

able agreement with the values in Table II. Most of the required group contributions to the entropy are missing for methoxy and methylthio substituents, but enthalpy components of D of 8.44 and 2.87 kcal/mol, respectively, may be calculated. The latter value is

near ours, but unless there is a remarkably large entropy contribution (11 eu) the value for methoxy is significantly larger than ours. For none of the other substituents are there enough parameters even to calculate the enthalpy component of D .

Electrophilic Substitution at Saturated Carbon. LI. Varieties of Pathways for Substituted-Ammonium Carbanide Ion Pairs to Reorganize¹

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Abstract: The stereochemical capabilities in *tert*-butyl alcohol of tertiary substituted-ammonium 3-*tert*-butyl-1-methylindenyl ion pairs have been examined. Changes in charge distribution in the protonated tertiary amine change the fate of the ion pair. Treatment of (–)-(R)-3-*tert*-butyl-1-methylindene ((–)-1-*h*) in *tert*-butyl alcohol-*O-d* (ROD) or (–)-(R)-3-*tert*-butyl-1-deuterio-1-methylindene ((–)-1-*d*) in *tert*-butyl alcohol-*O-h* (ROH) with triethylenediamine (TDA) or pentamethylguanidine (PMG) gave several reactions. Hydriodides of the tertiary bases were present in representative runs. Careful kinetics were studied for PMG-catalyzed isomerization of **1** to **2** and of racemization of equilibrated (–)-1-*h* and (+)-2-*h* in ROH. The results suggested the following conclusions. (1) For 1-*h* in ROD, the rate of isomerization exceeds that of racemization of the system by factors of 24–53 with the charge-delocalizing base (PMG), but by a factor of 4×10^4 with the charge-localizing base (TDA). (2) For 1-*h* and 2-*h* in ROD, PMG produced a dominant isoinversion component, whereas TDA produced a less dominant isoinversion component. (3) The isoinversion components were demonstrated to be due neither to a carbanion-carbon acid proton transfer nor to concerted thermal isomerizations with PMG as base. (4) The *suprafacial*, base-catalyzed isomerization reaction of (–)-1-*h* to (+)-2-*h* occurs by a conducted tour mechanism by the amine of the proton along the π face of the anion from the 1 to the 3 position, where collapse to the covalent state occurs. (5) The slower isoinversion reaction (*antarafacial*, intramolecular proton transfer) passes through a relatively nonstructured, achiral contact ion pair of higher energy than the structured ion pair of the conducted tour mechanism. (6) The dominant isotope effects of the system are in collapse of contact ion pairs to **2**, and in isotopic drowning of the amine's conjugate acid in the medium.

Earlier work demonstrated that charge-delocalizing tertiary amines such as pentamethylguanidine (PMG) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) affected the reactions of carbon acids differently from charge-localizing tertiary amines such as triethylenediamine (TDA).² In *tert*-butyl alcohol, 2- and 3-substituted 9-methylfluorene systems underwent PMG- and DBN-catalyzed isoinversion reactions in the absence of "conducted tour" functional groups. The data pointed to a nonstructured, contact ion-pair mechanism for isoinversion, with charge delocalization in both cation and anion. With TDA or tripropylamine as bases, isoinversion was observed only when the negative charge of the carbanion could be distributed by resonance on electronegative atoms, and a conducted-tour mechanism for isoinversion through contact ion pairs was available. In the absence of such groups, these charge-localizing tertiary amines largely gave racemization with isotopic exchange, presumably through solvent-separated ion pairs. A small bias toward isotopic exchange with retention was detectable, however. In the latter systems, invisible, but dominant, reactions of ionization and col-

lapse to starting material seemed probable based on isotope effects, and on the fact that introduction of traces of secondary amine into the tertiary amine led to isotopic exchange with high retention of configuration.²

In the present study, the behavior of (–)-(R)-3-*tert*-butyl-1-methylindene ((–)-1-*h*)³ in *tert*-butyl alcohol-*O-d* or (–)-(R)-3-*tert*-butyl-1-deuterio-1-methylindene^{3a,b} ((–)-1-*d*) in *tert*-butyl alcohol-*O-h* with tertiary amines was examined. These hydrocarbons provide many advantages for mechanistic study. (1) Isotopic exchange, rearrangement, and racemization reactions catalyzed by amine bases occur in a variety of solvents without side reactions at convenient temperatures.³ (2) The absolute configurations and maximum rotations of **1** and **2** are known.^{3b,4} (3) The equilibrium constants between starting olefin **1** and the product **2** of allylic rearrangement are known at 25° (7.5), 48° (6.6), and 102° (6.0).^{3b} (4) Isomers **1** and **2** can be separated by glc without thermal reac-

(3) (a) J. Almy, R. T. Uyeda, and D. J. Cram, *ibid.*, **89**, 6769 (1967); (b) J. Almy and D. J. Cram, *ibid.*, **91**, 4459 (1969); (c) A. Weidler, *Acta Chem. Scand.*, **17**, 1798 (1963); (d) A. Weidler and G. Bergson, *ibid.*, **18**, 1484 (1964).

(4) In ref 3b, the sign of rotation is coupled with the correctly drawn configuration for (+)-**2**, but (+)-**2** and its two precursors are incorrectly labeled *S*; they should have been labeled *R*. We thank Professor W. Klyne for calling our attention to this error.

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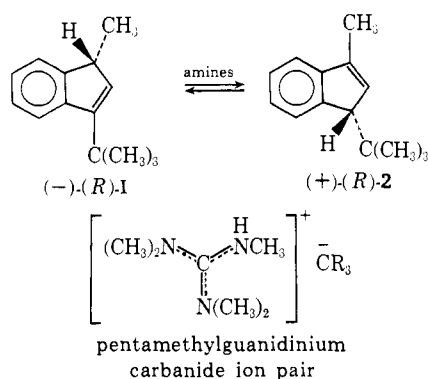
(2) K. C. Chu and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 3521 (1972).

Table I. Pentamethylguanidine (PMG) or Triethylenediamine (TDA) Catalyzed Isomerization, Racemization, and Isotopic Exchange of

Run no.	Starting material	Solv	Base		Temp, °C	Time, hr	10 ⁵ k _i , sec ⁻¹	10 ⁵ k _r , sec ⁻¹	% Obt	% exch
			Nature	Concn, M						
1	(-)-1- <i>h</i>	ROD ^c	PMG	0.395	25	9.5	2.7	0.35	43	1.7
2	(-)-1- <i>h</i>	ROD	PMG	0.417	25	48	2.6 ^d	0.34	12	4.8
3	(-)-1- <i>h</i>	ROD ^c	PMG	0.420	25	48	2.6 ^d	0.34	13	11.4
4	(-)-1- <i>d</i>	ROH	PMG	0.414	25	167	0.33 ^e	0.043	20	10 ± 2
5	(-)-1- <i>h</i>	ROD ^c	TDA	0.40	100	85.5	<i>f</i>		14.5	0.6 ± 0.5
6	(-)-1- <i>h</i> ^b	ROD ^d	TDA	0.268	100	1297	<i>f</i>		14.3	6.6 ± 1
7	(-)-1- <i>h</i> ⁱ	ROD ^d	TDA	0.254	100	4618	<i>f</i>		14.3	6.6 ± 1
8	(-)-1- <i>d</i> ⁱ	ROH	TDA	0.17	50	26.5	0.23 ^k	0.034 ^k	81	2.7
9	(-)-1- <i>h</i>	ROD ^c	TDA	0.256	100	0.53	32.3	5.4	56	

^a 0.99 atom of deuterium per molecule. ^b 0.99 atom of deuterium per molecule. ^c Solution was 0.0007 M in PMG·DI or PMG·HI. ^d Determined from two preliminary runs, 38 and 57% isomerized, but otherwise identical. ^e Determined by analysis of an aliquot taken after

tions and individually examined for optical activity and deuterium abundance.^{3b} (5) The indenyl anion contains a π system that provides a *suprafacial* conducted tour route for 1,3-proton transfer. Thus, at least some of the invisible *suprafacial* process of ionization and return to starting material in the fluorenyl systems becomes the revealed *suprafacial* process of ionization and rearrangement in the indenyl system (1 \rightarrow 2). (6) The indenyl system contains no functional group that provides an *antarafacial* conducted tour route for either 1,1 or 1,3 proton transfer. Thus any isoinversion (inversion without isotopic exchange) observed with either 1 or 2 cannot occur by a conducted tour mechanism.



Results

Stereochemical Courses of Reactions. In experiments designed for determining stereochemical reaction course, (-)-1-*h* in *tert*-butyl alcohol-*O-d* (or (-)-1-*d* in *tert*-butyl alcohol-*O-h*) was treated with either PMG or TDA, the reaction was interrupted, 1 and 2 were quantitatively separated by preparative glc, and each was analyzed polarimetrically^{3b} for racemization and mass spectrometrically^{3b} for isotopic exchange. From the data, one-point pseudo-first-order rate constants were calculated. The rate constant for isomerization of 1 to 2 (k_i) is 6.0 to 7.5 times that for the reverse reaction (k_r). Values of ($k_i + k_r$) were estimated from the glc analyses of mixtures in which the isomerization had been carried less than 1 half-life toward equilibrium. From $k_i + k_r$ values and the equilibrium constants, both k_i and k_r were estimated. Previously conducted control runs with internal standards established that even after complete equilibration, 99–100% of the starting material was accounted for as either 1 or 2.^{3b} The rate constants for (-)-1 \rightarrow (\pm)-1 ($k_a(1)$) and for (+)-2 \rightarrow (\pm)-2 ($k_a(2)$) were

estimated from the polarimetric data. Similarly, rate constants for 1-*h* \rightarrow 1-*d* or 1-*d* \rightarrow 1-*h* ($k_e(1)$) and for 2-*h* \rightarrow 2-*d* or 2-*d* \rightarrow 2-*h* ($k_e(2)$) were estimated. Since large isotope effects are evident, the values for k_i , k_r and k_a would ultimately change with time. The isotopic exchange was much slower than either isomerization or racemization of 1, and isotopic exchange of 1 never exceeded 20%. Thus, isotope effects should not greatly affect the estimates of $k_e(1)$ and $k_a(1)$. However, racemized and isotopically exchanged 2 arose mainly from already racemized and exchanged 1. This conclusion follows from the facts that at 25°, $k_i/k_r = 7$, and k_i possesses a large isotope effect ($k_i^{C-H}/k_i^{C-D} \sim 8$). Thus $k_e(2)$ and $k_a(1)$ values reflect mainly exchange and racemization of 1, followed by isomerization. In representative runs, low concentrations of hydriodides of the amines were present to act as potential isotopic pools of the same acidity (opposite isotopic variety) as the conjugate acids of the amines generated in ionization of the carbon acids. In all runs, the isotopic reservoir of the medium was not depleted materially. Table I records the conditions and results of these experiments.

Kinetics. The kinetics of isomerization of (-)-1-*h* in *tert*-butyl alcohol-PMG were followed by glc (run 10) through 1.7 half-lives, and polarimetrically (runs 11–17) through about 1 half-life at 25.0 \pm 0.1°. Table II records the results. The equilibrium constant for 1 \rightleftharpoons 2 was determined by glc (after 160 isomerization half-lives) to be $K = 7.54 \pm 0.14$, which agrees well with the previous value of 7.55 \pm 0.1 determined in tetrahydrofuran with propylamine as the catalyst.^{3b} The value of the pseudo-first-order rate constant for isomerization, k_i , was calculated in run 10 by eq 1 and 2.

$$k_i + k_r = -\frac{2.303}{t} \log \left[\frac{[\mathbf{1}]_t - [\mathbf{1}]_{\text{equil}}}{[\mathbf{1}]_{t=0} - [\mathbf{1}]_{\text{equil}}} \right] \quad (1)$$

$$K = k_i/k_r = 7.54 \quad (2)$$

The polarimetrically determined rate constants (k_i) of runs 11–16 were calculated through use of eq 2 and 3,

$$\log(\alpha_t - \alpha_\infty) = -t(k_i + k_r)/2.303 + \log(\alpha_0 - \alpha_\infty) \quad (3)$$

in which α_t is the observed rotation at time t , α_∞ represents the value for the rotation at $t = \infty$, and α_0 is the value at $t = 0$. Since racemization occurs concurrently with isomerization, although at a much slower rate, α_∞ was impossible to determine experimentally. Also, since the polarimeter cell was filled in a drybox, α_0 was

0.1 M Solutions of Optically Pure (–)-3-*tert*-Butyl-1-methylindene ((–)-1-*h* or (–)-1-*d*^a) in *tert*-Butyl Alcohol (ROD^b or ROH)

Isomer 1			Isomer 2				
10 ⁶ <i>k</i> _e (1), sec ⁻¹	% rac	10 ⁶ <i>k</i> _α (1), sec ⁻¹	% obt	% exch	10 ⁶ <i>k</i> _e (2), sec ⁻¹	% rac	10 ⁶ <i>k</i> _α (2), sec ⁻¹
0.51	8.7 ± 1	2.7	57	0.24	0.071	2.1 ± 1.0	0.63
0.28	23 ± 5	1.5	88	0.4	0.023	12 ± 1	0.75
0.71	32 ± 3	2.3	87	1.1	0.063	14.7 ± 1	0.92
0.17	76	2.4	80	20 ± 2	0.37	68 ± 1	1.9
0.02 ± 0.016	1.5 ± 1	0.048 ± 0.036	85.5	0.7 ± 0.5	0.023 ± 0.012	1.4 ± 0.5	0.044 ± 0.0016
0.011 ± 0.002	7.0 ± 0.7	0.016 ± 0.002	85.7	2 ± 1	0.0043 ± 0.0021	3.0 ± 0.7	0.0064 ± 0.0016
0.0041 ± 0.0008	14.8 ± 1.0	0.0096 ± 0.0008	85.6	6.3 ± 1.4	0.0038 ± 0.001	12.6 ± 1.0	0.0081 ± 0.0008
	0 ± 0.5		19	4.8		0 ± 0.5	
			44				

27.5 hr, 27% isomerized. ⁱ Solution at equilibrium. ^a Solution was 0.001 M in TDA·DI. ^b Solution 0.19 M. ^c Solution 0.18 M. ⁱ Run 9, Table III, ref 3b. ^k Calculated from $K = 6.7 = k_i/k_r$ at 48°, Table II, ref 3b.

Table II. Kinetics in *tert*-Butyl Alcohol-*O-h* at 25.0 ± 0.1° of Isomerization of Optically Pure (–)-3-*tert*-Butyl-1-methylindene ((–)-1-*h*) to (+)-1-*tert*-Butyl-3-methylindene ((+)-2-*h*) Catalyzed by Pentamethylguanidine (PMG)

Run no.	Concn, M		Number of		10 ⁶ <i>k</i> _i , sec ⁻¹ ^{a,b}	<i>k</i> _i /[PMG] × 10 ⁴ , sec ⁻¹ M ⁻¹ ^a
	(–)-1- <i>h</i>	PMG	Half-lives	Points		
10 ^c	0.0296	0.524	1.7	7	5.28 ± 0.05	1.01 ± 0.02
11 ^d	0.0296	0.524	1	42	5.38 ± 0.02	1.03 ± 0.01
12 ^d	0.0590	1.058	1	23	17.62 ± 0.04	1.66 ± 0.02
13 ^d	0.0296	1.058	1	29	17.81 ± 0.10	1.68 ± 0.02
14 ^d	0.0119	1.060	1	24	17.68 ± 0.08	1.67 ± 0.02
15 ^d	0.0296	0.260	1	47	1.996 ± 0.004	0.77 ± 0.02
16 ^d	0.0296	0.131	0.9	29	0.880 ± 0.003	0.67 ± 0.02

^a Two standard deviations. ^b Least-squares linear regression analysis. ^c Followed by glc. ^d Followed polarimetrically at λ 436 nm.

not measurable directly. Parameters α_0 and α_∞ were determined for run 12 as follows. From the concentration (±0.5%) of (–)-1-*h* and the known rotation of (–)-1-*h* in chloroform, α_0 was calculated as –3.17°. With this value and that for the equilibrium constant, α_∞ was calculated as +2.345°. These calculations involved the assumptions that the rotations were solvent and concentration independent.

With this value of α_∞ and the data of run 12, a linear plot of $\log(\alpha_t - \alpha_\infty)$ against time gave an intercept $\log(\alpha_0 - \alpha_\infty)$ from which was calculated a new α_0 of –3.060° (assuming the old α_∞). With this new α_0 value, a new value, $\alpha_\infty = 2.265^\circ$, was calculated (only 3.5% lower than the first). With this new α_∞ value, a good straight line was obtained now including the $t = 0$ point. For runs 11 and 13–16, α_∞ values were calculated by multiplying that of run 12 by the appropriate concentration factor. The good correspondence between the k_i values obtained in runs 10 and 11, followed by the two methods, points to the validity of the procedure.

In runs 12–14, the concentration of PMG was held constant and that of (–)-1-*h* was varied fivefold with <1% variation in k_i /[PMG]. In runs 10, 11, 13, 15, and 16, the concentration of (–)-1-*h* was held constant and the PMG concentration was varied eightfold. Values of k_i /[PMG] varied from $1.68 \times 10^{-4} \text{ sec}^{-1} \text{ M}^{-1}$ at 1.058 M base to $0.67 \times 10^{-4} \text{ sec}^{-1} \text{ M}^{-1}$ at 0.131 M base. The factor increase in rate produced by each doubling of the base concentration was plotted against the base concentration. The linear plot, extrapolated to zero base concentration, gave an intercept (factor) of 2. Clearly the isomerization is first order in **1** and is probably first order in PMG at low base concentrations. The changes in values of k_i /[PMG] with base concentration may reflect a medium effect, particularly since the PMG was contaminated with 0.15 mol of tetramethylurea per mol of PMG.

The kinetics of racemization of the equilibrated mixture, (–)-1-*h* ⇌ (+)-2-*h*, was followed polarimetrically. Table III records the results. Pseudo-first-order rate constants (k_α^{obsd}) were calculated with eq 4,

$$k_\alpha^{\text{obsd}} = 2.303/t \log(\alpha_0/\alpha_t) \quad (4)$$

where α_t is the observed rotation at time t , and α_0 is the observed rotation at $t = 0$. At infinity, α was assumed to be 0°. All runs but 23 were carried out from 2 to 4 half-lives, and the first-order plots exhibited good linearity. Values of k_α^{obsd} at constant PMG concentrations were essentially the same over a fivefold change in initial concentration of (–)-1-*h* (runs 17–20). With an eightfold change in concentration of PMG from 1.060 to 0.131 M, k_α^{obsd} /[PMG] values decreased steadily from 5.28 to $1.27 \times 10^{-6} \text{ sec}^{-1} \text{ M}^{-1}$, respectively. The factor increase in rate produced by each doubling of the base concentration was plotted against the base concentration. The nearly linear plot, extrapolated to zero base concentration, gave an intercept (factor) of 2. The results demonstrate the racemization reaction is first order in the equilibrating isomers, and suggest that at low PMG concentrations, the reaction approaches first order in base concentration.

Discussion

These results provide further insight into the character of carbanion-containing ion-pair reorganization reactions. Previously identified were base-catalyzed mechanisms for a *suprafacial*, 1,3-hydrogen shift,³ for isotopic exchanges of starting material and product with retention of configuration,^{3a,b} and for the stereochemically indiscriminate mechanisms that accompany ion-pair dissociation.^{5a} The current results provide evidence for an isoinversion process as well.

(5) (a) J. Almy, D. C. Garwood, and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 4321 (1970); (b) J. Almy and D. J. Cram, *ibid.*, **92**, 4316 (1970).

Table III. Kinetics in *tert*-Butyl Alcohol-*O-h* at $25.0 \pm 0.1^\circ$ of Racemization of an Equilibrated Mixture^a of (-)-3-*tert*-Butyl-1-methylindene ((-)-1-*h*) and (+)-1-*tert*-Butyl-3-methylindene ((+)-2-*h*) Catalyzed by Pentamethylguanidine (PMG)

Run no ^b	Concn, <i>M</i>		Number of		$10^6 k_\alpha^{\text{obsd}}$, sec^{-1} c, d	$10^6 k_\alpha^{\text{obsd}}/[\text{PMG}]$, $\text{sec}^{-1} M^{-1}$ c
	(-)-1- <i>h</i>	PMG	Half-lives	Points		
17 ^e	0.0590	1.058	4	45	5.240 ± 0.005	4.95 ± 0.04
18	0.0296	1.058	2	26	5.448 ± 0.013	5.15 ± 0.04
19	0.0296	1.058	2	21	5.437 ± 0.022	5.14 ± 0.05
20	0.0119	1.060	2	20	5.599 ± 0.049	5.28 ± 0.09
21	0.0296	0.524	3	30	1.262 ± 0.005	2.41 ± 0.02
22	0.0296	0.260	2	43	0.412 ± 0.001	1.59 ± 0.05
23	0.0296	0.131	0.25	9	0.165 ± 0.003	1.27 ± 0.04

^a Generated from optically pure (-)-1-*h* during 11 half-lives for isomerization. ^b All reactions followed polarimetrically at λ 436 nm except 19, where λ is 546 nm. ^c Two standard deviations. ^d Least-squares linear regression. ^e A polarimetric, 11-point run, 0.10 *M* (-)-1-*h* and 0.97 *M* PMG in *tert*-butyl alcohol-*O-d*, gave $k_\alpha^{\text{obsd}} = 6.4 \times 10^{-6} \text{ sec}^{-1}$.

Table IV. Rate Constant Ratios of Isotopic Exchange to Racemization for (-)-1 ($k_e(1)/k_\alpha(1)$), for (+)-2 ($k_e(2)/k_\alpha(2)$), and Rate Constant Ratios of Isomerization (k_i) to Racemization of Equilibrating 1 and 2 ($k_i/k_\alpha^{\text{equil}}$)^a

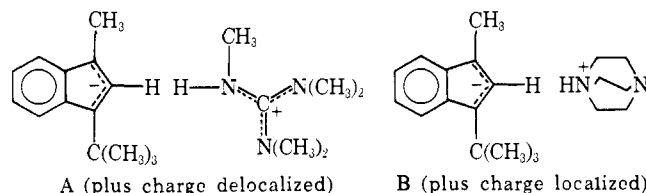
Run no.	Starting material	Base	Temp, °C	$k_e(1)/k_\alpha(1)$	$k_e(2)/k_\alpha(2)$	$k_i/(k_\alpha^{\text{equil}})$ ^a
1	(-)-1- <i>h</i>	PMG	25	0.2	0.1	31
2	(-)-1- <i>h</i>	PMG	25	0.2	0.03	31
3	(-)-1- <i>h</i>	PMG	25	0.3	0.07	24
4	(-)-1- <i>d</i>	PMG	25	0.07	0.2	1.7
5	(-)-1- <i>h</i>	TDA	100	0.4 ± 0.2	0.5 ± 0.8	
6	(-)-1- <i>h</i>	TDA	100	0.7 ± 0.2	0.7 ± 0.5	
7	(-)-1- <i>h</i>	TDA	100	0.4 ± 0.1	0.5 ± 0.16	
8	(-)-1- <i>d</i>	TDA	50	≈ 4.5	≈ 9	
7 + 9	(-)-1- <i>h</i>	TDA	100			4.0×10^{4b}

^a $k_\alpha^{\text{equil}} = (7.6k_\alpha(2) + k_\alpha(1))/8.6$ at 25° . ^b $k_\alpha^{\text{equil}} = (6.0k_\alpha(2) + k_\alpha(1))/7.0$ at 102° .

Evidence for an Isoinversion Reaction Path. The estimates of the values of the rate constants of Table I provide a means of identifying the isoinversion reactions of (-)-1 and (+)-2. Values of $k_e(1)/k_\alpha(1)$ and of $k_e(2)/k_\alpha(2)$ based on these estimates are found in Table IV. Although not strict measures of the ratio of rate constants for isotopic exchange to racemization, these values characterize the reaction mechanisms as having a dominant reaction component. The values less than 0.5 for these ratios indicate the presence of a process of racemization without isotopic exchange (isoinversion). Values from 0.5 to 1 point to either an isoinversion or an inversion with isotopic exchange component. Values greater than unity indicate that a process of isotopic exchange with retention is present. Examples of all three possibilities are found in Table IV.

With PMG as base, $k_e(1)/k_\alpha(1)$ and $k_e(2)/k_\alpha(2)$ values range from 0.07 to 0.3 (runs 1–4). Included are runs in which the isotopic label was in the solvent and in the carbon acid. Also included are runs in which added salt provides a potential relay pool of isotopic label of the same acidity as that of the pentamethylguanidinium ion generated by ionization of the carbon acid. Since in the anion of 1 and 2 no functional group is present that distributes negative charge in the plane of the carbon skeleton, a concerted tour mechanism is not available for isoinversion. Thus, a nonstructured ion pair is required whose reorganization at some point on the reaction coordinate must place in the skeletal plane of the carbanion the proton being transferred from one to the opposite face of anion by the amine. Contact ion pairs, A and B, provide the proper symmetry properties to account for this achiral point on the potential energy surface.

The isoinversion component is much more visible with the charge-delocalizing amine (PMG) than with the charge-localizing amine (TDA). The fact that the



$k_e(1)/k_\alpha(1)$ and $k_e(2)/k_\alpha(2)$ values in runs 5–7 are less than unity probably reflects the presence of a rather minor isoinversion component with the charge-localizing amine as catalyst. The greater isoinversion component catalyzed by PMG as compared to TDA is attributed to the lower energy cost in separating charge at the achiral point on the potential energy surface when both *plus* and *minus* are delocalized, as in A. The conjugate acid of TDA localizes plus charge, as in B.

Two alternatives to the isoinversion mechanism require discussion. The possibility exists that k_e/k_α values of less than 0.5 arose from proton or deuteron transfer from optically active carbon acid to planar carbanion in a chain reaction. The kinetic runs of Table III indicate that racemization of equilibrating mixtures of (-)-1-*h* and (+)-2-*h* is first order in carbon acid, and at low PMG concentration, first order in PMG. This fact rules out racemization by transfer of protons from carbon to carbon, particularly when PMG served as base. That isoinversion arises by two successive sigmatropic shifts is equally improbable. This thermal reaction when it occurs in this system provides racemized but isotopically nonexchanged product.^{5b} However, this thermal rearrangement occurs only very slowly at 140° in this system. The PMG-catalyzed reactions occur at 25° , and the TDA reactions at 100° . Since the racemization reactions of 1 and 2 with TDA occur only very slowly at 100° , there is a possibility that the small isoinversion component

observed is due to the intramolecular, thermal rearrangements. Clearly, the isotopic exchange reaction must be base catalyzed, as in the isomerization reaction itself.

Effect of Base Structure on Relative Rates of Isomerization and Racemization. The most dramatic effect of the structure of the base on the reaction course is found in the relative rates of isomerization and racemization. The isomerization is completely intramolecular (no isotopic exchange) and involves amine conduction of a proton along a single π face of the indenyl anion (conducted tour mechanism). The intramolecular component of the racemization process involves enough charge separation to allow the planar carbanion to rotate with respect to the alkylammonium ion. The values of the rate constant ratios, $k_i/(k_\alpha^{\text{equil}})$ of Table IV, provide an estimate of the relative rates of the isomerization and racemization processes, particularly for runs 1, 2, 3, and 9, in which $k_i > k_\alpha(1)$ or $k_\alpha(2)$. A similar but more accurate measure of the relative rates of isomerization and racemization is found in the values of the rate constant ratios, $k_i/k_\alpha^{\text{obsd}}$, which combine the data of Tables II and III. Table V records the

Table V. Ratios for the Rate Constants for Isomerization of (-)-1-*h* to (+)-2-*h* (k_i) to the Rate Constants for Racemization of an Equilibrated Mixture of (-)-1-*h* and (+)-2-*h* (k_α^{obsd}) Catalyzed by PMG in *tert*-Butyl Alcohol-*O*-*h* at 25°

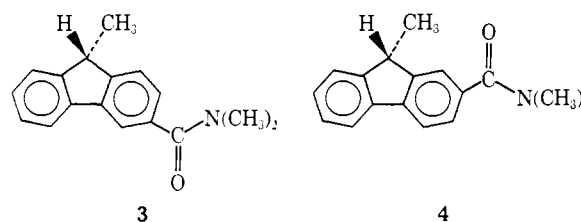
Runs used ^a	PMG concn, <i>M</i>	$k_i/k_\alpha^{\text{obsd}}$
12 + 17	1.058	34
13 + 18	1.058	33
14 + 20	1.060	32
11 + 21	0.524	43
15 + 22	0.260	48
16 + 23	0.131	53

^a Tables II and III.

values of the ratio for runs made under identical conditions of PMG and (-)-1-*h* concentrations. In runs 1, 2, and 3 with (-)-1-*h* in *tert*-butyl alcohol-*O*-*d* and ~ 0.4 *M* in PMG, $k_i/k_\alpha^{\text{equil}}$ ranged from 24 to 31. In runs 11 and 21 with (-)-1-*h* in *tert*-butyl alcohol-*O*-*h* and ~ 0.52 *M* in PMG, $k_i/k_\alpha^{\text{obsd}}$ was 43. This qualitative agreement is satisfactory, considering the isotope effect of the medium and the different means used in obtaining the data.

The charge-localizing base (TDA) provides a $k_i/k_\alpha^{\text{equil}}$ value of 4×10^4 (runs 7 + 9), whereas the charge-delocalizing base (PMG) gives a value of about 31 (run 2) (see Table IV). The isomerization reaction can occur without breaking the hydrogen bond between carbanion and the alkylammonium ion in the ion pair. The racemization reaction can only occur by breaking this hydrogen bond. The hydrogen bond should be stronger when the charge on nitrogen is localized than when the charge is delocalized. This expected difference in hydrogen bond strength provides an attractive explanation for the behavior of the two types of tertiary amine bases. The *suprafacial* conducted tour mechanism occurs by factors 24 to 53 faster than the nonstructured isoinversion mechanism with the charge-delocalizing catalyst, and by a factor of 4×10^4 with the charge-localizing catalyst. Thus, the structured reaction path dominates over the nonstructured in systems where the former is available. The same type of

dominance is visible in the high stereospecificity of the potassium *tert*-butoxide catalyzed *suprafacial* isomerization of open-chain aza-allylic systems⁶ in *tert*-butyl alcohol. The behavior with charge-localizing tertiary amines of carbon acid **3** exemplifies isoinversion going by a structured path when charge distribution in the anion is favorable.^{2,7} Carbon acid **4**, whose anion pro-



vides poor charge distribution for a conducted tour path for isoinversions, gives mainly isotopic exchange with racemization.²

Effect of Location of Isotope Label on Stereochemical Course of Isotopic Exchange. In runs 4 and 8 of Table IV, (-)-1-*d* in *tert*-butyl alcohol-*O*-*h* was employed, whereas in all the other runs, (-)-1-*h* in *tert*-butyl alcohol-*O*-*d* was used. The effect of the difference in position of the isotopic label is dramatic. With PMG as catalyst, $k_\alpha(1)/k_\alpha(1)$ and $k_\alpha(2)/k_\alpha(2)$ values indicate that isoinversion dominates with deuterium initially in either carbon acid or solvent. However, the value of $k_i/k_\alpha^{\text{equil}}$ for run 4 is only 1.7, as compared with the value of 24 for run 3 when the isotopic labels were in opposite initial positions. Runs 11 and 21 (Table V) were made with protium in both substrate and solvent, and at about the same PMG concentration as run 4. A value of $k_i/k_\alpha^{\text{obsd}} = 43$ was the result. The low value in run 4 of $k_i/k_\alpha^{\text{equil}} = 1.7$ is associated mainly with k_i (~ 8 times lower than k_i in run 3) and relatively little with k_α^{equil} . The isotope effects associated with ionization of and collapse to **1** are common to both k_i and k_α . This leaves the isotope effect associated with collapse to **2** as the main contributor to the k_i isotope effect. The large steric factors involved in protonation or deuteration at the position of the allylic anion carrying the *tert*-butyl group may be responsible for a large isotope effect for this stage of the isomerization. Abnormally large isotope effects associated with large steric effects have been observed previously.^{6a,8}

Comparison of $k_\alpha(1)/k_\alpha(1)$ and $k_\alpha(2)/k_\alpha(2)$ values for runs 7 and 8 (with TDA as base, Table IV) reveals a marked isotope effect on the stereochemical course of the reactions. With (-)-1-*h* in *tert*-butyl alcohol-*O*-*d*, values of 0.4 and 0.5 (isoinversion) were observed, respectively. With (-)-1-*d* in *tert*-butyl alcohol-*O*-*h*, the values were >4.5 and >9 (exchange with retention). This striking combination of isotope effects of carbon acid and solvent on ion-pair behavior is difficult to explain, but is part of a general pattern. With a variety of solvents and bases, several allylic and aza-allylic systems tend to undergo proton transfers intramolecularly^{3b,5a,6a,9} of both the 1,3-shift or isoinversion

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(b) S. M. Wong, H. P. Fischer, and D. J. Cram, *ibid.*, **93**, 2235 (1971).

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varieties more efficiently than deuterium transfers. In other words, isotopic drowning of BD species generated by deuterium extraction from a carbon acid in a protium-containing pool is a relatively more efficient process than isotopic drowning of a BH species in a deuterium-containing pool. The isotopic exchange with retention observed in run 8 might reflect a low equilibrium concentration of $R_3N^+HO-C(CH_3)_3$ acting as the active base in the visible isotopic exchange reaction. Abstraction of deuterium by $R_3N:$, although faster, might lead directly back to starting material, and thus be an invisible reaction.

Experimental Section

General. All glassware was cleaned with chromic acid, washed with dilute ammonia and distilled water, and dried at 120° for 12 hr before use. The *tert*-butyl alcohol was distilled from calcium hydride and stored in a sealed flask. Karl Fischer titration¹⁰ showed 0.0114 ± 0.0005% water by weight after a storage of 3 months. Pentamethylguanidine (PMG) was prepared¹¹ containing 8 mol % tetramethylurea (weight vs. titration). Triethylenediamine (TDA) was sublimed at 35° under high vacuum. The hydriodide salts of PMG and TDA have been reported^{8b, 12a} as has the preparation of the *tert*-butyl alcohol-*O-d* (0.99 atom of deuterium).^{12b} The carbon acids^{3b} were optically pure and were submitted to filtration chromatography on silica gel before use: (–)-1-*h*, $[\alpha]^{25}_D -125^\circ$, $[\alpha]^{25}_{375} -133^\circ$, $[\alpha]^{25}_{546} -153^\circ$, $[\alpha]^{25}_{436} -288^\circ$ (*c* 0.4, $CHCl_3$); (–)-1-*d* (99% atom excess deuterium per molecule), $[\alpha]^{25}_D -128^\circ$, $[\alpha]^{25}_{546} -158^\circ$, $[\alpha]^{25}_{436} -292^\circ$ (*c* 0.4, $CHCl_3$). The isomeric purity of (–)-1-*h* by analytical glc was 99.82% **1** and 0.18% **2** after 4 weeks of storage in *tert*-butyl alcohol, and less than 0.1% high boiling polymer was present. Glc analyses employed a Wilkens Model 204 gas chromatograph with flame ionization detector, and a 15 ft × 0.125 in. column, 4% Apiezon L on 80–100 mesh Chromosorb W at 125° with the injector and detector at 135 and 130°, respectively. The flow rate of nitrogen was 12 ml/min. Isomer **1** gave a 67-min and **2** a 75.5-min retention time with base-line separation. Peak areas were measured by integration on a Leeds and Northrup Speedomax W recorder equipped with a Model 244-4 Disc Integrator. Rotations were taken on a Perkin-Elmer Model 141 polarimeter, and deuterium analyses were performed with an AEI Model MS-9 mass spectrometer. Details of analytical procedures are reported elsewhere.^{3b} Preparative separations of **1** and **2** after runs 1–9 were made on a Varian-Aerograph Model A-90 gas chromatograph, with a 7 ft × 0.25 in. column containing 10% Apiezon L on 60–80 mesh firebrick with helium as carrier gas. The injector, detector, and column were all maintained at 150°. Retention times for **1** and **2** were 67 and 68 min, respectively, with near-base-line separation of peaks. Glass tube collectors were tightly fitted into a silicon rubber disk cut to accommodate the collector and exit port. The collectors were warmed when neces-

sary to maintain **2** as a liquid during collection to avoid fractionation of optically active and racemic material. The samples isolated in preparatory glc were greater than 99.5% pure by analytical glc.

Run 7. In 10 ml of *tert*-butyl alcohol-*O-d* containing 0.300 g of TDA and 2.7 mg of TDA·HI was dissolved 0.346 g of (–)-1-*h*. This solution under anhydrous conditions was transferred to a heavy-walled Pyrex tube, frozen at –78°, degassed by two freeze-thaw cycles, sealed under vacuum, and submerged in a 100 ± 1° constant-temperature bath. After 4618 hr, the solution was quenched in 1 *N* hydrochloric acid and extracted three times with pentane. The organic layers were combined, washed with brine, dried and concentrated, and submitted to analytical glc analysis and to preparative glc separation. The samples of **1** and **2** collected were each analyzed for isomer and optical purity and deuterium content. Runs 1–6 and 9 were similarly patterned.

Kinetics. Volumetric glassware was calibrated and corrections were applied. Stock solutions of (–)-1-*h* (0.1181 *M*) and of PMG (2.109 *M* by titration, 15 mol % tetramethylurea) in *tert*-butyl alcohol were prepared in a drybox, and the solutions and solvent were stored there until used. In the runs of Tables II and III, carefully measured volumes of *tert*-butyl alcohol and the stock solutions were syringed into a 2-ml volumetric flask which was stoppered and shaken for 1 min. Zero time was taken to be the point at which all the PMG solution had been added. Approximately 1 ml of this solution was drawn into a disposable pipet and used to fill the polarimeter cell, which was sealed with greased, ground-glass stoppers. The remainder of the kinetic solution was set aside for analysis of PMG concentration by titration. The polarimeter cell was removed from the drybox, and thermostated at 25.0 ± 0.1°. After 2 min, readings were taken (±0.003°) at 436 nm, except for run 19, where 546 nm was used with little change in rate constant from run 18. At the end of a kinetic run (longest was 40 days), the solution in the polarimeter cell was analyzed by titration for PMG in triplicate. An aliquot was syringed into ~5 ml of distilled water and titrated with 1.039 *N* HCl to a phenolphthalein end point. Analyses performed before and after runs usually differed by less than 0.5%. In run 22, it differed by 2.2%. No trend was apparent. Additionally, the base concentration in each run was calculated from known volumes and the known PMG stock solution concentration. In runs 12, 13, 14, 17–20, the calculated and mean titration values agreed to within 0.3%. In the other runs, the calculated values were up to 2.8% too high. The reported base concentrations (Tables II and III) are the average of all titration values.

In all kinetic runs the rate constant for racemization was calculated using data obtained after at least 11 half-lives (99.95% reaction) of the isomerization reaction. Runs 11 and 21, 12 and 17, etc., involved the same solutions, and differ only in the times at which data points were collected. First-order rate constants obtained through use of a least-squares first-order computer program checked within 1.6% of the k_1 's obtained graphically.

In run 10, isomerization was followed by glc. A 0.2-ml aliquot of the solution used to fill the polarimeter cell for runs 11 and 21 was introduced into a shell vial which was closed firmly with a serum cap. The vial was thermostated at 25.0 ± 0.1°, and at timed intervals 0.02-ml aliquots were withdrawn and injected into 5-ml aliquots of 1 *N* HCl in a stoppered flask. The flask was shaken with 4 ml of pentane and left stoppered until the end of the run. After conclusion of the run the pentane layers were separated, concentrated to about 0.1 ml, and analyzed by glc (see above).

At the conclusion of run 17 (160 half-lives for isomerization), the reaction solution was analyzed by glc. Three analyses yielded an average value of $K = 7.54 \pm 0.14$ for the equilibrium constant at 25° for **1** ⇌ **2**.

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