and 25 cps (100 Mc) in order of increasing field. These splittings can only be due to diastereoisomeric solute–solvent interactions; for example, splitting of the −3580-cps signal arises from the species (*l*)-Λ(+,+) and (*l*)-Δ(−,−), in which (*l*) indicates the optical sense of the solvent molecules in the immediate solvation spheres.[10] This observation is entirely analogous to those made on organic enantiomers in optically active solvents. Doubling of the −3010-cps signal requires that the asymmetric structural feature responsible for the differentiating solute–solvent interactions be the chirality of the tetrahedral forms of the Λ(+,−), Δ(+,−) enantiomeric pair and suggests a similar origin of splitting for the other two enantiomeric pairs.

The pmr spectrum of Ni(3*s*Bu,5Me-sal)$_2$bp dissolved in incompletely resolved α-pinene ($[\alpha]^{25}D$ −47.1° (neat)) revealed an unexpected and interesting time dependence shown in Figure 1. The first recorded spectrum after sample preparation (Figure 1a) displays the splitting of each signal into Δ, Λ components. Over ~30 min (Figure 1b–d) the separations of the components of each doublet decrease at rates unequal for each doublet. The components of each pair remain equally intense during the collapse and converge to a point slightly downfield of the lower field component of the initial pair in Figure 1a. In −52.2° α-pinene resolvable splittings were observed in the −2490-cps signal after 1 hr and in the −3580-cps signal after 1 week. This unusual behavior must be explained by a mechanism which converts diastereoisomeric entities, presumably solvates formed initially in solution, to enantiomers. In incompletely resolved α-pinene the solvation equilibria of the Δ and Λ isomers of each of the three pairs can be presented in an approximate manner as (1) and (2).

$$(d) + (l)\text{-}\Delta \rightleftharpoons (d)\text{-}\Delta + (l) \quad (1)$$

$$(d) + (l)\text{-}\Lambda \rightleftharpoons (d)\text{-}\Lambda + (l) \quad (2)$$

In the initially prepared solution, reactions 1 and 2 are both considered to lie heavily toward the left, as both Δ and Λ isomers are solvated by the *l*-pinene present in large excess, thereby rendering them magnetically inequivalent. Equilibrium is reached within 1 hr, under the conditions employed,[11] by rapid exchange of molecules between bulk solvent and the solvation sphere of the complex such that the signals of the Δ and Λ isomers represent a time average of the species in reactions 1 and 2, respectively. The time-dependent behavior of the spectra indicates that the equilibrium constants, K_{eq}, are unequal for reactions 1 and 2 such that, at equilibrium, the predominant species become (*l*)-Δ and (*d*)-Λ or (*d*)-Δ and (*l*)-Λ, depending on the relative magnitudes of K_{eq} for (1) and (2). The components of these pairs are strictly enantiomeric and thus are indistinguishable by pmr. The arguments presented above are easily generalized to the case in which more than one solvent molecule is involved in the solvation spheres. Reaction 1 then represents the end products in a series of reactions such as (*l*)(*l*)-Δ ⇌ (*l*)(*d*)-Δ ⇌ (*d*)(*d*)-Δ. The −52.2° α-pinene, in which this decay process is greatly retarded but not eliminated, is evidently not fully resolved. These results indicate that the Δ, Λ forms of these complexes manifest stereoselective solvation at equilibrium and that, compared to certain organic systems,[2] equilibrium solvation is not necessarily reached during the time required for an initial pmr measurement.

Finally, a similar but much smaller splitting of the azomethine signals of Ni(3*s*Bu,5Me-sal)$_2$bp into Δ and Λ components has been observed in solutions of *d*-limonene ($[\alpha]^{25}D$ +120.8° (neat)).

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Cyclopropanols. VIII. Low-Temperature Thermolysis of Cyclopropyl Nitrites

Sir:

Reactions in which a carbon free radical is formed are generally slightly accelerated by the presence of an adjacent cyclopropyl group, although the origin of the activating effect is still under discussion.[1,2] We wish to report that cyclopropyl groups enormously accelerate the rate of thermal homolysis of nitrite esters, so that substituted cyclopropyl nitrites undergo rearrangement at temperatures as low as −80°. In addition, we find that the rates of thermolysis are extremely sensitive to the nature of the 2 substituent on the cyclopropane ring, strongly suggesting that ring opening and O–NO bond breaking are concerted reactions. Thus, the results suggest that relief of strain in the transition state accounts for most, if not all, of the accelerating effect.

In a typical experiment, 1,2,2-trimethylcyclopropanol,[3] dissolved in CS_2 containing 2 equiv of pyridine-d_5, was cooled to −80° and treated with 1 equiv of NOCl. A portion of the cold solution was transferred to an nmr tube and the spectrum recorded at −60°. The spectrum was that expected for the nitrite ester,[4] and the cyclopropanol had been completely consumed. The probe temperature was gradually raised until changes in subsequent spectra indicated that decomposition was fairly rapid (*i.e.*, a half-life of ~1 hr). Further spectra were then recorded until complete decomposition had occurred. The product of the reaction, as shown in Scheme I, was the dimer of

(10) Assignment of the Δ, Λ components of each doublet, which is in principle possible by deliberately controlling the absolute configuration at the metal in the B = bmp complexes,[4] could not be accomplished due to the low solubility of isomers such as Λ-Ni(3-(+)-*s*Bu-sal)$_2$bmp in *l*-pinene with the resultant poorly resolved pmr spectra. The spectrum of this complex did, however, permit assignment of the low-field signals to the Λ(+,+) and Δ(−,−) isomers. Assignment of the other two doublets to the Λ(+,−), Δ(+,−) and Λ(−,−), Δ(+,+) isomers (*cf.* Figure 1) follows directly from relative intensities. Signal assignments are thus identical with those proven in $CDCl_3$ solution which in order of increasing field are independent of 5-X'.[4]

(11) At the concentrations used, 0.11 *M* solute in 90% resolved *l*-α-pinene, the mole ratio of *d*-α-pinene to Δ or Λ isomers is ~6:1.

(1) J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Lett.*, 4629 (1967).

(2) D. C. Neckers, A. P. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966); D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

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(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 371.

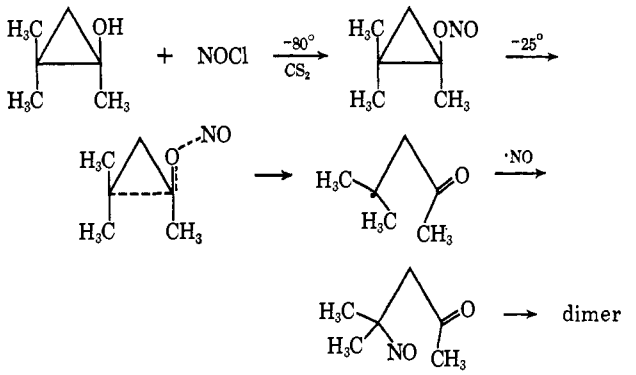
Table I. Decomposition Temperatures of Cyclopropyl Nitrites ($t_{1/2} \sim 1$ hr)

Nitrite[a]	Temp, °C	Product
2,2,3,3-Tetramethyl-1-methoxycyclopropyl	<−80	$(CH_3)_2C(NO)C(CH_3)_2CO_2CH_3$
2,2,3,3-Tetramethylcyclopropyl	−55	$(CH_3)_2C(NO)C(CH_3)_2CHO$
1,2,2,3,3-Pentamethylcyclopropyl[b]	−45	$(CH_3)_2C(NO)C(CH_3)_2COCH_3$
1,2,2-Trimethylcyclopropyl	−25	$[(CH_3)_2C(NO)CH_2COCH_3]_2$
trans-2-Phenylcyclopropyl	−20	3-Phenyl-5-hydroxy-2-isoxazoline[d]
trans,trans-2,3-Dimethyl-1-phenylcyclopropyl	−5	$[CH_3CH(NO)CH(CH_3)COC_6H_5]_2$
Cyclopropyl[c]	>0	5-Hydroxy-2-isoxazoline[d]
1-Phenylcyclopropyl[c]	>0	$(ONCH_2CH_2COC_6H_5)_2$
1-Methylcyclopropyl[c]	+20	$(ONCH_2CH_2COCH_3)_2$

[a] The nitrites were formed from the corresponding alcohols and nitrosyl chloride, at low temperatures. [b] The starting alcohol was synthesized by methyllithium treatment of the hemiketal. [c] See ref 6 for the preparation of the corresponding cyclopropanol. [d] These products can be visualized as cyclization products of the intermediate nitroso ketone, although the ketone has not been detected in the nmr.

4-nitroso-4-methyl-2-pentanone which was identified by comparison with an authentic sample.[5]

Scheme I



The temperature at which rapid decomposition of a cyclopropyl nitrite ester occurs correlates well with the radical-stabilizing ability of the 2 substituents (see Table I). Thus, the 1,2,2-trimethyl and the *trans*-2-phenyl[6] esters decompose near −25°, the isomeric 2,3-dimethyl-1-phenylcyclopropyl nitrites[7] decompose at −5°, while 1-methylcyclopropyl nitrite and nitrite esters of other cyclopropanols without 2 substituents are stable until near room temperature. Nitrite esters of 2,2,3,3-tetramethylcyclopropanols[8] are particularly unstable, the parent ester decomposing at −55° and the 1-methoxy derivative at −80°. Nitrite esters of ordinary alcohols undergo thermolysis only at elevated temperatures (150–200°), and the rates of their decomposition are not ordinarily sensitive to structure.[9]

The conversion of the cyclopropanols to the corresponding nitrite esters and their subsequent decompositions proceed in high yield. The nitroso ester from 2,2,3,3-tetramethyl-1-methoxycyclopropyl nitrite and the nitroso ketone from 1,2,2,3,3-pentamethylcyclopropyl nitrite can be isolated in >90% yield. In the other examples, no significant by-products were observed by nmr.

The alkyl radical intermediates in the cyclopropyl nitrite decompositions can readily be trapped. For example, ether solutions of the pentamethyl nitrite and its 1-methoxy analog were prepared, at −80°, in the presence of 10 equiv of bromotrichloromethane and allowed to decompose slowly in the dark. Subsequent analysis of the nmr spectra of the products indicated *ca.* 40:60 mixtures of the ring-opened nitroso compounds and the corresponding β-bromo carbonyl compounds. The bromo compounds were identical with those obtained by reaction of the appropriate cyclopropanol with brominating agents.

We anticipate that the low-temperature thermolysis of these esters will allow us to study the stereochemistry, spectra, and reactivity of a number of alkyl radicals, and experiments along these lines are already under way. We intend also to compare the nature of the radicals formed thermally with those formed by the photochemical decomposition of these same nitrites, a reaction which also occurs readily.[10]

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Trichlorosilane–Tertiary Amine Combinations as Reducing Agents for Polyhalo Compounds. Potential Analogies with Phosphorus Chemistry

Sir:

The effectiveness of organic bases as catalysts for the addition of trichlorosilane to acrylonitrile[1] and phenylacetylene[2,3] is suggestive of a little-explored aspect of organosilicon chemistry. In the course of our experiments in this area, we have discovered that in the presence of tertiary amines trichlorosilane undergoes facile reaction with a variety of organic halides, yielding products that are significant from both synthetic and mechanistic standpoints. Reported here is a series of reactions in which polyhalo compounds are reduced cleanly and selectively by the trichlorosilane–amine combination. The data are summarized in Table I.

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