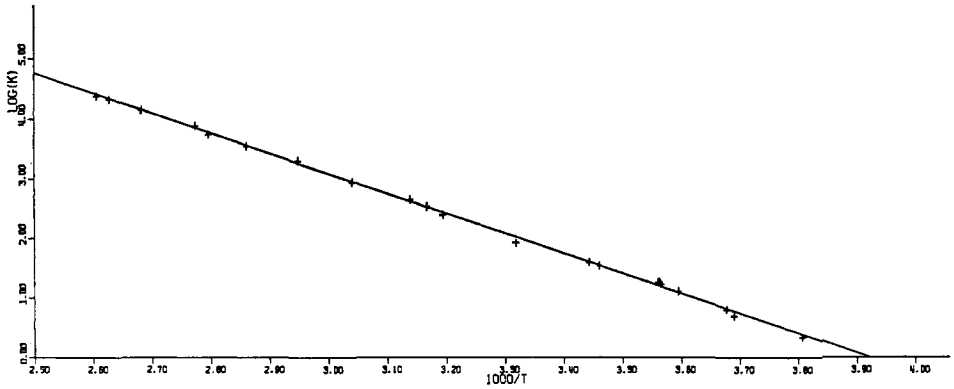
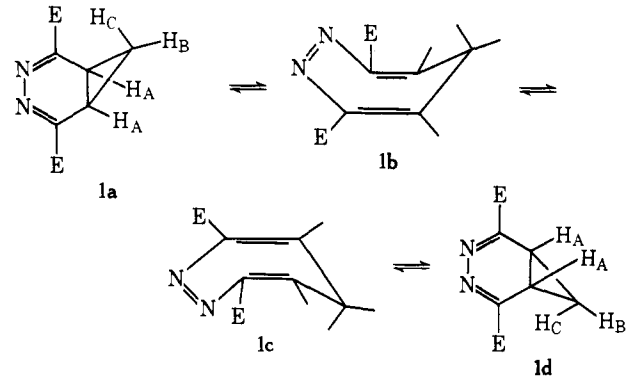


Figure 4. Arrhenius plot for the **1a** ⇌ **1d** exchange process.

processor time on a UNIVAC 1107 computer, which would be reduced to a fraction on the third-generation computers now in operation at many institutions.

On the basis of the extensive literature on the norcaradiene–cycloheptatriene problem[12,13] and its hetero analogs[12,14] it seems likely that the interconversion **1a** ⇌ **1d**, which is responsible for the temperature-dependent nmr spectra, proceeds through the diazacycloheptatrienes **1b** and **1c** as intermediates.



E = CO_2CH_3

The interesting question then arises as to what fraction of the observed activation energy is due to the bond-breaking process **1a** → **1b** (**1d** → **1c**) and what part arises from the barrier expected[15] for the inversion **1b** ⇌ **1c**. We shall address ourselves to this problem when we discuss the thermodynamic and kinetic data for a series of substituted diazanorcaradienes in the full paper.

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Solvent Assistance in the Solvolysis of Secondary Substrates. IV. The Solvolytic Behavior of the Di-*t*-butylcarbinyl System

Sir:

Highly crowded acyclic derivatives usually react rapidly in carbonium ion processes because of the opportunities for "B strain" relief in going from ground state to transition state.[1-4] On the basis of such reasoning and the very slow rate of $NaBH_4$ reduction of di-*t*-butyl ketone, Brown and Ichikawa[1b] predicted "a very fast rate of solvolysis for the tosylate of di-*t*-butylcarbinol." This prediction, though untested,[5] is supported by numerous theoretical arguments.[6] From the very low carbonyl stretching frequency of di-*t*-

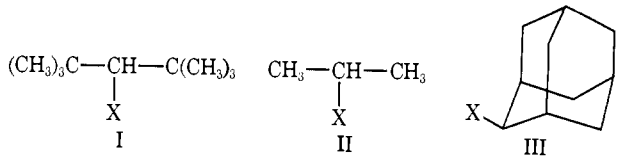
(12) The older literature is reviewed by G. Maier, *Angew. Chem.*, **79**, 446 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).
(13) For some recent references see E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454, 1458 (1967); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *ibid.*, **89**, 4076 (1967); J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968); T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967); T. Toda, M. Nitta, and T. Mukai, *ibid.*, 4401 (1969); M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968); *Angew. Chem.*, **81**, 83 (1969); M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969); M. Jones, Jr., and E. W. Petrillo, Jr., *Tetrahedron Lett.*, 3953 (1969); C. J. Rosteck and W. M. Jones, *ibid.*, 3957 (1969); D. Schönleber, *Angew. Chem.*, **81**, 83 (1969); *Chem. Ber.*, **102**, 1789 (1969); T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Jap.*, **42**, 2033 (1969); N. Görlitz and H. Günther, *Tetrahedron*, **25**, 4467 (1969).
(14) E. Vogel, *Angew. Chem.*, **79**, 429 (1967); M. A. Battiste and T. J. Barton, *Tetrahedron Lett.*, 1227 (1967); G. Maier and U. Heep, *Chem. Ber.*, **101**, 1371 (1968); H. Prinzbach and P. Vogel, *Helv. Chim. Acta*, **52**, 396 (1969).
(15) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964); A. Mannschreck, G. Rissmann, F. Vögtle, and D. Wild, *Chem. Ber.*, **100**, 335 (1967).

(1) (a) H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, **71**, 1845 (1949); **73**, 1317 (1951); (b) H. C. Brown and K. Ichikawa, *ibid.*, **84**, 373 (1962).
(2) P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968), and earlier papers therein cited.
(3) (a) E. D. Hughes, *Quart. Rev. Chem. Soc.*, **5**, 245 (1951); *Bull. Soc. Chim. Fr.*, C39 (1951); (b) F. Brown, T. D. Davies, I. Dostrovsky, O. J. Evans, and E. D. Hughes, *Nature* (London), **167**, 987 (1951).
(4) V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.*, **31**, 137 (1966).
(5) The earlier history is confused. Hughes[3] alluded several times to work with di-*t*-butylcarbinyl chloride (I, X = Cl), but full details were never published. The activation parameters for 80% ethanolysis of this compound were said to be "of quite the same order as for simpler secondary alkyl chlorides."[3b] Brown and Ichikawa were unable to prepare I (X = OTs), but quoted Hughes' work as showing that the corresponding chloride exhibited "unusually high reactivity."[1b] Apparently, the earlier reference was misread.
(6) A fuller analysis may be found in the Ph.D. Thesis of J. J. Harper, Princeton University, Princeton, N. J., 1968.

Table I. Solvolysis Data for Di-*t*-butylcarbinyl, 2-Adamantyl, and Isopropyl Derivatives

Compd	Solvent	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Di-*t*-butylcarbinyl chloride I, X = Cl	80% aq ethanol	120.0	4.50×10^{-5} [a]		
		111.7	2.15×10^{-5} [a]	25.9[c]	−13.2[c]
		100.4	7.52×10^{-6} [a]		
		25.0	8.91×10^{-10} [b]		
Isopropyl chloride, II, X = Cl	80% aq ethanol	100.0	5.25×10^{-6} [d]	22.5[d]	−23.0[d]
		25.0	2.07×10^{-9} [d]		
Di-*t*-butylcarbinyl tosylate I, X = OTs	80% aq ethanol	76.4	8.42×10^{-3} [a]		
		50.0	5.10×10^{-4} [a]	23.5	−1.2
		25.0	2.12×10^{-5} [b]		
	CH_3COOH	75.0	3.27×10^{-3} [e]		
		50.0	1.71×10^{-4} [e,f]	25.7[f]	+3.7[f]
		25.0	5.49×10^{-6} [b,f]		
	HCOOH	25.0	1.18×10^{-2} [a]	22.5	+8.2
		14.3	2.74×10^{-3} [a]		
	97% TFE	25.0	1.83×10^{-3}		
2-Adamantyl tosylate III, X = OTs[h]	80% aq ethanol	25.0	2.41×10^{-8} [b]	26.9	−3.0
	CH_3COOH	25.0	5.94×10^{-9} [b]	28.1	−2.1
	HCOOH	25.0	1.16×10^{-5} [b]	25.9	+5.6
	97% TFE	25.0	1.93×10^{-6} [g]		
Isopropyl tosylate II, X = OTs[h]	80% aq ethanol	25.0	2.94×10^{-6} [b]		
	CH_3COOH	25.0	7.74×10^{-8} [b]	24.7	−8.2
	HCOOH	25.0	3.69×10^{-5} [b]	19.5	−13.3

[a] Rate constants determined conductometrically. [b] Calculated from values at other temperatures. [c] From the Arrhenius activation parameters given by Hughes, *et al.*,[3b] $\Delta H^{\ddagger} = 26.0$ kcal/mol and $\Delta S^{\ddagger} = -12.7$ eu can be calculated. The agreement is very good. [d] Calculated from data of E. D. Hughes and V. G. Shapiro, *J. Chem. Soc.*, 1177 (1957). [e] Titrimetrically determined rate constants. [f] Independently prepared material, independently solvolyzed in the presence of sodium acetate, gave excellent agreement with these values. [g] R. Hall, unpublished results. [h] Reference 7b.



butyl ketone ($\nu_{C=O}$ = 1687 cm^{-1}), a rate enhancement for acetolysis of I (X = OTs) over isopropyl tosylate (II) of $10^{5.3}$ is anticipated[7a] (in the absence of steric effects involving the leaving group).[8] The greater electron-releasing inductive effect of *t*-butyl over methyl groups also leads to the expectation that I should react more rapidly than II.[8,9] Finally, to the extent that methyl participation occurs in the solvolysis of I, the rate should be further enhanced.

The actual experimental results are startlingly different from these expectations! A wide range of relative reactivities is actually found. At 25° in 80% ethanol the solvolysis rate of di-*t*-butylcarbinyl chloride (I, X = Cl)[10] actually is *slower* than that of isopropyl chloride (Tables I and II).[3,5] Di-*t*-butylcarbinyl tosylate (I, X = OTs)[11] reacts only eight times more rapidly than isopropyl tosylate in 80% ethanol at 25°, and 71 times more rapidly (instead of the predicted $10^{5.3}$)[7] in acetic acid (Tables I and II). In formic acid this ratio increases to 320 and in 97% trifluoroethanol to 630. We believe that this variation in behavior gives strong support to our contention[7b] that the solvolysis of isopropyl (and other simple secondary) derivatives is strongly nucleophilically solvent assisted ($k_s/k_c \gg 1$). Such solvent assistance is impossible with the di-*t*-butylcarbinyl system (I) because of severe backside hindrance. Thus, the greater the nucleophilic solvent assistance with isopropyl, the lower the di-*t*-butylcarbinyl (I)/isopropyl (II) rate ratio observed (Table II). Chlorides are believed to be more sensitive to solvent assistance than are tosylates;[7b,12] the lowest I/II ratio found is for the chlorides in 80% ethanol. For the tosylates, the I/II ratio *increases* as solvent nucleophilicity *decreases* along the series: 80% ethanol ~ acetic acid > formic > 97% trifluoroethanol.

To further substantiate this proposal, comparison of the behavior of I with 2-adamantyl (II) derivatives has been made (Table II). We have established that 2-adamantyl is a limiting (k_c) or nearly limiting substrate.[7b] Di-*t*-butylcarbinyl shows no tendency to undergo a k_s process; no substitution products were found from solvolysis of either I (X = Cl) or I (X = OTs). Rather, only rearranged olefin, 2,3,4,4-tetramethyl-1-pentene, was detected. Therefore, di-*t*-butylcarbinyl (I) is either a k_c (nucleophilically and anchimerically unassisted) or a k_Δ (methyl participation) substrate. As such, I should be insensitive to solvent nucleophilicity, as is III. The remarkable constancy

(7) (a) C. S. Foote, *J. Amer. Chem. Soc.*, 86, 1853 (1964); P. v. R. Schleyer, *ibid.*, 86, 1854, 1856 (1964). Modification of this treatment is now indicated.[7b] (b) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, 92, 2538 (1970); J. L. Fry, J. M. Harris, R. C Bingham, and P. v. R. Schleyer, *ibid.*, 92, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, 92, 2542 (1970).

(8) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965); H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, 56, 1653 (1966).

(9) *Cf.* P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, 87, 5169 (1965).

(10) Prepared by thermal decomposition of the chloroformate (M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, 19, 1150 (1954)) and isolated by glpc (25 ft × 3/8 in. FFAP, 192°). The structure was confirmed by nmr: δ (CCl_4) 3.58 (s, 1 H), 1.10 (s, 18 H).

(11) Readily prepared from di-*t*-butylcarbinol by the methyllithium method (H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Sheppele, *J. Amer. Chem. Soc.*, 89, 370 (1967)): mp 68–69°; nmr (CCl_4), δ 7.68 (AA′BB′, 4 H, J = 9 Hz), 4.29 (s, 1 H), 2.38 (s, 3 H), and 0.95 (s, 18 H). *Anal.* Calcd for $C_{16}H_{26}O_3S$: C, 64.39; H, 8.78. Found: C, 64.10; H, 8.56.

(12) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965); C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, 82, 2532 (1960).

Table II. Comparison of Di-*t*-butylcarbinyl (I), 2-Adamantyl (III), and Isopropyl (II) Systems

Characteristic	Di-*t*-butylcarbinyl (I)	2-Adamantyl (III)	Isopropyl (II)
	Relative Rates		
Chlorides, 25°			
80% ethanol	$10^{-0.3}$		1
Tosylates, 25°			
80% ethanol	$10^{0.9}$	$10^{-2.1}$	1
CH_3COOH	$10^{1.9}$	$10^{-1.1}$	1
HCOOH	$10^{2.6}$	$10^{-0.5}$	1
97% TFE	$10^{2.8}$	$10^{-0.2}$	1
CF_3COOH	$\sim 10^{5.1}$ [a]	$10^{2.1}$	1
	Derived Data[b]		
Apparent *m* values	0.88 (25°)	0.91 (25°)	0.40 (70°)[c]
α-CH_3/H, halides, 80% ethanol, 25°	$10^{5.3}$ (chlorides)	$10^{7.5}$ (bromides)	$10^{3.8}$ (bromides)
$(k_{aq\ alc}/k_{HOAc})_Y$	0.34 (25°)	0.18 (25°)	6 (70°)

[a] Estimated assuming the nearly constant I/III = $10^{3.0}$ ratio observed in other solvents. [b] See ref 7b for pertinent discussion. [c] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951).

of the I/III rate ratio (Table II) establishes this point.[13] The 10^3 magnitude of this ratio shows that the di-*t*-butylcarbinyl system does indeed exhibit enhanced reactivity.

It would be of interest to compare the behavior of I (X = OTs) with isopropyl tosylate in the very weakly nucleophilic solvent trifluoroacetic acid. Unfortunately, I (X = OTs) is too reactive ($k_1 \approx 10^1$ sec^{-1} at 25°) to be measured using regular techniques. However, if the constancy of the I/III ratio observed for other solvents (Table II) is assumed for CF_3COOH, a rate constant can be estimated. On this basis a lower limit estimate of the "inherent" (k_c *vs.* k_c) di-*t*-butylcarbinyl (I)/isopropyl (II) ratio, $\geq 10^{5.1}$, can be made. This large value confirms theoretical expectations. The acceleration is very much greater than that observed in the corresponding tertiary series. Shiner and Meier found that methyl di-*t*-butylcarbinyl chloride solvolyzed in 80% ethanol only 18.4 times faster than did *t*-butyl chloride; only a low percentage of products with a rearranged skeleton were formed.[4] Under comparable conditions (80% ethanol, 25°), the α-methyl/hydrogen ratio (methyl di-*t*-butylcarbinyl chloride/di-*t*-butylcarbinyl chloride) was $10^{5.3}$. Although this value would formerly have been considered to be rather high (especially in 80% ethanol!), it is less than our provisional estimate of α-CH_3/H = 10^8 for limiting solvolysis.[7b] The reduction from 10^8 to $10^{5.3}$ indicates that the secondary system is assisted to a greater extent than is the tertiary. This is also shown by comparison of the estimated limiting I/II ratio ($10^{5.1}$) with the methyl di-*t*-butylcarbinyl/*t*-butyl value ($10^{1.3}$). It seems probable that the chief factor responsible for the difference in secondary *vs.* tertiary di-*t*-butylcarbinyl behavior is methyl participation. This is consistent with the observation that the products in the tertiary series are largely unrearranged while solvolysis of secondary substrate (I) gives rearrangement exclusively.

Inductive and "B strain" effects would be somewhat different in secondary and tertiary series. Using the Peterson $\Sigma\sigma$ plot for trifluoroacetolysis,[9] an estimated acceleration of $10^{4.2}$ for I (X = OTs) over isopropyl tosylate is obtained. The actual difference is $10^{0.9}$ greater. It is difficult to estimate quantitatively the difference in "B strain" effects (or even their direction!)

We conclude that the solvolyses of di-*t*-butylcarbinyl derivatives are probably assisted to a modest extent by methyl participation ($k_\Delta/k_c \approx 10^1$–$10^2$).[14] Steric ("B strain") and inductive factors also contribute to an inherently greater reactivity over isopropyl. This inherently greater reactivity is masked in many solvents by nucleophilic solvent assistance in isopropyl solvolysis, thus reducing the observed I/III ratios, sometimes to very low values.

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(13) This constancy is due to the similarity in "apparent *m*" values of I and III (Table II).[7b] Limiting (k_c) and anchimerically assisted (k_Δ) substrates do not necessarily have constant rate ratios, but their response to solvent changes should exhibit proportionality especially with the same leaving groups.

(14) We have no evidence to exclude the possibility suggested by a referee that this participation may be occurring after intimate ion pair formation. See V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969); V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969).

(15) National Institutes of Health Postdoctoral Fellow, 1969–1970.

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Stereochemistry of Alkaline Cleavage of *cis*- and *trans*-1-Benzyl-4-methyl-1-phenylphosphorinanium Bromide

Sir:

Recently there has been considerable interest shown in the stereochemical behavior of phosphorus in cyclic systems in which phosphorus is the only heterocyclic atom.[1] Ordinarily, cleavage of acyclic phosphonium

(1) (a) I. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961); S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967); K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967); S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968); K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7393