Dynamic NMR Studies of Diastereomeric Carbamates: Implications toward the Determination of Relative Configuration by NMR

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Diastereomeric carbamates, derived from an optically pure amine of known configuration and racemic secondary carbinols, exhibit NMR line broadening, a process observed in only one of a pair of diastereomers. This line broadening and the associated hindered rotational process have been studied in detail for a variety of diastereomeric pairs, and it has been found that although the diastereomeric pairs differ in their NMR behavior, they are conformationally quite similar. The implications of these findings are discussed in reference to the determination of the configuration at the carbinyl center by NMR differences between a pair of diastereomers.

Diastereomeric carbamates similar to 1 are being used increasingly for the chromatographic resolution of chiral alcohols.[1-8] Complimenting the widespread chromatographic separability of these diastereomeric carbamates is the ease of retrieval of the resolved alcohol under mild nonracemizing conditions and the ability to determine the configuration at the carbinyl carbon from NMR spectral differences between the diastereomeric derivatives.[9] These spectral differences arise from the preferential population of the *Z* rotamer, the conformational rigidity of the carbamate backbone, and the resultant stereochemically dependent shielding by the α-naphthyl substituent.

The NMR spectra of some type 1 carbamate diastereomers show line broadening at ambient temperatures owing to a hindered rotational process in the amide portion of the carbamate. This NMR line broadening, which can sometimes complicate the mechanics of configurational assignment, offered a means for further refinement of our earlier correlations of NMR spectral differences, chromatographic elution orders, and relative configurations.[9,10] These correlations were adduced on the basis that the *Z* rotamer is the only one to contribute significantly to the aforementioned properties. However, NMR line broadening *requires* the nontrivial population of the *E* rotamer as well. Therefore, we felt it important to understand more fully the reasons underlying the occasional observation of this hindered process.

Lanthanide-induced chemical shift studies have shown that type 1 carbamates largely populate the *Z* conformation depicted.[10] In the absence of shift reagent, most of the originally studied type 1 carbamates showed neither line broadening nor spurious resonances. With incremental addition of shift reagent, minor resonances arise and were taken to indicate the "freezing" of the dynamic equilibrium between the *Z* and *E* rotamers.[11]

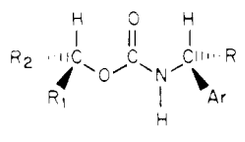

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Table I. Rotamer Populations[13] and Nonequivalence Data for Carbamates 2b-12b and 13-19 in $CDCl_3$ at Low Temperature

carbamate	% *Z*	% *E*	$\delta_Z - \delta_E$, ppm
2b	85	15	0.30 ($OCHCH_3$)
3b	85	15	0.55 ($OCHCH_2CH_3$)
4b	~85[a]	~15[a]	0.47 ($OCH(CH_2)_2CH_3$)
5b	~85[a]	~15[a]	0.41 ($OCH(CH_2)_3CH_3$)
6b	84	16	0.18 ($OCH_2CH_2CO_2CH_3$)
7b	81	19	0.18 ($OCH_2CH_2CO_2CH_3$)
8b	78	22	0.15 (p-CH_3-C_6H_4)
9b	73	27	0.16 (p-CH_3-C_6H_4)
10b	80	20	0.16 (p-CH_3-C_6H_4)
11b	~80[b]	~20[b]	−0.40 (carbonyl carbon)
12b	75	25	0.53 ($OCHC(CH_3)_3$)
13	~80[b]	~20[b]	−0.47 (carbonyl carbon)
14	87	13	0.32 ($OCHCH_3$)
15	83	17	0.37 ($OCHCH_2Cl$)
16	84	16	0.06 (OCH_3)
17	90	10	0.13 (OCH_3)
18	82	18	0.09 ($OCH(CH_3)_2$)
19	82	18	0.09 ($OCH(CH_3)_2$)

[a] Determination complicated by rotameric nonequivalence of the methylene protons. [b] Populations *estimated* by comparison of ^{13}C signal intensities.

Table II. ^{13}C Rotamer Nonequivalence Data for Carbamates 8b-12b and 13-19 in $CDCl_3$ at Low Temperature

	carbon ($\delta_E - \delta_Z$), ppm				
carbamate	carbonyl	CH_3-(α-NEA)	NH-CH	O-CH	R_2-($ArCH_3$)
8b	0.47	*a*	0.87	*b*	1.13
9b	0.33	1.13[a]	0.73	*b*	
10b	0.27	*a*	0.80	*b*	0.53
11b	0.40	1.00[a]	0.87	*b*	0.60
12b	0.40	1.07	1.20	0.67	0.67
13	0.47	1.20	1.13	0.60	
14	0.47	*c*	0.87	0.60	
15	0.27		0.80	0.80	
16	0.27		0.67	0.27	
17	2.27			0.93	
18	1.83			1.13	
19	2.20		0.33	1.20	

[a] Observation of nonequivalence for this carbon is complicated by overlap with the resonance for the aromatic methyl carbon. [b] Observation of nonequivalence for this carbon is complicated by two-bond carbon-fluorine coupling ($^2J_{C-F}$ ~ 30 Hz). [c] Observation of nonequivalence for this carbon is complicated by overlap with the resonance for the isopropyl methyl carbon.

(1) E. J. Corey, R. L. Danheiser, S. Chandrasekaran, G. Keck, B. Goplan, S. Larsen, P. Siret, and J. Gras, *J. Am. Chem. Soc.*, **100**, 8034 (1978).
(2) G. Schmid, T. Fukuyana, K. Akasaka, and Y. Kishi, *J. Am. Chem. Soc.*, **101**, 259 (1979).
(3) T. Fukuyana, C. Wang, and Y. Kishi, *J. Am. Chem. Soc.*, **101**, 260 (1979).
(4) T. Fukuyana, K. Akasaka, D.Karanewsky, C. Wang, G. Schmid, and Y. Kishi, *J. Am. Chem. Soc.*, **101**, 262 (1979).
(5) W. H. Pirkle and P. E. Adams, *J. Org. Chem.*, **43**, 378 (1978).
(6) W. H. Pirkle and C. W. Boeder, *J. Org. Chem.*, **43**, 2091 (1978).
(7) W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, **43**, 3083 (1978).
(8) W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, **44**, 1025 (1979).
(9) One actually determines the configuration at the carbinyl carbon relative to the known absolute configuration of the amine-derived portion of the carbamate.
(10) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42**, 1839 (1977).

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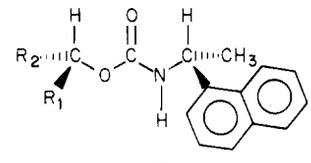
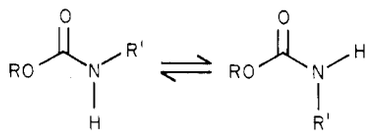
Chart I



Z

2b, R_1 = C≡CH; R_2 = CH_3
3b, R_1 = C≡CH; R_2 = CH_2CH_3
4b, R_1 = C≡CH; R_2 = $CH_2CH_2CH_3$
5b, R_1 = C≡CH; R_2 = $(CH_2)_3CH_3$
6b, R_1 = C≡C-*n*-C_8H_{17}; R_2 = $CH_2CH_2CO_2CH_3$
7b, R_1 = C≡CH; R_2 = $CH_2CH_2CO_2CH_3$
8b, R_1 = CF_3; R_2 = 4-CH_3-C_6H_4
9b, R_1 = CF_2CF_3; R_2 = 4-CH_3-C_6H_4
10b, R_1 = $CF_2CF_2CF_3$; R_2 = 4-CH_3-C_6H_4
11b, R_1 = CF_3; R_2 = 3-NO_2-C_6H_4
12b, R_1 = CH_3; R_2 = $C(CH_3)_3$
13, R_1 = H; R_2 = H
14, R_1 = CH_3; R_2 = CH_3
15, R_1 = CH_2Cl; R_2 = CH_2Cl
2a–12a, R_1 and R_2 interchanged



Z *E*

16, R = CH_3; R' = CH_3
17, R = CH_3; R' = $C(CH_3)_3$
18, R = CH_2CH_3; R' = $C(CH_3)_3$
19, R = $C(CH_3)_3$; R' = $C(CH_3)_3$

Results and Discussion. Diastereomeric carbamates were prepared from a series of racemic carbinols and chromatographically separated as previously described. Diastereomers **2a–12a** are the most chromatographically mobile (high R_f). Care was taken to ensure that each carbamate was diastereomerically pure. With the exception of **12a**,[12] no high R_f diastereomer shows detectable line broadening or the presence of a second rotamer *even at low temperature*. However, low R_f carbamates **2b–12b** show noticeable line broadening of some resonances at ambient temperature. At low temperature, the *Z* and *E* rotamers have nonequivalent ^1H and ^{13}C resonances for R_1 and R_2. Table I presents *Z* and *E* rotamer populations and nonequivalence data for carbamates **2b–12b** and **13–19**, while Table II presents ^{13}C nonequivalence data for these carbamates.

In both the ^1H and ^{13}C spectra, the resonance for R_2 in the major *Z* rotamer is downfield of the corresponding resonance in the minor *E* rotamer[14] (a low-field sense of rotameric nonequivalence).[15] It should be noted that carbons in the backbone of all the low R_f carbamates show a high-field sense of rotameric nonequivalence (i.e., resonances of the major rotamer are *upfield* of those of the minor rotamer). This nonequivalence appears to be unrelated to the nature of the alcohol or the amine in the carbamate (carbamates **13–19** show this same behavior) and may arise from differential steric crowding or differential angular distortion of the backbone carbons in the two rotamers.[16] (See Figure 1.)

It is important to note that the populations of the *Z* and *E* rotamers of carbamates **2b–12b** seem to be essentially independent of the structure of the alcohol. The populations remain roughly 80% *Z* and 20% *E*, even when one

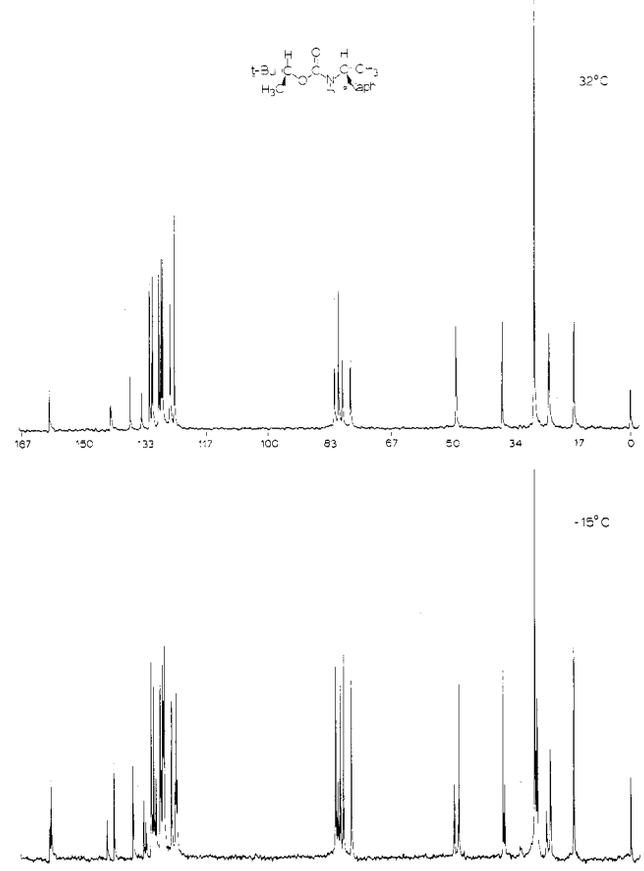


Figure 1. ^{13}C NMR spectra of the above carbamate showing rotameric nonequivalence.

Table III. Energy of Activation for Rotamer Interconversion in Carbamates 6b and 7b from Line Shape Analysis

carbamate	$\Delta G^{\ddagger}_{Z\rightarrow E}$,[a,b] kcal/mol	$\Delta G^{\ddagger}_{E\rightarrow Z}$,[a,b] kcal/mol
6b	14.9 ± 0.5	14.1 ± 0.5
7b	14.9 ± 0.5	14.0 ± 0.5

[a] At 270 K. [b] Obtained from the Eyring equation assuming a transmission coefficient of unity.

(11) Others have used shift reagents to effect interconversion rate and equilibrium position in carbamates. See, for example, S. Tanny, M. Pickering, and C. Springer, *J. Am. Chem. Soc.*, **95**, 6227 (1973).

(12) The diastereomeric carbamates **12a,b**, derived from 3,3-dimethyl-2-butanol and *R*-(−)-1-(1-naphthyl)ethyl isocyanate, exhibit anomolous chromatographic behavior. Based upon the observed sense of rotameric nonequivalence for the *tert*-butyl and methyl groups and the optical rotation of the carbinol retrieved from each diastereomer (low R_f: $[\alpha]^{25}_D$ −7.3 ± 2° (*c* 4.8, Et_2O); high R_f: $[\alpha]^{25}_D$ +3.1 ± 2° (*c* 2.9, Et_2O)),[20] the low R_f diastereomer (least chromatographically mobile) corresponds to the *R,R* configuration while the high R_f diastereomer corresponds to the *S,R* configuration. From our prior studies[10] of the factors which determine the relative elution orders of diastereomeric carbamates, the *S,R* diastereomer would have been expected to be the last eluted. We presently have no rationalization for the unanticipated elution order.

(13) Integration of the rotamer NMR signals at various low temperatures has shown the *Z* and *E* rotamer populations to be independent of temperature over the range studied.

(14) The carbinol portions of carbamates **2a,b–7a,b** and **12a,b** are of known absolute configuration.

(15) The sense of "rotameric" nonequivalence can serve as another method of assigning the relative configuration of the chiral centers, provided the major (so far, always *Z*) rotamer is known. "Rotameric" nonequivalence is analogous to the general phenomenon of NMR nonequivalence due to diastereomeric environments. Other examples include diastereomeric solvates formed between chiral substrates and chiral solvating agents (see W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, **43**, 4475 (1979)) and nonequivalence shown by diastereomeric carbamates.[10]

(16) Differential steric compression of the *n*-butyl groups has been used to explain the ^{13}C chemical shift difference of these groups in *N,N*-di-*n*-butylformamide. See G. C. Levy and G. L. Nelson, *J. Am. Chem. Soc.*, **94**, 4897 (1972).

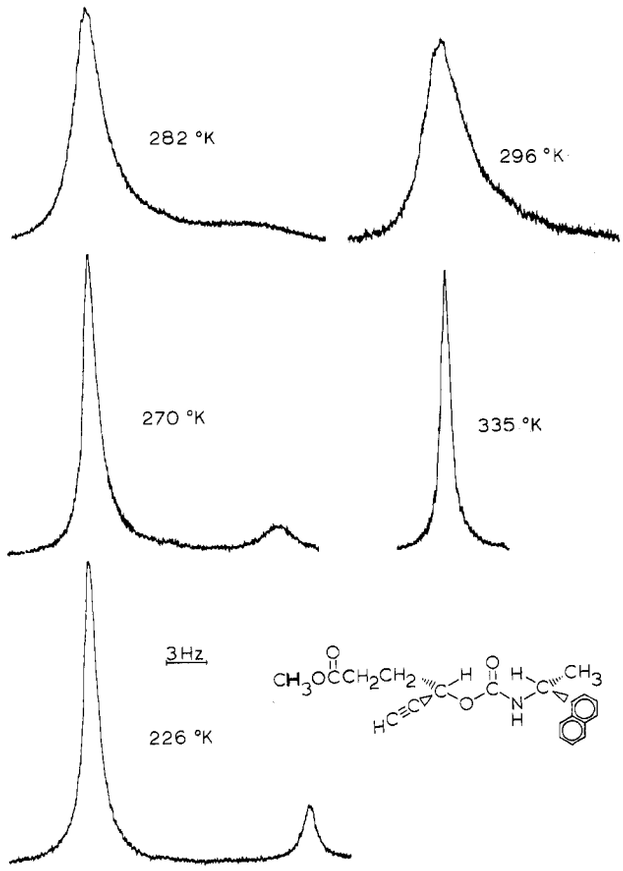


Figure 2. ^{1}H NMR spectra vs. temperature for the above low R_f carbamate.

deliberately includes bonding donor–acceptor interactions (i.e., **11b**) or repulsive steric interactions (i.e., **12b**) in an effort to perturb the *Z*:*E* ratio. The obvious inference is that R_1 and R_2 have no significant interactions with the α-naphthyl or methyl substituents owing to the intervening distance.[17] This reasonable inference poses a dilemma: if R_1 and R_2 are too remote to interact with the methyl or α-naphthyl substituents, then why do the high R_f diastereomers *not* show the NMR line broadening shown by their low R_f counterparts?

There are three interrelated criteria for NMR observation of an exchange process: the activation energy for exchange must be of adequate magnitude, both exchanging species must be adequately populated, and there must be an adequate chemical shift difference between the exchanging species. High R_f diastereomers **2a**–**11a** presumably fail to meet at least one of these criteria.

Figure 2 shows the resonance(s) of the methoxyl protons of **7b** at various temperatures. Line shape analysis of the methoxyl resonance(s) of **6b** and **7b** afforded the activation energies given in Table II. Our computed values for $\Delta G^{\ddagger}$ agree well with the usual values reported for a large variety of carbamates (13.9–15.9 kcal/mol).[18] Although we can only measure $\Delta G^{\ddagger}$ for the low R_f diastereomers, it seems unlikely that the barrier to rotation about the carbonyl carbon–nitrogen bond would be appreciably different than the barrier for the high R_f diastereomers. Evidence supporting this view will be presented subsequently.

(17) However, this distance is not so great as to totally preclude shielding by the α-naphthyl group.

(18) (a) E. Lustig, W. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967); (b) T. M. Valega, *ibid.*, **31**, 1150 (1966); (c) W. E. Stewart and J. H. Siddall, *Chem. Rev.*, **70**, 517 (1970); (d) S. van der Werf and J. B. F. N. Engberts, *Tetrahedron Lett.*, 3311 (1968).

Table IV. *Z* Rotamer Population vs. Solvent Polarity

	% *Z*		
carbamate	$CDCl_3$	$(CD_3)_2CO$	CD_3OD
8b	78	80	
12b	75	80	85
16	84	86	

Table V. Percent *Z* Rotamer from Variable Temperature and Lanthanide Shift Reagent Studies

carbamate	% *Z*	carbamate	% *Z*
8b	78[a]	**10b**	80[a]
8a	81[b]	**10a**	83[b]
9b	73[a]	**16**	84,[a] 81[b]
9a	69[b]	**17**	90,[a] 82[b]

[a] Variable temperature. [b] Lanthanide shift reagent.

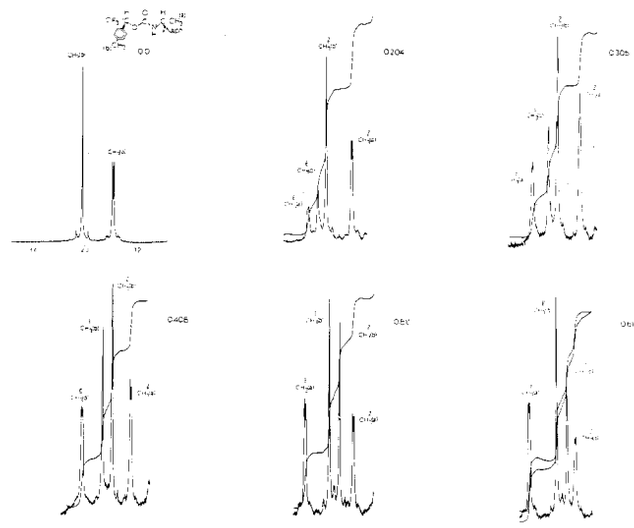


Figure 3. Effects of added shift reagent on the *Z*:*E* ratio of the above high R_f carbamate. ^{1}H NMR spectra vs. equivalents of added $Eu(fod)_3$.

It is known that solvent polarity can influence the position of rotameric equilibria. A conceivable rationalization for the dissimilar NMR behavior of the high R_f and low R_f diastereomers might be that dissimilar solvation leads to dissimilar *Z*:*E* ratios. This was a troubling thought since, to the extent that chromatographic adsorption might resemble solvation, chromatographic separability of diastereomeric carbamates might be more closely related to relative rotamer populations than we had previously supposed.[10] We do know that coordination of $Eu(fod)_3$ to a carbamate increases the *E*:*Z* ratio, and it seemed reasonable that solvation or adsorption might do the same, especially since it is the most strongly adsorbed (low R_f) diastereomers that seemingly showed the highest population of the *E* rotamer. Attempts to appreciably alter *E*:*Z* ratios by increasing solvent polarity (Table IV) show that the solvent has no strong effect on these ratios; indeed, the data suggest that increasing solvent polarity slightly favors the *Z* rotamer.

On the other hand, initial additions of $Eu(fod)_3$ to $CDCl_3$ solutions of carbamates cause a *linear* decrease in the logarithm of the population of the *Z* rotamer with increasing shift reagent concentration (Figure 3). Extrapolation of a plot of the logarithm of the *Z* rotamer population vs. shift reagent concentration to zero shift reagent concentration affords the unperturbed *Z* rotamer population for the carbamates. Several pairs of diastereomers have been so studied (Table V), and it is clear that the high R_f diastereomers *do* appreciably populate the *E* rotamer

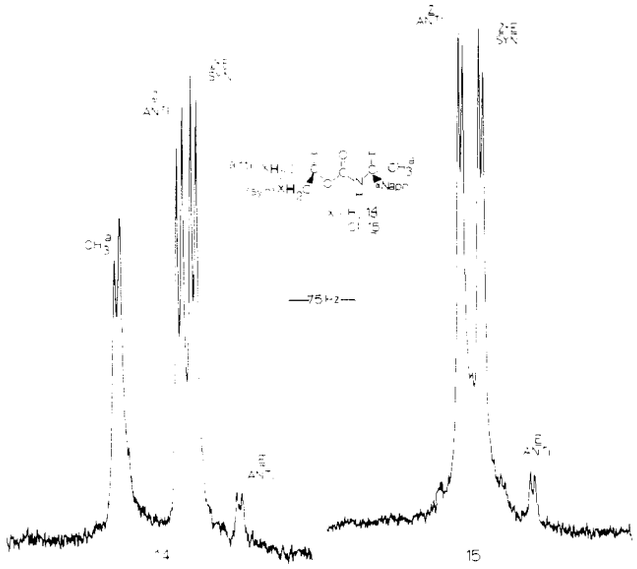
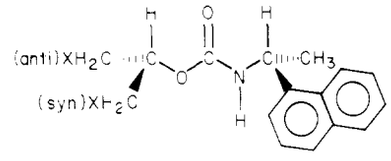


Figure 4. ^{1}H NMR spectra (220 MHz) for carbamates **14** and **15** in the stopped exchange region (−45 °C).

and to essentially the same extent as does the corresponding low R_f diastereomer. In view of the demonstrated similarity of rotamer populations for either diastereomer, the failure of the high R_f diastereomer to exhibit rotameric nonequivalence at low temperature suggests that the magnetic environments within its rotamers are very similar. Consistent with this view is the NMR behavior of the diastereotopic methyl and methylene groups in the rotamers of carbamates **14** and **15**.

Carbamates **14** and **15** each serve as simultaneous



14, X = H
15, X = Cl

models for the previously discussed high and low R_f diastereomers. The obvious difference between the diastereotopic methyl and methylene groups in **14** and **15** is that while one is syn to the α-naphthyl (in the depicted *Z* rotamer conformation) the other is anti. Bearing in mind the shielding effect of the α-naphthyl, we make our syn-anti assignments, as usual,[10] on the basis of the relative chemical shifts of these groups in the fast exchange limit. Figure 4 shows the appropriate regions of the 220-MHz ^{1}H NMR spectra of **14** and **15** in the *stopped exchange* limit. From these spectra, one clearly observes rotameric nonequivalence for the *anti*-methyl (or methylene) group but no rotameric nonequivalence for the *syn*-methyl (or methylene) group. The assignments shown in Figure 4 were reached from considerations of the relative chemical shifts and populations of the rotamers (Table I).

The failure of the syn groups to show rotameric nonequivalence cannot have its origin in the magnitude of the *Z*–*E* rotational barrier, since the anti groups do show rotameric nonequivalence. This "failure" parallels the behavior of the R_1 substituents in high R_f diastereomers **2a**–**11a**. We infer similar origins for the parallel behavior; that is, the high and low R_f diastereomers do not have appreciably different *Z*–*E* rotational barriers, but rather the magnetic environment of syn groups (i.e., R_1 in **2a**–**11a**) is not much different in the *Z* and *E* rotamers. However, the magnetic environments of anti groups (R_2 in **2b**–**12b**) do differ between the *Z* and *E* rotamers, the anti group being more highly shielded in the *E* rotamer.

One may qualitatively rationalize the preceding rotameric nonequivalence data on the basis that the conformations depicted in **20** approximately represent the time-averaged conformations of the *Z* and *E* rotamers of both diastereomers of carbamates **2**–**12**. One can perceive that R_1 is shielded by the α-naphthyl group in both the *Z* and *E* rotamers, whereas R_2 is shielded in the *E* but not the *Z* rotamer. The lack of rotameric nonequivalence for R_1 (syn) groups and the low-field sense of rotameric nonequivalence for R_2 (anti) groups is so explained. For the carbamates investigated, rotameric nonequivalence for the anti group (R_2) is always larger than diastereotopic nonequivalence in the *Z* rotamer (e.g., 0.32 vs. 0.070 ppm in **14** and 0.37 vs. 0.10 ppm in **15**). This behavior is thought to stem from the preferred conformation of the α-naphthyl group with respect to the nitrogen, methyl, and methine hydrogen substituents on the α-carbon. Essentially, the α-naphthyl ring is positioned roughly perpendicular to the carbamate backbone with its peri hydrogen near the methine hydrogen. Thus, in the *Z* rotamer, a syn group is positioned so that it is off center of and only partially shielded by the α-naphthyl system. Since an anti group is too remote for any appreciable shielding, only a modest diastereotopic nonequivalence results between the *Z* rotamers (i.e., 0.07 and 0.10 ppm for **14** and **15**, respectively). In the *E* rotamer, the originally anti group is now positioned directly over the α-naphthyl system and, hence, is heavily shielded relative to the anti group in the *Z* rotamer. Thus, a large amount of rotameric nonequivalence is observed for the anti group (i.e., 0.32 and 0.37 ppm for **14** and **15**, respectively). However, the originally syn group is off center of the α-naphthyl system in the *E* rotamer, as it was in the *Z* rotamer, and therefore exhibits little, if any, rotameric nonequivalence.[19] Shielding effects fall off rapidly with increasing distance, and the present simplistic rationalization takes no explicit heed of intervening distances. Note, however, that while diastereomeric nonequivalence is small between the syn and anti groups of **14** and **15** in the *Z* rotamer, its greater magnitude in the *E* rotamer (i.e., 0.27 ppm for **15**) is at least partially a consequence of the closer approach to the α-naphthyl system.

Substitution of phenyl for α-naphthyl caused, in the instances studied, essentially no change in conformational populations or senses of nonequivalence. Nonequivalence magnitudes were reduced considerably, however.

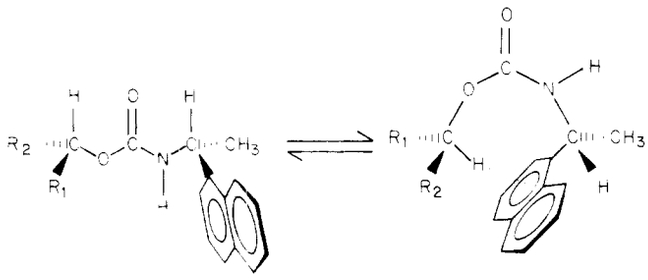
Insofar as we do not understand the origins of the ^{13}C rotameric nonequivalence of carbamates **8b**–**12b** and **13**–**19**, we cannot comment upon the applicability of the *E* rotamer depicted in **20** in rationalizing the lack of rotameric ^{13}C nonequivalence in **8a**–**11a**.

Experimental Section

Carbamates **2**–**15** were prepared by heating to reflux in toluene a mixture of racemic alcohol (1 equiv) and (*R*)-(−)-1-(1-naphthyl)ethyl isocyanate (1 equiv) for ca. 30 h, by which time

(19) This potential rotameric nonequivalence is not observed at 220 MHz but begins to manifest itself for **15** at 360 MHz (~30 Hz, 0.08 ppm). Even though the syn group is off center of the α-naphthyl group in both rotamers, it is presumably closer to the α-naphthyl in the *E* rotamer and the low-field sense of nonequivalence observed is so rationalized.

(20) The diastereomers from which the carbinol samples were retrieved were incompletely separated from one another. Hence, the carbinols are not enantiomerically pure. The absolute configuration of 3,3-dimethyl-2-butanol is known and is *S*(+) and *R*(−). See J. Jacobus, Z. Majerski, K. Mislow, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 1998 (1969). The diastereomer samples used for the NMR experiments were recrystallized until free of cross contamination.



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the isocyanate band at 2260 cm^{-1} mostly disappeared. Then diastereomeric carbamates **2a,b**–**12a,b** were chromatographed while carbamates **13**–**15** were recrystallized from the appropriate solvent.

Carbamates **16**–**18** were prepared by the reaction of the appropriate chloroformate (1 equiv) with the amine (1 equiv) in CH_2Cl_2 with 1 equiv of triethylamine added.

Carbamates **2a,b**,[10] **3a,b**,[10] **5a,b**,[10] and **7a,b**[6] have been reported previously.

1-(1-Octynyl)-3-carbomethoxypropyl *N*-[1-(1-Naphthyl)ethyl]carbamate (6a,b). These carbamates were generously provided by Paul E. Adams. **6a**: ^1H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.30 (broad s, 12 H), 1.63 (d, 3 H), 2.1 (m, 4 H), 2.45 (t, 2 H), 3.60 (s, 3 H), 5.1–5.8 (m, 3 H), 7.2–8.1 (m, 7 H); IR (film) 3320, 2230, 2030, 1740, 1510, 1440, 1230, 1050 cm^{-1}; MS (70 eV), *m/e* (rel intensity) 451 (M^+, 2.5), 254 (14), 237 (12), 215 (11), 214 (37), 200 (24), 197 (33), 182 (22), 170 (34), 156 (33), 155 (100), 154 (15), 153 (14), 129 (24), 127 (15), 124 (12). **6b**: ^1H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.30 (broad s, 12 H), 1.63 (d, 3 H), 2.1 (m, 4 H), 2.45 (m, 2 H), 3.66 (s, 3 H), 5.05–5.75 (m, 3 H), 7.2–8.1 (m, 7 H); IR (film) 3320, 2230, 2030, 1740, 1510, 1440, 1230, 1050 cm^{-1}; MS (70 eV), *m/e* (rel intensity) 451 (M^+, 1.6), 254 (13), 214 (33), 200 (19), 197 (30), 155 (100), 154 (14), 153 (13), 129 (20), 127 (16).

1-Ethynylbutyl *N*-[1-(1-Naphthyl)ethyl]carbamate (4a,b). **4a**: mp 94–95 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.3–1.9 (m, 4 H), 1.66 (d, 3 H), 2.35 (d, 1 H), 5.1–5.7 (m, 3 H), 7.2–8.2 (m, 7 H); IR ($CHCl_3$) 3430, 3310, 2970, 2260, 1740, 1510, 1380, 1220, 1060 cm^{-1}; MS, *m/e* (rel intensity) 295 (M^+, 18), 215 (15), 214 (100), 200 (15), 170 (57), 156 (29), 155 (62), 154 (20). **4b**: mp 114–116 °C (CH_3OH/H_2O); ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.3–1.9 (m, 4 H), 1.66 (d, 3 H), 2.31 (d, 1 H), 5.1–5.7 (m, 3 H), 7.2–8.2 (m, 7 H); IR ($CHCl_3$) 3450, 3315, 2985, 2260, 1740, 1510, 1380, 1220, 1060 cm^{-1}; MS, *m/e* (rel intensity) 295 (M^+, 21), 215 (17), 214 (100), 200 (17), 170 (63), 156 (33), 155 (71), 154 (23), 153 (25), 129 (70), 128 (18), 127 (23).

1-(4-Methylphenyl)-2,2,2-trifluoroethyl *N*-[1-(1-Naphthyl)ethyl]carbamate (8a,b). **8a**: mp 133–134 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.70 (d, 3 H), 2.30 (s, 3 H), 5.1–5.4 (broad s, 1 H), 5.6 (quintet, 1 H), 6.1 (quartet, 1 H), 7.1–8.1 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 387 (M^+, 30.2), 328 (8.5), 215 (11.1), 214 (74.7), 182 (13.1), 174 (9.9), 173 (100), 170 (40.7), 156 (12.8), 155 (48.3), 154 (18.0), 153 (16.4), 129 (35.1), 128 (12.5), 127 (21.3), 123 (37.2), 77 (9.9), 42 (27.3); IR ($CHCl_3$) 3690, 3620, 3440, 2980, 1735, 1500, 1350, 1270, 1185, 1135, 1070, 810, and 720 cm^{-1}. Anal. Calcd for $C_{22}H_{20}NO_2F_3$: C, 68.21; H, 5.20; N, 3.62. Found: C, 67.88; H, 5.07; N, 3.50. **8b**: mp 141–142 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 2.40 (broad s, 3 H), 5.1–5.4 (broad d, 1 H), 5.6 (quintet, 1 H), 6.1 (quartet, 1 H), 7.1–8.2 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 387 (M^+, 28.8), 328 (7.6), 215 (19.1), 214 (66.4), 182 (15.1), 173 (100), 171 (13.7), 170 (37.4), 156 (12.5), 155 (51.8), 154 (16.5), 153 (17.8), 129 (33.2), 128 (14.0), 127 (22.0), 123 (37.4), 77 (11.0); IR ($CHCl_3$) 3690, 3620, 3440, 3040, 2980, 1735, 1505, 1270, 1185, 1135, 1065, 810, and 720 cm^{-1}. Anal. Calcd for $C_{22}H_{20}NO_2F_3$: C, 68.21; H, 5.20; N, 3.62. Found: C, 68.02; H, 5.02; N, 3.70.

1-(4-Methylphenyl)-2,2,3,3,3-pentafluoropropyl *N*-[1-(1-Naphthyl)ethyl]carbamate (9a,b). **9a**: mp 115–116 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 2.30 (s, 3 H), 5.2–5.5 (broad d, 1 H), 5.6 (quintet, 1 H), 6.2 (doublet of doublets, 1 H), 7.0–8.1 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 437 (M^+, 39.9), 378 (9.4), 223 (88.3), 215 (14.5), 214 (100), 182 (14.0), 173 (12.4), 171 (10.8), 170 (52.1), 156 (17.6), 155 (69.5), 154 (36.8), 153 (26.4), 129 (44.4), 128 (15.5), 127 (24.1), 121 (10.6), 91 (14.6), 86 (41.2), 84 (66.6), 70 (10.8), 51 (29.2), 49 (96.7), 47 (17.4), 42 (32.1); IR ($CHCl_3$) 3690, 3620, 3440, 3030, 2970, 1735, 1500, 1375, 1180, 1145, 1065, 1035, 810, and 740 cm^{-1}. **9b**: mp 126–128 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 2.30 (broad s, 3 H), 5.1–5.5 (broad s, 1 H), 5.6 (quintet, 1 H), 6.15 (doublet of doublets, 1 H), 7.0–8.1 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 437 (M^+, 38.0), 378 (9.1), 224 (9.3), 223 (85.8), 215 (15.3), 214 (100), 197 (9.7), 183 (9.8), 182 (19.0), 173 (12.5), 171 (12.1), 170 (54.6), 156 (18.2), 155 (78.0), 154 (41.9), 153 (28.7), 129 (45.9), 128 (16.9), 127 (27.2), 121 (15.8), 91 (17.6), 77 (11.7), 70 (10.4), 42 (32.9); IR ($CHCl_3$) 3690, 3620, 3440, 3030, 2980, 1735, 1500, 1375, 1180, 1145, 1065, 1035, 810, and 715 cm^{-1}.

1-(4-Methylphenyl)-2,2,3,3,4,4,4-heptafluorobutyl *N*-[1-(1-Naphthyl)ethyl]carbamate (10a,b). **10a**: mp 138–139 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 2.35 (s, 3 H), 5.1–5.3 (broad d, 1 H), 5.55 (quintet, 1 H), 6.2 (doublet of doublets, 1 H), 7.0–8.1 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 487 (M^+, 35.6), 273 (65.7), 215 (14.2), 214 (100), 182 (12.5), 171 (11.4), 170 (47.9), 156 (17.1), 155 (74.0), 154 (58.9), 153 (23.0), 129 (38.8), 128 (12.9), 127 (20.6), 121 (12.2), 91 (12.2), 70 (10.2), 42 (27.3); IR ($CHCl_3$) 3690, 3620, 3440, 3030, 2980, 1735, 1500, 1350, 1280, 1110, 1065, 810, and 720 cm^{-1}. Anal. Calcd for $C_{24}H_{20}NO_2F_7$: C, 59.14; H, 4.14; N, 2.87; F, 27.29. Found: C, 59.12; H, 4.05; N, 2.71; F, 26.91. **10b**: mp 150–151 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 2.35 (broad s, 3 H), 5.1–5.3 (broad d, 1 H), 5.6 (quintet, 1 H), 6.2 (doublet of doublets, 1 H), 7.1–8.1 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 487 (M^+, 48.6), 273 (64.5), 215 (14.2), 214 (100), 182 (17.1), 171 (11.5), 170 (47.5), 156 (16.8), 155 (74.9), 154 (61.6), 153 (24.7), 129 (39.7), 128 (13.2), 127 (22.8), 121 (17.2), 91 (13.8), 77 (10.0), 70 (10.9), 42 (29.4); IR ($CHCl_3$) 3690, 3620, 3440, 3040, 2980, 1735, 1505, 1350, 1240, 1130, 1070, 810, and 720 cm^{-1}. Anal. Calcd for $C_{24}H_{20}NO_2F_7$: C, 59.14; H, 4.14; N, 2.87. Found: C, 59.25; H, 4.17; N, 2.72.

1-(3-Nitrophenyl)-2,2,2-trifluoroethyl *N*-[1-(1-Naphthyl)ethyl]carbamate (11a,b). **11a**: mp 141–142 °C (hexane–CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.70 (d, 3 H), 5.3–5.7 (broad s, 1 H), 5.6 (quintet, 1 H), 6.15 (quartet, 1 H), 7.2–8.3 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 418 (M^+, 65.0), 403 (38.8), 359 (16.2), 215 (15.3), 214 (100), 204 (68.8), 197 (25.6), 182 (42.8), 170 (56.8), 168 (10.1), 158 (26.8), 156 (12.1), 155 (83.7), 154 (94.5), 153 (34.0), 152 (48.1), 129 (56.5), 128 (37.1), 127 (54.4), 115 (9.8), 105 (9.6), 77 (23.3), 42 (48.8); IR ($CHCl_3$) 3690, 3620, 3040, 2980, 1740, 1540, 1505, 1355, 1265, 1180, 1140, 1070, 810, and 720 cm^{-1}. Anal. Calcd for $C_{21}H_{17}N_2O_4F_3$: C, 60.29; H, 4.10; N, 6.70. Found: C, 59.93; H, 3.90; N, 6.46. **11b**: mp 109–110 °C (hexane–CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 5.3–5.7 (broad s, 2 H), 6.10 (quartet, 1 H), 7.2–8.3 (m, 11 H); MS (70 eV), *m/e* (rel intensity) 418 (M^+, 74.5), 404 (10.4), 403 (49.3), 359 (17.9), 215 (14.9), 214 (98.1), 204 (72.0), 197 (26.5), 182 (47.7), 170 (59.7), 158 (28.6), 156 (13.3), 155 (94.9), 154 (100), 153 (34.8), 152 (52.8), 129 (59.3), 128 (38.8), 127 (55.5), 126 (10.2), 115 (10.2), 105 (10.1), 77 (25.3), 51 (10.4), 42 (50.6); IR ($CHCl_3$) 3690, 3630, 3420, 3040, 1740, 1540, 1505, 1355, 1190, 1140, 1070, 810, and 740 cm^{-1}. Anal. Calcd for $C_{21}H_{17}N_2O_4F_3$: C, 60.29; H, 4.10; N, 6.70. Found: C, 60.09; H, 4.05; N, 6.56.

2-(3,3-Dimethyl)butyl *N*-[1-(1-Naphthyl)ethyl]carbamate (12a,b). **12a**: mp 113–115 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.80 (s, 9 H), 0.95–1.20 (broad d, 3 H), 1.60 (d, 3 H), 4.50 (quartet, 1 H), 4.9 (broad d, 1 H), 5.6 (quintet, 1 H), 7.2–8.1 (m, 7 H); MS (70 eV), *m/e* (rel intensity) 299 (M^+, 27.7), 215 (66.4), 214 (43.6), 201 (10.4), 200 (83.4), 182 (16.5), 170 (28.4), 156 (49.6), 155 (100), 154 (22.2), 153 (21.3), 129 (27.6), 128 (15.0), 127 (21.1), 85 (25.8), 57 (28.0), 43 (73.8), 42 (12.9), 41 (27.3); IR ($CHCl_3$) 3690, 3020, 2980, 1710, 1510, 1460, 1380, 1250, 1080, 1060, and 900 cm^{-1}. **12b**: mp 81–83 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.80 (broad s, 9 H), 1.10 (d, 3 H), 1.60 (d, 3 H), 4.50 (quartet, 1 H), 4.8 (broad d, 1 H), 5.5 (quintet, 1 H), 7.2–8.1 (m, 7 H); MS (70 eV), *m/e* (rel intensity) 299 (M^+, 26.3), 216 (11.1), 215 (56.1), 214 (35.3), 201 (13.5), 200 (67.1), 170 (22.9), 156 (41.0), 155 (100), 154 (19.3), 153 (17.5), 129 (24.2), 128 (12.0), 127 (15.3), 85 (24.6), 57 (25.4), 43 (74.6), 42 (12.0), 41 (23.7); IR ($CHCl_3$) 3685, 3020, 2980, 1710, 1505, 1460, 1380, 1240, 1080, 1060, and 900 cm^{-1}.

Methyl *N*-[1-(1-napthyl)ethyl]carbamate (13): mp 89–90 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.60 (d, 3 H), 3.65 (s, 3 H), 5.1 (broad d, 1 H), 5.60 (quintet, 1 H), 7.3–8.2 (m, 7 H); IR ($CHCl_3$) 3680, 3620, 3440, 3020, 2980, 1710, 1500, 1240, 1110, 1060, and

800 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.60; N, 6.11. Found: C, 73.43; H, 6.50; N, 5.91.

Isopropyl *N*-[1-(1-naphthyl)ethyl]carbamate (14): mp 92–94 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.20 (d, 6 H), 1.60 (d, 3 H), 4.90 (septet, 1 H), 4.8–5.1 (broad d, 1 H), 5.60 (quintet, 1 H), 7.2–8.2 (m, 7 H); IR ($CHCl_3$) 3680, 3620, 3440, 3020, 2980, 1710, 1500, 1240, 1110, 1060, and 810 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.54; H, 7.29; N, 5.57.

2-(1,3-Dichloropropyl) *N*-[1-(1-naphthyl)ethyl]carbamate (15): mp 104.5–105.5 °C (hexane–CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.63 (d, 3 H), 3.68 (broad d, 4 H), 5.10 (quintet, 1 H), 5.2 (broad d, 1 H), 5.60 (quintet, 1 H), 7.3–8.2 (m, 7 H); IR ($CHCl_3$) 3690, 3620, 3440, 3030, 2980, 1725, 1505, 1240, 1200, 1065, and 810 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2Cl_2$: C, 58.91; H, 5.25; N, 4.29; Cl, 21.74. Found: C, 58.98; H, 5.24; N, 4.12; Cl, 21.83.

Methyl *N*-methylcarbamate (16): clear, colorless liquid; bp 76–78 °C (45 torr); ^1H NMR ($CDCl_3$) δ 2.75 (d, 3 H), 3.70 (s, 3 H), 5.0–5.4 (broad s, 1 H); IR (film) 3350, 2940, 1725, 1540, 1340, 1260, 1000, 900, and 775 cm^{-1}.

Methyl *N*-*tert*-butylcarbamate (17): clear, colorless liquid; bp 57–58 °C (15 torr); ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 3.58 (s, 3 H), 4.5–4.9 (broad s, 1 H); IR (film) 3350, 2950, 1715, 1530, 1350, 1260, 1215, 1180, 1100, 930, 775, and 715 cm^{-1}.

Ethyl *N*-*tert*-butylcarbamate (18): clear, colorless liquid; bp 66–67 °C (15 torr); ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H), 1.35 (s, 9 H), 4.05 (quartet, 2 H), 4.5–4.8 (broad s, 1 H); IR (film) 3350, 2950, 1715, 1525, 1450, 1380, 1260, 1210, 1080, 925, 870, and 775 cm^{-1}.

***tert*-Butyl *N*-*tert*-Butylcarbamate (19).** To a solution of di-*tert*-butyl dicarbonate (7.21 g, 33 mmol) in 25 mL of CH_2Cl_2 was added slowly a solution of 2.20 g (30 mmol) of *tert*-butylamine and 3.10 g (31 mmol) of triethylamine in 15 mL of CH_2Cl_2. The reaction was stirred for 1 h, extracted with 3 N HCl (2 × 25 mL) and H_2O (1 × 25 mL), and dried ($MgSO_4$). Evaporation of the solvent gives 4.62 g of **19** (89%): bp 72–73 °C (15 torr); clear, colorless liquid which solidifies in receiving vessel; mp 37–39 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 1.45 (s, 9 H), 4.3–4.6 (broad s, 1 H).

Dynamic Nuclear Magnetic Resonance Studies. Proton spectra were obtained on Varian Associates EM-390 (90 MHz) or HR-220 (220 MHz) spectrometers. Carbon spectra were obtained on a Jeol JNM-FX60 spectrometer operating in the FT mode, using 8 K data points and a frequency width of 2500 Hz (167 ppm), corresponding to a data point resolution of 0.61 Hz (0.04 ppm). Temperature calibration was done using Varian's standard methanol sample. Samples were prepared in the appropriate solvent at about 0.5 M concentration. Experimental line shapes were matched to the Block-McConnell theoretical line shapes calculated with an IBM 360/75 computer.

Conclusion

Since the ^1H NMR and the chromatographic behavior of diastereomeric type 1 carbamates are strongly influenced by their conformational behavior, demonstration that a pair of diastereomers behaves very similarly in conformational terms is reassuring. All such diastereomers herein studied predominantly populate the *Z* conformation to an extent of ca. 82 ± 5%, a value but slightly perturbed by solvent polarity. In view of these findings, our earlier correlations of NMR spectral differences and chromatographic behavior are still reliable. However, the present study has shown that NMR measurements made in the stopped exchange region have greater informational content and lead to even more facile assignments of stereochemistry.

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Registry No. 2b, 71927-70-3; **3b**, 65337-09-9; **4a**, 71871-94-8; **4b**, 71871-95-9; **5b**, 65337-07-7; **6a**, 71871-96-0; **6b**, 71871-96-0; **7b**, 65414-55-3; **8a**, 71885-03-5; **8b**, 71885-04-6; **9a**, 71871-97-1; **9b**, 71885-37-5; **10a**, 71871-98-2; **10b**, 71885-05-7; **11a**, 71927-76-9; **11b**, 71885-06-8; **12a**, 71871-99-3; **12b**, 71872-00-9; **13**, 71872-01-0; **14**, 71872-02-1; **15**, 71885-38-6; **16**, 6642-30-4; **17**, 27701-01-5; **18**, 1611-50-3; **19**, 71872-03-2; di-*tert*-butyl dicarbonate, 24424-99-5; *tert*-butylamine, 75-64-9.

Selectivity of Olefin Formation from Platinacyclobutanes

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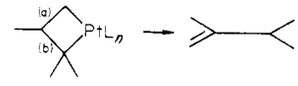
Platinacyclobutanes were shown to prefer olefin formation along the least-substituted edge of the platinacyclobutane when the olefin formed via a β-hydrogen abstraction from a ring carbon. In addition, the formation of olefins was sensitive to α substituents, which led to a preference for cis over trans olefins.

We recently reported[1] upon labeling experiments with dichlorobis(pyridine)(1,1,2-trimethylpropane-1,3-diyl)-platinum(IV) (1), which indicated the *mode* of olefin formation from this platinacyclobutane occurred via a β-hydrogen abstraction–reductive elimination process rather than by an α-hydrogen abstraction–reductive elimination process. In the same study, we also established that a β-hydrogen could be abstracted from a methyl substituent as well as from a ring carbon. While hydrogen abstraction from a substituent can lead to only one olefin, hydrogen abstraction from a ring carbon can often lead to two different olefins. In this study we report upon the *selectivity* in forming olefins from platinacyclobutanes.

The platinacycle 1 produced 2,3-dimethyl-1-butene as the only olefin although one could, theoretically, also form 2,3-dimethyl-2-butene from 1. We thought it was interesting that the olefin formed upon what would be the least-substituted edge (a) of the platinacycle. This gave a thermodynamically less stable olefin than if the olefin formation had occurred along the more-substituted edge (b). Hydrogen abstraction from a substituent methyl was shown to occur in conjunction with hydrogen abstraction from a ring carbon. This process, however, could lead only



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