Table III

—Undeuterated—		—Deuterated—	
m/e	(%)	m/e	(%)
98	(<1.0)		
99	(37.1)	99	(<1.0)
100	(5.8)	100	(44.2)
101	(3.0)	101	(7.5)
102	(<1.0)	102	(<1.0)
114	(<1.0)		
115	(12.9)	115	(<1.0)
116	(3.8)	116	(12.1)
117	(<1.0)	117	(9.1)
118	(<1.0)	118	(2.2)
271	(<1.0)		
272	(19.6)	272	(<1.0)
273	(<1.0)	273	(18.3)
274	(1.4)	274	(<1.0)
275	(<1.0)	275	(<1.0)

was reduced with deuterium gas (99.5% D). Filtration and concentration provided material recrystallized from ether–hexane to yield the pure deuterated trans carbomethoxy compound, mp 145–148°,[6] whose mass spectrum had molecular ion peaks at m/e 318 (2.3% of base), 319 (4.5), 320 (12.8), and 321 (4.5). Molecular ion peaks for the corresponding undeuterated material appeared at m/e 318 (16.5), 319 (4.0), 320, and 321 (<1.0%). When undeuterated 2, R = COOMe, was treated as described above with D_2 and Pd/C, then recovered and purified, its molecular ion peak intensities were m/e 318 (18.0), 319 (4.0), 320, and 321 (<1.0).

The liquors from crystallization of the deuterated trans carbomethoxy material, which were relatively rich in the cis product,

were subjected to vpc–ms; compound 3, R = COOMe, from this source gave a mass spectrum whose molecular ion distribution was similar to that of 2, R = COOMe.

Hydroxymethyl Substituent. Compound 1, R = CH_2OH, was deuterated catalytically using the procedure and conditions described above. The product was filtered, concentrated in vacuo, and trimethylsilylated directly for vpc–ms. The major mass spectral peaks and their intensities for both the undeuterated and deuterated cis product are shown in Table I. In addition, the following peaks and intensities for fragments containing C-3, shown in Table III, are of particular value in assessing the extent of deuterium incorporation.

Mass spectra of the undeuterated and deuterated trans products, 2, R = CH_2OSiMe_3, were obtained from the same preparations and had major mass spectral peaks similar to those of 3, R = CH_2-$OSiMe_3$, and indicating a similarly small extent of excess deuterium incorporation.

An entire undeuterated hydrogenation mixture containing both 2 and 3, R = CH_2OH. was treated with D_2 as described above. When reisolated and trimethylsilylated, this material was subjected to vpc–ms and gave spectra indicating negligible deuterium incorporation.

Alkylation of Tertiary Alkyl Halides with Trialkylaluminums. A Model for Initiation and Termination in Cationic Polymerizations

J. P. Kennedy,* N. V. Desai,[1a] and S. Sivaram[1b]

Contribution from the Institute of Polymer Science, The University of Akron, Akron, Ohio 44304. Received January 23, 1973
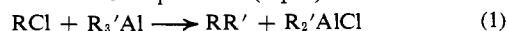
Abstract: The alkylation of *tert*-butyl halide with trimethylaluminum, a reaction which quantitatively and rapidly yields neopentane, can be viewed as a model for cationic polymerization initiation and termination. In an attempt to gain insight into the mechanism of these reactions, we have examined the effect of methyl chloride, methyl bromide, methyl iodide, and cyclopentane solvents on the rate of alkylation of *tert*-butyl chloride, bromide, and iodide with trimethylaluminum in the temperature range +50 to −80°. The reactivity of *tert*-butyl halides toward alkylation was found to decrease in the order *t*-BuCl > *t*-BuBr > *t*-BuI. The nature of the solvent also exerts a significant influence, the rates of alkylation decreasing in the order MeCl > MeBr > MeI ≫ cyclopentane. While the individual rates were significantly different, the activation energies calculated for the alkylation of *tert*-butyl halides with trimethylaluminum were found to be constant both in the three methyl halide solvents (10–11.5 kcal/mol) and in cyclopentane (15–16.5 kcal/mol). A mechanism consistent with these observations has been proposed. The stereochemistry of alkylation has been investigated by the reaction of optically active α-phenethyl chloride with triethylaluminum. The significance of these results for the understanding of the mechanism of initiation and termination of cationic polymerization is discussed.

In a previous publication[2] we reported the facile, quantitative reaction of *tert*-alkyl chlorides with trialkylaluminums in MeCl solvent at −78° to produce

(1) (a) Taken in part from the Masters Thesis of N. V. D., submitted to the University of Akron, December 1972; (b) Postdoctoral research associate.

(2) J. P. Kennedy, *J. Org. Chem.*, **35**, 532 (1970).

quarternary carbon compounds (eq 1). The reaction

$$RCl + R_3'Al \longrightarrow RR' + R_2'AlCl \qquad (1)$$

was proposed to involve the intermediacy of a carbenium ion–counteranion pair (*e.g.*, *t*-Bu⁺ Me₃AlCl⁻). The same *tert*-butyl cation–counteranion pair has also been invoked to explain the initiation of cationic polymer-
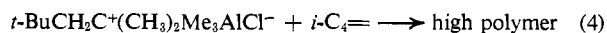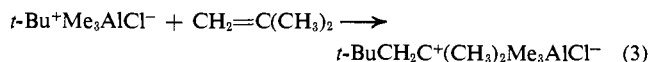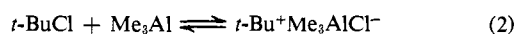
Table I. Rates of Alkylation of tert-Butyl Halides with Trimethylaluminum in Various Solvents

Solvent	t-BuCl	E_a, kcal/mol	t-BuBr	E_a, kcal/mol	t-BuI	E_a, kcal/mol
			k, l./(mol sec) × 10³, temp, °C			
CH₃Cl	~18,[a] −80 (estimated)		1.7, −60		0.40, −20	
				10.0		9.7
CH₃Br	1.4, −50		4.9, −50 1.8, −40		0.86, −10 0.36, 0	
		11.4		10.0		10.0
CH₃I	4.1, −40 2.0, −40		10.0, −20 0.10, −40		0.69, +10 0.26, +10	
		10.0		10.0		11.5
	4.9, −30		0.30, −30 0.58, −20		0.52, +20	
Cyclopentane	0.07, −10		0.03, −10		0.03, +40	
		16.5		15.0		16.0
	0.20, 0		0.22, +10		0.07, +50	

[a] Reaction too fast for rate measurement even at −80°.

ization using the t-BuCl–Me₃Al initiator–coinitiator system.[3,4]

Extensive studies have shown that cationically polymerizable olefins can be stirred in a variety of solvents in the presence of trialkylaluminums for long periods of time without reaction. However, upon addition of tertiary alkyl halides to these quiescent systems, immediate and vigorous polymerization commences and high polymer is obtained.[5-7] For example, the polymerization of isobutylene by the t-BuCl–Me₃Al system has been explained in terms of the following events (eq 2-4).

$$t\text{-BuCl} + Me_3Al \rightleftharpoons t\text{-Bu}^+Me_3AlCl^- \quad (2)$$

$$t\text{-Bu}^+Me_3AlCl^- + CH_2{=}C(CH_3)_2 \longrightarrow$$
$$t\text{-BuCH}_2C^+(CH_3)_2Me_3AlCl^- \quad (3)$$

$$t\text{-BuCH}_2C^+(CH_3)_2Me_3AlCl^- + i\text{-}C_4{=} \longrightarrow \text{high polymer} \quad (4)$$

In this sense the alkylation of t-BuCl with Me₃Al can be viewed as a model for initiation followed by immediate termination. Therefore, we have extended our alkylation studies by Me₃Al to a series of tert-butyl halides (t-BuCl, t-BuBr, t-BuI) in polar (MeCl, MeBr, MeI) and nonpolar (cyclopentane) solvents in the temperature range +50 to −80°.

The reaction of halohydrocarbons with trialkylaluminums and dialkylaluminum halides in solvents other than methyl halides and at temperatures higher than 0° has been studied previously.[8] However, under these conditions, product analysis showed medium to high conversions to a variety of products, which arose by a variety of reaction paths, i.e., coupling, reduction, elimination, and polymerization.

Results

Figures 1 and 2 show representative data of conversions to neopentane as a function of time for a series of tert-butyl halides in MeBr solvent, and for tert-butyl bromide in a series of methyl halide solvents, respectively. In Table I are compiled pseudo-second-order rate constants determined graphically by plotting the

(3) J. P. Kennedy in "Polymer Chemistry of Synthetic Elastomers," Part 1, J. P. Kennedy and E. Tornqvist, Ed., Interscience, New York, N. Y., 1968, Chapter 5A, p 291.
(4) J. P. Kennedy and J. K. Gillham, Advan. Polym. Sci., 10, 1 (1972).
(5) J. P. Kennedy, U. S. Patent 3,349,065 (1967).
(6) J. P. Kennedy, J. Polym. Sci., Part A-1, 6, 3139 (1968).
(7) J. P. Kennedy, J. Macromol. Sci., Chem., 5, 861 (1969).
(8) D. B. Miller, J. Org. Chem., 31, 908 (1966); S. Pasynkiewicz and W. Kuran, J. Organometal. Chem., 16, 43 (1969).

inverse of tert-butyl halide concentrations against time. Only the initial, linear parts of the rate plots were used to calculate rates. In general, beyond approximately 50% conversions, the linear slopes showed a sharp increase which is most likely due to the intervention of Me₂AlCl, MeAlCl₂, etc. at the latter stages of the reaction (eq 1). For purposes of comparison, all rates shown in Table II have been interpolated or extrapolated

Table II. Rates of Alkylation of tert-Butyl Halides with Trimethylaluminum at −40°

	k, l./(mol sec) × 10⁶			
t-BuX	MeCl	MeBr	MeI	Cyclopentane
t-BuCl	>10⁹ [a]	4100	2000	1.2
t-BuBr	13,000	1800	100	0.7[b]
t-BuI	75[c]	15[c]	3.2[c]	0.005[b]

[a] Calculated from the observed rate at −80°, assuming an activation energy of ~10 kcal/mol. [b] Calculated from the measured rates in the temperature range −0 to +50°. [c] Calculated from the measured rates in the temperature range −20 to +20°.

to −40°. Activation energies were calculated from rates at two temperatures and are accurate within ±1.0 kcal/mol.

In all cases, alkylation proceeded without side reactions (e.g., elimination) to yield neopentane quantitatively.

Independent low temperature nmr studies of Me₃Al in various methyl halide solvents show that the rate of bridge-terminal methyl group exchange in the trimethylaluminum dimer is fastest in MeCl followed by MeBr and MeI. Experimentally one observes in the nmr spectrum a splitting of the methyl singlet into two signals characteristic for the bridge and terminal methyl groups at −80° for MeCl, −70° for MeBr, and at −55° for MeI.

Discussion

Examination of Table II reveals that (a) in all solvents t-BuCl is alkylated fastest followed by t-BuBr and t-BuI; (b) alkylation is faster in polar methyl halide solvents than in nonpolar cyclopentane; (c) among the methyl halides, alkylation is fastest in MeCl followed by MeBr and MeI; (d) the activation energies for the alkylation of tert-butyl halides with Me₃Al are the same in all methyl halides (10–11.5 kcal/mol); and (e) the

Figure 1. Relative reactivities of various *tert*-butyl halides with trimethylaluminum in MeBr solvent.

Figure 2. Relative reactivity of *tert*-butyl bromide with trimethylaluminum in various methyl halide solvents.

activation energies obtained for the alkylation of *tert*-butyl halides in cyclopentane solvent are about 50% higher (15–16.5 kcal/mol) than those obtained for alkylations in methyl halides. A mechanism consistent with these findings is proposed in Scheme I.

Scheme I. Proposed Mechanism of Alkylation of *tert*-Butyl Chloride by Trimethylaluminum in Methyl Chloride Solvent[a]

[a] The hydrogen atoms in trimethylaluminum have been omitted.

Trimethylaluminum is dimeric in the solid,[9a] liquid,[9b] and gaseous states.[9c] It has also been shown that a

(9) (a) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953); (b) K. S. Pitzer and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **68**, 2204 (1946); (c) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941).

rapid exchange of the bridge and terminal methyl groups occurs at room temperature.[10] However, upon cooling to $-40°$, methyl exchange is frozen out, as indicated by the appearance of two signals in the nmr spectrum. The precise mechanism of methyl exchange in $(Me_3Al)_2$ is still a matter of speculation. It can either involve complete dissociation to monomer followed by recombination (eq 5)[11] or can occur intra-

$$[Me_3Al]_2 \rightleftharpoons 2Me_3Al \qquad (5)$$

molecularly, wherein only one of the methyl bridges is broken followed by bond rotation (Scheme I).[10,12]

According to earlier investigations,[13] the relatively slow rate of the bridge-terminal methyl exchange in $(Me_3Al)_2$ in cyclopentane solvent is significantly increased by the addition of methyl chloride ("bridge opener"). This rate-accelerating effect of methyl chloride was explained by postulating the half-bridged intermediate **2** (*cf.* in Scheme I). In the presence of large amounts of methyl chloride (*i.e.*, in methyl chloride solution) intermediate complex **2** rapidly further dissociates into monomeric trimethylaluminum–methyl chloride complex, the active form of trimethylaluminum. The monomeric species **3** and the half-bridged dimer complex **2** are in a rapid equilibrium. There is no direct nmr evidence (chemical shift of methyl groups on the aluminum bearing the coordinated methyl chloride) for $(CH_3)_3Al\leftarrow ClMe$ or $(CH_3)_6$-$Al_2\leftarrow ClMe$ complexes, most likely because the concentration of these species is very low and/or the coordination equilibrium is too rapid. In contrast to

(10) N. Muller and D. E. Pritchard, *ibid.*, **82**, 248 (1960).
(11) K. C. Williams and T. L. Brown, *ibid.*, **88**, 5460 (1966).
(12) K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. F. Borchert, *J. Phys. Chem.*, **69**, 3418 (1965).
(13) J. P. Kennedy and G. E. Milliman, *Advan. Chem. Ser.*, No. 91, 287 (1969).

this system, nmr evidence is available for the existence of an i-Bu$_3$Al←ClMe complex.[13]

Nmr experiments indicate that the rate of bridge-terminal methyl group exchange in (Me$_3$Al)$_2$ is fastest in MeCl followed by MeBr and in turn by MeI. The rate of opening the (Me$_3$Al)$_2$ by methyl halides decreases in the order MeCl > MeBr > MeI. This sequence is probably due to the increasing size and decreasing basicity of the halogen in the above series.

If t-BuCl is added to trimethylaluminum in methyl chloride, the tertiary chloride, on account of its more basic chlorine atom, displaces a methyl chloride molecule from complex 3 and produces complex 4. According to our kinetic results, the reaction between (CH$_3$)$_3$Al←ClMe and t-BuCl is rate determining. The driving force of the reaction is provided by the formation of the $tert$-butyl cation. The collapse of the incipient ion pair to give rise to neopentane is a rapid subsequent event. In the presence of a cationically polymerizable monomer the transitory carbenium ion may initiate polymerization.

The present study shows that t-BuCl is alkylated by trimethylaluminum at a rate of about 10^9 faster in methyl chloride than in cyclopentane. We propose that this enormous difference in rates is due to the fact that dimeric trimethylaluminum which exists in cyclopentane is a relatively poor alkylating agent, and that methyl chloride promotes alkylation by opening the dimer giving rise to highly active monomeric species (cf. Scheme I). The reason why alkylation occurs in cyclopentane at all is probably because t-BuCl itself is able to break up the dimer, albeit much slower than MeCl and at higher temperatures. Previous observations by Kennedy and Milliman[13] that the addition of methyl chloride to a cyclopentane solution of trimethylaluminum at −40° caused the coalescing of the nmr peaks assigned to the bridge and terminal methyl groups bear out this postulate.

The rate of neopentane formation with a given $tert$-butyl halide decreases in the order MeCl > MeBr > MeI. The difference in the rate of alkylation of $tert$-butyl chloride with trimethylaluminum in methyl iodide and methyl chloride of almost 10^6 is too large to be attributed to differences in solvent polarity alone and is indicative of a more intricate structural involvement in the alkylation. This trend is explained by assuming that the rate of displacement by the t-BuX of the MeX from the Me$_3$Al←XMe complex is slowed down by the increased strength of the Al ← X coordinative bond in the order Al←I > Al←Br > Al←Cl. This sequence of coordination strengths would be due to the decreasing polarizabilities of the halogens I > Br > Cl.
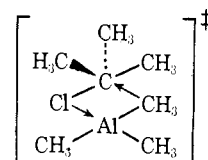
The results also show that in a given methyl halide solvent, the rate of alkylation (displacement) decreases in the order t-BuCl > t-BuBr > t-BuI. It appears that the halogen which represents the least steric hindrance and has the highest basicity toward aluminum is able to accomplish displacement most efficiently.

The reaction in cyclopentane is also (pseudo) second order; however, in this case the rate-determining step is not the displacement of a "bridge opener" by the $tert$-butyl halide because no suitable molecule (e.g., methyl halide) is available. In this system,

we propose that the $tert$-butyl halide fulfills a dual role: it functions as a dimer-bridge opener (a rather inefficient one, which explains the relatively slow rates) and as a source of carbenium ions. The decreasing rate of neopentane formation in the order t-BuCl > t-BuBr > BuI in cyclopentane solvent is most likely due to the decreasing rate of Me$_3$Al dimer bridge opening by the decreasing basicity and/or increasing bulk of the halogens in the above sequence.

The overall activation energies measured for all the methyl halide solvents are 10.3 ± 1, and those obtained with cyclopentane diluent are 15.8 ± 1 kcal/mol. Evidently nonspecific solvation of the $tert$-butyl cation by the methyl halides significantly enhances the driving force of the alkylation under consideration.

The final step in the alkylation, i.e., the transfer of the methyl group to the tertiary carbon, can occur either through a relatively "loose" [t-Bu$^+$ Me$_3$AlX$^-$] ion–counteranion pair 5 or through a relatively "tight" transition state.

$$\begin{bmatrix} & & CH_3 & & \\ H_3C & & | & CH_3 & \\ & & C & & \\ Cl & & & CH_3 & \\ CH_3 & & Al & CH_3 & \end{bmatrix}^{\ddagger}$$

Stereochemistry of Alkylation. To gain deeper insight into the nature of the intermediate(s) involved in the final step of these alkylations, we have investigated the reaction of optically active α-phenethyl chloride with triethylaluminum at −65° in ethyl chloride solvent. The reaction proceeds cleanly to give two products, 2-phenylbutane and ethylbenzene, in the relative proportions of 70:30 (eq 6). The product of interest,

$$(-)PhCHCl + Et_3Al \longrightarrow PhCHEt +$$
$$\qquad | \qquad\qquad\qquad\qquad\quad |$$
$$\qquad Me \qquad\qquad\qquad\qquad\quad Me$$
$$\qquad\qquad PhCH_2Me \,(+ Et_2AlCl + C_2H_4) \quad (6)$$

2-phenylbutane, was isolated and examined for optical purity. It had a rotation α^{23}D −0.7° (l = 1, neat) which would mean that the alkylation had proceeded with 4% net retention based on the maximum known value of rotation of 24° for 2-phenylbutane[14] and correcting for the fact that the starting α-phenethyl chloride was only 68% optically pure. Thus the stereochemical consequence of alkylation is predominant racemization. This result is consistent with the proposal that the intermediate involved in alkylation is a conventional carbenium ion–counteranion pair (i.e., [PhCH$^+$CH$_3$ Et$_3$AlCl$^+$]), sufficiently long-lived to undergo inversion and retention with the latter slightly predominating.

Cationic polymerization of olefins initiated by alkyl halide–alkylaluminum systems also probably involves similar carbenium ion–counteranion pairs (e.g., t-Bu$^+$ Me$_3$AlCl$^-$, PhCH$^+$CH$_3$ Et$_3$AlCl$^-$, etc). As mentioned above, these efficient initiators of olefin polymerizations give rise to high polymers, which indicates that propagation (addition of the monomer to the growing cation) must successfully compete with alkylation at the growing cation (alkylation of the cation is equivalent to termination of the kinetic chain). It has been previously observed that cationic polymeriza-

(14) D. J. Cram, J. Amer. Chem. Soc., 74, 2137, 2149 (1952).

tions of olefins (e.g., isobutylene) using t-BuCl–Me₃Al initiator–coinitiator systems do not proceed or proceed only with difficulty in nonpolar solvents such as n-pentane or cyclopentane. However, in methyl chloride high rates of polymerizations can be obtained.[3,4] Therefore, we conclude that similar to the alkylation model reaction, the function of methyl chloride in polymerization systems is to open the trimethylaluminum dimer and thus increase the rate of formation of the active cationic species. In addition, the polar methyl halide solvents also provide a favorable solvating medium for ion formation and separation.[15]

Experimental Section

All experiments were performed in a stainless steel enclosure under N₂ atmosphere (<50 ppm moisture).[13] Trimethylaluminum, triethylaluminum (Texas Alkyl Co.), and other chemicals were commercially available materials (Matheson Coleman and Bell) and were freshly distilled before use. Nmr analyses were done on Varian A-60 or T-60 instruments equipped with a low temperature probe. Optical rotation measurements were carried out using a Rudolph photoelectric Model 200 polarimeter.

Rate studies were carried out in nmr tubes and a representative procedure is described. Separate molar solutions of tert-butyl chloride and trimethylaluminum were prepared in methyl chloride at −60°. Trimethylaluminum solution (0.5 ml) was placed in an nmr tube and frozen in liquid N₂. An equal volume of the tert-butyl chloride solution was added to the tube and the tube was capped and sealed in vacuo. Subsequently, the nmr tubes were warmed up to ∼−90° to liquefy the reactants, mixed, and placed in the nmr probe maintained at a preselected temperature. Temperature equilibrium was generally established within 60 sec, at which instance the zero time was marked. The extent of the reaction was followed by observing the increase in the intensity of neopentane protons and the decrease in the intensity of protons

in tert-butyl chloride. In general, all rate measurements were done in duplicate.

α-Phenethyl alcohol, α^{23}D +36° (l = 1, neat), 84% optically pure (available commercially from Norse Laboratories, Calif.), was converted to the corresponding chloride using phosphorus oxychloride, pyridine, and tetra-n-butylammonium chloride in methylene chloride at −20° in 65% overall yield.[16] The α-phenethyl chloride, bp 58–59° (5 mm) (lit.[17] bp 68° (8 mm)) had a rotation α^{23}D −75.1° (l = 1, neat) (corrected for optically pure alcohol[18] α^{23}D −92°). The nmr spectrum (CCl₄, δ) showed a singlet at 7.3 (aromatic, 5 H), a quartet centered at 5.0 (methine, 1 H), and a doublet at 1.8 (methyl, 3 H).

Reaction of (−)-α-Phenethyl Chloride with Triethylaluminum. In a three-necked round-bottom flask equipped with a glass-jacketed addition funnel, thermometer, and stirrer and cooled to −65° was placed 26.5 g (0.115 mol) of triethylaluminum dissolved in 200 ml of ethyl chloride. (−)-α-Phenethyl chloride, 16.1 g (0.115 mol), was dissolved in 200 ml of ethyl chloride and added dropwise through the precooled addition funnel. After 15 min stirring, the reaction was quenched by the addition of 25 ml of prechilled methanol. The aluminum methoxide was coagulated using a saturated aqueous solution of potassium sodium tartrate and the organic material was extracted into n-pentane. The pentane extract was washed three times with water and dried over anhydrous sodium sulfate. After removal of solvent, the product was distilled under reduced pressure. Initial fractions consisting mainly of ethylbenzene were discarded and the fraction boiling at 53–54° (13 mm) was collected. Its nmr spectrum (CCl₄, δ) showed a singlet at 7.1 (aromatic, 5 H), a sextet at 2.56 (methine, 1 H), a quartet at 1.5 (methylene, 2 H), a doublet at 1.22 (methyl, 3 H), and a triplet at 0.8 (methyl, 3 H), consistent with the structure for 2-phenylbutane. The product had a rotation α^{23}D −0.69° (l = 1, neat) corresponding to a net retention of 4%.

(15) The possibility that in methyl halide solvents the actual alkylating (and propagating) intermediate is a tert-butyl methyl halonium ion (t-Bu-X⁺-Me) cannot be ruled out: G. A. Olah and J. R. DeMember, ibid., 91, 2113 (1969); 92, 718 (1970).

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Reversible Dimerization and Some Solid-State Properties of Two Bicyclic Nitroxides[1]

G. D. Mendenhall[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. Received February 21, 1973

Abstract: In isopentane at 25° a 0.1 M solution of nortropane N-oxyl (1) contains 0.0618 M of the free radical and a 0.1 M solution of 9-azabicyclo[3.3.1]nonane N-oxyl (4) contains 0.0854 M of radical. Measurements at lower temperatures show that the thermodynamic parameters for the dimerization of these two nitroxides are very similar. However, the solid-state properties of 1 and 4 show striking differences. Thus, at room temperature 1 is yellow, diamagnetic, and has a strong band in its infrared spectrum attributable to the NO group at 1332 cm⁻¹ in KBr. In contrast, 4 is red, paramagnetic, and has only a few weak bands in this region.

The reversible coupling of free radicals in solution to yield diamagnetic dimers is a feature common to such diverse organic radicals as triarylmethyls,[3] phe-

noxys,[4] alkylperoxys,[5,6] and iminoxys.[7] A few of the many stable nitroxides that are known[3] also dimerize

(1) Issued as National Research Council of Canada No. 13420.
(2) National Research Council of Canada Postdoctorate Fellow, 1971–1973.
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