The presence of intramolecular rotation results in $(T_1)_{calcd}$ on the basis of (1) and (2) being too small. That is, the mode of relaxation is less efficient than assumed in (1).[3] If molecular reorientation is anisotropic, then the reorientation time calculated from (2) is too small; that is, T_1 is too long.[4] Since cyclohexane and cyclopentane possess additional modes of angular reorientation, *e.g.*, the boat–chair interchange in the former, which have lifetimes short compared to the relaxation times observed,[7] estimates of relaxation times on the basis of (1) and (2) can be expected to be too short.

The following conclusions may be drawn from examination of Table I. The results obtained are much more understandable if a magnetic resonance microviscosity factor of $f = {}^1/_{12}$ is assumed for the pure liquids. After this correction the molecules possessing internal degrees of freedom may be picked out because their observed/calculated ratios are significantly greater than 1. Methyl cyanide, which has been one of the most popular for internal rotation studies,[1,2] has the least free rotation. The methyl groups on toluene, xylene, acetophenone, acetic anhydride, and methyl iodide are much more free. There does not appear to be internal rotation in such liquids as acetone and dimethyl sulfoxide. This is in accord with the barriers to internal rotation found for their gas phases (3.07 kcal/mole for DMSO[8] and 0.738 kcal/mole for acetone[9]) which will surely be higher in the condensed materials. The effect of internal degrees of freedom in the cycloalkanes is apparent.

It therefore appears that a modified Debye–Stokes–Einstein equation such as (2) describes magnetic resonance relaxation in a number of liquids despite the presence of association and/or anisotropic reorientation. Internal degrees of freedom exist in several molecules other than those already studied, and more complete studies on these should be of interest.

The wider variety of accurately determined deuteron quadrupole coupling constants which have recently become available make it clear that the values of these constants are remarkably invariant to substitution on an atom β to the one the deuteron is attached to in a given series of molecules. α substitution, as would be expected, has a large effect.

The following conclusions are made.

(1) A wide variety of molecules have reorientation times described by eq 1 with a microviscosity factor of ${}^1/_{12}$ rather than ${}^1/_6$. This is without recourse to other assumptions such as anisotropic rotational reorientation.

(2) Rather free internal rotation exists for methyl groups in several molecules. This is especially true in several not yet studied in detail. The presence of rapid conformational changes in the cycloalkanes effects intramolecular relaxation processes.

(3) An illustration of the utility of these relaxation techniques is provided by the various *specifically* labeled propyl halides. The results show conclusively that there is no internal rotation in the chain. Similar experiments with longer chains should prove fruitful in studies of hydrocarbon chain flexibility and conformation.

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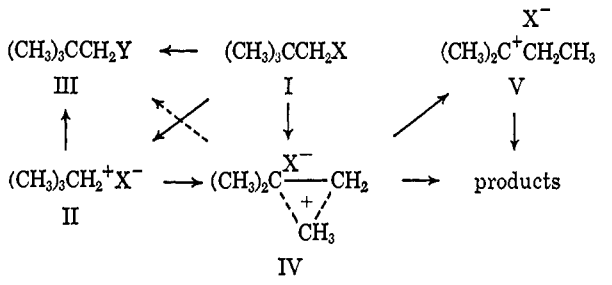
The Acetolysis of Chiral 1-Adamantylcarbinyl-1′-*d* Tosylate. Evidence for a Bridged Intermediate in a Neopentyl Solvolysis

Sir:

The problem of concerted *vs.* stepwise mechanisms in the carbonium ion rearrangements of simple aliphatic substrates has remained a conundrum for many years, as exemplified by the exceptional amount of work on the neopentyl (I) and related systems.[1,2]



The deoxidation of chiral neopentyl alcohol-1-*d*,[2a] the deamination of chiral neopentylamine-1-*d*,[2d] and the ethanolysis of chiral neopentyl tosylate-1-*d*[2g] have all been shown to give rise to chiral 2-methyl-1-butene-3-*d*, formed with inversion of configuration. While these results exclude the intermediacy of a free, long-lived neopentyl cation, the possibility of a stepwise process is still not eliminated, at least for solvolysis. If the rate-determining step is ion-pair formation (I → II), and if the ion pair is so "tight" that no racemization (of deuterated substrate) occurs, conversion of chiral I to chiral V can occur without any rate enhancement due to methyl participation.[1]

Another problem, still not settled, is whether bridged structure IV is an intermediate, or merely a transition state.[2f] IV can, in principle, give rise to both primary (III) and tertiary (*via* V or directly) products, although the latter would be expected strongly to be favored. Nevertheless, it has been demonstrated recently that the use of the more nucleophilic ethanol–water solvents gives rise to appreciable (2–10%) amounts

(1) For a review and a discussion of the pertinent literature, see J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966). For more recent references, see footnote 2.
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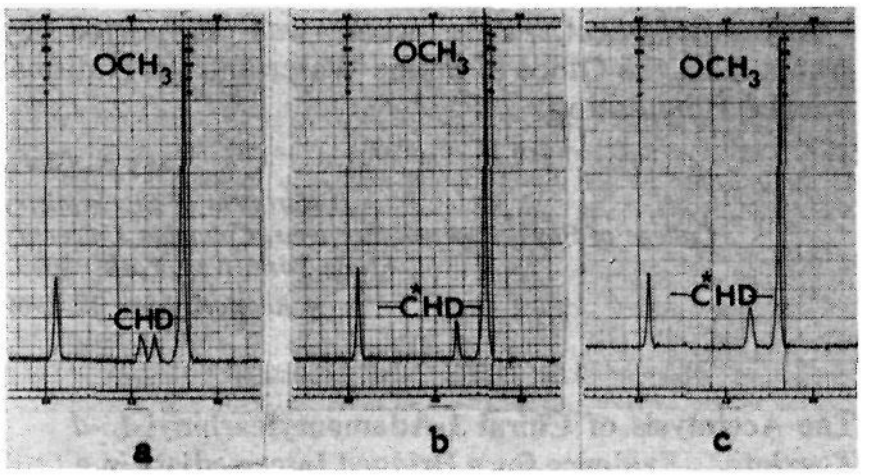
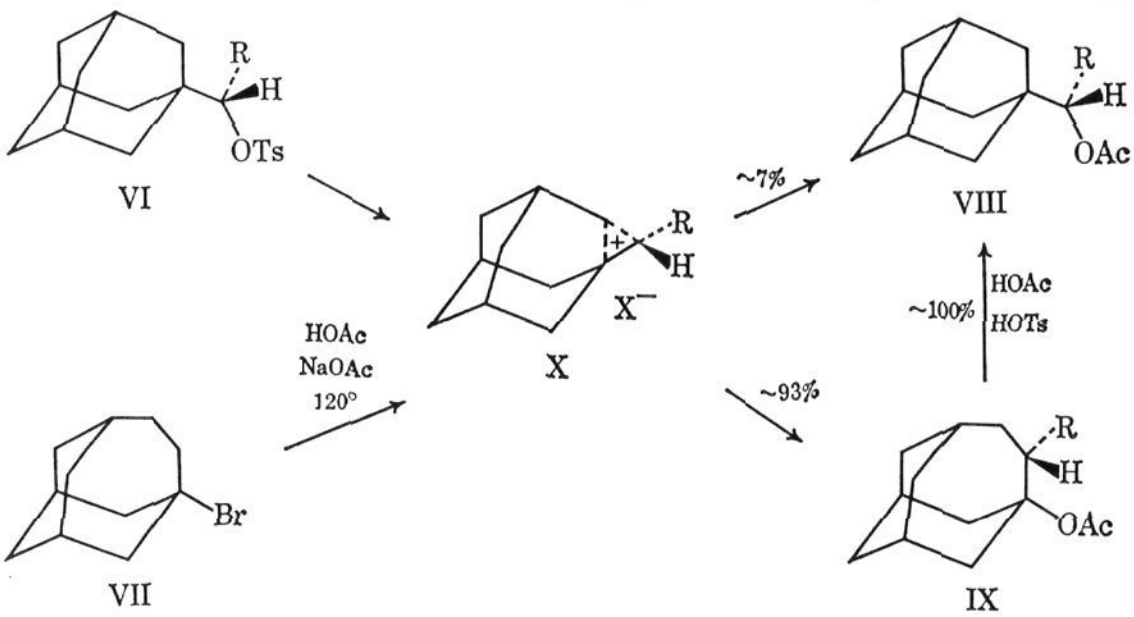


Figure 1. Partial 60-MHz nmr spectra in benzene (relative to benzene) of (a) racemic 1-AdCHDOCOC*HOCH$_3$C$_6$H$_5$; (b) O-methylmandelate ester of product XIV (R = D); (c) O-methylmandelate ester of starting alcohol XIV (R = D).

of neopentyl products (III) in the solvolysis of neopentyl tosylate.[2f,g] Unfortunately, the optical fate of these products (III) has not yet been determined.[2g] Inverted III would be expected from I or II, but III with retained configuration from IV. In the less nucleophilic solvent, acetic acid, practically no neopentyl products are found.[1,2b,d] Of course, neopentyl products are not expected from *t*-amyl starting materials.

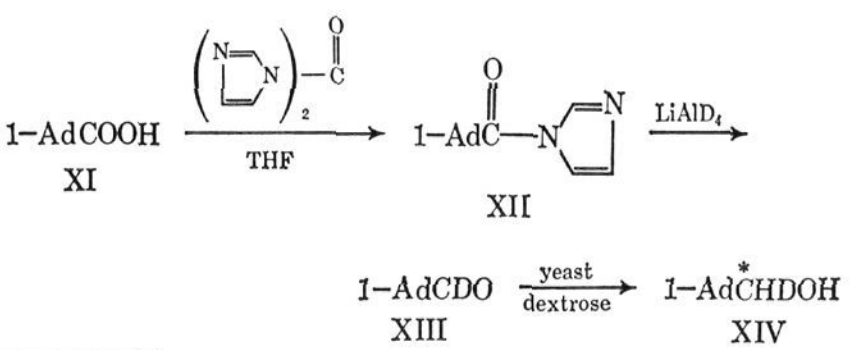


In contrast, 1-adamantylcarbinyl (VI, VIII) and 3-homoadamantyl (VII, IX) systems are interconvertible, because of offsetting carbonium ion stability and ring-strain factors.[1] Acetolysis of both 1-adamantylcarbinyl tosylate (VI, R = H) and 3-homoadamantyl bromide (VII) under the same conditions gave the same mixture of acetate products by kinetic control: *ca.* 93% 3-homoadamantyl acetate (IX, R = H) and 7% 1-adamantylcarbinyl acetate (VIII, R = H). These systems are thus ideally suited for the study of the possible intermediacy of bridged ion X. We report here the stereochemical course of the acetolysis of chiral 1-adamantylcarbinyl-1′-*d* tosylate (VI, R = D).

Synthesis of VI (R = D) was accomplished by treating 1-adamantanecarboxylic acid[3] (XI) with N,N-carbonyldiimidazole[4] followed by the lithium aluminum deuteride reduction[5] of the resulting imidazolide[6] XII to 1-adamantanecarboxaldehyde-1′-*d* (XIII). Yeast reduction[2b,7] of XIII led to chiral 1-adamantylcarbinol-1′-*d* (XIV),[8] which was then converted to the tosylate ester VI (R = D) by the usual procedure.[1,9]

The optical purity of chiral XIV was shown to be 97 ± 3% by nmr analysis of its O-methylmandelate ester.[10,11] The partial nmr spectrum of racemic 1-adamantylcarbinyl-1′-*d* O-methylmandelate (Figure 1a) shows *two* diastereotopic –CHDO– signals (δ 3.88 and 3.73 ppm, relative to benzene), but only *one* such signal (at δ 3.73 ppm) is present in the spectrum of chiral product (Figure 1b). By mixing racemic and chiral O-methylmandelates, it was determined that the nmr method employed was capable of detecting 3% of diastereomeric impurity.

Acetolysis of chiral tosylate VI (R = D) in the presence of 0.08 *M* sodium acetate and 1% acetic anhydride at 120° for 72 hr yielded a mixture of 7% VIII (R = D) and 93% IX (R = D). Preparative glpc isolation of VIII (R = D, Carbowax 20 M, 210°) was followed by saponification with 25% aqueous–methanolic NaOH to 1-adamantylcarbinol-1′-*d* (XIV)[12] and conversion to its O-methylmandelate ester.[11] The chemical shift of the single observable carbinyl proton (δ 3.73 ppm relative to benzene) for both the mandelate ester of starting material XIV (Figure 1c) and product XIV (Figure 1b) were identical, thus indicating that the reaction oc-



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(11) XIV was esterified by the acid chloride derived from (*R*)-O-methylmandelic acid.
(12) Mass spectral analysis of XIV from solvolysis showed the absence of any deuterium loss.

cured with *complete retention of configuration* (within the limits of the detection method used).

The chirality of the major acetolysis product, 3-homoadamantyl-4-*d* acetate (IX, R = D), was not determined directly. However, this product was rearranged to the thermodynamically more stable 1-adamantylcarbinyl-1'-*d* acetate (VI, R = D) by catalytic amounts of toluenesulfonic acid in acetic acid.[1] The optical purity of this rearranged ester was determined by saponification, conversion[11] to the O-methylmandelate, and nmr analysis. Again, only the δ 3.73 ppm band was observed. This indicates that both the conversion of VI (R = D) to IX (R = D) and the latter to VIII (R = D) had proceeded with optical integrity, both processes presumably involving inversion at the chiral center.

This evidence, along with that previously acquired,[1,2i] strongly implicates bridged ion X as the intermediate in the reactions described.

According to our present view of solvolysis reactions,[13] simple primary carbonium ions are energetically inaccessible in the usual solvents. Only two mechanistic routes are available for primary solvolysis: k_s (solvent assisted), which would lead only to unrearranged products and ester with inverted configuration, and k_Δ (neighboring group assisted). This is the only available mechanism which can lead to rearranged products. It follows then that the observation of *any* rearrangement accompanying the solvolysis of a simple, primary system can be taken as *prima facie* evidence for neighboring group participation. Thus, contrary to our former tentative conclusion,[1] the solvolysis of neopentyl tosylate must be assisted by methyl participation.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society, and by a grant-in-aid by the Union Carbide Corporation.

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Conformational Stability of Tris(ethylenediamine)ruthenium(II) Ion in Solution

Sir:

The possibility of conformational isomerism in chelated ethylenediamine ligands has long been recognized,[1] and a detailed analysis has been presented by Corey and Bailar.[2] They predicted that the most stable conformer of a Λ-tris(ethylenediamine)metal ion would have each ethylenediamine ligand in the δ conformation with the carbon–carbon axis of each ligand parallel to the C_3 axis of the complex, in preference to the λ conformation in which the carbon–carbon bond forms an obtuse angle with the C_3 axis. This agrees with the observed crystal structures of $Co(en)_3^{3+}$ in several salts[3-5] and with that of $[Ni(en)_3](NO_3)_2$.[6] In each case the metal–ethylenediamine rings were observed to be *gauche* and in the $\delta\delta\delta$ conformation for a Λ configuration about the metal.

For both the δ and the λ conformations of the ethylenediamine ligand the hydrogens on both the amine nitrogen and methylene carbon atoms adopt approximately axial and equatorial positions and would be expected to produce a complex proton nmr spectrum. In particular, in the absence of coupling with the amine protons, which may be eliminated by deuteration, the methylene protons would be expected to produce an AA'BB' spectrum. Such complex spectra have not been observed, however, for the trisethylenediamine complexes of Pt(IV)[7] or Rh(III),[8] which exhibit single resonances only several cycles wide, or of Co(III) which gives a single broader line of 18 Hz width.[9] The absence of the expected multiplets has been attributed to rapid conformational equilibration between the δ and λ forms during which the axial protons become equatorial, and *vice versa*, with the result that the methylene protons become equivalent.[8,9] There have been several recent reports of nmr evidence from the amine proton spectra for distinct conformations of $Co(en)_3^{3+}$, but there seems to be no case of well-resolved fine structure for the methylene resonances of a trisethylenediamine complex.[9,10]

The tris(ethylenediamine)ruthenium(II) ion in contrast has a methylene proton spectrum with very well resolved fine structure. Both the 60- and 100-MHz spectra of the deuterated complex, shown in Figure 1, have typical AA'BB' multiplet structures with the center of the band 2.55 ppm downfield from DSS. A detailed analysis of these spectra is in progress. In the spectrum of the nondeuterated complex two distinct broad amine proton resonances can be observed in the region 2.8–4.5 ppm downfield from DSS. Quite remarkably the multiplet structure of the methylene protons persists in 0.1 *M* trifluoroacetic acid solution up to 100°.

The bromide salt of $Ru(en)_3^{2+}$ used in this study was obtained from the less soluble $[Ru(en)_3]ZnCl_4$ or $[Ru(en)_3]ZnBr_4$[11] by dissolving the latter in an acetate-buffered solution of Na_2H_2EDTA and adding a concentrated solution of NaBr to effect precipitation. Previous studies of the optical activity[12] of $Ru(en)_3^{2+}$ and of its electron-exchange reaction[11a] with $Ru(en)_3^{3+}$ indicate that the complex ion is monomeric and substitution inert, as are the trisethylenediamine complexes of Co(III), Rh(III), and Pt(IV). The facile air oxidation of $Ru(en)_3^{2+}$ was avoided by preparing solutions in an

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