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TRI-*t*-BUTYLCYCLOPROPENYL AZIDE. DEGENERATE ISOMERIZATION

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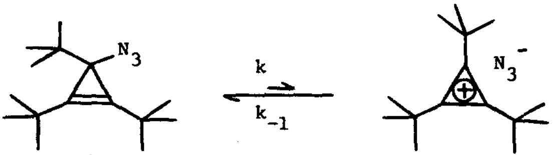
We wish to describe the novel properties of tri-*t*-butylcyclopropenyl azide (1),[1-3] a compound which exhibits solvent as well as temperature dependent nmr spectra, and present evidence that this behavior is attributed to a degenerate isomerization *via* an ionization-recombination pathway. Reaction of tri-*t*-butylcyclopropenium fluoroborate or perchlorate with sodium azide in acetonitrile at 0° followed by aqueous work-up afforded 1 in quantitative yield as a colorless oil[4]; short path distillation, pot temp 40-50° (0.03-0.05 mm), mp ≈ +2°; *Anal*. Calcd for $C_{15}H_{27}N_3$: C, 72.24; H, 10.91; N, 16.85; mw 249; Found: C, 72.36; H, 10.96; N, 16.74; mw 250 (osmometric, CCl_4); mass spectrum m/e 207 (M-42, tri-*t*-butylcyclopropenium ion), 123, 57; ir (ν_{max} CCl_4) 2085 (vs, azide), and 1810 cm^{-1} (w, cyclopropene); uv (λ_{max}, cyclohexane) 295 mμ (ε 28). The nmr spectrum of the neat azide at *ca*. 40° exhibited a symmetrical exchange-broadened singlet at 1.21δ (60 MHz, $W_{1/2}$ = 9 Hz). The appearance of solution spectra was a function of solvent and temperature and in CCl_4 (0.6 M) varied from two sharp singlets (-10°, $W_{1/2}$ ≈ 1 Hz) at 1.28 and 0.94δ



1 2

in a 2 to 1 ratio respectively to one singlet (+75°, $W_{1/2}$ = 2 Hz) at 1.17δ (approximate weighted average position). By comparison the completely ionic tri-*t*-butylcyclopropenium perchlorate or fluoroborate exhibits a sharp singlet at 1.58δ in $CDCl_3$. Some experimental (left) and computer calculated (right)[5] nmr spectra in CCl_4 (60 MHz, 0.6 M) at various temperatures are presented in Figure 1; activation parameters are: E_a = 15.3 ± 0.5 kcal/mole; $\Delta S^{\ddagger}$ = - 5.2 e.u.

This behavior may be ascribed to a dynamic process in which the azide function is exchanging between three equivalent sites. The intramolecular nature of this isomerization was established on the basis of dilution experiments which revealed no significant dependence of rate on alkyl azide concentration. The observed small changes in rate were attributed to medium effects (*vide infra*).

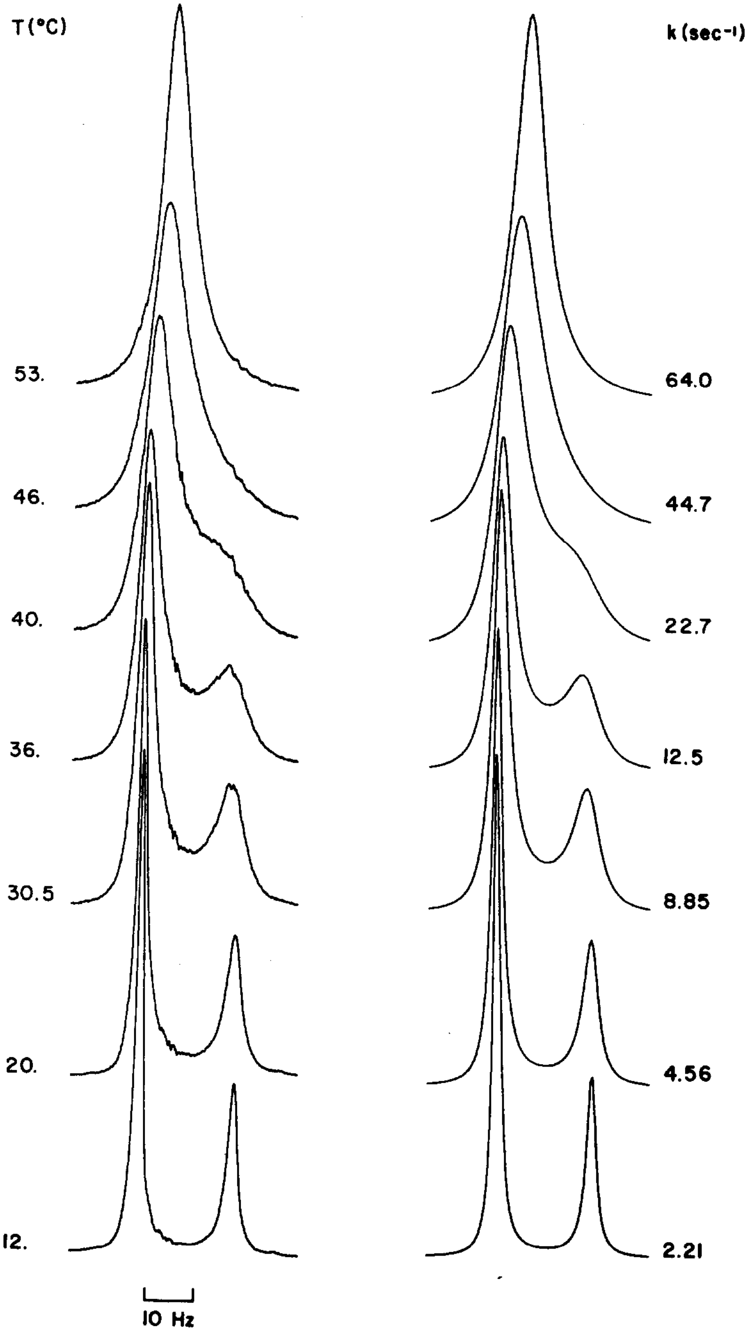
Evidence for the ionic nature of the isomerization was provided by the dramatic solvent effect data presented in Table 1. The expected solvent effects for an ionic process were observed with the exception of $CDCl_3$ and CD_2Cl_2 which exhibited anomalously fast rates.[2] In all solvents except SO_2 the equilibrium lies almost entirely in favor of covalent azide **1**. Apparently the forward and reverse rate constants k_1 and k_{-1} respectively are more sensitive to changes in solvent than is the equilibrium constant K.[6] However, in liquid SO_2 at -42°, the position of absorption of the singlets from both the tri-*t*-butylcyclopropenium fluoroborate or perchlorate and azide were superimposable at 1.58δ indicating that in this solvent **1** exists as the completely dissociated species **2**.[7]

Table 1

Solvent	Coalescence temp, °C [a]	k_{rel}
CCl_4	+40	1
CD_3COCD_3	-12.5	120
$CDCl_3$	-40	4×10^3
CD_2Cl_2	-40	4×10^3
CD_3CN	<-40[b]	-
CD_3OD	-52	2×10^4

[a] 60 MHz; [b] CH_3CN freezes at -42°

Figure 1



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4. In contrast to the triphenyl and trimethyl analogues, **1** does not rearrange to the corresponding v-triazine.
5. A total line shape analysis (TLS) method was employed invoking temperature dependent chemical shifts and rate constants. The experimental spectra were digitized into about 50 points and least-squares fitted to the Bloch equations modified for chemical exchange. See R. R. Shoup, E. D. Becker, and M. L. McNeel, J. Phys. Chem., **76**, 71 (1972), and references cited therein.
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