for the Amine–Ammonium Equilibrium at 51.29° Using Experimental Frequencies

Assignment	Vibrational mode	Trimethyl-phenylammonium ion[a]	N,N-Dimethylaniline[a]	ZPE contbn to K_D/K_H
A	Methyl stretch	9.3795	9.6593	0.7558
	Methyl deformation	5.0394	5.1349	0.9050
	Methyl rock	1.9492	1.4230	1.6924
			K_D/K_H =	1.163
B	Methyl stretch	9.3795	9.6593	0.7558
	Methyl deformation	5.0727	5.0505	1.022
	Methyl rock	0.9070	0.3774	1.6710
			K_D/K_H =	1.311
C	Methyl stretch	9.3795	9.6593	0.7558
	Methyl deformation	4.7752	5.0150	0.7868
	Methyl rock	1.9890	1.4230	1.7616
			K_D/K_H =	1.050

[a] $(hc/2kT)\sum_j[(\omega_H - \omega_D)]$, ω in cm^{-1}.

great deal more CD bending motion present in the CD$_3$ stretching modes than there is CH bending in the CH$_3$ stretching vibrations.

This is not entirely unexpected. Coupling generally occurs between frequencies which are close

together (provided they are of the same symmetry species). Although the methyl stretching frequencies are quite high compared to most other frequencies, they are even higher for CH_3 than CD_3, and might therefore couple less. For example, the lowest CH stretching frequency (symmetric) observed for N,N-dimethylaniline (2801 cm^{-1}) is much higher (by 1358 cm^{-1}) than the highest observed CH_3 symmetric bend (probably at 1443 cm^{-1}), compared to the difference (of 990 cm^{-1}) between the lowest CD stretching vibration (2054 cm^{-1}) and the highest symmetric CD_3 deformation (1064 cm^{-1}).

For the product cations (salts), the lowest CH stretch (2822 cm^{-1}) is 1406 cm^{-1} higher than the highest symmetric CH_3 bend at 1416 cm^{-1}, whereas the lowest CD stretching frequency (2080 cm^{-1}) is 1027 cm^{-1} higher than the CD_3 deformation mode at 1053 cm^{-1}.

It should also be noted that the ratios of the CH to CD stretching vibrations in both the reactants and products are substantially less (1.31–1.36) than the "ideal" value of 1.41 (observed when $\mu_H \simeq \mu_D/2$), indicating incorporation of zero-point differences into other normal modes.

Since the total effect of the changes in the methyl stretching frequencies on going from reactant to product is to produce a normal isotope effect, the observed inverse kinetic effect should therefore be due to increased bending force constants, or, in other words, to the steric effect.

Assignment B, which produces the most reasonable

calculated isotope effect, shows a decrease for methyl deformations and rocking modes on going from reactant to product. In the absence of a more complete vibrational assignment, including the frequencies below 740 cm^{-1}, we cannot decide for certain whether assignment B is entirely reasonable and the observed decreases result from coupling with lower vibrations, or assignment B is in error. Though the analysis of the spectra is made more uncertain by such extensive coupling, we believe that eventually more reliable assignments based on further theoretical and experimental study can give a relatively simple answer in terms of valence force constant changes.

In analyzing the observed kinetic isotope effects, one cannot yet be certain whether the smaller effect for the phosphine than for the amine results from a decreased equilibrium effect for the phosphine, or from a more reactant-like transition state, or both.

Stereochemistry of Deuteron Attack of a Strained Bond in exo-Tricyclo[3.2.1.0²,⁴]octane[1]

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Abstract: exo-Tricyclo[3.2.1.0²,⁴]octane was treated with sulfuric acid-d_2 in acetic acid-d_1 solution to determine the stereochemistry of electrophilic attack on the C_2–C_4 bond. The principal product, exo(axial)-bicyclo[3.2.1]octan-2-ol-4-d_1 acetate was converted to the corresponding alcohol, ketone, and hydrocarbon. By taking the difference in shift values (per cent) for the two principal peaks (m/e 67 and 80) in the mass spectrum of the ketone, the percentage deuterium at C_4, the point of electrophilic attack, was determined to be 86%. The two principal fragmentation modes of bicyclo[3.2.1]octan-2-one was ascertained through mass spectral studies with labeled ketones. Examination of the hydrocarbon, bicyclo[3.2.1]octane-exo(axial)-, and -endo(equatorial)-2-d_1 in the C–D stretching region of the infrared revealed the identity of the hydrocarbon with the exo(axial) isomer. Therefore, it was concluded that deuteron attack on the C_2–C_4 bond must be "end on" and results in inversion of configuration.

Conceptually, there are two ideal ways by which a strained carbon–carbon bond might interact with an electrophile. In one of these, the electrophile and strained bond approach each other orthogonally. This mode of interaction results in retention of configuration at the carbon atom forming the new bond with the electrophile. In the other mode of interaction, the electrophile approaches the strained bond

from along an extended axis joining the two carbon atoms; that is, the electrophile approaches the bond "end on" and interaction ultimately results in inversion of configuration at the carbon atom forming the new electrophile–carbon bond.

The steric mode of electrophilic attack of strained carbon–carbon bonds is a question which has received some attention in connection with studies of acid- and base-catalyzed transformations of cyclopropanols to aldehydes and ketones. DePuy[3] concludes on the

(1) (a) Paper VII in a series dealing with carbon–carbon bond fission in cyclopropanes. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this work.
(2) National Science Foundation Cooperative Fellow, 1963–1964.

(3) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966).