Conformation of Protected Amino Acids. V.[1] Application of Lanthanide-Shift Reagents for Conformational Studies of *tert*-Butoxycarbonyl α-Amino Acid Esters: Equilibrium Changes and Kinetics of the Isomerization

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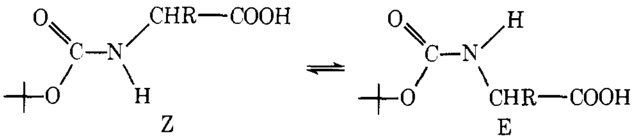
Abstract: ^{1}H and ^{13}C NMR studies show that in the *E,Z*-conformational equilibrium of Boc α-amino acid esters (Gly, Ala, Phe) the *Z* rotamer dominates. The addition of Eu(fod)$_3$ increases the amount of the *E* rotamer by preferred complexation. This directly observable change in equilibrium is caused by the increased size of the complexed urethane carbonyl group accompanied by the higher steric hindrance in the *Z* rotamer. Complete line shape analysis of Boc-Gly-OCH$_3$-d_3 at four different concentrations of Eu(fod)$_3$-d_{27} proves that the observed barrier of rotation ($\Delta G^{\ddagger}{}_{Z\rightarrow E}$ = 66.8 kJ/mol, $\Delta H^{\ddagger}{}_{Z\rightarrow E}$ = 65.7 kJ/mol, $\Delta S^{\ddagger}{}_{Z\rightarrow E}$ = 4.7 J/deg mol) reflects the barrier of the uncomplexed substrate. The change in the isomerization barriers $E \rightarrow Z$ with increasing LSR concentration parallels the ground state stabilization of the *E* rotamer.

Lanthanide-shift reagents (LSR) have developed as a very important tool for conformational studies during the past few years.[2] One problem of concern in this way is the change of the conformational equilibrium of nonrigid molecules by the addition of LSR. For the most part such changes are not directly observable. Indirect conclusions that have been drawn from changes of the coupling constants[3] and/or the quantitative lanthanide-induced shifts[4] (LIS) are more or less uncertain. Often the influence of the addition of LSR on the conformational equilibrium is neglected.[5] On the other hand it has been found that the change of the population by the addition of LSR can be followed directly, if the isomerization is near the range of the NMR time scale.[1,6-9] Furthermore, in such cases the temperature dependence of the spectra offers a method of determining the barrier of isomerization.[7]

The method of dynamic NMR spectroscopy requires an observable chemical-shift difference of the exchanging nuclei and a difference in the population of the isomers that is not too large. We will show in this paper that the application of LSR can influence chemical shift differences and populations in a positive way.

Change of Equilibrium

The equilibrium of *Z,E* isomers around the CN urethane bond of Boc amino acids can be observed in the ^{1}H and ^{13}C nmr spectra.[1,10] In those compounds the intramolecular hydrogen bond between the acid proton and the urethane carbonyl group are important for the stability of the isomers, and therefore it seemed of interest to investigate the corresponding esters. With one exception[11] no splitting of a signal was observed in the 90 MHz ^{1}H NMR spectra from −60 to +130 °C. The addition of Eu(fod)$_3$ to a solution of Boc-X-OCH$_3$ (X = Gly, Ala, Phe) at 0 °C shows a doubling of all signals. With increasing amounts of LSR the population of the minor component increases. The latter, which is assigned to the *E* conformer (see below) is shifted at low LSR concentrations much more than the *Z* isomer. At higher LSR concentrations the *Z* isomer is also shifted in a comparable amount (Figure 1A). These observations can be explained by steric effects. The complexation increases the size of the carbonyl groups so much that the "larger substituent" at the nitrogen prefers the trans arrangement to that group (*E* conformer). Without the shift reagent, the *Z* rotamer is the most stable conformation, but the preferred complexation of the *E* rotamer favors the latter in the equilibrium.



The assignment of the signals was made on the basis of the LIS data. One expects for the *Z* rotamer a larger shift of the C$_\alpha$ protons caused by the shorter distance to the lanthanide ion. To compare the shifts of the C$_\alpha$H groups of the two rotamers an indication of the amount of complexation with respect to the rotamers is required. For that reason we took the LIS of the *tert*-butyl group as a reference. This procedure includes the reasonable assumption that the LIS of the *tert*-butyl group is comparable in both isomers. Accordingly, the ratios $r = \Delta_{C_\alpha H}/\Delta_{Boc}$ were used for the assignment. Whereas these values always were larger than 1 for the *Z* isomers ($r^Z{}_{Gly}$ = 3.9, $r^Z{}_{Ala}$ = 22, $r^Z{}_{Phe}$ = 13), the corresponding ones for the *E* isomers were much smaller ($r^E{}_{Gly}$ = 0.33, $r^E{}_{Ala}$ = 0.18, $r^E{}_{Phe}$ = 0.11). In that respect it is interesting to see that LSR measurements for assignment of a mixture of isomers has to be carried out carefully; up to 30% LSR the C$_\alpha$H signal of the *E* isomer is shifted more than that of the *Z* isomer, which is unexpected considering only the distance from Eu ion. To prevent wrong assignments one must make measurements at different LSR concentrations.

From the data we can extrapolate the LSR concentration zero and in that way determine the population ratio of the Boc α-amino acid methyl esters without LSR at 7 °C. The amounts of *E* isomer are: Gly, 11 ± 2%; Ala, 12 ± 2%; and Phe, 9 ± 2%. In the case of Phe the directly determined value of 10 ± 2% is in good agreement with these values.[11]

The ^{13}C NMR spectra exhibit the same behavior. With an increasing amount of shift reagent an increasing set of signals appears (Figure 2). The unusual high field shift of the urethane carbonyl signal with Eu(fod)$_3$ is caused by the strong contact interaction with the paramagnetic ion. As quantitative studies have shown, the contact contribution dominates the pseudocontact contribution of Eu(fod)$_3$ induced shifts of an urethane carbonyl signal.[12] This provides unequivocal proof for the urethane carbonyl complexation of Boc amino acid esters.

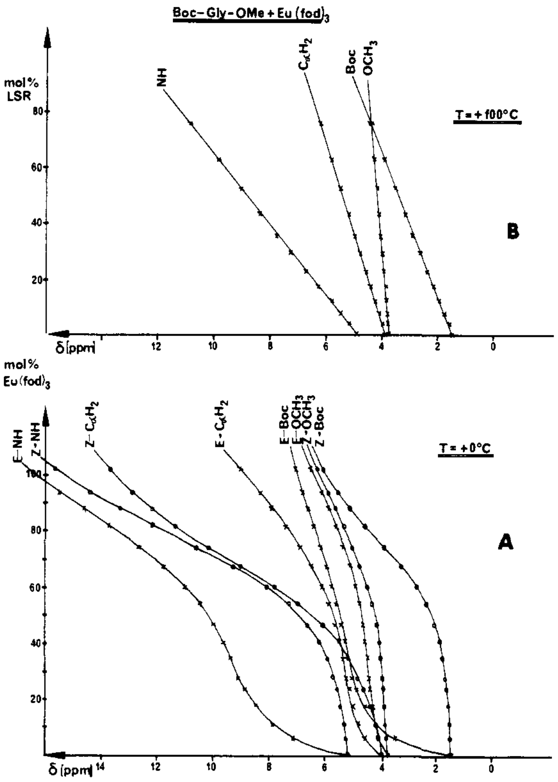


Figure 1. ^1H NMR chemical shifts of Boc-Gly-OCH_3 in $C_2D_2Cl_4$ vs. the Eu(fod)$_3$ concentration; (A) slow rotation about the CN bond; (B) fast rotation about the CN bond.

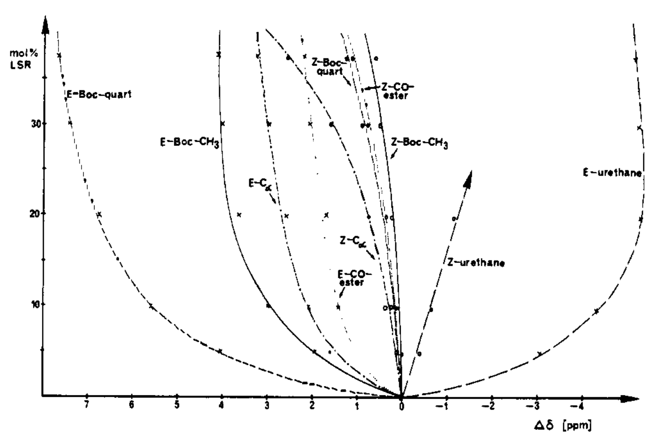


Figure 2. Eu(fod)$_3$ lanthanoid-induced shifts of the ^{13}C NMR signals of Boc-Gly-OCH_3 in $CDCl_3$ at 0 °C.

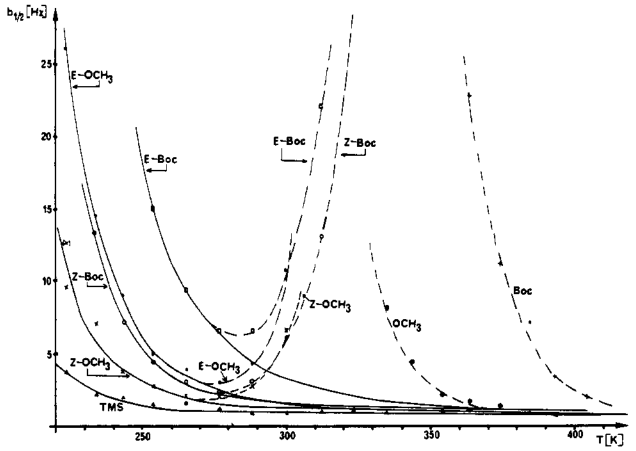


Figure 3. Determination of the line width parameters ($b_{1/2}$) for line shape analysis of Boc-ND-CD_2-$COOCH_3$ in the presence of 22.4 mol% Eu(fod)$_3$-d_{27} in $C_2D_2Cl_4$ at different temperatures.

A simulation of the usual case, where a change of the equilibrium by LSR cannot be directly observed, can be achieved by measurement at 100 °C. At that temperature the equilibrium is fast with respect to the NMR time scale, and the normal linear correlation of the induced shift with the concentration of LSR is observed (Figure 1B). It is reasonable to assume, and has been proven by the line shape analysis (see below), that at higher temperatures the ratio of the isomers also depends on the LSR concentration. Therefore, in using LIS data for quantitative studies of nonrigid molecules, caution is required.

Kinetic Studies

A four side equilibrium is to be taken into account for the investigated system of Boc α-amino acid methyl esters and LSR. The equilibrium between the complexed and uncomplexed isomers in the relevant temperature range is fast with respect to the NMR time scale in this system. Such an equilibrium can be frozen out at rather low temperatures only in the rare cases of very basic substrates.[13-15] The exchange between the *E* and *Z* rotamer can occur either in the uncomplexed or in the complexed state. Complexation of an amide with a Lewis acid at the carbonyl group leads to an increased double bond character of the CN bond and an increased barrier of rotation about that bond.[16] Consequently, the rotation should be faster in the uncomplexed Boc amino acid ester, and the determination of the rotational barrier of the uncomplexed species by the aid of LSR should be possible in those cases. We have proved the correctness of that assumption in the case of Boc-Gly-OCH_3-d_3 at four different LSR concentrations.

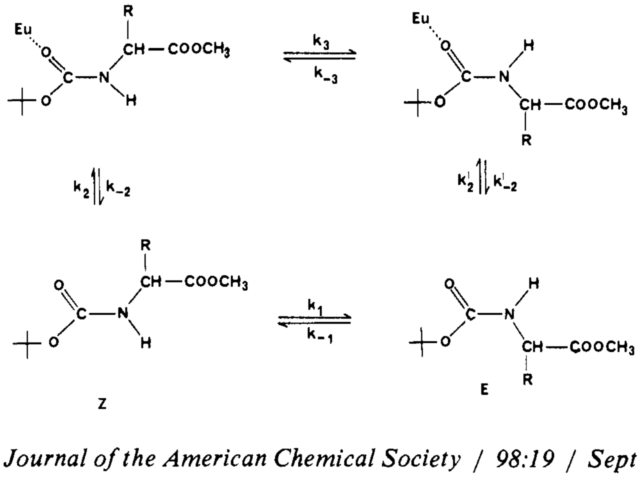


Figure 1 shows that in Boc-Gly-OCH_3 considerable overlap of the different signals occurs. The determination of the exact chemical shifts and population was complicated for that reason. Actually, we used α-C and *N*-deuterated Boc-Gly-OCH_3-d_3 in which the problem is simplified by the analysis of the two uncoupled systems. The presence of LSR in the sample causes substantial line broadening, especially at low temperatures which produce additional problems for line shape analysis. Consequently the often used procedure to reproduce the line width parameter by the value of the Me_4Si signal cannot be applied here. Accordingly, we extrapolated the line width at half-height from low and high temperatures into the exchange region as shown in Figure 3 and chose these values for the calculations. We think that such a procedure has to be done in all line shape studies. Otherwise systematic errors which are not detectable in the Eyring plot are produced because normally the line broadening of substrate signals at low temperatures is larger than that for the Me_4Si signals. The chemical shifts for the two isomers in the exchange region have been

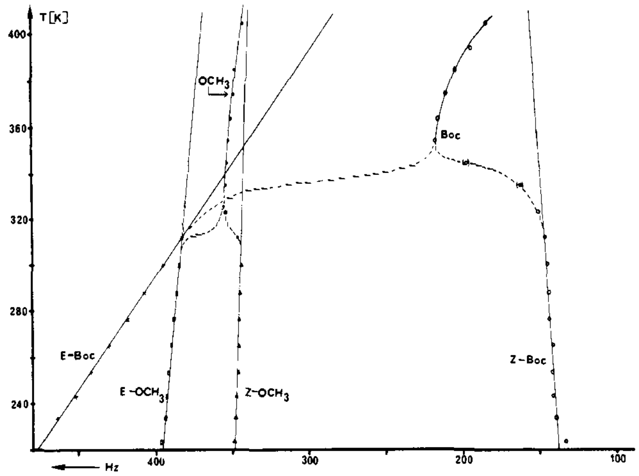


Figure 4. Determination of the chemical-shift parameters for line shape analysis of Boc-ND-CD_2-$COOCH_3$ in the presence of 22.4 mol% Eu(fod)$_3$-d_{27} in $C_2D_2Cl_4$ at different temperatures.

extrapolated also (Figure 4). The population of the isomers were determined at low temperature by electronic and planimetric integration and linearly extrapolated to the higher temperature by the van't Hoff treatment (plot of ln P_A/P_B vs. 1/T; Figure 5). Each extrapolation obviously is a source of error. Nevertheless we believe that due to the very large difference in the chemical shift (up to 300 Hz) and the concomitantly large temperature range (about 100 °C), which is sensitive to variations in the life time τ, the accuracy of the results is satisfying.

To evaluate the errors we also determined the τ values at each temperature, which were certainly wrong, and used only those optimal τ values for the Eyring plot, for which the deviations were less than 10%. Normally, those deviations are smallest near the coalescence temperature. In our case the very large chemical-shift difference of the exchanging nuclei causes a small signal to noise ratio in the exchange broadened spectra near the coalescence temperature. The concentration of the solution is limited by the solubility of the LSR at low temperatures. A further increase of the H_1 power to improve the signal to noise ratio could not be applied to avoid saturation effects. Accordingly, the errors in τ are about 10% in this range. Similar problems are common in ^{13}C DNMR studies.[17] The temperature was determined with a methanol or glycol sample before and after recording each spectrum.[18] The error in the temperature was determined to be less than 1 °C. The errors, calculated by using the formula of K. Schwetlick,[19] result in $\Delta\Delta H^{\ddagger} = \pm 1.5$ kJ/mol and $\Delta\Delta S^{\ddagger} = \pm 3.6$ J/K mol. The errors in $\Delta G^{\ddagger}$ are smaller than 0.4 kJ/mol.[29] These calculations do not take into account the errors which result from the extrapolation in the above mentioned parameters.

In Figure 6 one example of the comparison of calculated and experimental spectra is exhibited. The results of the line shape studies at different LSR concentrations are represented in Table I.

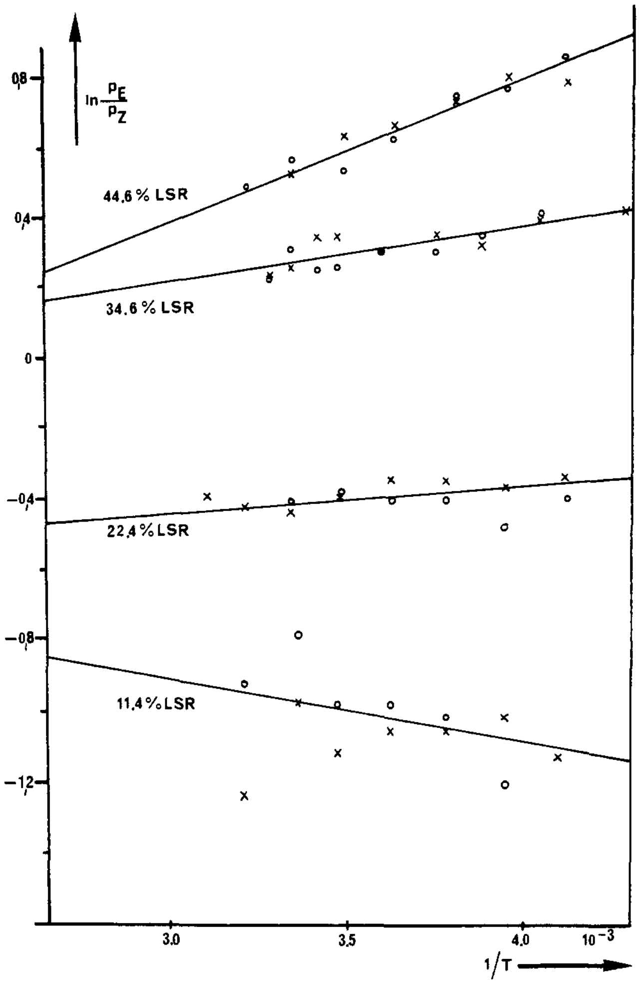


Figure 5. Extrapolation of the populations parameters for line shape analysis of Boc-ND-CD_2-$COOCH_3$ in the presence of different concentrations of Eu(fod)$_3$-d_{27} in $C_2D_2Cl_4$ at different temperatures. Intensities were determined by electronic (×) and planimetric (○) integration.

Discussion

Lanthanide-shift reagents were used in some cases for investigation of intramolecular rotations. Cheng and Gutowsky[20] used Eu(fod)$_3$ to increase the chemical-shift difference of the diastereotopic CH_3 groups of several *N,N*-dimethyl amides and in that way increased the coalescence temperature by more than 50 °C. Springer et al.[21] were able to do line shape analysis at constant temperature by the variation of the $\Delta\nu$ parameter brought about by successive additions of LSR. Quite another approach has been used by A. Mannschreck et al.[22] in the application of an optically active LSR as an auxiliary com-

Table I. Kinetic Data of CN Bond Rotation in Boc-ND-CD_2-$COOCH_3$ in Presence of Eu(fod)$_3$-d_{27}[a]

LSR[b]	$Z \rightarrow E$			$E \rightarrow Z$			
concentration	$\Delta G^{\ddagger}_{25}$, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, kJ/deg mol	$\Delta G^{\ddagger}_{25}$, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/deg mol	$\Delta G^{\circ}_{Z\rightarrow E}$, kJ/mol
0				62.3[c]			5.2
11.3	67.2	65.3	−6.0	64.7	63.9	−2.7	0.62
22.4	67.1	66.1	−3.1	65.9	66.7	+2.4	0.22
34.6	66.6	66.9	+0.8	67.2	67.9	+2.0	−0.15
44.6	66.2	64.4	−5.8	67.4	67.3	−0.2	−0.30

[a] 0.4 M solution of the substrate in $C_2D_2Cl_4$; errors see text. [b] Given in mol% relative to the substrate. [c] Calculated using $\Delta G^{\circ}_{Z\rightarrow E}$, see text.

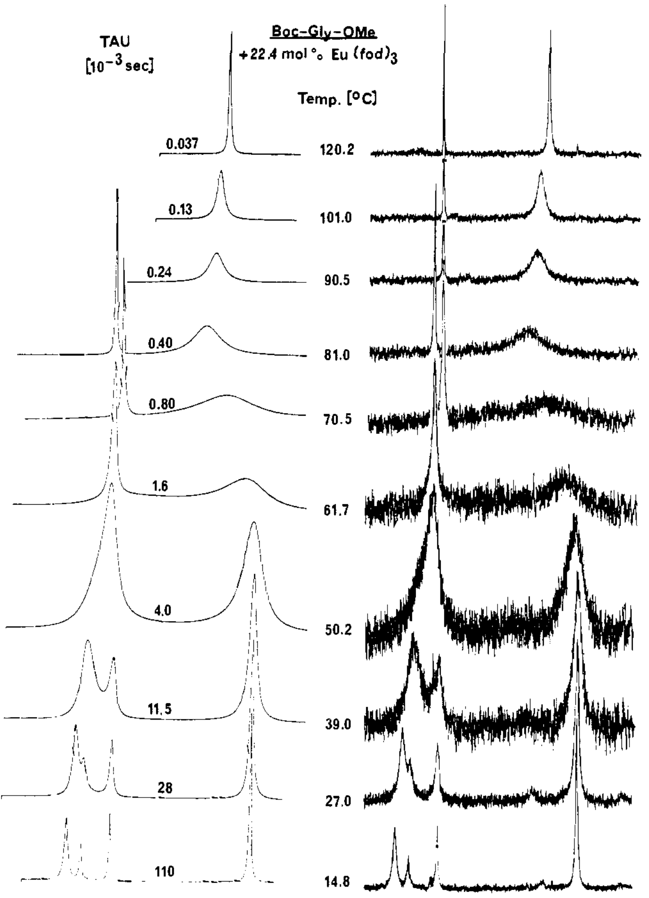


Figure 6. Comparison of calculated and experimental spectra of Boc-ND-CD_2-$COOCH_3$ in the presence of 22.4 mol% Eu(fod)$_3$-d_2 in $C_2D_2Cl_4$ at different temperatures.

pound to convert enantiotopic groups into diastereotopic ones that could be used to detect intramolecular rate processes. All these investigations are based on the assumption that the measured rate processes are not influenced by the shift reagent. While there are some indications that this requirement is fulfilled, we think our results give a clear-cut proof of it.

Comparing the $\Delta G^{\ddagger}$ values in Table I, we note that the variation of the LSR concentration does not influence the barrier of the isomerization $Z \rightarrow E$ in a significant way. On the other hand, the barrier $E \rightarrow Z$ increases with increasing LSR concentration. From the observed LIS data we know that in the concentration range that was used, the E rotamer is predominantly complexed (see Figure 7). This complexation stabilizes the E with respect to the Z conformer, which is also reflected in the population ratios. Consequently the barrier from E to Z has to rise by the same amount as the ground state of the E rotamer was stabilized, if the barrier is not influenced by the shift reagent. Hence, with increasing LSR concentration the change in $\Delta G^{\ddagger}{}_{E \rightarrow Z}$ should represent the change in $\Delta G^{\circ}{}_{Z \rightarrow E}$, whereas the barrier from $Z \rightarrow E$ remains constant in that case. Within the experimental error, our data fulfill these requirements. This gives an unequivocal proof that the observed barrier is the barrier of the uncomplexed substrate and that the addition of LSR does not increase the barrier. The measured barriers in $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are typical for rotations about urethane CN bonds.[1,10,23,24] The $\Delta S^{\ddagger}$ values are small as can be expected for an intramolecular rotation.[25]

Experimental Section

Boc-ND-CD_2-$COOCH_3$ was prepared from Glycin-d_5 (Firm Carl Roth, No. 1-7575) by reaction with Boc-N_3 in the usual way[26] and subsequent esterification with diazomethane and purified by distillation (bp 93.5 °C/0.2 Torr). Eu(fod)$_3$-d_{27} (Merck Sharp and Dohme) was dried for 1 week over P_2O_5 at 0.1 Torr and used without further purification.

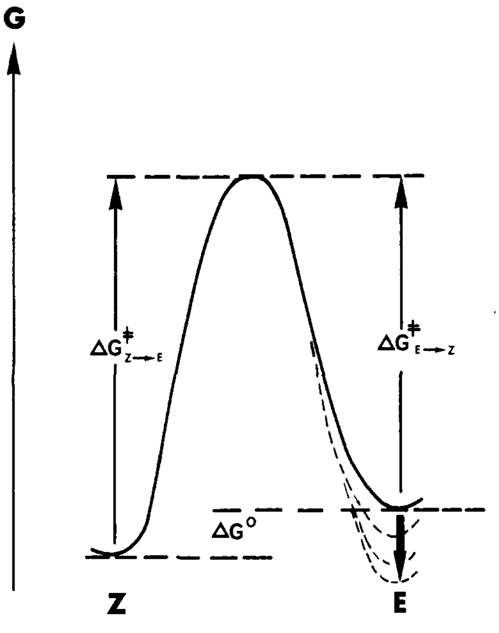


Figure 7. Schematic representation of the influence of LSR on the Z,E equilibrium of Boc-Gly-OCH_3.

The ^1H NMR spectra were recorded at 90 MHz with a Bruker HX 90 spectrometer in the CW mode.

The ^{13}C NMR spectra were recorded on the PFT mode at 22.63 MHz with the same spectrometer equipped with the Nicolet 1080 computer (program NIC. 80/S-7202-D).

The line shapes were calculated by the modified CLATUX program of Binsch[27,28] by the UNIVAC 1108 computer at the Hochschulrechenzentrum of the Universität of Frankfurt a.M.

Acknowledgment. The computer calculations were done at the Hochschulrechenzentrum der Universität Frankfurt a.M. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: (5 pp) Figure S 1 shows the extrapolation of the E,Z isomeric population on Boc-Ala-OCH_3, Boc-Gly-OCH_3, and Boc-Phe-OCH_3 as a function of LSR concentration. Tables S 1-4 give the NMR parameters for line shape calculations of Boc-ND-CD_2-$COOCH_3$ and the resulting τ values at the different LSR concentrations. Ordering information is given on any current masthead page.

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(29) The often reported "errors" from regression analysis are not realistic and give only the reproducibility of the data.

Reductive Demercuration of Hex-5-enyl-1-mercuric Bromide by Metal Hydrides. Rearrangement, Isotope Effects, and Mechanism

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Abstract: The use of the rearrangement of hex-5-enyl radical intermediates as a mechanistic probe has been examined in the reductive demercurations of hex-5-enyl-1-mercuric bromide (**1**). Methylcyclopentane and 1-hexene are the major products from reductions of **1** by sodium borohydride, lithium aluminum hydride, and tri-*n*-butyltin hydride. The formation of methylcyclopentane and the absence of cyclohexane are consistent with a noncage, free-radical chain mechanism for these reductions. The sodium amalgam reduction of **1** produces only 1-hexene. Hex-5-en-1-ol and a peroxide are formed from sodium borohydride reductions of **1** in the presence of molecular oxygen. Isotope effects for transfer of hydrogen to the intermediate hex-5-enyl radicals have been determined from the 1-hexene/methylcyclopentane product ratio, since rearrangement of the 5-hexenyl radical competes with hydrogen abstraction. The magnitude of these isotope effects (1.8 ± 0.2) is the same for reductive demercurations of **1** by sodium borohydride, lithium aluminum hydride, and tri-*n*-butyltin hydride; these results provide evidence for a common hydrogen-transfer agent, such as hex-5-enyl-1-mercuric hydride, for all of these metal-hydride reductions. The validity of the competing rearrangement method of determining hydrogen isotope effects has been demonstrated by determining the isotope effect for the tri-*n*-butyltin hydride reduction of 6-bromo-1-hexene (2.8 ± 0.2) at 40 °C.

Versatile synthetic procedures for the Markownikoff conversion of alkenes,[2] allenes,[3] and cyclopropanes[4] to alcohols, ethers, amides, amines, peroxides, and azides have been developed using the mercuration–reductive demercuration sequence.[5] Since metal hydrides, particularly sodium borohydride, have generally been used to effect the reductive demercuration of the intermediate alkylmercuric salts, the mechanisms of these reductions have received careful scrutiny recently. The significant mechanistic observations are that reductive demercurations by sodium borohydride are characterized by loss of stereochemical integrity,[5-8] rearrangement,[6,7,9] and incomplete incorporation of label from sodium borodeuteride.[7,8] These results as well as the efficient trapping of alkyl radical intermediates by molecular oxygen[9,11] and 2,2,6,6-tetramethylpiperidoxyl[11] have been explained in terms of mechanisms for the reductive demercurations by sodium borohydride involving either solvent-cage reactions (eq 1–3) or radical-chain processes (eq 4–6); an alkylmercuric hydride, RHgH, is the assumed source of hydrogen for the radicals.[7] Furthermore, the product distributions from reductions of norbornenyl-, nortricyclyl-, and isomeric norbornylmercuric salts using a variety of metal hydrides ($NaBH_4$, $(n\text{-Bu})_3SnH$, $(C_6H_5)_3SnH$, Et_2AlH, and $HCuP(n\text{-Bu})_3$) have been interpreted in terms of a common source of hydrogen (RHgH) for reductions using different metal hydrides.[7,10]

$$\mathrm{RHgX} \xrightarrow{\mathrm{NaBH_4}} \mathrm{RHgH} \tag{1}$$

$$\mathrm{RHgH} \rightarrow \overline{\mathrm{R\cdot} + \cdot\mathrm{HgH}} \tag{2}$$

$$\overline{\mathrm{R\cdot} + \cdot\mathrm{HgH}} \rightarrow \mathrm{RH} + \mathrm{Hg(0)} \tag{3}$$

or

$$\mathrm{RHgX} \rightarrow \mathrm{R\cdot} \tag{4}$$

$$\mathrm{R\cdot} + \mathrm{RHgH} \rightarrow \mathrm{RH} + \mathrm{RHg\cdot} \tag{5}$$

$$\mathrm{RHg\cdot} \rightarrow \mathrm{R\cdot} + \mathrm{Hg(0)} \tag{6}$$

We have been exploring the scope and limitations of using rearrangement as a mechanistic probe for radical intermediates. Earlier studies of the sodium borohydride reduction of 2,2,2-triphenylethylmercuric chloride provided the first evidence for relatively long-lived radical intermediates in reductive demercuration, since the major product in the absence of oxygen was the rearranged hydrocarbon, 1,1,2-triphenylethane.[9] These studies also provide the first report of successful trapping of radical intermediates in these reactions; the major product of reductive demercuration of 2,2,2-triphenylethylmercuric chloride by sodium borohydride in the presence of oxygen was the rearranged alcohol, 1,1,2-triphenylethanol. However, the extrapolation of these results to simple alkyl systems was regarded as tenuous. As an extension of these studies, we report herein results obtained for the reductive demercuration of hex-5-enyl-1-mercuric bromide (**1**) by various metal hydrides.[12] These studies provide direct evidence regarding: (a) the lifetimes of the radical intermediates in reductive demercuration; (b) the nature of the common hydrogen source; and (c) the cause of the relatively low amounts of deuterium incorporation (80–90% d_1) reported for reductive