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Temperature and Viscosity Dependence in the Stereoselective Formation of the Inverted Housane for the Photochemical Nitrogen Loss from the Deuterium-Stereolabeled Parent Diazabicyclo[2.2.1]hept-2-ene

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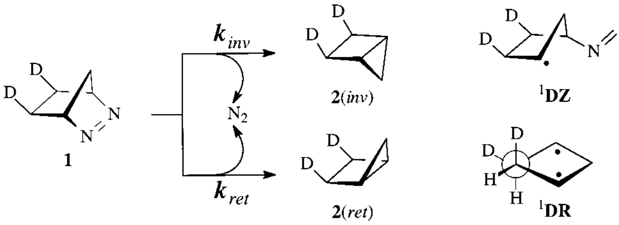
Abstract: For the liquid-phase photolytic denitrogenation of the stereolabeled DBH derivative *exo*-d_2-diazabicyclo[2.2.1]heptene (*exo*-d_2-**1**), the $k_{\mathrm{inv}}/k_{\mathrm{ret}}$ ratio of the inverted [**2**(*inv*)] and retained [**2**(*ret*)] housanes (bicyclo[2.1.0]pentanes) depends on the viscosity of the medium. For this purpose, the viscosity was varied by changing the solvent (various alcohols and diols, *n*-hexane, and acetonitrile) at constant temperature and by changing the temperature (−50 to +100 °C) in one single solvent, namely *n*-butanol. This viscosity effect is consistent with a stepwise denitrogenation mechanism in the liquid-phase photolysis of DBH, which proceeds through an unsymmetrical, nitrogen-containing transient, namely the singlet diazenyl diradical. The simple *free-volume* model adequately accounts for the observed viscosity behavior of the $k_{\mathrm{inv}}/k_{\mathrm{ret}}$ ratio in terms of frictional effects. The temperature dependence discloses a small but measurable difference in the internal activation energies for the inversion and retention processes of the proposed diazenyl diradical.

Introduction

An intriguing feature of the nitrogen extrusion in the denitrogenation of diazabicyclo[2.2.1]hept-2-enes (DBH), shown in Scheme 1 for the appropriately stereolabeled *parent* DBH (**1**), is the preferred formation of the inverted bicyclo[2.1.0]-pentane (housane) product **2**(*inv*).[1] A long-standing mechanistic query on this unique stereoselective process pertains to whether the diazenyl (^{1}**DZ**) or the nitrogen-free cyclopentane-1,3-diyl (^{1}**DR**) diradical intervenes in the product branching point (Scheme 1) to afford the diastereomeric housanes **2** in this denitrogenation process. In this scheme, the inverted housane **2**(*inv*) is produced through the intramolecular homolytic displacement of the nitrogen molecule by backside attack (the so-called S_H2 process[1a,2]) in the diazenyl diradical ^{1}**DZ**. The retained housane **2**(*ret*) is formed through the competitive denitrogenation of ^{1}**DZ** to the cyclopentanediyl diradical ^{1}**DR**. The latter C_2-symmetric species[3] is destined to cyclize to equal amounts of the **2**(*ret*) and **2**(*inv*) housanes, as demonstrated in the triplet-sensitized photolysis of *exo*-d_2-**1**.[4]

A recent computational study on the *thermolysis* of the parent DBH has concluded that the lower energy pathway of deazetation is the concerted expulsion of N_2 directly to the ^{1}**DR** species.[5] The observed stereoselection, namely more **2**(*inv*) than **2** (*ret*), was interpreted in terms of a dynamic effect, for which the nonstatistical C_2-symmetric ^{1}**DR** diradical is responsible.

Scheme 1. Competitive Pathways for the Denitrogenation of the Stereolabeled *exo*-d_2-DBH (**1**)



Computational[6] and experimental[7] work exists in favor of the stepwise nitrogen elimination in the photolysis of azoalkanes, which implicate the intervention of a diazenyl radical species. Thus, a recent theoretical study on the parent DBH discloses the singlet diazenyl diradical ^{1}**DZ** as lowest energy transient on n,π^* excitation.[6] Similarly, computational results on the

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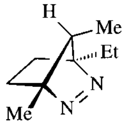
photolysis of azomethane suggest a stepwise mechanism for the denitrogenation.[8] Indeed, simple symmetry considerations in terms of the Dauben−Salem−Turro theory on photochemical transformations[9] predict a stepwise process.[7c] Nevertheless, it was important to scrutinize the validity of the stepwise deazetation mechanism for the photolysis of the parent DBH, properly stereolabeled in the form of *exo*-d_2-**1** (Scheme 1). In this context, we have recently demonstrated that viscosity (η) serves as a sensitive mechanistic probe to diagnose photochemical transformations with differentiated volume requirements. For example, the photolysis of *syn*-2,3-diaza-4,7-dimethyl-1-ethylbicyclo-[2.2.1]heptene, the substituted DBH derivative **3**, manifested a pronounced decrease in the **2**(*inv*)/**2**(*ret*) housane ratio at increased viscosity for a broad set of solvents, which included nonpolar, polar, and protic ones.[10] A temperature variation in *n*-butanol disclosed that the difference in the activation energies of the *inversion* and *retention* processes was negligible for the photolysis of the substituted DBH derivative **3**.[10b] The observed viscosity dependence of the k_{inv}/k_{ret} ratio was attributed to the larger spatial displacement of the methylene bridge in the denitrogenation of the diazenyl diradical ^{1}**DZ** during the inversion process of the azoalkane **3** photolysis.



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Mechanistically it may be argued that the viscosity dependence for the DBH derivative **3** is imposed by the bridgehead and methylene-bridge substitution and, thus, does not constitute an inherent feature of the azoalkane. It was, therefore, of import to examine the viscosity dependence of the nitrogen extrusion for the *unsubstituted* case, that is, the properly stereolabeled *exo*-d_2-DBH **1**. Herein we report a pronounced viscosity dependence of the stereoselectivity in the photolysis of the *exo*-d_2-DBH in liquid media by variation of the solvent and temperature.

Results and Discussion

The viscosity at constant temperature (20 °C) and ambient isobaric conditions was varied over a wide range (from 0.6 to 89.2 cP) of properly chosen alcohol solvents, as well as the nonprotic solvents *n*-hexane (nonpolar) and acetonitrile (polar). The temperature dependence was conducted in *n*-butanol over a broad (from −50 to 100 °C) temperature range.

The experimental results are displayed in Figure 1. As we have expected, the viscosity increase through both the solvent (dashed line) and the temperature (solid line) variations results in the decrease of the stereoselectivity, as expressed by the k_{inv}/k_{ret} ratio. However, contrary to the substituted DBH **3**,[10b] the constant-temperature and temperature-dependent viscosity profiles of the k_{inv}/k_{ret} ratio for the *exo*-d_2-DBH (**1**) do not coincide. To rationalize this viscosity behavior for the deuterium-labeled azoalkane **1**, we apply the same free-volume model that we have previously used for its substituted analogue **3**.[10]

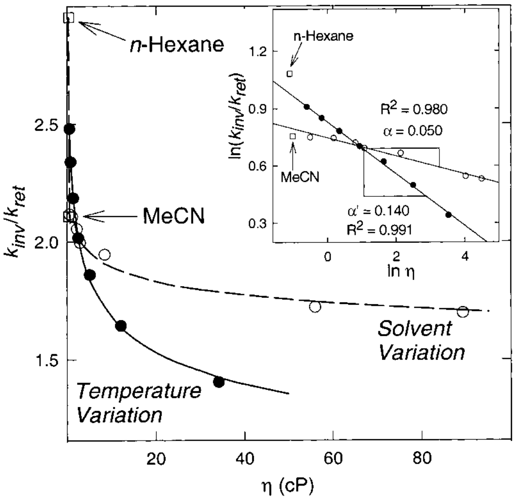

Figure 1. Viscosity dependence of the k_{inv}/k_{ret} ratio for the diastereomeric housane products (Scheme 1) as a function of the solvent at 20 °C for *n*-hexane [0.33 cP] and MeCN [0.36 cP], both codified by {□}, and alcohols methanol [0.6 cP], ethanol [1.2 cP], *n*-propanol [2.26 cP], *n*-butanol [2.95 cP], *n*-octanol [8.5 cP], 1,2-propanediol [56.0 cP], and 1,4-butanediol [89.2 cP], all codified by {○}, and as a function of temperature (100 °C [0.54 cP], 75 °C [0.84 cP], 50 °C [1.4 cP], 25 °C [2.55 cP], 0 °C [5.18 cP], −25 °C [12.1 cP], −50 °C [34.2 cP]) in *n*-butanol, codified by {●}; the insert displays the respective double-logarithmic plots of the viscosity k_{inv}/k_{ret} data as a function of the solvent {○, □} and temperature {●} variations (η expressed in cP).

The latter approach affords eq 1 for the k_{inv}/k_{ret} ratio in the liquid phase, in which the constants A and k^0_{inv} are the

$$k_{inv}/k_{ret} = (k^0_{inv}/k_{ret})(A/\eta)^{\alpha} \tag{1}$$

preexponential factors for the viscosity (η) and inversion rate constant (k_{inv}) in terms of the free-volume model;[11] α refers to the fraction of the van der Waals volume involved in the molecular reorganization.[11c−g] The double-logarithmic form of eq 1 predicts a linear plot for the $\ln(k_{inv}/k_{ret})$ versus $\ln(\eta)$, whose slope equals −α. Indeed, as seen from the insert in Figure 1, this plot is linear for the alcoholic solvents. The k_{inv}/k_{ret} value in acetonitrile, a polar aprotic solvent, fits in well within the viscosity data of the alcohols ($R^2 = 0.980$). This is most gratifying, because hydrogen-bonding effects are therewith not responsible for the observed viscosity behavior in Figure 1. However, in the nonpolar *n*-hexane, the k_{inv}/k_{ret} ratio is significantly higher than expected from the $\ln(k_{inv}/k_{ret})$ versus $\ln(\eta)$ plot (this data point has been excluded from the statistical treatment). Such viscosity behavior is not surprising when different types of solvents are used in the viscosity studies of unimolecular[11d,e,12] as well as bimolecular[13] processes. Thus, it is customary to assess the viscosity dependence in one type of solvent, to keep as constant as possible the solvent parameters other than viscosity. Herein, we have chosen a set of alcohol solvents whose advantage is the large viscosity range that may be spanned, in the present case ca. 150-fold! Nevertheless, it is

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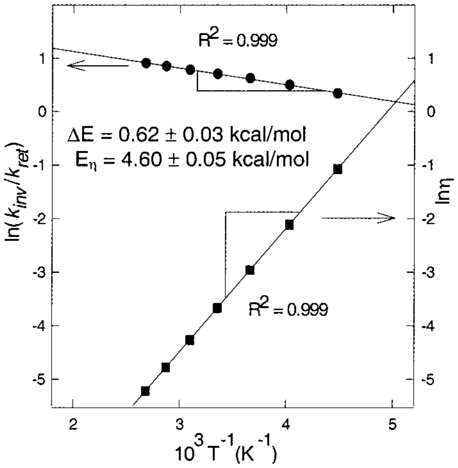

Figure 2. Arrhenius plots for the temperature dependence of the $k_{\text{inv}}/k_{\text{ret}}$ ratio according to eq 3 (●) and of the viscosity (η in P) for *n*-butanol according to eq 2 (■).

noteworthy that for the substituted azoalkane **3**, the $k_{\text{inv}}/k_{\text{ret}}$ data in all the protic and aprotic solvents obey the *same* viscosity dependence according to eq 1; however, this is happenstance rather than the rule for molecular rearrangements.[14]

As seen from Figure 1, the viscosity dependence for the temperature variation in *n*-butanol is markedly steeper than that for the solvent variation at constant temperature. What is the origin of the observed difference in the solvent- and temperature-varied viscosity profiles of the $k_{\text{inv}}/k_{\text{ret}}$ ratio? Below, we show that the difference ($\Delta E^i = E^i_{\text{inv}} - E^i_{\text{ret}}$) in the internal activation energies of the inversion (E^i_{inv}) and retention (E^i_{ret}) reaction channels accounts for the viscosity behavior in Figure 1.

In terms of the temperature dependence, the solvent viscosity may be expressed in the conventional Arrhenius−Andrade form by eq 2 and the $k_{\text{inv}}/k_{\text{ret}}$ ratio is given by eq 3, in which A_{inv} and

$$\eta = \eta_0 \exp(E_\eta/RT) \tag{2}$$

$$k_{\text{inv}}/k_{\text{ret}} = (A_{\text{inv}}/A_{\text{ret}}) \exp(-\Delta E/RT) \tag{3}$$

A_{ret} are the preexponential factors for the rate constants k_{inv} and k_{ret}; ΔE is the difference in the activation energies for the inversion versus retention channels, which consists of the *internal* (ΔE^i) and the *external* (ΔE^e) energy terms. While the former term represents the difference in the activation energies for the inversion versus retention channels at zero viscosity, the latter corresponds to the energy required to overcome the frictional impediment provided by the medium for the inversion mode [it is reasonable to assume that for the retention process frictional effects with the medium are negligible, since there are only minor geometrical differences between the DBH azoalkane and retained housane **2**(*ret*)]. Thus, the ΔE^e term is linearly proportional to the activation energy (E_η) of the solvent fluidity (η^{-1}) by the proportionality coefficient α in the relation $\Delta E^e = \alpha E_\eta$, which represents the fraction of the molecule involved in the molecular reorganization. According to eq 3, the difference in the experimental activation energy, $\Delta E = \Delta E^i + \alpha E_\eta$, may be assessed from the slope of the linear plot of $\ln(k_{\text{inv}}/k_{\text{ret}})$ versus $1/T$ (cf. Figure 2), which gives the value $\Delta E = 0.62 \pm 0.03$ kcal/mol for the present case.

To assess the internal (ΔE^i) and external ($\Delta E^e = \alpha E_\eta$) contributions to the experimental ΔE value, the α and E_η data are required. According to eq 1, the α value is given by the slope of the double-logarithmic plot of the $k_{\text{inv}}/k_{\text{ret}}$ ratio versus η (cf. insert in Figure 1), which takes the value $\alpha = 0.050 \pm 0.003$ for the viscosity data at constant temperature. The value $E_\eta = 4.60 \pm 0.05$ kcal/mol is given by the slope of the Arrhenius plot for the temperature dependence of the *n*-butanol viscosity (Figure 2).[15] Thus, the external (frictional) contribution to the experimental activation energy takes the value $\alpha E_\eta = 0.23 \pm 0.01$ kcal/mol; consequently, for the difference in the internal activation energy of the inversion versus retention channels we obtain the value $\Delta E^i = \Delta E - \alpha E_\eta\ (=\Delta E^e) = 0.62 - 0.23 = 0.39 \pm 0.03$ kcal/mol.

For the *exo*-d_2-DBH (**1**), a small but measurable difference ΔE^i in the internal activation energies for the inversion and retention channels is observed. This difference manifests the two competitive pathways of the photochemical denitrogenation in Scheme 1: (i) The N_2 displacement from the ^{1}**DZ** diradical by a backside attack of the unpaired electron in the carbon-centered 2p orbital to afford the inverted **2**(*inv*) housane[1,7c] and (ii) the nitrogen extrusion from the ^{1}**DZ** species to afford the nitrogen-free ^{1}**DR** diradical, which subsequently cyclizes to yield equal amounts of the diastereomeric housanes. Although the value $\Delta E^i = 0.39$ kcal/mol is small, its effect on the viscosity dependence of the $k_{\text{inv}}/k_{\text{ret}}$ ratio obtained by varying the temperature is evident in the steeper falloff for the solid curve in Figure 1, which shall be substantiated by the following analysis of the shape for the viscosity profiles.

In eq 1, the factor $k^0_{\text{inv}}/k_{\text{ret}}$ represents the conventional Arrhenius exponential temperature dependence, i.e., $k^0_{\text{inv}}/k_{\text{ret}} \sim \exp(-\Delta E^i/RT)$. Hence, on substitution of this expression, eq 1 may be rewritten as eq 4 for the temperature-dependent viscosity profile (solid curve in Figure 1), in which viscosity (η) and

$$k_{\text{inv}}/k_{\text{ret}} \sim \exp(-\Delta E^i/RT)\eta^{-\alpha} \tag{4}$$

temperature (T) are variables. With the help of eq 2, which describes the temperature dependence of the viscosity, eq 4 may be expressed solely in terms of the viscosity variable. For this purpose, eq 2 is rearranged as $E_\eta/RT = \ln(\eta/\eta_0)$; division of both sides of this expression by E_η and multiplication by ΔE^i leads to eq 5. Substitution of $\Delta E^i/RT$ from eq 5 into eq 4 gives finally eq 6 for the thermally varied η. According to eq 6, the

$$\Delta E^i/RT = (\Delta E^i/E_\eta) \ln(\eta/\eta_0) \tag{5}$$

$$k_{\text{inv}}/k_{\text{ret}} \sim \eta^{-(\alpha + \Delta E^i/E_\eta)} \tag{6}$$

double-logarithmic plot for the $k_{\text{inv}}/k_{\text{ret}}$ data versus the thermally varied viscosity provides a straight line, as seen in the insert of Figure 1 (solid symbols). Its slope is given by $\alpha' = \alpha + \Delta E^i/E_\eta$ (the α terms determine the shape of the viscosity profiles), from which ΔE^i may be calculated as $(\alpha' - \alpha)E_\eta$. Substitution of $\alpha' = 0.14$ (obtained from the viscosity dependence of the $k_{\text{inv}}/k_{\text{ret}}$ ratio for the thermally varied η, solid symbols in Figure 1), $\alpha = 0.05$ (assessed from the viscosity dependence at constant temperature, open symbols in Figure 1), and $E_\eta = 4.6$ kcal/mol (for *n*-butanol fluidity) affords $\Delta E^i \approx 0.4$ kcal/mol. Thus, the observed steeper falloff for the temperature-dependent (solid line) viscosity curve versus the constant-temperature curve

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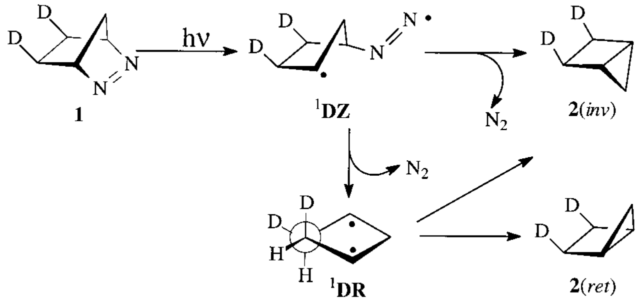
Scheme 2. Proposed Mechanism for the Diastereoselective Formation of the Inverted Housane in the Liquid-Phase Photodenitrogenation of the Stereolabeled *exo*-d_2-DBH (**1**) Azoalkane



(dashed line) in Figure 1 is accounted for by the difference in the internal activation energy (ΔE^i) of the inversion and retention channels.

The viscosity tool discloses two mechanistically relevant findings on the inversion process for the liquid-phase photodenitrogenation of the stereolabeled *exo*-d_2-DBH (**1**): The temperature dependence displays a small but measurable difference in the internal activation energies ($\Delta E^i = 0.39 \pm 0.03$ kcal/mol) for the formation of inverted and retained housanes **2**(*inv*) and **2**(*ret*), an experimental fact that implicates two distinct transition structures which lead to these diastereomeric housane molecules; the viscosity dependence reveals a small but measurable difference in the external activation energies ($\Delta E^e = 0.23 \pm 0.01$ kcal/mol) for the formation of **2**(*inv*) and **2**(*ret*), an experimental fact that results from the frictional effects with the medium, which are more pronounced for the inversion than for the retention process. These experimental results are consistent with the mechanism proposed in Scheme 2, with the singlet diazenyl diradical ^{1}**DZ** as the product branching point for the housane diastereomers **2**(*inv*) and **2**(*ret*). The concerted denitrogenation (inversion) of the ^{1}**DZ** species leads to the **2**(*inv*) housane, which is favored over the competitive nitrogen loss to the C_2-symmetrical cyclopentane-1,3-diyl diradical ^{1}**DR**. The latter symmetrical species is predestined to give equal amounts of the retained and inverted housanes **2**(*inv*) and **2**(*ret*). The stereodifferentiating species of the two distinct transients that intervene is the nitrogen-containing diazenyl diradical ^{1}**DZ**, the one responsible for the dominant formation of the inverted housane **2**(*inv*). Such diazenyl structures have been computationally[6] and experimentally[7] documented in the photochemical deazetation of azoalkanes. Thus, in view of the larger spatial displacements during the motion of the methylene bridge and the hydrogen atoms at the bridgehead for the inversion $^1\mathbf{DZ} \rightarrow \mathbf{2}(inv)$ than for the denitrogenation $^1\mathbf{DZ} \rightarrow {}^1\mathbf{DR}$ (Scheme 2), expectedly, the unsymmetrical transient ^{1}**DZ** should be subject to more pronounced frictional impediments exerted externally by the liquid medium ($\Delta E^e = 0.23 \pm 0.01$ kcal/mol). For the C_2-symmetric, nitrogen-free cyclopentadiyl diradical ^{1}**DR**, frictional effects cannot differentiate between the formation of **2**(*inv*) and **2**(*ret*) and, consequently, equal amounts of each are produced. Moreover, for the diazenyl transient ^{1}**DZ** different activation energies should be manifested for the inversion and retention events, as experimentally confirmed ($\Delta E^i = 0.39 \pm 0.03$ kcal/mol).

These new experimental facts, taken together with the results of previous work,[6−10] are in accord with the mechanism proposed in Scheme 2. Other mechanisms to rationalize the stereoselective inversion in liquid-phase photolysis of *exo*-d_2-DBH (**1**) may operate, e.g., the dynamic model proposed for the thermolysis of *exo*-d_2-DBH (**1**) in supercritical media,[5] but we favor the one offered in Scheme 2.

Finally, the following experimental difference in the viscosity behavior of the substituted derivative **3** and the stereolabeled parent DBH **1** deserves comment: Contrary to the parent DBH **1**, for the substituted DBH **3**, no difference has been measured in the internal activation energies (ΔE^i).[10b] It should be noticed, however, that the larger substituted DBH derivative **3** possesses a much greater frictional effect ($\Delta E^e = 1.24 \pm 0.06$ kcal/mol) compared to the smaller parent DBH **1** ($\Delta E^e = 0.23 \pm 0.01$ kcal/mol). Since for the substituted DBH **3** the external frictional contribution dominates, we speculate that the difference in the internal activation energies becomes more difficult to assess by the viscosity probe, at least in the examined viscosity range. To clarify this intrinsic behavior of diazenyl diradicals, it should be of mechanistic relevance to examine the viscosity dependence of the liquid-phase photolysis of a set of tailor-made substituted DBH derivatives.

We conclude that the viscosity is a sensitive probe to diagnose such a complex mechanistic question as the origin of the stereoselective inversion in the photodeazetation of azoalkanes. In the present case, this tool furnishes detailed mechanistic insight into the denitrogenation process for the *the liquid-phase photolysis* of the stereolabeled DBH derivative *exo*-d_2-**1** to the housanes **2**(*inv*) and **2**(*ret*). The frictional effects imposed by the liquid medium control the stereoselectivity ($k_{\mathrm{inv}}/k_{\mathrm{ret}}$) in the photochemical denitrogenation of DBH.

Experimental Section

Synthesis of Starting Materials. The *exo*-d_2-diazabicyclo[2.2.1]hept-2-ene (**1**) and the housanes **2**(*inv*) and **2**(*ret*) were synthesized as previously described.[7c]

Product Studies. Samples (0.7 mL) of the azoalkane *exo*-d_2-**1** (0.31 mmol) in the solvents (distilled prior to use) methanol, *n*-hexane, acetonitrile, ethanol, *n*-propanol, *n*-butanol, *n*-octanol, 1,2-propanediol, and 1,4-butanediol were transferred to an NMR tube, deaerated with a slow stream of argon gas for 10 min, and irradiated with the 333-, 353-, and 364-nm lines of the argon-ion laser (INNOVA 100, Coherent Company) at 20 °C. Additionally, *n*-butanol solutions of **1** (0.31 mmol) were irradiated with the same laser lines in the temperature range from −50 to 100 °C. The photolyzates were degassed in an ultrasonic bath and the product ratios were determined by ^{2}H NMR spectroscopy (Bruker Avance 400) by electronic integration of the peak areas for the corresponding signals (error ±5%).

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