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Reactivities of Stable Rotamers. XVIII. Reactions of 9-[2-(1-Hydroxyethyl)-1-naphthyl]fluorene Rotamers with Sulfuric Acid and Thionyl Chloride[1)]

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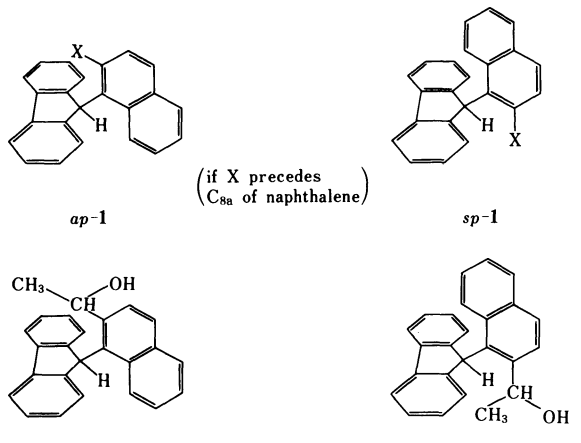
Treatment of the title compound with 70% sulfuric acid in 1,2-dimethoxyethane caused cyclization for the *ap* isomer, whereas it did dehydration to produce a vinyl compound smoothly for the *sp*. The same treatment with 10% sulfuric acid in 1,2-dimethoxyethane afforded the corresponding vinyl compounds from both rotamers. Treatment of the alcohol with thionyl chloride afforded the corresponding chloride in the case of the *sp*-alcohol, while it gave the *sp*-vinyl compound in addition to the *ap*-chloride in the case of the *ap*-alcohol. The change in solvents in the reaction of the *ap* form caused the change in the ratio of the olefin vs. the chloride: The polar solvents enhance the rates of formation of the chloride. Introduction of three deuteriums to the methyl group of the *ap*-form of the title compound suppressed the formation of the olefin to some extent. The results are explained on the grounds of steric effects in the ion-pair formation from the chlorosulfites and the contribution of the C–H stretching in the transition state of the elimination.

In previous papers of this series, it was postulated that a reaction is slow in the ap conformer of 9-arylfluorenes, one of which examples is 9-(2-substituted 1-naphthyl)fluorene (**1**), if the reaction takes a space-demanding transition state[2,3)] and that a cation formed in the benzylic position of the aryl group shows intramolecular interactions with the π-electron system of the fluorene moiety.[4)] Since 9-[2-(1-hydroxyethyl)-1-naphthyl]fluorene (**2**) should form a cationic species if treated with an acid and derivation of the alcohol to the corresponding chloride with the use of thionyl chloride should proceed with a cyclic transition state,[5)] the rotamers of compound **2** might show interesting difference in their behaviors in these reactions. Thus we investigated these reactions of the alcohol **2**. This paper is to report the results of the investigation and to discuss the origin of the difference.

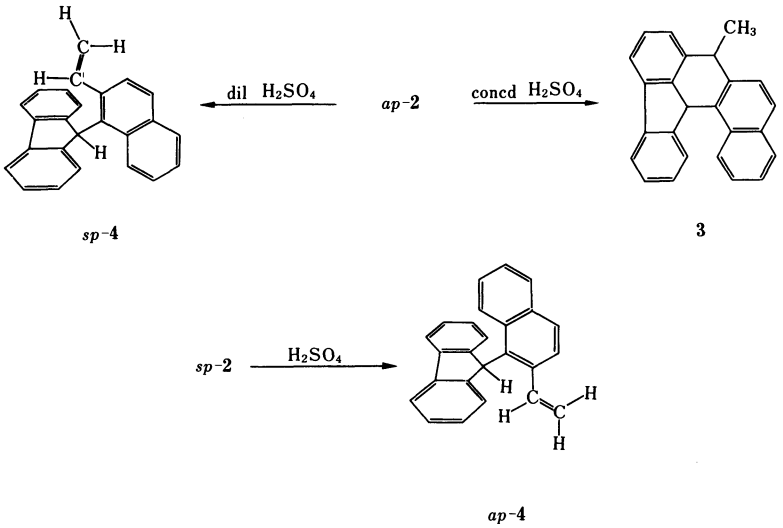


ap-1 *sp*-1

ap-2 *sp*-2

The barrier to rotation about the C_9(fluorene)-to-C_1(naphthalene) bond in the compound **2** has not been determined but may be assumed to be high enough to examine reactions without giving any complexity due to isomerization at room temperature for the following reasons. The barrier to rotation in 9-(2-methyl-1-naphthyl)fluorene (**1**: X=CH_3) is known to be ca. 29 kcal mol^{-1} (1 cal=4.18 J).[6,7)] Substitution of one of the hydrogens in the methyl group of 9-(2-methyl-1-naphthyl)fluorene does not significantly affect the barrier height (ca. 29 kcal mol^{-1}).[8)] In a series of 9-(2-substituted phenyl)fluorenes, the change in the substituent from methyl to ethyl and then to isopropyl causes a slight increase in the barrier height (16, 17, and 18 kcal mol^{-1}, respectively, for the *ap*→*sp* process).[6,9)] Similarly, 9-[2-(1-methoxycarbonylethyl)phenyl]fluorene exhibits ca. 18 kcal mol^{-1} barrier.[10)] Furthermore, the barrier to rotation in 9-[2-(α-hydroxybenzyl)-1-naphthyl]fluorene (*ap*→*sp*) is known to be ca. 30 kcal mol^{-1} at room temperature.[2b)] Thus the barrier to rotation about the C_9(fluorene)–C_1-(naphthalene) bond should be higher than 29 kcal mol^{-1}.

Reaction with Sulfuric Acid. Treatment of *ap*-**2** in 1,2-dimethoxyethane with sulfuric acid, of which concentration was high in the same solvent, afforded a product of which elemental analysis was consistent with a structure derived by dehydration of *ap*-**2**. From the ^{1}H NMR spectrum of the product and from our experience that has shown cyclization be possible for the *ap*-isomer if a cation is formed,[4)] we assigned a planar structure **3** for the product. By contrast, the *sp*-isomer afforded *ap*-9-(2-vinyl-1-naphthyl)fluorene (**4**) in good yields. If the concentration of sulfuric acid in 1,2-dimethoxyethane was low, both *ap*-**2** and *sp*-**2** afforded the respective rotamer of **4**, although the former is often contaminated by **3**.

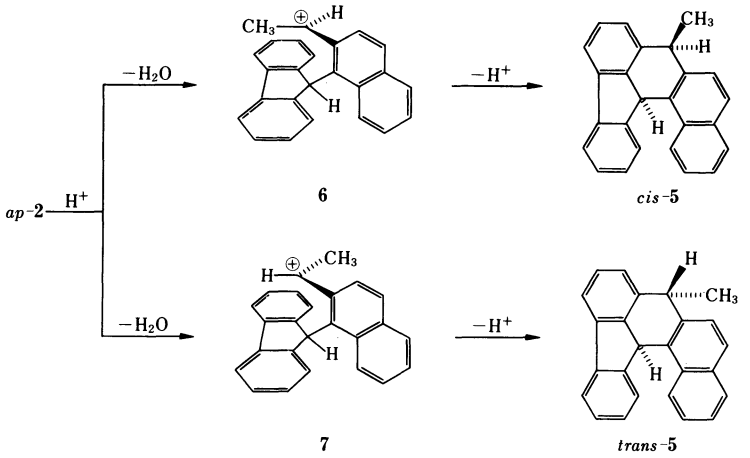


The reason for the fact that, whereas the *ap* form of **2** cyclized, *sp*-**2** failed to give any cyclized product, must be the geometry of the cation that is formed during the reaction. The cation from *sp*-**2** is in the plane of the fluorene ring. Since rotation about the C_9(fluorene)–C_1(naphthalene) bond must take place for the cation from *sp*-**2** for cyclization, of which barrier is high, deprotonation from the cation is a preferred process even in the concentrated sulfuric acid medium. In contrast, cyclization is favored in the cation from *ap*-**2** because the cationic center is very close to the π-system of the fluorene ring. It seems that, if the concentration of sulfuric acid is low, water or hydrogensulfate anion can remove a proton from the intervening cation from *ap*-**2** favorably.

If the π-participation in forming the benzylic cation from *ap*-**2** is really important, the dehydration of the *ap*-alcohol may be facilitated relative to the *sp*-alcohol, since formation of the cation is expected to be rate-determining. Competitive dehydration of *sp*-**2** and *ap*-**2** revealed that the relative rate, k_{sp}/k_{ap}, was 0.36, as determined by the formation of the olefins. Although this ratio might seem small, it must be taken as an indication that the π-participation is considerable, especially because the solvent molecules are good at stabilizing carbocations. For the cation from *ap*-**2**, solvation shell is formed by participation of the fluorene ring in addition to the solvent molecules, the latter being more favorable than the former.[4]

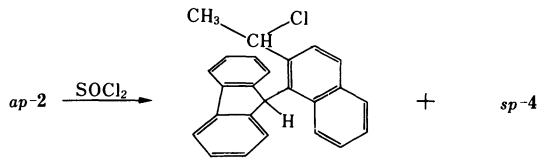
As to the stereostructure of **3**, there are two possibilities, *cis* and *trans*, with respect to the 8-H and 14c-H. For the stereochemical assignments of 9,10-dihydroanthracene derivatives, coupling constants in ^{1}H NMR are known to be useful.[11] Since the 14c-H should take the axial position because of the geometrical requirement, if the methyl group at the 8-position is equatorial, a large coupling constant between the protons in question is expected. Since they showed a small coupling constant, the ^{1}H NMR spectrum supports the stereochemistry in that the 8-H and the 14c-H are *trans* with each other.

Consideration of the reaction mechanism also supports the conclusion drawn from the ^{1}H NMR spectrum. The alcohol (**2**) will form a cationoid species when it is treated with sulfuric acid, since it is a benzylic alcohol.[12] Then there are two over-simplified reaction intermediates (**6** and **7**) possible, as

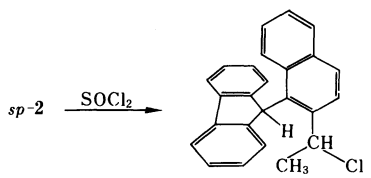


shown in the preceding page. Of the two, the one in which the methyl group is located over the fluorene ring **6** should be of high energy than the other **7** in which the hydrogen is over the fluorene ring. If cyclization takes place from **6**, the 8-H/14c-H stereochemistry is *cis*, whereas it is *trans* when cyclization takes place from **7**. Thus, *trans* stereochemistry should be favored in the product. In support of this, we observed formation of another isomer, of which ^{1}H NMR doublet signal appeared at δ 1.82 due to the methyl protons, in addition to the main product which showed the same peak at δ 1.53, in the reaction run by adding sulfuric acid to 1,2-dimethoxyethane solutions of *ap*-**2**, when temperature rose spontaneously.

Reactions with Thionyl Chloride. The reactions of the alcohol (**2**) with thionyl chloride was carried out generally as dichloromethane solutions at 0 °C. *sp*-**2** afforded the corresponding chloride (**8**) smoothly, whereas *ap*-**2** afforded *sp*-9-(2-vinyl-1-naphthyl)fluorene (**4**) in addition to the chloride (**8**). Since the reaction of 1-(2-naphthyl)ethanol under the same conditions gave the corresponding chloride only, as had been reported,[13] the anomaly is in *ap*-**2** rather than in *sp*-**2**. Formation of olefins in treatment of secondary alcohols with thionyl chloride has been reported in purely aliphatic series,[14] but not for the benzylic alcohols. We have examined whether hydrogen chloride reacted with *sp*-**4** to form *ap*-**8** and *ap*-**8** decomposed to produce *sp*-**4** under the conditions. The results were all negative. Thus the ratio *sp*-**4**/*ap*-**8** can be taken as intrinsic.



ap-**8**



sp-**8**

The formation of a chloride from a chlorosulfite ester which is derived by the reaction of an alcohol with thionyl chloride is believed to proceed via an ion pair that is produced by a cyclic transition state.[5b] The rate-determining step in the olefin formation from secondary alcohols and thionyl chloride has been deduced to be the formation of the ion pair as well from the kinetic isotope effect.[15] However, it is necessary for the chloride anion to move in the deprotonation from the methyl group in the case of *ap*-**2**. Therefore, if the elimination to form *sp*-**4** and the substitution to form *ap*-**8** are competing, solvent effects due to the polarity are expected. Thus we carried out the reactions of **2** with thionyl chloride in various solvents. The results are shown in Table 1. The olefin **4** is never found in the product of the reaction of *sp*-**2**, as far as the present method of detection concerns, but the formation of the olefin from *ap*-**2** is dependent on the polarity of the solvent used: The more polar is the solvent, the more is the chloride produced.

Table 1. Dehydration versus Chlorination in the Reaction of **2** with Thionyl Chloride

Solvent	Dielectric constant of solvent	From *ap*-alcohol (*sp*-**4**/*ap*-**8**)	From *sp*-alcohol (*ap*-**4**/*sp*-**8**)
Hexane	1.88[b]	71/29	<5/>95
Dioxane	2.21[b]	67/33	<5/>95
Dichloromethane	8.93[b]	60/40	<5/>95
Thionyl chloride	9.25[c]	38/62	<5/>95
Nitromethane	35.9[b]	20/80	<5/>95

a) Reactions were carried out with ice-cooling except for the hexane solutions which were heated at 40 °C. b) From Ref. 16. c) From Ref. 17.

In order to get further insight into the reaction, we measured ^{1}H NMR spectra of mixtures of **2** and thionyl chloride in dichloromethane at 0 °C. Surprisingly, we found signals due to the starting material and the products, the olefin **4** and/or the chloride **8**, but not those due to chlorosulfites. Whereas the signals due to **2** decreased in their intensities and those due to the products increased in their intensities, we did not observe any signals ascribable to the chlorosulfite. This means either that the rate determining step in the reaction is not the step leading to the cyclic transition state or that the chlorosulfite is highly unstable, though its decomposition is rate-determining. It is not possible to conclude which is the case from the results of the present work. The rate determining step may vary also, as the polarity of the solvent changes.

We further carried out the reaction of *ap*-**2**-methyl-d_3 under the same conditions with the protium compound in dioxane to find that the ratio *sp*-**4**/*ap*-**8** changed from 2.0 in the protium compound to 1.0 in the deuterium compound. Although it was not possible to run the kinetic studies due to the fact that the chlorosulfites were unstable and thus the kinetic isotope effects were not determined, this change in the product ratio is interesting. The results would mean that the hydrogen-abstraction step is contributing to the overall reaction rates.

The implication of the results made it necessary to reexamine the reported kinetic isotope effect.[15] Close examination of the reported rates of decomposition of

1-methylbutyl-methyl,2,2-$d_{4.3}$ chlorosulfite reveals that the isotope effects are 1.4 and 3.3 in dioxane and isooctane, respectively. The secondary α-kinetic isotope effects are normally 10—15% per deuterium for the S_Ni type ionizations.[18] While the β-kinetic isotope effects are stereochemistry-dependent, they never exceeds 2.0.[19] The data obtained for the dioxane solutions are within the range for normal ionization reactions, but those for the isooctane solutions exceeds the range of the normal ionization, if the secondary isotope effects are assumed. This would mean that solvents change the mechanisms or the contributions to the transition states of the rate-determining step considerably, because the solvent polarity affects the transition state energy.

The isotope effects on the product ratio then could be used for the diagnosis of the reaction mechanisms, since the primary isotope effects are expected to be more than 3.0 for the normal cases.[20] From the data of the solvent effects on the product ratios, it was expected that the isotope effects on the product ratio *sp*-**4**/*ap*-**8** were to be the highest in hydrocarbons. Accordingly, examination of the product ratio *sp*-**4**/*ap*-**8** in hexane would be interesting. The reaction had to be carried out at 40 °C in hexane because of its slowness, while reactions were practically complete at 0 °C in other solvents. This operation will cause reduction in the *sp*-**4**/*ap*-**8** ratio relative to the data at 0 °C in other solvents.[21] Yet the ratio was 7:3 for the protium compound, a little higher value than that obtained with the dioxane solution at 0 °C (Table 1). Thus the solvent effect on the *sp*-**4**/*ap*-**8** ratio, favoring the formation of *sp*-**4** in less polar media, is still valid. The same treatment of *ap*-**2**-methyl-d_3 in hexane gave the *sp*-**4**/*ap*-**8** ratio of 1.5, which is still higher than that obtained with the dioxane solution of the deuterium compound.

From the above results, we can conclude that 1) the olefin formation from *ap*-**2** is favored in less polar media than in more polar media and 2) the deuterium isotope effects on the product ratio is more significant in less polar media than in the more polar. Any explanation of the mechanisms must accommodate these facts together with the results that have been published.

The formation of the olefin (*sp*-**4**) from *ap*-**2** may be explained by the steric effects. Molecular models of the cyclic transition state to form an ion pair from the *ap*-chlorosulfite suggest that the transition state of the reaction receives considerable steric hindrance from the fluorene ring. In nonpolar media, the ion pair must be tight, while it is loose in polar media. This will mean that the transition state for the ion-pair formation in polar media is attained earlier than that in nonpolar media. Since the $C_\alpha \cdots Cl$ distance in this assumed transition state in nonpolar media is shorter than that in polar media, the steric effect that is received by the former must be severer than the latter. By contrast, the elimination reaction which involves the contribution of the C–H stretching will receive far less steric effect of the fluorene ring because one of the C–H bonds in the methyl group is always far from the fluorene moiety. In addition to the above, there is a factor that must be taken into account. That is, the ionic reactions, that form the chloride in this case, are generally favored in polar solvents, whereas the olefin formation should be less affected by the polarity of the media, as judged from the participation of the C–H stretching to the olefin formation, which means that the nonionic cyclic transition state is contributing. Thus we conclude that due to the factors discussed above the chloride formation becomes relatively favored in polar media, while the olefin formation is favored in nonpolar media.

Experimental

9-[2-(1-Hydroxyethyl)-1-naphthyl]fluorene (2). A solution of 2.0 g (5.9 mmol) of a rotameric mixture (ca. 1:1) of 9-(2-formyl-1-naphthyl)fluorene[2] in 150 mL of ether was added to a Grignard solution, which was prepared from 0.37 g (15 mmol) of magnesium, 1.1 mL (18 mmol) of methyl iodide, and 15 mL of ether. The mixture was stirred for several minutes and decomposed with aqueous ammonium chloride. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layer was dried over magnesium sulfate and the solvent was evaporated to afford a mixture of the rotameric alcohols. The mixture was separated by silica-gel chromatography (hexane–ether eluent) to give 1.0 g each of *sp* and *ap* rotamers, which were identical with those previously reported.[2]

ap-9-[2-(2,2,2-Trideuterio-1-hydroxyethyl)-1-naphthyl]fluorene (*ap*-**2**-methyl-d_3) was similarly prepared from methyl-d_3 iodide and the *ap*-aldehyde (**1**: X=CHO) and purified by thin-layer chromatography (3:2 dichloromethane–hexane). MS (*m/z*): 339 (M^+, $C_{25}H_{17}D_3O$), 321 (base peak, M−CD_3), 320 (M−HDO). ^{1}H NMR ($CDCl_3$) δ=3.77 (1H, s), 6.10 (1H, s), 7.1—8.0 (13H, m), 8.4—8.6 (1H, m). The OH proton signal was not detected.

Reaction with Dilute Sulfuric Acid. A solution of 1.0 g of the *sp*-alcohol (**2**) in 50 mL of 1,2-dimethoxyethane was mixed with a mixture of 10 mL of concentrated sulfuric acid and 150 mL of 1,2-dimethoxyethane with ice-cooling. The mixture was stirred for 5 d at room temperature, poured into water, and extracted with ether. The ethereal extract was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane eluent). The product was recrystallized from pentane to give pure *ap*-9-(2-vinyl-1-naphthyl)fluorene (**4**), mp 119.0—119.5 °C, in 90% yield. Found: C, 94.14; H, 5.41%. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%. ^{1}H NMR ($CDCl_3$) δ=5.4—5.9 (2H, m), 5.87 (1H, s), 6.3—8.0 (15H, m).

Similar treatment of the *ap*-alcohol (**2**) with sulfuric acid afforded *sp*-olefin (**4**), mp 134.5—135.5 °C, in 85% yield. Found: C, 94.58; H, 5.41%. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%. ^{1}H NMR ($CDCl_3$) δ=4.4—5.3 (2H, m), 5.4—5.8 (1H,

m), 6.11 (1H, s), 7.1—8.0 (13H, m), 8.4—8.7 (1H, m).

Reaction with Concentrated Sulfruic Acid. A solution of 1.0 g of *ap*-alcohol (**2**) in 10 mL of 1,2-dimethoxyethane was mixed with a mixture of 30 mL of 1,2-dimethoxyethane and 30 mL of concentrated sulfuric acid and stirred overnight at room temperature. The mixture was poured into water and extracted with ether. The ethereal extract was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silca gel (hexane eluent) to afford *trans*-8-methyl-8,14c-dihydrodibenz[*a,l*]aceanthrylene (**5**), mp 173.0—174.0 °C, in 90% yield. Found: C, 94.27; H, 5.40%. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%. ^{1}H NMR ($CDCl_3$) δ=1.53 (3H, d, J=7 Hz), 4.11 (1H, dq, J=1 and 7 Hz), 5.14 (1H, d, J=1 Hz), 6.9—8.8 (13H, m).

Similar treatment of the *sp*-alcohol afforded the *ap*-olefin only which was identical with that described above.

Competitive Reaction of *ap*-2 and *sp*-2 with Sulfuric Acid. A solution of 20 mg each of *ap*-**2** and *sp*-**2** in 50 mL of 1,2-dimethoxyethane was mixed with a mixture of 10 mL of concentrated sulfuric acid and 50 mL of 1,2-dimethoxyethane with ice-cooling. The whole was stirred at room temperature for 3 h and treated similarly as above thereafter. The conversion was less than 10% under the conditions. The ratio of the rotameric olefins, *sp*-**4**/*ap*-**4**, was analyzed with the use of HPLC. The HPLC instrument was a Waters M-600 Chromatograph equipped with a UV detecter at 254 nm. At a flow rate of 3.1 mL min^{-1} of hexane on a Microporasil column, the retention times were, *ap*-**4** 6.1 min and *sp*-**4** 7.1 min. The formation ratio, *sp*-**4**/*ap*-**4**, was 0.36.

Since the reaction can be assumed to be first-order in each of the substrate and sulfuric acid is used in large excess and since the reaction was discontinued at early stages, the formation ratios were taken as the relative rates of the reaction.

9-[2-(1-Chloroethyl)-1-naphthyl]fluorene (8). A solution of 100 mg (0.30 mmol) of the *sp*-alcohol in 50 mL of nitromethane was mixed with 0.5 mL (4.3 mmol) of thionyl chloride which was freshly distilled from a mixture of thionyl chloride and triphenyl phosphite, with ice-cooling. The mixture was stirred at 40 °C for 10 min and the solvent was evaporated. The residue was chromatographed on silica-gel TLC to give ca. 80% *sp*-chloride, oil, which was rather unstable. High resolution MS gave very weak M$^+$ peak at m/z 354.1192, whereas the calcd value for $C_{25}H_{19}{}^{35}Cl$ is 354.1175. ^{1}H NMR ($CDCl_3$) δ=2.13 (3H, d, J=7 Hz), 5.86 (1H, s), 6.00 (1H, q, J=7 Hz), 6.3—8.0 (14H, m). No impurity was detected by ^{1}H NMR spectra.

Similar treatment of the *ap*-alcohol gave a mixture of *sp*-9-(2-vinyl-1-naphthyl)fluorene and *ap*-9-[2-(1-chloroethyl)-1-naphthyl]fluorene in 18 and 72% crude yields, respectively. The *ap*-chloride, oil, was again unstable but showed a very weak M$^+$ peak in high resolution MS at m/z 354.1166, whereas the calcd value for $C_{25}H_{19}{}^{35}Cl$ is 354.1175. No impurity peaks were detected in the ^{1}H NMR spectra of *ap*-**8**. ^{1}H NMR ($CDCl_3$) δ=1.02 (3H, d, J=7 Hz), 4.03 (1H, q, J=7 Hz), 6.10 (1H, s), 7.0–8.0 (13H, m), 8.4–8.6 (1H, m).

Solvent Dependence of the Thionyl Chloride Reaction with the Alcohol (2). Except for hexane solutions, the following is the typical procedure. The alcohol (*ap*-**2**) (30 mg) in appropriate solvent (50 mL) was mixed with 0.5 mL of thionyl chloride, which was purified as above, with ice-cooling, and the mixture was stirred for 5 min at that temperature and then at 40 °C for 10 min. The reaction mixture was treated similarly as above and the ratios (olefin/chloride) were determined by ^{1}H NMR spectra of the products in chloroform-*d* with the use of a Varian EM-390 spectrometer.

For hexane solutions, the reaction was carried out for 10 h at 40 °C with the same ratios of the reactants and the solvent and the mixture was treated similarly as above. Under the competitive conditions, 15% of the *ap*-alcohol remained unreacted, whereas 28% of the *sp*-alcohol was found unreacted after 10 h at 40 °C, when 50 mg each of the rotameric alcohols and 0.5 mL of thionyl chloride in 80 mL of hexane were used.[22]

Reaction of *ap*-2-Methyl-d_3 with Thionyl Chloride. The reaction was carried out in either dioxane or hexane as described in the Solvent Dependence section and the product ratios were determined by ^{1}H NMR spectra. The alcohol was less reactive than the protium compound, giving 35.5% unreacted alcohol after 10 h in hexane at 40 °C. The following ^{1}H NMR spectra were recorded. *ap*-**8**-methyl-d_3: 4.01 (1H, s), 6.10 (1H, s), 7.0—8.0 (13H, m), 8.4—8.6 (1H, m). *sp*-**4**-methylene-d_2: 5.54 (1H, s), 6.10 (1H, s), 7.0—8.0 (13H, m), 8.4—8.6 (1H, m).

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21) In one experiment in which thionyl chloride was added to a nitromethane solution of *ap*-**2** at room temperature followed by heating at 40 °C, no detectable amount of the olefin (*ap*-**4**) was formed. This lends support as well to the idea that the olefin formation is suppressed at a high temperature.
22) In hexane, it seems that the rate-determining step is the decomposition of the corresponding chlorosulfites, because addition of thionyl chloride to a hexane solution of *sp*-**2** caused a change in the chemical shift due to the methine proton in ^{1}H NMR spectra. However, the huge peaks due to the solvent prevented us performing any reliable, quantitative study.