2,3:4,5 structure has generally been formulated.[3,7]
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(15) The thermal parameters of the atoms (Table IV) and observed and calculated structure factors are available as supplementary material; see paragraph at end of paper.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 35. The Search for a Dialkylaminyl Rearrangement. Ring Opening of *N*-Cyclobutyl-*N*-*n*-propylaminyl[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada. *Received June 4, 1979*

Abstract: A search for a dialkylaminyl radical which rearranges at a rate suitable for study by kinetic EPR spectroscopy has shown that cyclobutyl-*n*-propylaminyl is such a species. This radical undergoes ring opening, and the rate constant for this process can be represented by $\log (k_r/s^{-1}) = (12.8 \pm 1.5) - (10.5 \pm 1.5)/\theta$, where $\theta = 2.3RT$ kcal/mol.

The most generally useful method for determining the rate at which a substrate reacts with a particular class of free radicals is to utilize a radical from this class which can undergo a competitive, irreversible rearrangement or scission. The kinetic scheme can be represented as

$$\begin{array}{l} R_A^{\cdot} + \text{substrate} \xrightarrow{k_A} \text{product A} \\ \quad\downarrow k_r \\ R_B^{\cdot} + \text{substrate} \longrightarrow \text{product B} \end{array}$$

Provided that the rate constant for the rearrangement, k_r, and the concentration of the substrate are both known, then the desired rate constant, k_A, can be calculated from the product ratio, i.e.

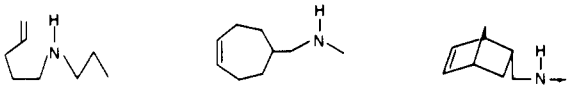
$$k_A = k_r \frac{[\text{product A}]}{[\text{product B}][\text{substrate}]}$$

There is now a well-filled stable[3] of primary alkyls for which rearrangement rates have been measured over a range of temperature by kinetic EPR spectroscopy.[4-10] There are also a few specific carbon-centered radicals from other classes for which the rearrangement rates have been measured by EPR (e.g., secondary alkyl,[11] acyl,[7,12] and alkoxycarbonyl[13]). Comparable data on heteroatom-centered radicals are almost nonexistent.[14] For example, no absolute rate constant has been measured for *any* unimolecular reaction of a dialkylaminyl radical. This is not to say that dialkylaminyl rearrangements are unknown. Indeed, a number of alkenylalkylaminyls have been shown to undergo intramolecular additions under neutral conditions[15] to form monocyclic,[16,17] bicyclic,[18,19] and even tricyclic[20] products. However, these results are of qualitative significance only. Cyclization rates were not measured and the experiments were such[15] that not even a rough estimate of rate can be made.

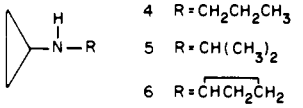
In this paper we report on our search by EPR for a suitably "paced" dialkylaminyl rearrangement. Naturally, this search began among the known rearrangements, but all were found to proceed much too slowly for study by EPR. Our investigation of other potential dialkylaminyl rearrangements uncovered several that were too fast and one that was too slow, but eventually the ring opening of cyclobutyl-*n*-propylaminyl proved to be "just right".

Experimental Section

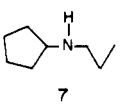
Materials. Amines. *N*-4-Pentenyl-*N*-*n*-propylamine, **1**, was prepared from bromopent-4-ene (0.05 mol) and *n*-propylamine (0.5 mol) by using the procedure described by Surzur et al.[21] We are also indebted to Professor C. J. Michejda for a sample of this amine and the derived tetrazene. Amines **2** and **3** were gifts from Dr. O. E. Edwards



1 **2** **3**



4 R = $CH_2CH_2CH_3$
5 R = $CH(CH_3)_2$
6 R = $\overline{CHCH_2CH_2}$



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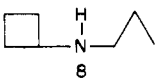
and from Professor B. Waegell and Dr. R. Furstoss, respectively. The cyclopropylamines **4**, **5**, and **6** were prepared by heating cyclopropylamine (0.5 mol) with the appropriate alkyl bromide (0.05 mol) in sealed tubes at 70 °C for 20 h. The amine, **7**, was prepared by the same general procedure as **1**.

N-Cyclobutyl-*N*-*n*-propylamine, **8**, was prepared from cyclobutanecarboxylic acid (which was itself prepared from trimethylene dibromide and diethyl malonate)[22] via the Schmidt reaction.[23] To 25



8

g (0.25 mol) of cyclobutanecarboxylic acid in a 1-L distillation flask were added 200 mL of $CHCl_3$, 50 mL of concentrated H_2SO_4, and 16.9 g (0.26 mol) of solid NaN_3 in such portions as to maintain the well-stirred mixture at 45 °C. After standing for 48 h at room temperature, the solution was rendered alkaline with 150 g of KOH in 300 mL of water and the cyclobutylamine was distilled into 50 mL of

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concentrated HCl. Upon evaporation, 24.2 g (89.7%) of the amine hydrochloride remained as white crystals. The amine was liberated with aqueous KOH and converted to **8** by reaction with 1-bromopropane following the general procedure outlined above. Compound **8** was purified by preparative VPC: ^{1}H NMR ($CDCl_3$) δ values in parts per million downfield from Me_4Si 0.8–1.1 (t, 3 H, CH_3), 1.1–2.4 (m, 9 H $CH_2CH_2CH_2C$, CCH_2C, and NH), 2.4–2.6 (t, 2 H, NCH_2C), 3.0–3.5 (m, 1 H, C_2CHN). Anal. Calcd for $C_7H_{15}N$: C, 74.33; H, 13.27; N, 12.38. Found: C, 74.14; H, 13.12; N, 12.44.

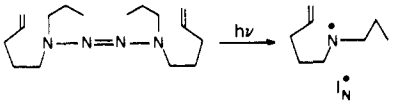
Dialkylaminodiethoxyphosphines. These compounds were prepared by the slow addition under nitrogen of 1.5 g of diethyl chlorophosphite in 10 mL of pentane to 0.01 mol of dialkylamine and 1.0 g (0.01 mol) of triethylamine in 50 mL of pentane. The triethylamine hydrochloride precipitated and was filtered off, and the pentane was then evaporated under nitrogen. In the case of **8**, for example, the yield of aminophosphine was 1.5 g (64%).

EPR Experiments. Our general experimental procedure and the techniques used to measure the absolute rate constants for free-radical rearrangements over a range of temperatures have been described in some detail in earlier publications.[4-11] All samples were carefully deoxygenated and all traces of hydroperoxides were removed from the solvents and reagents in order to avoid the formation of nitroxide radicals. Spectra were recorded on a Varian E 104 EPR spectrometer, and the EPR parameters were measured by using a ^{1}H NMR field marker and microwave frequency counter, with correction for the placement of the field marker.

Radical Generation. The most satisfactory (i.e., "cleanest" and simplest) method for generating all the dialkylaminyls (or their rearrangement products) was found to be by direct hydrogen atom abstraction from the amine in cyclopropane by using photochemically produced *tert*-butoxy radicals.[24]

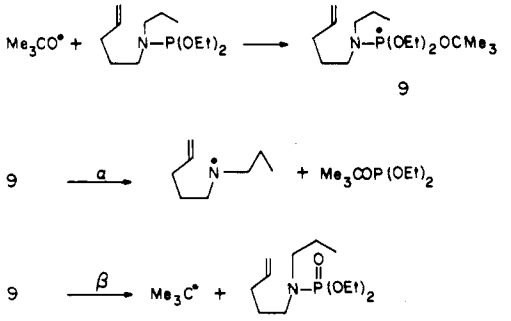
$$Me_3CO\cdot + R_1R_2NH \rightarrow Me_3COH + R_1R_2N\cdot$$

Why this route should be so effective is a bit of a mystery.[26] That is, the hydrogen atoms attached to the α carbons might be expected to be the most labile in view of the stabilization of the resultant aminoalkyl radical by conjugative electron delocalization with the nitrogen lone pair. In fact, attack at the α carbon does appear to be favored at high temperatures.[28] However, there can be no doubt that the amino hydrogen is abstracted in all cases. This was confirmed for the radical from **1** by showing that the same radical, $\mathbf{1}_N^{\cdot}$, was produced by photolysis of the corresponding tetrazene.



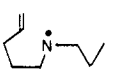
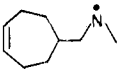
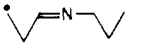
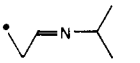
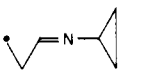
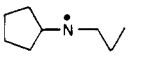
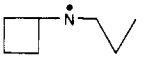
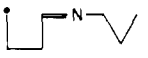
$\mathbf{1}_N^{\cdot}$

The same radical was also produced on photolysis of di-*tert*-butyl peroxide and the corresponding aminodiethoxyphosphine,[25,29] though in this case the *tert*-butyl radical was also observed above 210 K indicating that the intermediate phosphoranyl radical, **9**, underwent β as well as α scission.



Several other amine derived radicals were also shown to be identical with the radicals derived from the corresponding aminophosphines. Because of the presence of the *tert*-butyl radical in these systems, the amine/di-*tert*-butyl peroxide system was used in the kinetic work on the cyclobutyl-*n*-propylaminyl ring-opening reaction. Qualitatively similar results were obtained with the aminophosphine but rate constants could not be evaluated reliably because of the *tert*-butyl "contaminant".

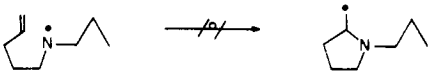
Table I. EPR Parameters and Structures of Radicals Derived from Amines **1–8**[a]

amine	radical	temp range, K[b]	g	a^N	a^H [c]
1		180–400	2.0047	14.2	36.1 (4)
2		170–350	2.0040	14.6	37.8 (2) 27.2 (3)
3		170–250	2.0043	14.5	37.5 (2) 26.0 (3)
4		135–275	2.0027		29.2 (2) 22.1 (2)
5		135–275	2.0027		29.2 (2) 22.1 (2)
6		135–275	2.0027		29.2 (2) 22.1 (2)
7		150–350	2.0040	14.2	36.4 (2) 29.2 (1)
8		170[d]	2.0039_6	14.1	36.2 (2) 29.0 (1)
8		270[d]	2.0025_2		28.1 (2) 21.8 (2)

[a] Hyperfine splittings are given in gauss. Typical experimental conditions were 0.1 M amine and 0.7 M di-*tert*-butyl peroxide in cyclopropane at temperatures below 300 K and in *n*-heptane or *n*-hexadecane at higher temperatures. The EPR spectra of $\mathbf{1}_N^{\cdot}$, $\mathbf{4}_C^{\cdot}$, $\mathbf{7}_N^{\cdot}$, and $\mathbf{8}_N^{\cdot}$ were confirmed by generating the radicals from the corresponding aminodiethoxyphosphine at 193 K ($\mathbf{1}_N^{\cdot}$ from 173 to 400 K). $\mathbf{1}_N^{\cdot}$ was also generated from the corresponding tetrazene. [b] The maximum temperature was, in general, the temperature above which the signal could no longer be observed. [c] The numbers of equivalent hydrogens are given in parentheses. [d] See text.

Results and Discussion

The reaction of **1** with photochemically generated *tert*-butoxy radicals gave the EPR spectrum of the corresponding aminyl radical, $\mathbf{1}_N^{\cdot}$, at temperatures from 180 to 400 K. This radical was identified by its characteristic g value[30] and by its nitrogen and β-hydrogen hyperfine splittings[31] (see Table I). Its identity was further confirmed by its independent generation from the corresponding tetrazene[17,25,32] and aminophosphine[29] (see Experimental Section). At no temperature was there any sign of the hoped-for primary alkyl which would certainly have been observed if the rate constant for cyclization were $\geq$ca. 10^3 s^{-1}. If we assume an Arrhenius preexponential factor for cyclization equal to that found for cyclization of 6-hepten-2-yl, viz.,[11] $10^{9.8}$ s^{-1}, then the absence of $\mathbf{1}_C^{\cdot}$ at 400 K means that the activation energy for cyclization of $\mathbf{1}_N^{\cdot}$ is $\geq$12.4 kcal/mol, and that the rate constant at 25 °C is $\leq$5 s^{-1}.

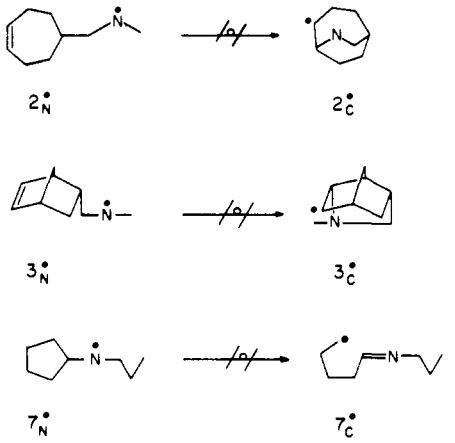


$\mathbf{1}_N^{\cdot}$ $\mathbf{1}_C^{\cdot}$

The amines **2**, **3**, and **7** also gave only the corresponding aminyl radicals, $\mathbf{2}_N^{\cdot}$, $\mathbf{3}_N^{\cdot}$, and $\mathbf{7}_N^{\cdot}$, at all temperatures where radicals could be observed (see Table I).

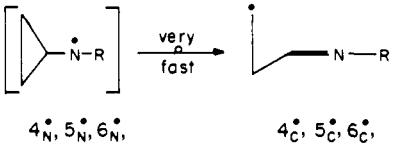
Table II. Rearrangement of $8_N^{\cdot}$ to $8_C^{\cdot}$ in Cyclopropane

temp, K	$[8_N^{\cdot}] \times 10^8$, M	$[8_C^{\cdot}] \times 10^8$, M	$k_r/2k_t^{CC} \times 10^8$, M
198	$11._3$	0.9	0.97
208	$10._3$	1.9	2.2
218	8.4	3.6	5.1
227	7.1	5.7	$10._2$
237	5.6	8.1	$19._9$
247	3.7	$10._9$	43



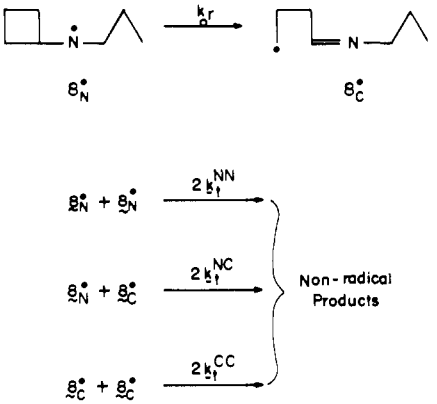
By way of contrast, even at 135 K the cyclopropylamines, **4, 5,** and **6,** all gave radicals with identical EPR spectra, the parameters for which (Table I) clearly label these radicals as the ring-opened primary alkyls, $4_C^{\cdot}$, $5_C^{\cdot}$, and $6_C^{\cdot}$.[33]

Since $4_N^{\cdot}$, $5_N^{\cdot}$, and $6_N^{\cdot}$ underwent very rapid ring opening whereas $7_N^{\cdot}$ does not appear to undergo such a reaction, we next



turned our attention to the intermediate case of a cyclobutylaminyl. The amine, **8**, gave the corresponding aminyl, $8_N^{\cdot}$, at 170 K and a primary alkyl, $8_C^{\cdot}$ at 270 K (see Table I). It is clear that $8_N^{\cdot}$ rearranges to $8_C^{\cdot}$ and, since both radicals could be observed together at intermediate temperatures, it was a comparatively straightforward matter[4-13] to measure the rate of this dialkylaminyl rearrangement.

The overall kinetic scheme can be represented by



Provided the rate constant for the cross-reaction between $8_N^{\cdot}$ and $8_C^{\cdot}$, $2k_t^{NC}$, is equal to the rate constant for the bimolecular self-reaction of $8_C^{\cdot}$, $2k_t^{CC}$, then the rate constant for the rearrangement, k_r, can be determined from the concentration of $8_N^{\cdot}$ and $8_C^{\cdot}$ present under steady illumination via the equation[4-11]

$$\frac{k_r}{2k_t^{CC}} = [8_C^{\cdot}](1 + [8_C^{\cdot}]/[8_N^{\cdot}]) \quad (1)$$

Since $8_C^{\cdot}$ is an unhindered alkyl radical its bimolecular self-reaction will certainly be diffusion controlled,[4,8,9,35-38] and this was confirmed by the usual kinetic EPR method[39] which gave $2k_t^{CC} = 6.0 \times 10^9$ and 1.1×10^{10} M^{-1} s^{-1} at 237 and 247 K, respectively, in cyclopropane. The aminyl radical also decayed with "clean" second-order kinetics at temperatures where the rearrangement was unimportant. At 179 K in cyclopropane, $2k_t^{NN} = 8.7 \times 10^8$ M^{-1} s^{-1} which indicates that this reaction also proceeds at, or close to, the diffusion-controlled limit. It is therefore safe to assume that the cross-reaction is diffusion controlled, i.e., $2k_t^{NC} = 2k_t^{CC}$, and so eq 1 is applicable to this rearrangement.

Values of $k_r/2k_t^{CC}$ based on experimental data obtained in cyclopropane and calculated according to eq 1 are given in Table II. The temperature dependence can be represented by

$$\log (k_r/2k_t^{CC}/M^{-1}) = (0.2 \pm 0.5) - (7.5 \pm 0.5)/\theta \quad (2)$$

where $\theta = 2.3RT$ kcal/mol.

The experimental rate constants for the bimolecular self-reactions of $8_N^{\cdot}$ and $8_C^{\cdot}$ in cyclopropane taken together can be represented by

$$\log (2k_t/M^{-1} s^{-1}) = (12.6 \pm 1.0) - (3.0 \pm 1.0)/\theta \quad (3)$$

which is in reasonable agreement with the equation

$$\log (2k_t/M^{-1} s^{-1}) = (11.6 \pm 0.5) - (2.1 \pm 0.5)/\theta$$

obtained previously for the diffusion-controlled bimolecular self-reaction of cyclopentylcarbinyl (the radical product of the 5-hexenyl cyclization) in cyclopropane.[8]

Combining eq 2 and 3 we obtain the following Arrhenius equation for the rearrangement of $8_N^{\cdot}$

$$\log (k_r/s^{-1}) = (12.8 \pm 1.5) - (10.5 \pm 1.5)/\theta \quad (4)$$

The preexponential factor of $10^{12.8\pm1.5}$ s^{-1} is in the range anticipated[40] for a simple ring-opening radical rearrangement. The extrapolated rate constant at 25 °C is 1.2×10^5 s^{-1}, and this value is probably reliable to within a factor of two or three. It would appear that the cyclobutyl-*n*-propylaminyl radical undergoes ring opening at about the same rate at ambient temperatures as the 5-hexenyl radical undergoes ring closure (viz., $k_r^{25°C} = 1.06 \times 10^5$ s^{-1}).[8] We hope that it will eventually play as important a role in quantitative kinetic studies of dialkylaminyl radical chemistry as 5-hexenyl has played in primary alkyl radical chemistry.

Acknowledgment. We should like to thank Professor C. J. Michejda, Professor B. Waegell, and Dr. R. Furstoss for the chemicals which helped to get this work underway. We should also like to thank Dr. D. Griller for his help and advice during this work and Professor J.-M. Surzur for some very useful comments.

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(15) Protonated and metal complexed aminyls are known to be much more reactive than neutral aminyls and, if their structure is appropriate, they cyclize readily.[14] Our present results confirm the low reactivity toward intramolecular additions of neutral aminyls and serve to put an upper limit on the rate constant for cyclization (see Results and Discussion). Since cyclization is undoubtedly rather slow, we tentatively suggest that in at least some prior work the conditions may not have been quite as neutral (nonacidic) as the investigators believed.
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Propellanes. 13. On the Magnitude of the Norcaradiene–Cycloheptatriene Energy Difference

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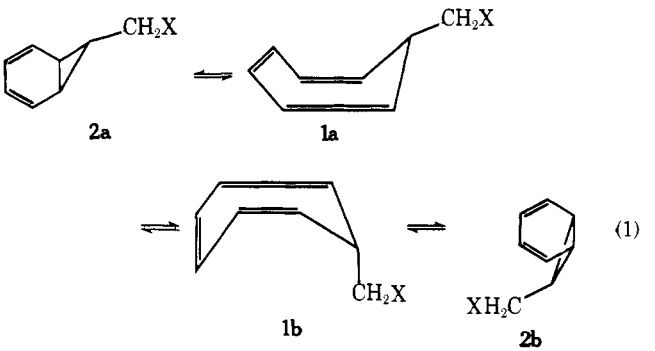
Abstract: The synthesis and solvolysis of dinitrobenzoates **15c–22c** are described. From the kinetic data, one can conclude that the *anti*-norcaradienylcarbinyl ion from **18c** is electronically stabilized relative to the syn ion derived from **22c.** More importantly, the data reveal that the norcaradiene–cycloheptatriene energy gap for a 7-alkyl substituted cycloheptatriene is only 4.0–4.5 kcal/mol, which is far below the previously estimated value (11 ± 4 kcal/mol).

Introduction

The norcaradiene–cycloheptatriene equilibrium problem was rejuvenated by Doering's demonstration[2] that Büchner's esters[3] were actually cycloheptatrienes rather than norcaradienes. Since that time, numerous substituted systems have been synthesized,[4] including some for which one could observe both norcaradiene and cycloheptatriene tautomers. The energy difference between the valence isomers for the parent system was unknown, but was estimated as 11 ± 4 kcal/mol by Doering and Willcott.[5] This widely quoted estimate, which is unfortunately still sometimes utilized,[6] came from a consideration of bond energy terms. An experimental approach[7] to the determination of the desired equilibrium constant, patterned upon Huisgen's[8] dilatometric study of the cyclooctatetraene–bicyclooctatriene valence equilibrium, was thwarted when the authors put more faith in the Doering–Wilcott estimate than in their own data. Their results in fact lead to a free energy difference of 4.0–4.5 kcal/mol, a value in full accord with our data[9] (vide infra).

Our approach to the determination of the norcaradiene–cycloheptatriene energy gap is based on Sargent's demonstration[10] that cycloheptatrienylcarbinyl systems solvolyze via preequilibrium isomerization to norcaradienylcarbinyl de-



(1)

rivatives. Conformational factors permit two distinct geometries for the monocyclic series (eq 1). Thus while Hoffmann[11] and Günther[12] have discussed the symmetry factors which stabilize the ions derived from **2a** and **2b** (and other seven-electron-withdrawing-group-substituted norcaradienes), they have not distinguished between them.

Paquette[13] has investigated the solvolysis of the conformationally fixed bicyclic systems **3** and **4**. Although not initially apparent,[13a] low temperature ^{13}C NMR indicated that **4** is closer in energy to its solvolytically reactive tricyclic tautomer

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