By observing the methyl proton double-doublet due to labeling at C_1 and C_3 only, and irradiating the carbon frequencies in steps from 20 to 2 Hz, we could demonstrate that ${}^3J_{C_3H_M}$ and ${}^1J_{C_1C_3}$ have opposite signs, the same result as above. More importantly, however, ${}^1J_{C_1C_3}$ and ${}^2J_{C_1H_M}$ were shown to have the same sign by noting that low frequency carbon irradiation enhanced the low frequency proton peak whereas higher frequency irradiation enhanced the high frequency proton peak. Thus the signs are uniquely determined (based on ${}^1J_{C_MH_M}$ being positive[10]).

It should be noted also that placing the ${}^{13}C$ irradiating frequency to a position 5 ppm more shielded than that carbon decoupling frequency needed to reduce the proton double-doublet of C_1–C_3 dilabeled material to a doublet (J = 7.3 Hz) results in another doublet (J = 2.7 Hz). This means the less shielded carbon, C_3 (29.02 ppm from TMS),[2] is coupled to H_M with the smaller J while the more shielded carbon, C_1 (24.02 ppm),[2] is coupled to H_M by the larger J.

Finally, since little is known about the signs of carbon-carbon coupling constants[13] except that ${}^1J_{CC}$ is positive[5,14,15] (with the exception of ${}^1J_{C_1C_3}$ in bicyclobutane) it would be inappropriate to discuss the significance of a negative ${}^2J_{C_3C_M}$. It should also be noted that as expected,[10c] the signs of ${}^1J_{CH}$, ${}^2J_{CH}$, and ${}^3J_{CH}$ alternate. In addition the sign of ${}^2J_{CH}$ is expected to be negative for a system where the H is attached to an sp^3 hybridized C which in turn is bonded to either an sp^2 or sp hybridized C,[16] which is the case in a 1-methylbicyclobutane.[3a]

We would also like to point out that all of the signs and values for the coupling constants reported agree in sign and approximate value with those calculated by Schulman in 1-methylbicyclobutane using the INDO coupled Hartree-Fock approxmation.[17]

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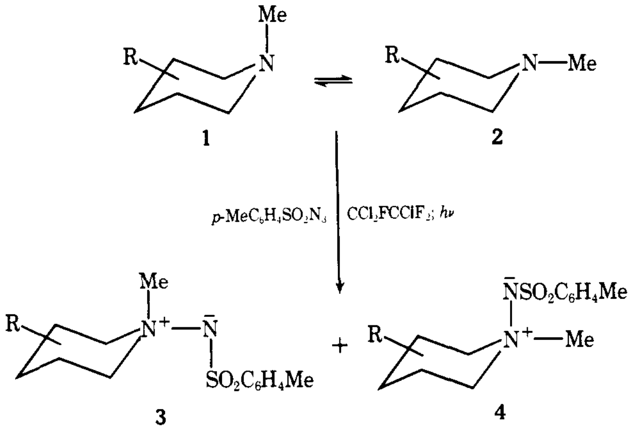
Lack of Selectivity in the Electrophilic Addition of *p*-Toluenesulfonylnitrene to Tertiary Amines. Conformational Equilibrium in *N*-Methylpiperidines

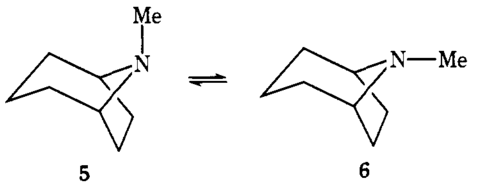
Sir:

The position of the *N*-methyl equilibrium in *N*-methylpiperidines ($\mathbf{1} \rightleftharpoons \mathbf{2}$) is a problem of considerable current interest.[1-3] We report some results obtained by a novel photochemical procedure, the rationale of which has been outlined previously.[4]

p-Toluenesulfonylnitrene, *p*-$MeC_6H_4SO_2N$, photochemically generated in situ from the azide, was shown[4] in competition experiments not to discriminate between dimethyl sulfide and diisopropyl sulfide in the reaction to produce iminosulfuranes *p*-$MeC_6H_4SO_2N^-S^+R_2$, and we have now found a similar lack of discrimination between butyl- and isobutyldimethylamines in the competitive conversion into aminimides *p*-$MeC_6H_4SO_2N^-N^+Me_2R$. These quantitative comparisons (rate-constant ratio 1.0:1 in each case[5]) are supported by further examples of lack of selectivity of the nitrene probe for competitive additions to nucleophiles in systems where precise quantitative assessments are adventitiously more difficult. There appears to be little if any discrimination between dimethyl sulfide and di-*ter*-butyl sulfide despite the ready thermal conversion of the iminosulfurane from the latter into the sulfenamide *p*-$MeC_6H_4SO_2NHSCMe_3$ presumably because of internal steric compressions. Likewise, the nitrene adds about equally readily to each nitrogen atom of 1,2,4-trimethylpiperazine.[6] Our deductions in the sequel are based on the expectation, which accords with all our available experimental evidence, that *p*-toluenesulfonylnitrene will be kinetically unselective between tertiary piperidine conformers such as **1** and **2** or **5** and **6** in the reaction to yield diastereoisomeric aminimides.

From 1-methyl-4-*tert*-butylpiperidine ($\mathbf{1} \rightleftharpoons \mathbf{2}$; R = equatorial 4-*t*-Bu) and the nitrene only one aminimide (formulated as **4**; R = equatorial 4-*t*-Bu) was observed by examination of the ${}^1H$ NMR spectrum of the appropriate product fractions. We were just able to detect 1% of the diastereoisomer **3** in the spectra of calibration mixtures,[7] 2% being very clearly evident. *We deduce that the 4-tert-butyl base and hence the parent N-methylpiperidine* ($\mathbf{1} \rightleftharpoons \mathbf{2}$; R = H) *has no more than about 1% of the conformation* **1** *with axial N-methyl* ($-\Delta G^\circ_{300} \geqslant 2.7$ kcal mol^{-1} in CCl_2FCClF_2)[8]. 1,4-Dimethylpiperidine and the nitrene gave mixed diastereoisomeric imides in ratio 22:1, a value we interpret in terms of two predominating conformers **2** (R = equatorial 4-Me) and **2** (R = axial 4-Me) in the reactant base, in ratio controlled by the 4-methyl conformational preference, which is presumably similar to that[10] of methyl-





cyclohexane ($-\Delta G°_{305} = 1.70$ kcal mol^{-1} or $K = 17$). Tropane[11] (**5** ⇌ **6**) gave mixed aminimides in ratio 4.2:1 ($-\Delta G°_{300} = 0.86$ kcal mol^{-1} in CCl_2FCClF_2) and, by application of the kinetically controlled protonation procedure,[3,13] diastereoisomeric salts in ratio 5.8:1 ($-\Delta G°_{300} = 1.05$ kcal mol^{-1} in CCl_2FCClF_2 or cyclohexane near the interface with aqueous sulfuric acid). Agreement between the two methods is satisfactory[14] in view of the obvious difference in physical conditions.

In application of the photochemical method, all bases (or mixtures of bases) were converted into aminimides by irradiation through Pyrex of solutions in CCl_2FCClF_2 containing *p*-toluenesulfonyl azide and a large excess of base, using a 450-W medium-pressure Hanovia lamp and a water-jacketed reaction cell with temperature controlled to ±2°. Yields of aminimide (based or decomposed azide) were typically 2–3% (8–9% with tropane); numerous by-products were evident, but under the experimental conditions chosen the high yields of by-products do not affect the quantitative conclusions on conformational equilibria.[4,15] Aminimides were readily isolated chromatographically and monitored by their characteristic ir spectra (strong bands at ca. 1090, 1130, and 1260 cm^{-1}). Rigorous checks with calibration mixtures (some in high ratios) indicated no tendency toward thermal or photochemical equilibration of products, and no loss of minor component during isolation procedures.

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(7) The difficulty of measuring high ratios by NMR spectroscopy (cf. ref 3 and comments thereon in ref 2) is eased considerably by the separate availability of the components of the mixtures. Both aminimides **3** and **4** (R = equatorial 4-*t*-Bu) were obtained from 1-amino-4-*tert*-butylpiperidine by successive treatments with methyl iodide, potassium *tert*-butoxide (in tetrahydrofuran), and *p*-toluenesulfonyl chloride; the 4-methyl analogues were similarly obtained. All new compounds have been characterized by elemental and spectroscopic analysis.
(8) So far as comparison is possible between results obtained by different methods on different models, our value accords with the highest previously recorded[3] ($-\Delta G°_{288} = 2.7 \pm 0.2$ kcal mol^{-1} to unspecified confidence limits) from kinetically controlled protonation of **1**, *cis*-3,5-trimethylpiperidine. We note that our *minimum* value is still correct even in the unlikely event that the nitrene is discriminatory between the conformers, with a higher rate constant for equatorial addition to the axial *N*-methyl conformer; this would lead to an observed product aminimide ratio lower than the reactant conformer ratio. The difficulty in *initial* bending of the axial *N*-methyl[2,9] group to relieve syn–axial interactions, relative to bending of *C*-methyl in axial methylcyclohexane, appears likely to be a substantial factor in the observed difference in conformational ratios for *N*-methylpiperidine and its hydrocarbon analogue.
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Tunneling Rotation of the Methyl Radical in the $CH_3COONa{\cdot}3D_2O$ Crystal

Sir:

Since Freed[1] theoretically predicted the quantum tunneling effect of the methyl group in radicals, several interesting experimental investigations[2] have been reported on the effect. However, these ESR studies on the quantum tunneling effect have been restricted to the systems for the methyl group in free radicals. In this paper, we wish to report the tunneling rotation of the methyl radical about the threefold symmetry axis of the molecule in a crystal.

We have measured temperature dependence of ESR spectra of the methyl radical produced by γ irradiation of a single crystal of $CH_3COONa{\cdot}3D_2O$ at temperatures below 77 K. The crystal was mounted in a quartz tube of high purity for the γ irradiation and the ESR measurements. The insertion type liquid helium Dewar[3] was used for the ESR measurements at the temperatures below 77 K. The temperature dependence could be examined for about 4 h until the sample temperature reaches 4.2 K, by keeping the crystal inside of the sample tube vacuo so that the thermal conduction might take place only through direct contact of the crystal with the glass wall. The ESR spectra shown in Figure 1b–e were observed during the first 2 h in the sample cooling process, and the spectrum of Figure 1f was observed during the last 2 h. After the sample temperature reached equilibrium with the liquid helium temperature, ESR absorption could not be observed for the sake of the microwave power saturation effect.

As Figure 1 shows, the γ irradiated crystal of