(0.4 mm)] gave an analytical sample, mp 139–140°. The ir spectrum showed peaks at 1710 and 800 cm$^{-1}$. The nmr spectrum showed peaks at $\tau$ 5.50–5.80 (m, H-4$_{exo}$, $J$ = 4.2, 6.4 Hz), 6.18 (dd, H-3$_{endo}$, $J$ = 4.0, 2.4 Hz), 6.70–7.70 (m, H-1, H-2, H-5, H-6, H-12a), 7.80–8.20 (m, H-7–H-10, H-12s).

*Anal.* Calcd for $C_{12}H_{16}Cl_2O$: C, 58.31; H, 6.53; Cl, 28.69. Found: C, 58.55; H, 6.50; Cl, 28.50.

**Tricyclo[4.4.1.1$^{2,5}$]dodec-3-en-11-one (4).**—A mixture of 3.90 g of **14**, 2.0 g of zinc chloride, and 21.3 g of zinc dust in 215 ml of 95% ethanol was refluxed at 100° for 25 hr. The mixture was allowed to cool to room temperature, the gray solid was filtered off, and the ethanol solution was diluted with ether. The ether was washed twice with water and the water was back extracted twice with ether. The combined ether fractions were dried over magnesium sulfate, the drying agent was filtered off, and the ether was evaporated. Purification of the resulting crystals by sublimation [100° (12 mm)] yielded 2.52 g (91%) of pure **4** identical in all respects with a sample prepared from deoxygenation of **3** (*vide supra*).

**Catalytic Hydrogenation of Tricyclo[4.4.1.1$^{2,5}$]dodec-3-en-11-one (4).**—A solution of 48 mg of **4** in 3 ml of 95% ethanol was exposed to hydrogen gas in the presence of 35 mg of 10% palladium on charcoal. After 25 min the uptake ceased; no additional hydrogen was taken up over the next 15 min. The solution was filtered and the solvent was evaporated to give 48 mg (98%) of pure colorless **12**.[25] The nmr spectrum showed only a complex multiplet between $\tau$ 7.2 and 8.9.

**Acknowledgment.**—We would like to thank the National Research Council of Canada for their generous financial support of this work.

**Registry No.**—**1**, 4668-70-6; **2**, 40696-03-5; **3**, 40696-04-6; **4**, 40696-05-7; **12**, 6824-69-7; **13**, 40696-06-8; **14**, 40696-07-9.

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# The Isomerization of Tri-*tert*-butylcyclopropenyl Azide[1]

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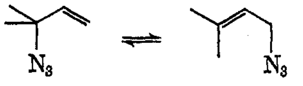
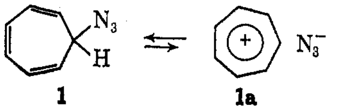
Tri-*tert*-butylcyclopropenyl azide has been synthesized by the reaction of tri-*tert*-butylcyclopropenyl perchlorate or fluoroborate with sodium azide. The nmr spectra exhibited both solvent and temperature dependence as the result of chemical exchange of the azide function between three equivalent annular sites. Total line shape analyses of the spectra provided activation parameters in six widely different solvents. The sensitivity of the degenerate isomerization rate to the nature of the solvent suggests that the process proceeds *via* an ionization–recombination (ion-pair) mechanism.

In recent years much interest has been devoted to the problem of structure and reactivity of organic azides.[2] The rates of rearrangement of allylic azides (eq 1) have been shown to be relatively insensitive to alkyl substitution and changes in solvent polarity.[3] These results are consistent with a concerted mechanism involving a [3,3] sigmatropic shift. On the other hand, Wulfman, *et al.*,[4] have suggested that the temperature and solvent dependence of the nmr spectrum of tropyl azide (1) can be rationalized on the basis of a mechanism involving ionization to the tropylium ion–azide ion pair (1a). Upon warming a solution of **1** in acetone-$d_6$ at −35 to −15°, all nmr (60 MHz) spin–spin splitting disappears, whereas, at 30°, all chemical shifts are indistinguishable and the spectrum exhibits a single broad maximum. The position of the center of gravity of the spectrum at −35°, namely $\delta$ 5.85, is identical with the corresponding position at 52° but is much further upfield than the tropylium ion resonance ($\delta$ 10.0). The independence of the spectra of concentration provided evidence that the protons in tropyl azide approach equivalency *via* an intramolecular degenerate isomerization process. However, it was shown that **1** in the presence of added tropylium perchlorate exhibits spectra ranging from those showing a single sharp line between tropylium ion and exchanging azide peaks, through those showing broad absorption in the same region, to those showing separate peaks. Furthermore, it was reported that under certain conditions these spectra show extreme concentration dependence attributed to an intermolecular exchange process between tropyl azide and tropylium perchlorate *via* an ion triplet 2.



(1)



**1** **1a**

$$C_7H_7^+ \quad N_3^- \quad C_7H_7^+$$

**2**

Since cyclopropenyl azides are (4$n$ + 2) vinylogs of tropyl azide (**1**), it was of interest to establish whether they revealed in their nmr spectra any of the unusual features exhibited by **1**. However, it has been reported that the reaction of triphenylcyclopropenyl bromide with sodium azide in DMF gives the unstable covalent triphenylcyclopropenyl azide (**3**) which undergoes facile rearrangement to the *v*-triazine **4**.[5,6]

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[1] A preliminary communication of this work has appeared in which a different total line shape analysis (TLS) program was employed: R. Curci, V. Lucchini, P. J. Kocienski, G. T. Evans, and J. Ciabattoni, *Tetrahedron Lett.*, 3293 (1972).

[2] E. Lieber, J. S. Curtice, and C. N. R. Rao, *Chem. Ind. (London)*, 586 (1966).

[3] A. Gagneux, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **82**, 5956 (1960).

[4] (a) C. E. Wulfman, C. F. Yarnell, and D. S. Wulfman, *Chem. Ind. (London)*, 1440 (1960); (b) D. S. Wulfman, L. Durham, and C. E. Wulfman, *ibid.*, 859 (1962); (c) D. S. Wulfman and J. J. Ward, *Chem. Commun.*, 276 (1967); (d) D. S. Wulfman, Ph.D. Thesis, Stanford University, 1962.

[5] E. A. Chandross and G. Smolinsky, *Tetrahedron Lett.*, 19 (1960).

[6] I. A. D'yakanov and R. R. Kostikov, *Russ. Chem. Rev.*, **36**, 557 (1967).

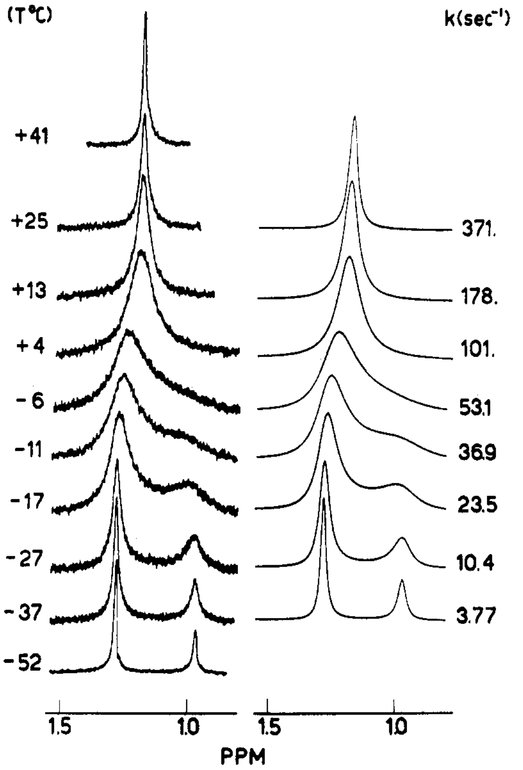
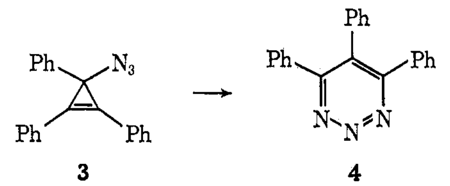


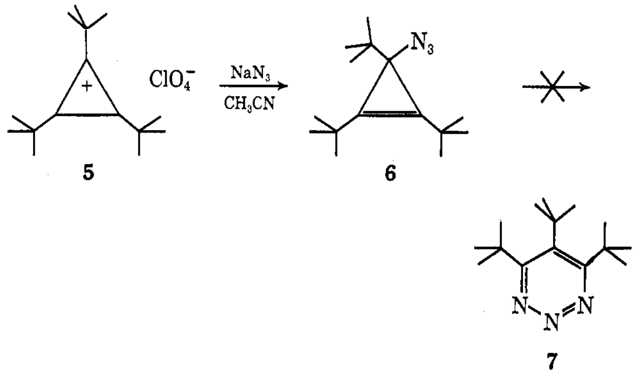
Figure 1.—Experimental (left) and computer-calculated (right) nmr spectra (90 MHz) of tri-*tert*-butylcyclopropenyl azide (0.08 *M*) in acetone-$d_6$ at various temperatures.

Nevertheless, the tendency of trialkylcyclopropenyl azides such as tri-*tert*-butylcyclopropenyl azide (**6**) toward ionization is *a priori* expected to be increased relative to **3**, since the tri-*tert*-butylcyclopropenyl



cation ($pK_{R^+}$ = 6.5 in 50% $H_2O$-$CH_3CN$)[7] is considerably more stable than the corresponding triphenyl derivative ($pK_{R^+}$ = 3.1 in 50% $H_2O$-$CH_3CN$).[8] Tri-*tert*-butylcyclopropenyl azide was selected on the basis of the above reasoning as well as the fact that it would be expected to exhibit a simple nmr spectrum.

## Results and Discussion



Reaction of tri-*tert*-butylcyclopropenyl fluoroborate[9] or perchlorate[10] (**5**) with sodium azide in acetonitrile at 0° followed by aqueous work-up afforded tri-*tert*-butylcyclopropenyl azide (**6**) in nearly quantitative yield as a stable, colorless oil which could be distilled under reduced pressure. Azide **6** has been stored neat in the crystalline state at about −10° (mp *ca.* 2°) for periods exceeding 6 months with no detectable decomposition. Unlike **3** no evidence was found for the rearrangement of **6** to *v*-triazine **7**. The infrared, ultraviolet, and nmr spectra were consistent with the covalent formulation **6**. In the infrared ($CCl_4$) **6** exhibited strong characteristic azide absorption at 2085 $cm^{-1}$ and weak cyclopropene (C=C) absorption at 1810 $cm^{-1}$.[11] The ultraviolet spectrum (cyclohexane) showed the characteristic azide maximum at 295 nm ($\epsilon$ 28).[12] The nmr spectrum exhibited a symmetrical exchange-broadened singlet at $\delta$ 1.21 (60 MHz, $W_{1/2}$ = 9 Hz). The appearance of solution spectra was a function of solvent and temperature and in acetone-$d_6$ (0.08 *M*) varied from two sharp singlets (−52°, 90 MHz, $W_{1/2}$ = 1.2 Hz) at $\delta$ 1.28 and 0.96 in a 2:1 ratio, respectively, to one singlet (41°, 90 MHz, $W_{1/2}$ = 1.2 Hz) at $\delta$ 1.19 (approximate weighted average position). By comparison the completely ionic tri-*tert*-butylcyclopropenyl perchlorate or fluoroborate exhibits a sharp singlet at $\delta$ 1.58 in $CDCl_3$. Although the mass spectrum of **6** did not reveal a parent ion, an intense peak at *m/e* 207 (M − 42) was observed corresponding to the cyclopropenyl cation. The lability of the azide was demonstrated by the reaction of a solution of **6** in ethanol with aqueous silver nitrate, affording an immediate white precipitate of silver azide. Furthermore, a solution of the cyclopropenyl azide **6** in acetonitrile reacted slowly with potassium cyanide to give the corresponding tri-*tert*-butylcyclopropenyl nitrile in 80% yield. This nitrile proved to be identical in all respects with an authentic sample prepared by the reaction of tri-*tert*-butylcyclopropenyl perchlorate with potassium cyanide.

The nmr spectra of **6** were recorded in a series of solvents of widely different characteristics at various temperatures. At sufficiently low temperatures the spectrum consisted of two sharp singlets of relative intensity 2:1. However, as the temperature was increased, the two peaks broadened, coalesced, and finally merged into one sharp peak whose position approximated the weighted-average position of the two singlets at low temperature (see Figure 1). This nmr behavior suggests that **6** is in equilibrium among its three congruent isomers.[13] Chemical shift data of azide **6** as well as the ionic tri-*tert*-butylcyclopropenyl perchlorate (**5**) in a series of solvents are presented in Table I.

In order to obtain rates and activation parameters for the apparent degenerate isomerization process in which the *tert*-butyl groups become magnetically equivalent, the spectra in six representative solvents were subjected to a total line shape analysis (TLS).

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[7] J. Ciabattoni and E. C. Nathan, *Tetrahedron Lett.*, 4997 (1969).

[8] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

[9] J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Syn.*, in press.

[10] J. Ciabattoni and E. C. Nathan, *J. Amer. Chem. Soc.*, **91**, 4766 (1969).

[11] G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966).

[12] W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.*, **85**, 290 (1963).

[13] R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970).

TABLE I

POSITIONS OF NMR ABSORPTION OF TRI-*tert*-BUTYLCYCLOPROPENYL AZIDE AND TRI-*tert*-BUTYLCYCLOPROPENYL PERCHLORATE IN VARIOUS SOLVENTS

| Solvent | Azide **6**[a] | Cation **5**[a] | Temp, °C | Dielectric constant[b] |
|---|---|---|---|---|
| Neat | 1.21 | | 40 | |
| | 1.18 | | 75 | |
| $CCl_4$ | 1.18 | | 70 | 2.24 |
| | {0.92 (9 H)<br>1.27 (18 H) | | −35 | |
| $CDCl_3$ | 1.17 | 1.58 | 40 | 4.81 |
| | {0.95 (9 H)<br>1.27 (18 H) | | −65 | |
| $CD_2Cl_2$ | 1.17 | 1.58 | 40 | 9.08 |
| Acetone-$d_6$ | 1.19 | 1.62 | 40 | 20.7 |
| | {0.96 (9 H)<br>1.28 (18 H) | 1.62 | −40 | |
| $CD_3OD$ | 1.18 | | 40 | 32.6 |
| | {0.95 (9 H)<br>1.26 (18 H) | | −65 | |
| $CD_3NO_2$ | 1.19 | 1.60 | 40 | 35.8[c] |
| DMF-$d_7$ | 1.17 | 1.54 | 40 | 37.6[d] |
| | {0.95 (9 H)<br>1.26 (18 H) | | −60 | |
| $CD_3CN$ | 1.18 | 1.51 | 40 | 37.5 |
| | {0.96 (9 H)[e]<br>1.28 (18 H)[e] | | −40 | |
| Ethylene carbonate | 1.16 | 1.56 | 40 | 95.0 |
| $SO_2$ (liquid) | 1.58 | 1.58 | −42 | 14.1 |

[a] All positions are given in units of $\delta$ to ±0.01 ppm. [b] Dielectric constants for undeuterated solvents at 20° except as noted. [c] At 30°. [d] At 25°. [e] Estimated values from spectra at −40°.

The line shapes were computer-calculated employing Binsch's DNMR program[14a] and rate constants were estimated by determining the best fit between experimental and theoretical spectra; in most instances (see Table II) the experimental spectra were fed point by point into the computer and the theoretical curves representing the best fit were found by a least squares method.[14b–d] The results of typical fits are shown in Figure 1. Statistical least squares analyses of Eyring plots provided approximate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.[14b] These activation parameters are shown in Table II together with their uncertainties. It should be pointed out, however, that systematic errors may be significantly larger than these estimates.[15] It is apparent from Table II that no significant changes in the activation parameters were found on changing the cyclopropenyl azide concentration, consistent with an *intramolecular* rather than an intermolecular exchange process.

The effect of added salts was also investigated. The addition of 0.07 *M* lithium perchlorate to a solution of **6** in acetone-$d_6$ resulted in a decrease in the coalescence temperature and an increase in rate at 25°. Similarly, the addition of 0.05 *M* tri-*tert*-butylcyclopropenyl perchlorate (**5**) resulted in the observation of a positive salt effect (see Table II). On the other hand, when an equimolar quantity of **5** was added to a solution of **6** in $CD_3CN$ or $CD_3NO_2$ at 40°, only a single sharp peak was observed halfway between the singlet for pure cation and the singlet for pure azide. The results suggest that in these polar solvents there is rapid intermolecular exchange of the azide function between **5** and **6** in analogy with the tropyl azide–tropylium perchlorate system (*vide supra*). However, the temperature-dependent nmr spectrum of **6** in the presence of **5** in acetone-$d_6$ (Figure 2) reveals that the above intermolecular azide group exchange actually occurs between the cation and the dynamic tri-*tert*-butylcyclopropenyl azide molecule, which is already undergoing a fast intramolecular isomerization process on the nmr time scale.

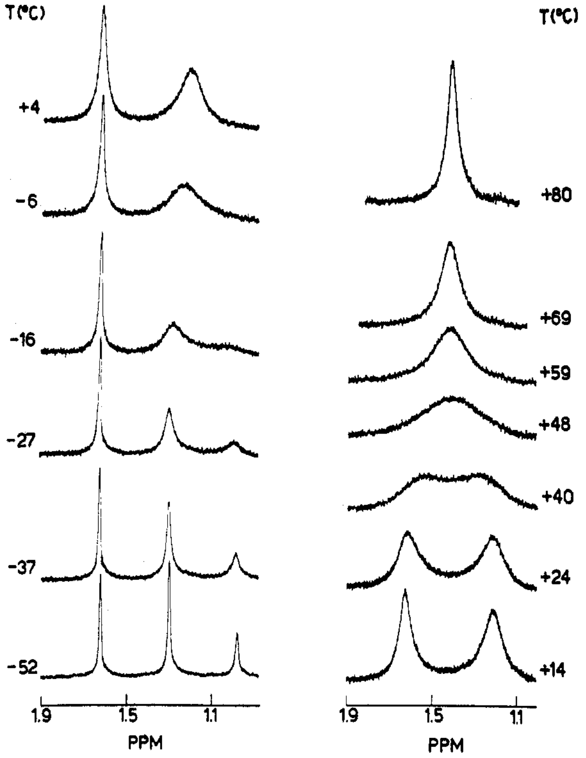

Figure 2.—The nmr spectra (90 MHz) of tri-*tert*-butylcyclopropenyl azide (0.08 *M*) in the presence of tri-*tert*-butylcyclopropenyl perchlorate (0.05 *M*) in acetone-$d_6$ at various temperatures.

It can be seen from Table II that the rate of intramolecular isomerization of **6**, like that of **1**, is very sensitive to the nature of the solvent in contrast with the analogous rearrangement of allylic azides.[3] The observed solvent effects, instead, are consistent with an ionic process involving the ionization of **6** to an ion pair **6a**[16] as depicted in Scheme I (path a). However, the concurrent intervention of a concerted pathway b cannot be excluded on the basis of our data. A concerted [1,3] sigmatropic shift is of course forbidden but a [${}_\omega2 + {}_\pi2 + {}_\sigma2$] process and a [3,3] sigmatropic shift represent possible allowed processes.[17]

Inspection of the data in Table I does not reveal any significant solvent effect on the single resonance position of **6**, which in every case, with the exception of $SO_2$, was about 0.4 ppm upfield from the signal of cation **5**. This suggests that the position of equi-

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[14] (a) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969); (b) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968); (c) R. R. Shoup, E. D. Becker, and M. L. McNeel, *J. Phys. Chem.*, **76**, 71 (1972); (d) L. G. Sillen, *Acta Chem. Scand.*, **18**, 1085 (1964), and references cited therein.

[15] B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4472 (1971).

[16] A more elaborate scheme would include a solvent-separated ion pair and dissociated ions depicting various degrees of association between the azide ion and cyclopropenyl cation.

[17] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

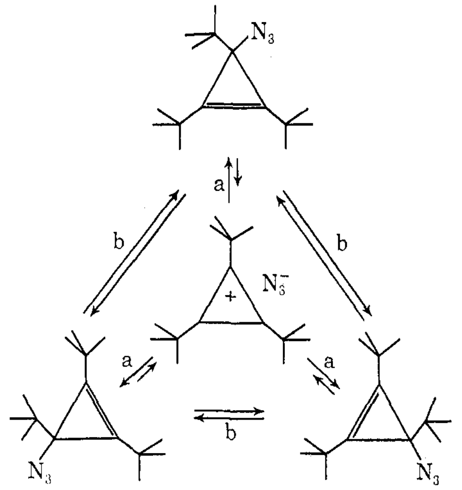
TABLE II

ACTIVATION PARAMETERS[a] AND RELATIVE RATES FOR THE ISOMERIZATION OF **6** IN VARIOUS SOLVENTS

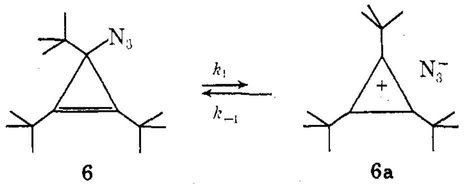
| Solvent | Dielectric constant | Azide, *M* | $\Delta H^{\ddagger}$ [b] | $\Delta S^{\ddagger}$ [c] | $\Delta G^{\ddagger}_{25°}$ [b] | Relative rates (25°)[d] | $T_c$, °C[e] |
|---|---|---|---|---|---|---|---|
| Acetone-$d_6$ | 20.7 | 0.02 | 10.7 ± 0.3 | −10.4 ± 1 | 13.8 ± 0.4 | | −2.5 |
| | | 0.06 | 10.7 ± 0.2 | −10.8 ± 0.5 | 13.9 ± 0.2 | 0.95 × $10^2$ | −1.5 |
| | | 0.08 | 10.0 ± 0.2 | −13.6 ± 0.5 | 14.0 ± 0.2 | | −2.5 |
| | | 0.14 | 10.4 ± 0.2 | −11.6 ± 0.5 | 13.9 ± 0.2 | | −2.5 |
| | | 0.29 | 10.7 ± 0.3 | −10.7 ± 0.5 | 13.9 ± 0.3 | | −1.0 |
| Acetone-$d_6$, 0.05 *M* **5** | | 0.08 | 11.5 ± 0.3 | −6.6 ± 0.5 | 13.5 ± 0.3 | 1.9 × $10^2$ | −8.5 |
| Acetone-$d_6$, 0.07 *M* $LiClO_4$ | | 0.08 | 9.8 ± 0.2 | −12.5 ± 0.5 | 13.5 ± 0.2 | 1.9 × $10^2$ | −11.0 |
| $CCl_4$ | 2.24 | 0.02 | 13.3 ± 0.3 | −10.8 ± 0.5 | 16.5 ± 0.3 | | 62.5 |
| | | 0.10 | 13.1 ± 0.3 | −11.5 ± 0.5 | 16.5 ± 0.3 | | 63.5 |
| | | 0.19 | 13.7 ± 0.3 | −9.6 ± 0.5 | 16.6 ± 0.3 | 1 | 63.5 |
| $CDCl_3$ | 4.81 | 0.12 | 7.8 ± 0.1 | −17.6 ± 0.5 | 13.0 ± 0.1 | 4.4 × $10^2$ | −31.5 |
| DMF-$d_7$ | 37.6 | 0.10 | 10.4 ± 0.2 | −10.0 ± 0.5 | 13.4 ± 0.2 | 2.2 × $10^2$ | −18.0 |
| $CD_3CN$ | 37.5 | 0.31 | 7.8 ± 0.3 | −17.4 ± 0.5 | 13.0 ± 0.3 | 4.4 × $10^2$ | −31.5 |
| $CD_3OD$ | 32.6 | 0.09 | 10.6 ± 0.2 | −4.8 ± 0.5 | 12.0 ± 0.2 | 2.4 × $10^3$ | −38.0 |

[a] Calculated from rate data obtained by a computer-determined point by point fit of experimental to theoretical spectra at various temperatures. Uncertainties arise from statistical analysis of random errors. Any systematic errors could result in much larger errors in the derived parameters; this might be particularly true for activation parameters estimated for the intramolecular isomerization process in the presence of added **5** (sixth entry) because of some contribution from the intermolecular exchange process (see text and Figure 2). [b] kcal $mol^{-1}$. [c] cal $deg^{-1}$ $mol^{-1}$. [d] ±10%. [e] Coalescence temperature (90 MHz).

SCHEME I



librium between **6** and **6a** must lie almost entirely in favor of the covalent form (eq 2). In liquid $SO_2$



(2)

**6** **6a**

at −42°, however, the chemical shift of the azide was identical with that of **5** (δ 1.58), demonstrating that in this solvent **6** exists as a completely ionized species. This is not surprising in view of the well-documented ability of $SO_2$ to complex strongly with inorganic anions, forming monosolvates.[18]

From the data in Table II it is evident that there is no simple correlation between the dielectric constant of the solvent and activation parameters or relative rates, although with the exception of chloroform, which exhibits a higher rate than expected, a rough trend does exist between the log of the rates and Kosower's *Z* values.[19] The observed order of relative rates apparently reflects, at least in part, specific solvation interactions. The high rate in $CDCl_3$ could be attributed to hydrogen bonding to the azide function.[20] This effect may also contribute to the fast rate observed in methanol relative to the rates in aprotic solvents of comparable dielectric constant such as DMF and acetonitrile (Table II). It can also be seen that the $\Delta S^{\ddagger}$ value in methanol is significantly less negative than that found in DMF and acetonitrile. This appears to be consistent with the ionic path a (Scheme I), since the separation of opposite charges in going from covalent azide to transition state should require less reorganization of methanol molecules than the molecules of aprotic solvents.[20,21] Furthermore, the positive salt effects observed in acetone-$d_6$ are consistent with a process involving ionization in poorly ionizing media.[22]

After this work was completed, a brief paper by Closs and Harrison appeared describing a similar nmr study of trimethylcyclopropenyl azide.[23] Our results are in substantial agreement with those reported by these authors, who also suggested an ionic pathway for the isomerization. It should be mentioned, however, that tri-*tert*-butylcyclopropenyl azide, in contrast with trimethylcyclopropenyl azide, does not exhibit rearrangement to a *v*-triazine in competition with the degenerate isomerization process.[23]

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[18] (a) E. J. Woodhouse and T. H. Norris, *Inorg. Chem.*, **10**, 614 (1971); (b) G. Illuminati, *Rend. Accad. Naz. Lincei*, **11**, 303 (1968); (c) T. C. Waddington, "Non-Aqueous Solvent Systems," Academic Press, New York, N. Y., 1965, pp 256–259.

[19] (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 293 ff; (b) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry," Wiley-Interscience, London, 1971, p 40 ff.

[20] C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972), and references cited therein.

[21] (a) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968); (b) P. Haberfield, L. Clayman, and J. S. Cooper, *ibid.*, **91**, 787 (1969).

[22] (a) S. Winstein, S. Smith, and D. Darwish, *J. Amer. Chem. Soc.*, **81**, 5511 (1959); (b) A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961), and references cited therein; (c) R. A. Sneen and W. A. Bradley, *ibid.*, **94**, 6975 (1972), and references cited therein.

[23] G. L. Closs and A. M. Harrison, *J. Org. Chem.*, **37**, 1051 (1972).

## Experimental Section

Melting points are uncorrected. High-purity commercial solvents were employed for all spectral determinations. Infrared and ultraviolet spectra were recorded with a Perkin-Elmer Model 337 and a Cary Model 14 recording spectrophotometer, respectively. Mass spectra were obtained on a Hitachi RMU-6D mass spectrometer. The nmr spectra were recorded on a Bruker HFX-10 (90 MHz) or a Varian A-60A (60 MHz) instrument with variable-temperature capability. Line shapes were calculated by a CDC-6600 computer using the DNMR program developed by Binsch.[14] The rate-dependent *tert*-butyl resonances of 6 were simulated for the azide moiety exchanging among three equivalent sites. High-quality experimental spectra were obtained on the Bruker HFX-10 instrument by constantly checking the field homogeneity with an internal standard. The same scale (2.00 Hz/cm) was employed for both the experimental and computer-simulated spectra. Sample temperatures were determined by the chemical shift method employing a capillary containing methanol (or ethylene glycol) which was inserted into the sample tube. Reference to revised calibration curves provided the temperatures.[14c,24]

**1,2,3-Tri-*tert*-butyl-3-azidocyclopropene (6).**—To a solution of 1.00 g (3.28 mmol) of tri-*tert*-butylcyclopropenyl perchlorate in 10 ml of acetonitrile was added 0.228 g (3.51 mmol) of sodium azide (Matheson Coleman and Bell) in one portion. The mixture was stirred at 0° for 1 hr, after which dilution with 50 ml of water resulted in the separation of a colorless oil. The oil was then extracted into two 15-ml portions of ether. After the ether layer was washed with five 10-ml portions of water and dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo* to afford the cyclopropenyl azide (0.815 g, 100%) as a colorless oil which crystallized upon refrigeration. Azide 6 is quite stable and has been stored neat in the crystalline state at about −10° for periods exceeding 6 months with no detectable decomposition. Purification, if necessary, may be effected by short-path distillation, pot temperature 40–50° (0.03–0.05 mm): mp $\sim$2°; $\nu_{max}$ ($CCl_4$) 2950 (s), 2900 (m), 2870 (m), 2085 (vs), 1810 (w), 1475 (m), 1455 (m), 1390 (m), 1365 (m), 1258 (m), and 910 $cm^{-1}$ (m); $\lambda_{max}$ (cyclohexane) 295 nm ($\epsilon$ 28); mass spectrum *m/e* (rel intensity) 207 (33), 206 (11), 166 (23), 150 (16), 123 (68), 108 (10), 95 (18), 93 (10), 82 (10), 81 (15), 69 (18), 68 (15), 67 (23), 57 (100), 56 (10), 55 (23), 53 (12), 43 (27), 42 (38), 41 (29), and 39 (19).

*Anal.* Calcd for $C_{15}H_{27}N_3$: C, 72.24; H 10.91; N 16.85; mol wt, 249. Found: C, 72.36; H, 10.96; N, 16.74; mol wt, 250 (osmometric, $CCl_4$).

Reaction of azide 6 with potassium cyanide in aqueous acetonitrile followed by work-up as described above gave 1,2,3-tri-*tert*-butyl-3-cyanocyclopropene (80%), which was identical in all respects with an authentic sample prepared by the reaction of cation 5 with potassium cyanide: mp 30–31°; $\nu_{max}$ ($CCl_4$) 2970 (s), 2900 (m), 2870 (m), 2210 (m), 1845 (w), 1610 (w), 1475 (m), 1455 (m), 1380 (m), 1365 (m), and 1040 $cm^{-1}$ (m); nmr ($CCl_4$) $\delta$ 1.00 (9 H, s) and 1.27 (18 H, s); mass spectrum *m/e* (rel intensity) 233 (4), 176 (100), 162 (13), 150 (19), 135 (12), 57 (72), and 41 (40).

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**Registry No.**—5, 19985-80-9; 6, 38409-72-2; 1,2,3-Tri-*tert*-butyl-3-cyanocyclopropene, 40893-42-3.

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[24] (a) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); (b) *ibid.*, **40**, 2227 (1968).

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# Substituent Effects in the Ring Expansion Reactions of Isopropenylcycloalkanols by *tert*-Butyl Hypochlorite

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1-Isopropenylcyclobutanol was prepared by the conventional Grignard method. 1-Isopropenylcyclopropanol was synthesized by the addition of isopropenylmagnesium bromide to 1,3-dichloroacetone followed by ferric chloride induced coupling. The cyclobutanol underwent the chlorinative ring expansion with *tert*-butyl hypochlorite to produce 2-methyl-2-(chloromethyl)cyclopentanone in 81% yield. The cyclopropanol proved to be so labile that it spontaneously rearranged to 2,2-dimethylcyclobutanone. The acid-catalyzed ring expansion of 1-isopropenylcyclobutanol was accomplished with sulfuric acid in the presence of 2,4-dinitrophenylhydrazine. A slight preference for phenyl migration over methylene migration (60:40) was demonstrated in the reaction of 1-isopropenyl-1-indanol with *tert*-butyl hypochlorite. The substituent effect studies were extended to *trans*-1-isopropenyl-2-methylcyclopentan-1-ol and *exo*-2-isopropenylnorbornan-2-ol. Structure assignments for the ring expansion products from these two substrates were based on an nmr study. Methine carbon migration was shown to predominate over methylene carbon migration. These results were rationalized in terms of a nonconcerted mechanism with some carbonium-ion character in the transition state. The observed stereochemistry of the product ketones was explained on the basis of the conformational preference of the isopropenyl group in the reactant alcohol.

## Part A

Carbocyclic ring expansion is a useful synthetic trick of the organic chemist.[1] Some of the classical methods applied to ring homologation by one carbon atom are the Demjanov[2] rearrangement, the Tiffeneau–Demjanov[2] rearrangement, and the pinacol[3] rearrangement. Well-known ring homologation methods which incorporate a heteroatom into the ring are the Baeyer–Villiger reaction (oxygen)[4] and the Beckmann rearrangement (nitrogen).[5] Several years ago we discovered a chlorinative ring-expansion reaction which homologates a ring by one carbon atom (eq 1).[6] This

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[1] C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

[2] P. A. Smith and D. R. Baer, "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, p 157.

[3] Y. Pocker in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Wiley, New York, N. Y., 1964, p 1.

[4] C. H. Hassall, "Organic Reactions," Vol. 9, Wiley, New York, N. Y., 1957, p 73.

[5] L. G. Donaruma and W. Z. Heldt, "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, p 1.

[6] C. R. Johnson, C. J. Cheer, and D. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).