Chromasorb W, and a 0.25 in. by 6 ft column of 10% SE-30 on acid-washed Chromasorb W.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Materials and Syntheses, General Data. All reagents were commercially available reagent grade chemicals unless otherwise noted. Purity of pK_a samples was ascertained by VPC, thin-layer chromatography (TLC; on Eastman Chromagram sheets No. 13181, silica gel with fluorescent indicator), HPLC, NMR, IR, and melting and boiling point, whenever applicable. Thick-layer chromatography was performed by Quantum Industries Quanta/Gram PQ6F or PQ5F plates.

Ethyl Phenylacetate. A commercial sample (Matheson Chemical Co.) was distilled under vacuum [75 °C (1.5 mm)] and found pure by VPC.

***N,N*-Dimethyl-α-phenylacetamide** was prepared from phenylacetyl chloride, and a crystallization from hexane was repeated until no further change in melting point was observed: white needles mp 38–40 °C (lit.[22] mp 43.5 °C); NMR δ 2.92 (6 H, s, $N(CH_3)_2$), 3.65 (2 H, s, $PhCH_2$), 7.15 (5 H, s, Ar).

Methyl Cyanoacetate. A commercial sample (Matheson Chemical Co.) was vacuum distilled [85 °C (~5.5 mm)] and found to be pure by VPC.

1-(Cyanoacetyl)pyrrolidine. A commercially available sample from Parish Chemical Co. was found to be pure enough for the pK_a measurement.

9-Carboxamidofluorene. A sample to 9-fluorenecarboxylic acid generously provided by Professor R. T. Arnold was converted to the amide by using thionyl chloride and a concentrated ammonium hydroxide solution. Multiple recrystallizations from absolute ethanol gave pure white needles: mp 255–256 °C (lit. mp 251 °C); NMR (Me_2SO-d_6) δ 4.54 (1 H, s), 6.9–7.7 (8 H, m).

***tert*-Butyl Acetate.** A commercially available sample (Matheson) was distilled through a 15-cm Vigreux column at atmospheric pressure: bp 95.5 °C; pure by VPC.

***N,N*-Dimethylacetylacetamide.** A commerical sample (Parish Chemical Co.) was vacuum distilled: bp 93 °C (3.8 mm); pure by VPC.

***tert*-Butyl phenylacetate** was prepared from phenylacetyl chloride and *tert*-butyl alcohol. Kugelrohr distillation [80 °C (1 mm)] gave the pure product [lit. bp 110 °C (15 mm)]: NMR δ 1.41 (9 H, s, $C(CH_3)_3$, 3.51 (2 H, s, $PhCH_2$), 7.28 and 7.35 (5 H, 2 s).

Ethyl (trimethylammonio)acetate (chloride salt) was prepared from chloroacetate and anhydrous trimethylamine in ethanol. The white solid was recrystallized twice from acetonitrile and dried under vacuum [100 °C (1.5 mm)] for 30 h: mp 151–153 °C; NMR (D_2O) δ 3.27 (9 H, s, $N(CH_3)_3$), 1.30 (3 H, t, CH_2CH_3), 4.22 (2 H, s, $Me_3NCH_2^+$), 4.21 (2 H, q, CH_2CH_3).

***N,N*-Dimethyl-α-(trimethylammonio)acetamide (chloride salt)** was prepared from chloroacetic acid, thionyl chloride, and diethylamine in benzene.

The oily amide was added directly to a solution of trimethylamine in absolute ethanol, and the solution was refluxed for 6 h, cooled to room temperature, and concentrated in vacuo to yield a brown water-soluble solid. Recrystallization of the product from ethyl acetate/ethanol followed by repeated trituration with hot ethyl acetate afforded a white, granular solid. The product dried in a drying pistol (100 °C, 36 h) under vacuum, melted at 214.5–16.0 °C (with evolution of gas): NMR (D_2O) δ 1.20 (2 t, 6 H), 3.24 (s, 2 H), 3.44 (s, 9 H), 3.44 (m, 4 H).

Ethyl phenylthioacetate and *N,N*-dimethylphenylthioacetamide were prepared by standard procedures from phenylthioacetic acid (Parish Chemical Co.).

Equilibrium acidity measurements were carried out by the method described earlier.[8,12] As pointed out by the referees, it is possible that addition to the carbonyl functions in these compounds may complicate the measurements. Addition of the 9-phenylxanthenyl carbanion to the carbonyl group of benzophenone or ethyl benzoate occurs rapidly, but the equilibrium concentration of adduct is low with the more weakly basic indicator anions that were used in the pK_a measurements reported in Table I.[11] For this reason, and because of the internal consistency of the results, we do not believe that carbonyl addition competes appreciably with the equilibrium deprotonation of esters or ketones in the pK_a range below 25.

Acknowledgment. We are grateful to the National Science Foundation for support of this investigation. We thank Timothy Ungermann for measurements of the acidities of $PhSCH_2CO_2Me$ and $PhSCH_2CONMe_2$ and acknowledge a generous gift of dimethyl sulfoxide from the Chemical Products Division of Crown Zellerbach.

Registry No. Phenylacetyl chloride, 103-80-0; 9-fluorenecarboxylic acid, 1989-33-9; *N,N*-diethylacetamide, 685-91-6; $[Me_3NCH_2CO_2Et]^+Cl^-$, 3032-11-9; $[Me_3NCH_2CONEt_2]^+Cl^-$, 69371-33-1; $PhCH_2CO_2$-*t*-Bu, 16537-09-0; $PhCH_2CO_2Et$, 101-97-3; $PhCH_2CONMe_2$, 18925-69-4; $PhSCH_2CO_2Me$, 17277-58-6; $PhSCH_2CONMe_2$, 78698-19-8; 9-$CONH_2$-FlH, 7471-95-6; $CH_3COCH_2CO_2Et$, 141-97-9; $CH_3COCH_2CONMe_2$, 2044-64-6; $CNCH_2CO_2Me$, 105-34-0; $CNCH_2CON(CH_2)_4$, 14227-95-3; $PhSCH_2CO_2Et$, 7605-25-6; 9-CO_2Me-FlH, 3002-30-0.

Deaminative Rearrangements of 1-Phenylthio- and 1-Oxy-Substituted Chrysanthemylamines

Christopher K. VanCantfort[1] and Robert M. Coates*

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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Metalation of chrysanthemic nitrile **1** with lithium diisopropylamide followed by sulfenylation with diphenyl disulfide or oxygenation with a molybdenum peroxide complex gave chrysanthemic nitrile derivatives bearing phenylthio (**3** and **4**) or hydroxyl (**6**) substituents at C-1. These compounds provided access to the following series of 1-substitued chrysanthemylamines: 1-(phenylthio)chrysanthemylamine (**5**), 1-methoxychrysanthemylamine (**8**), 1-methoxydihydrochrysanthemylamine (**10**), and the *N*-nitrosooxazolidinone (**13**) derived from 1-hydroxychrysanthemylamine (**11**). Nitrous acid deamination of **5** and **8** and hydrolytic deamination of **13** gave acyclic alcohols (**14**, **17**, and **18**) related in structure to yomogi alcohol as major products by cleavage of the 1–3 cyclopropane ring bond. Products formed by cleavage of the 1–2 cyclopropane ring bond (**15** and **24**) and related in structure to santolinatriene were obtained in lesser amounts from the deamination of **5** and **13**. Pinacol-type ring expansion to the isomeric cyclobutanones **19** and **20** was observed as a minor reaction pathway in the deaminations of **8** and **13**. In contrast, deamination of **10** gave dihydrocyclobutanones **21** and **22** as the major isolated products.

The heterolytic reactions of chrysanthemol derivatives have been studied extensively in recent years as a model reaction for the biogenesis of acyclic terpenoids and as an interesting substrate for investigation of cyclopropyl car-

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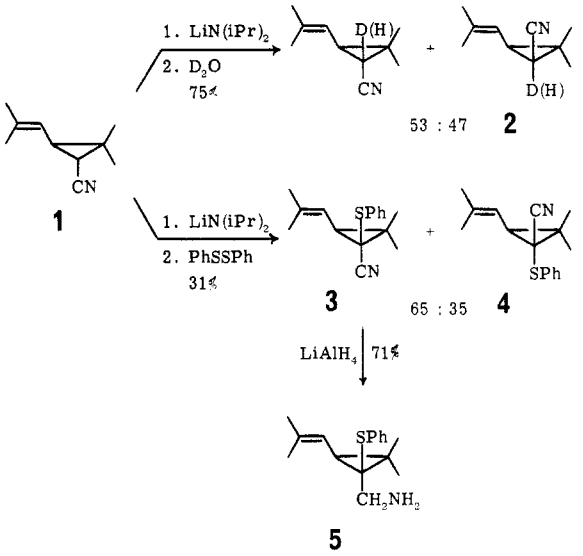
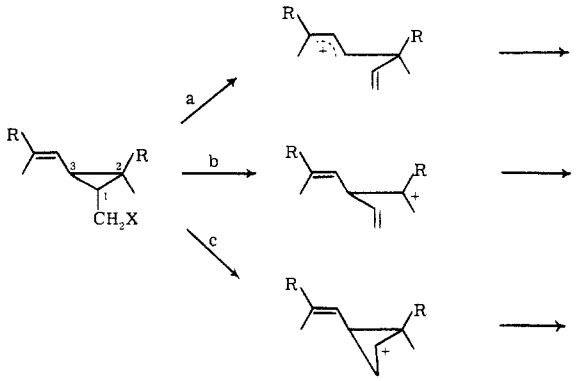
Scheme I

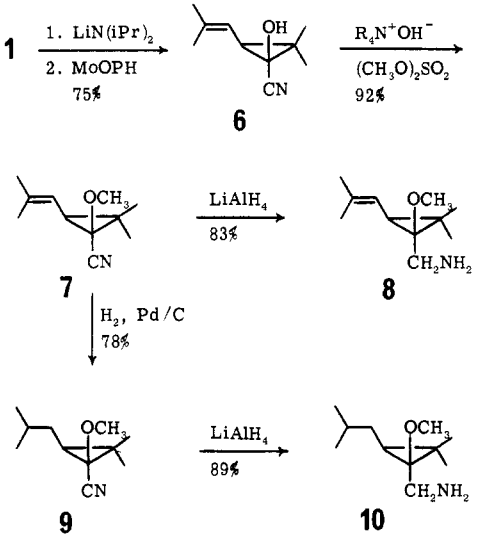


binyl rearrangements.[2-5] The predominant mode of reaction of the chrysanthemyl ion is ring opening by cleavage of the 1–3 cyclopropane ring bond (path a), a process which

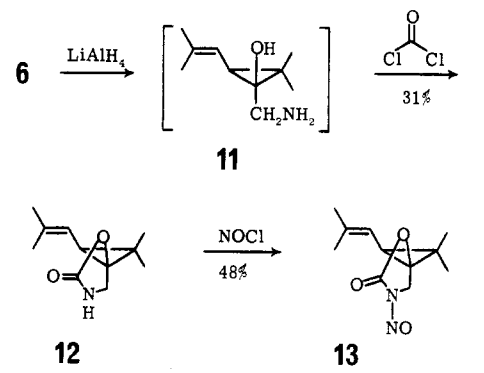


simulates the biogenesis proposed for the artemisia family of irregular monoterpenes.[6,7] Although cleavage of the other cyclopropane ring bond (path b) occurs to a minor extent,[4a,5] this alternative ring opening pathway is favored in the solvolysis of dihydrochrysanthemyl derivatives and gives rise to products possessing the santolina monoterpene skeleton.[3,4a] The ring-expansion pathway (path c) to the cyclobutyl cation (transition state or intermediate), which has been advanced as the initial step in the biosynthetic conversions of presqualene pyrophosphate (R = homogeranyl, X = OPP) to squalene[8,9] and of prephytoene pyrophosphate (R = homofarnesyl, X = OPP) to phytoene,[10]

Scheme II



Scheme III



does not, however, compete effectively with the ring opening of the chrysanthemyl ion. A solvolysis product formed via ring expansion was detected at the level of 0.02% in the solvolysis of *N*-methyl(chrysanthemyloxy)-pyridinium iodide.[4]

Since electron-donating substituents such as alkylthio and alkoxy groups exert a profound effect on the stability of carbonium ions[11] and on the course of their rearrangements,[12] we presumed that the presence of such a donor substituent at C-1 on chrysanthemyl ion might serve to direct the reaction along the ring-expansion pathway. As pertinent examples, the acid-catalyzed rearrangements of 1-(phenylthio)cyclopropylcarbinols[13] and the deaminative ring expansion of 1-(1-ethoxyethyl)cyclopropylcarbinylamine[14] to cyclobutanones may be cited. We have prepared a series of chrysanthemyl amines bearing phenylthio and oxy substituents at C-1 and subjected them to nitrous acid deamination to determine the extent of the pinacol-type rearrangements to the two possible cyclobutanones.

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Syntheses

The hetero substituents were introduced by sulfenylation and oxygenation of the carbanion obtained by metalation of chrysanthemic nitrile **1** as illustrated in Schemes I–III. The commercially available mixture of the ethyl esters of *cis*- and *trans*-chrysanthemic acid was equilibrated and partially transesterified with sodium *tert*-amyloxide in toluene at reflux.[15] Saponification of the ester mixture afforded *trans*-chrysanthemic acid (75%) which was converted to the acid chloride and amide by standard procedures (86%). Dehydration of the amide to chrysanthemic nitrile **1** was accomplished in 81% yield by reaction with *p*-toluenesulfonyl chloride in pyridine at room temperature.[16,17]

The *α-lithio derivative of chrysanthemic nitrile* was readily formed by deprotonation with lithium diisopropylamide in tetrahydrofuran at −78 °C for 30 min.[17] Reaction of the anion with deuterium oxide afforded a 53:47 mixture of *trans*- and *cis*-chrysanthemic nitriles which evidently had incorporated deuterium to the extent of about 60%. The incomplete deuteration may be explained by partial exchange with the NH proton of diisopropylamine during hydrolysis, possibly in combination with a kinetic isotope effect.[17]

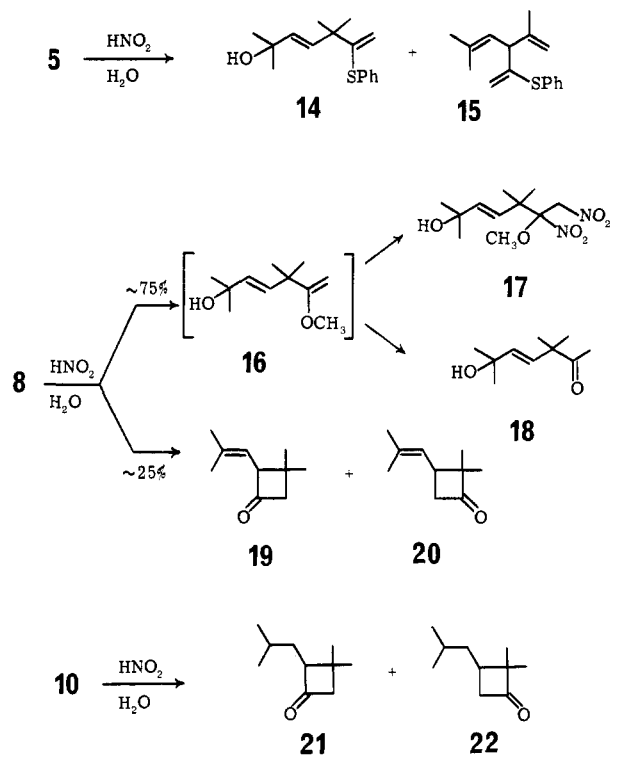
A 65:35 mixture of the isomeric α-phenylthio nitriles **3** and **4** was obtained from sulfenylation of the anion with diphenyl disulfide at -78 °C.[18] Owing to partial decomposition during chromatographic purification on silica gel and recrystallization, the isolated yields of the individual isomers were only 28% and 3.4%, respectively. Oxygenation of the lithiated nitrile was effected with molybdenum perioxide–pyridine–hexamethylphosphoramide complex (MoOPH) in tetrahydrofuran at −20 °C for 1 h.[19] The stable cyanohydrin **6** was obtained as a 82:18 mixture of trans and cis isomers in 75% yield after vacuum distillation. This mixture of isomers was utilized in subsequent reactions; consequently all of the compounds prepared from **6** contained 15–20% of the corresponding cis epimer.

The trans stereochemistry is tentatively assigned to the major products from the sulfenylation and oxygenation reactions on the basis of NMR chemical shift comparisons. Thus, the cyclopropane ring protons at C-3 of **1** and **3** appear at δ 1.86 and 2.00 whereas this same proton in the minor isomer resonates at δ 2.30. The chemical shift for the vinyl proton (δ 5.02) of the minor cyanohydrin corresponds closely to that of the cis nitrile **2** (δ 5.05) while the vinyl proton of the major isomer is found at higher field (δ 4.93).

The racemization of the lithium keteniminate from (−)-(*R*)-2,2-diphenylcyclopropylnitrile in ether[20] and the partial stereochemical isomerization of arylcyclopropyl nitriles following deprotonation with lithium dialkylamides and deuterolysis[17] have been reported. If the anion is assumed to be a planar lithium cyclopropylketeniminate, then the variations in the isomer ratios found in the present work could be a consequence of different steric requirements for the three electrophiles used. However, alternative explanations based on relatively rapid (or slow) electrophilic substitution on slowly (or rapidly) equilibrating stereoisomeric pyramidal α-lithio nitriles with retention (or inversion) of configuration could also account for the observed stereoselectivities.

Since aminohydrin **11** proved to be quite unstable, the cyanohydrin was converted to the corresponding methyl ether (**7**) in 92% yield by reaction with dimethyl sulfate. Reduction of the phenylthio and methoxy nitriles with lithium aluminum hydride in ether gave the corresponding 1-(phenylthio)- and 1-methoxychrysanthemylamines (**5** and **8**). Catalytic hydrogenation of the isobutenyl side chain of **7** followed by lithium aluminum hydride reduction provided 1-methoxydihydrochrysanthemylamine (**10**). Since hydrolysis of *N*-nitrosooxazolidinones from 1-(aminomethyl)-1-cycloalkanols effects a pinacol-type ring expansion to cyclic ketones under suitable conditions,[21] oxazolidone **12** was prepared by acylation of the unstable aminohydrin **11** with phosgene in a two-phase mixture of benzene and aqueous potassium hydroxide. Nitrosation of **12** with nitrosyl chloride and acetic anhydride in pyridine at 10–15 °C afforded *N*-nitrosooxazolidone **13**.

Scheme IV



Deaminations

The three chrysanthemylamines **5**, **8**, and **10** were subjected to deamination with sodium nitrite in aqueous acetic acid according to literature procedures (Scheme IV).[14,22] The product mixtures from **5** and **10** were treated with potassium carbonate in methanol to convert acetates to alcohols prior to purification by column chromatography on silica gel. The two major products formed in the deamination of the phenylthio amine **5** were identified as the dienol **14** (39%) and triene **15** (27%) by their IR and NMR spectra. The NMR spectral data for **14** and **15** are

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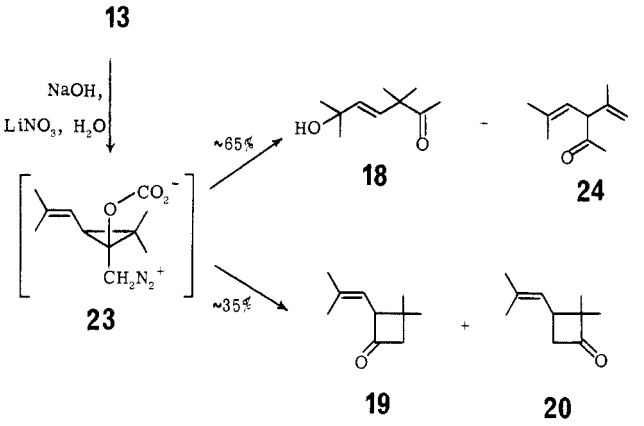
very similar to those reported for the monoterpenes yomogi alcohol[23] and santolinatriene.[24]

The methanolysis step preceding purification was omitted in the case of the deamination of methoxy amine **8** since acetates did not appear to be formed to a significant degree and since two of the products (**17** and **19**) were demonstrated to be unstable under these conditions. The four products were isolated by a combination of preparative TLC and GC. The unusual dinitro alcohol **17**, the major product from **8**, was identified primarily from its IR and NMR spectra. The two most intense bands in the IR spectrum of **17** appear at 1553 and 1348 cm^{-1} which is typical for the nitro group[25] and is consistent with IR spectral data for vicinal dinitro compounds.[26] The NMR spectrum exhibits an AB pattern for the vinyl hydrogens and a singlet for the methyl groups on the hydroxyl-bearing carbon which are quite similar to those appearing in the spectrum of methyl ketone **18**. The appearance of a distinct AB pattern (J_{AB} = 18 Hz) for the geminal protons α to the nitro group requires the presence of at least one chiral center in the compound. Unfortunately the exact oxidation level of the nitrogens in this compound could not be confirmed directly. The mass spectrum did not exhibit a parent peak and an elemental analysis of a sample judged to be pure by TLC and GC analyses indicated a higher content of nitrogen, carbon, and hydrogen than was calculated for the dinitro structure. Thus the possibility that this product contains a nitroso group on the methoxy-bearing carbon cannot be rigorously excluded, although this nitro–nitroso structure seems less likely.

Since nitrous acid in aqueous solution is known to undergo facile disproportionation to nitric acid and nitric oxide via N_2O_3 and N_2O_4,[27] we presume that the dinitro alcohol arises by addition of N_2O_4 to the enol ether **16**, the expected product of ring cleavage. The addition of N_2O_4, or for that matter N_2O_3, to olefins to give vicinal dinitro adducts has been reported.[26,28] Furthermore the disproportion of nitrous acid to nitric acid, and presumably the generation of N_2O_4, has been demonstrated to occur under standard deamination conditions similar to those used in the present work.[22,29]

The other three compounds isolated from the mixture of deamination products from **8** were the acyclic keto alcohol **18** and the two isomeric cyclobutanones **19** and **20**. The NMR spectrum of **18** in chloroform-*d* is deceptively simple owing to the fortuitous coincidence of the chemical shifts for the two vinyl protons. However, the expected AB pattern (J_{AB} = 15 Hz) for the nonidentical trans vinyl hydrogens was observable when the NMR spectrum was run in benzene-d_6. Cyclobutanone **20** had been prepared previously in our laboratories[30] and was readily identified by spectral comparison and chromatographic mobility. The IR and NMR spectra of the other cyclobutanone (**19**) are quite similar to those of **20** and form the basis for the identification of this product; a distinctive doublet at δ 3.77 in the NMR spectrum of **19** arises from the allylic hydrogen α to the carbonyl group. The ratio of the four products (**17**/**18**/**19**/**20**) was 53:21:18:8 and the combined, isolated yield was 38%. GC analyses and NMR spectra obtained with the crude product demonstrated that these compounds were indeed the major deamination products. The relatively low isolated yield may be attributed to losses during purification and possibly further reactions of the products with nitorgen oxides generated from nitrous acid. The instability of olefins to standard deamination conditions has been noted recently.[31]

Scheme V



Deamination of methoxydihydrochrysanthemylamine **10** followed by methanolysis afforded a 60:40 mixture of the isomeric saturated cyclobutanones **21** and **22** which was isolated in 21% yield by column chromatography. Inspection of the NMR spectrum of the crude product (83%) indicated that, despite the low isolated yield, **21** and **22** were the major products of the reaction and that the isomer ratio was not altered appreciably during purification. Although the individual isomers **21** and **22** were not separated, it was possible to identify the minor saturated cyclobutanone as **22** by comparison of the NMR spectrum of the mixture with the very distinctive spectrum of an authentic sample prepared by catalytic hydrogenation of **20**. The other peaks in the NMR spectrum of the mixture are all assignable to the major component and are in good agreement with the isomeric cyclobutanone structure **21**. The coincidence of the GC retention times of authentic **22** and the minor saturated cyclobutanone provided further support for this conclusion. Mass spectra of **21** and **22** obtained by GC/MS confirmed the isomeric nature of the two products and were generally consistent with the structural assignments.

Newman and Beard[21] have demonstrated that spiro-*N*-nitrosooxazolidones undergo hydrolytic deamination to ring-expanded ketones in highly ionic aqueous solution. For example, hydrolysis of the *N*-nitrosooxazolidone derived from 1-(aminomethyl)cyclopentanol with 1 equiv of sodium hydroxide in 5:1 (v/v) water/1,2-dimethoxyethane saturated with lithium nitrate afforded cyclohexanone in 96% yield. Diazonium carbonates analogous to **23** were proposed as intermediates in this pinacol-type rearrangement. Hydrolysis of *N*-nitrosooxazolidone **13** under these conditions afforded a four-component mixture of ring-cleavage products (**18** and **24**) and ring-expansion products (**19** and **20**) in the ratio 54:11:15:20 (45% isolated yield).

Discussion

The predominant reaction observed in the deamination of the 1-substituted chrysanthemylamines **5** and **8** and the

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N-nitrosooxazolidone **13** was ring opening to compounds (i.e., **14**, **17**, and **18**) related in structure to yomogi alcohol. Cleavage of the other cyclopropane ring bond to give olefinic products (**15** and **24**) related to santolinatriene was a major competing pathway in the deamination of **5** and a relatively minor pathway in the hydrolytic deamination of **13**. Although cyclobutanones **19** and **20** were obtained as minor products from **8** and **13** and were not found in the product mixture derived from the phenylthio-substituted substrate, ring expansion to cyclobutanones **21** and **22** became the major pathway in the deamination of **10** which lacks the side-chain double bond. It is apparent that, despite the presence of a phenylthio or oxy substituent at C-1, the course of these deamination reactions is dominated by the isobutenyl group at C-3. Since a methoxy group should be substantially more effective at stablizing a carbonium ion than an isobutenyl group,[32,33] it is of interest to consider possible explanations for the relatively inefficient ring expansion observed with the unsaturated chrysanthemylamines bearing oxy substituents.

A vast literature exists on the effects of substituents upon the rates and products from the solvolysis of cyclopropylcarbinyl compounds.[34-37] In general, stabilizing groups (alkyl, aryl, heteroatom) positioned at either C-1 or C-2 direct the reactions to cyclobutyl or homoallyl products, respectively. Unfortunately, relatively little data seems to be available on the competitive effect of two groups in 1,2-disubstituted cyclopropylcarbinyl derivatives. Solvolysis rates are enhanced to a greater extent when such groups are located at the trans C-2 position than at C-1, and the effects are cumulative to a first approximation. For example, the relative solvolysis rate of *trans*-2-anisyl- and *trans*-2-phenylcyclopropylcarbinyl 3,5-dinitrobenzoates is 15.1 (75% aqueous dioxane at 130 °C)[36] whereas a rate ratio of only 1.5 (50% aqueous dioxane at 90 °C) is reported for the isomers with the aryl substituent at C-1.[37b] Since these 3,5-dinitrobenzoates very likely ionize to short-lived cyclopropylcarbinyl carbonium ions prior to rearrangement to the respective aryl-substituted 3-buten-1-ols or cyclobutanols, the relative rate data reflect mainly the substituent effect on the stability of the substituted cyclopropylcarbinyl ions. It is therefore evident that the delocalization of charge into the aryl group is more pronounced at C-2 than at C-1.

The distribution of products observed in the deaminations of the 1-substituted chrysanthemylamines is presumably determined by a kinetic competition between the ring-opening and ring-expansion pathways in an initially formed chrysanthemyl cation.[38] The possibility that the acyclic products might be formed indirectly by a cyclopropylcarbinyl → cyclobutyl → homoallyl route is unlikely because solvolysis of related cyclobutyl tosylates leads to entirely different acyclic products.[9,30] It is reasonable to suppose that the ring expansion of the chrysanthemyl ion involves the conversion of a bicyclobutonium ion over a puckered cyclobutyl transition state to a classical cyclobutyl carbonium ion.[34,39,40] If the transition state (puckered cyclobutyl ion) lies nearer the bicyclobutonium ion and as a consequence the degree of rehybridization at C-1 is small, then the conjugative interaction with a donor substituent at this position will be minimal. On the other hand, the extent of rehybridization at C-3 in the transition state for ring opening is presumably greater, and as a result the delocalization with a conjugating substituent such as the isobutenyl group is enhanced.

Steric interactions and conformational effects may also play a role in the partitioning of the substituted chrysanthemyl ions into the two ring opening modes and the ring expansion pathway. The relatively large proportion of product arising from cleavage of the 1–2 cyclopropane ring bond in the deamination of the phenylthio-substituted amine (**5**) may be the result of steric interactions between the isobutenyl and phenylthio groups.

The use of oxy and thio substituents to direct the course of carbonium ion rearrangements in general and cyclopropylcarbinyl rearrangements in particular[12] is a common tactic in organic synthesis. Although the formation of highly stabilized oxonium ions[11,33] affords a powerful thermodynamic driving force for such pinacol-type rearrangements, the kinetic stabilizing effect of these heteroatom substituents on competing processes may be relatively small in comparison.[41]

Experimental Section

Proton nuclear magnetic resonance spectra were recorded on Varian Associates EM-390 or HR-220 spectrometers. Infrared spectra were obtained with a Perkin-Elmer 237B model spectrophotometer. Mass spectra were run on Varian MAT Model CH-5, 112 (GC/MS), 311A (GC/MS), and 731 (high-resolution GC/MS) instruments by J. C. Cook and Associates. Elemental analyses were carried out at the University of Illinois microanalytical laboratory by J. Nemeth and associates. Melting points were determined in open end capillaries with a Büchi melting point apparatus and are uncorrected. Preparative gas chromatography was performed on an Aerograph A90-P3 (Wilkens Instrument and Research, Inc.) equipped with a thermal-conductivity detector and using helium as the carrier gas under the indicated conditions. Analtical gas chromatography was performed on a Varian Model 3700 instrument equipped with a flame-ionization detector and using helium as the carrier gas under the indicated conditions.

Silica gel with a particle size range of 0.05–0.3 mm, supplied by Machery-Nagel and Co., was used for gravity-flow column chromatography. Preparative medium-pressure liquid chromatography was performed by using glass columns of the indicated length and diameter as previously reported.[42] A Milroyal D controlled-volume pump, supplied by Milton Roy Co., was used.

Analytical thin-layer chromatography was conducted on 2.5 × 10 cm precoated plates (silica gel 60F-254, layer thickness 0.25 mm) manufactured by E. Merck and Co. Preparative thin-layer chromatography was carried out on 20 × 20 cm plates precoated with a 2.0-mm layer of silica gel G-200 UV_{254}, supplied by Ma-

(32) The rate of ethanolysis of chloromethyl methyl ether has been estimated to be 7×10^4 that of 1-chloro-3-methyl-2-butene.[33]

(33) Ballinger, P.; de la Mare, P. B. D.; Kohnstam, G.; Prestt, B. M. *J. Chem. Soc.* **1955**, 3641–7.

(34) (a) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26. (b) Richey, H. G., Jr. *Ibid.*, Chapter 25.

(35) Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321–2.

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(37) (a) Roberts, D. D. *J. Org. Chem.* **1968**, *33*, 2712–5. (b) Roberts, D. D. *Ibid.* **1969**, *34*, 285–7. (c) Roberts, D. D.; Watson, T. M. *Ibid.* **1970**, *35*, 978–81.

(38) The rate of solvolysis of chrysanthemyl methanesulfonate is only 3 times faster than its dihydro analogue in 90% aqueous acetone at 0 °C. Since the former gives mainly products arising from cleavage of the 1–3 cyclopropane ring bond whereas the products from the latter result from exclusive rupture of the 1–2 bond, it is clear that ring opening occurs subsequent to ionization under these solvolytic conditions.[4a]

(39) (a) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016–8. (b) Staral, J. S.; Roberts, J. D. *Ibid.* **1978**, *100*, 8018–20. (c) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *Ibid.* **1979**, *101*, 5537–9.

(40) Since 1-phenylcyclobutyl cation exists as classical, delocalized species, the same should hold for a cyclobutyl cation bearing a phenylthio or oxy substituent at C-1. See: Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94* 146–56. Olah, G. A.; Prakash, G. K. S.; Donovan, D. J.; Yavari, I. *Ibid.* **1978**, *100*, 7085–6.

(41) The limitations of methoxy groups as probes for charge delocalization in carboniums ions produced by solvolysis of saturated precursors have been pointed out: Schleyer, P. v. R.; Stang, P. J.; Raber, D. J. *J. Am. Chem. Soc.* **1970**, *92* 4725–8.

(42) Baker, W. R.; Coates, R. M. *J. Org. Chem.* **1979**, *44*, 1022–4.

cherey-Nagel. Thin-layer chromatograms were visualized with phosphomolybdic acid reagent and/or ultraviolet light. All reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated.

Pyridine was dried by distillation from calcium hydride and stored over barium oxide. Diisopropylamine was distilled from sodium hydroxide and stored over the same in an amber bottle with a septum cap under nitrogen. Tetrahydrofuran was dried over sodium hydride and distilled from sodium benzophenone ketyl. *n*-Butyllithium in hexane (Alfa) and methyllithium–lithium bromide complex in ether (Alfa) were titrated[43] before use. Pentane used in recrystallizations was repeatedly washed with concentrated sulfuric acid and then distilled before use. Molybdenum oxide was used as supplied (Mallinkrodt) for the preparation of molybdenum peroxide–pyridine–hexamethylphosphoramide complex.[19b] Ethyl chrysanthemate (Columbia Organic Chemical Co., Inc.) was obtained as a 36:64 mixture of cis and trans isomers.

***trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carboxylic Acid (*trans*-Chrysanthemic Acid).** The equilibration and hydrolysis of ethyl chrysanthemate was performed in a manner similar to that reported by Julia et al.[15] A solution of sodium 2-methyl-2-butoxide was prepared[44a] by heating 14.2 g (0.617 mol) of sodium and 61.3 mL (0.561 mol) of *tert*-amyl alcohol in 400 mL of toluene at reflux temperature under nitrogen for 24 h. Unreacted sodium was removed, and 85.1 g (0.434 mol) ethyl chrysanthemate as a mixture of cis and trans isomers was added. The solution was stirred and heated under reflux for 45 min and then stirred without external heating for 10 min. After cautious addition of 400 mL of water, the organic phase was separated, washed with water, and dried ($MgSO_4$). Evaporation of the solvents at reduced pressure provided 87.5 g of a mixture of ethyl and *tert*-amyl *trans*-chrysanthemate.

A solution of 53.8 g of the ester mixture and 21.4 g (0.375 mol) of potassium hydroxide in 214 mL of 95% ethanol was heated at reflux for 24 h. The solution was concentrated under reduced pressure to give an orange, oily solid which was dissolved in 250 mL of water. The resulting aqueous solution was concentrated further to a volume of 100 mL and extracted with three 100-mL portions of chloroform. The chloroform extracts were combined, dried ($MgSO_4$), and evaporated to give 6.2 g of *tert*-amyl-*trans*-chrysanthemate as a clear, red-gold liquid: IR (neat) 1725 (C=O), 1380 and 1365 (*gem*-dimethyl), 1280, 1235, 1190, 1140, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.90 (d, 1, J = 8 Hz, C=CH), 1.85 (t, 1, J = 7 Hz, C=CCH), 1.72 (s, 6, $(CH_3)_2C$=C), 1.45 (s, 6, $OC(CH_3)_2$), 1.30 (s, 3, ring CH_3), 1.15 (s, 3, ring CH_3), 0.90 (t, 3, J = Hz, CH_2CH_3).

The basic aqueous phase was acidified to pH 2.0 with 6 M hydrochloric acid and extracted with three 100-mL protions of chloroform. The extracts were combined, dried ($MgSO_4$), and evaporated. Distillation of the resulting oil under reduced pressure gave 28.6 g (73%) of a clear, colorless liquid, bp 94 °C (0.7 mm). The liquid solidified upon cooling to a white, crystalline solid with IR and NMR spectral characteristics identical with those reported[45] for *trans*-chrysanthemic acid, mp 49–51 °C (lit[46] mp 54 °C).

***trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carbonyl Chloride.** A solution of 68.9 g (0.410 mol) of *trans*-chrysanthemic acid in 100 mL of anhydrous diethyl ether was stirred at room temperature as 51.5 mL (0.718 mol) of freshly distilled thionyl chloride in 52 mL of anhydrous diethyl ether was added over 1 h.[47] The solution was heated under reflux for 1 h and allowed to stand at room temperature for 17 h. The excess thionyl chloride and ether were removed under water aspirator vacuum. Slow distillation of the residual liquid to minimize bumping and foaming afforded 72.6 g (95%) of the acid chloride as a clear, slightly yellow liquid: bp 96–97 °C (15 mm) [lit.[47] bp 99–101 °C (13 mm)]; IR (neat) 1785 (C=O), 1450 and 1385 (*gem*-dimethyl), 760 (C—Cl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.00 (d, 1, J = 7 Hz, C=CH), 2.30 (t, 1, J = 6 Hz, C=CCH), 2.05 (d, 1, J = 5 Hz, CHCOCl), 1.80 (br s, 6, $(CH_3)_2C$=C), 1.36 (s, 3, ring CH_3), 1.30 (s, 3, ring CH_3).

***trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carboxamide.** *trans*-Chrysanthemic acid chloride (72.6 g, 0.390 mol) was added over a period of 1.25 h to 700 mL of concentrated ammonium hydroxide (28.5% NH_3) which was stirred and maintained at ice bath temperature. After another 1.25 h at 0 °C the reaction mixture was filtered, and the white solid was washed repeatedly with water until the filtrate was neutral to litmus paper. The white, granular solid was dried under aspirator vacuum to yield 58.3 g (90%) of *trans*-chrysanthemylamide: mp 123–124 °C (lit.[46] mp 126 °C); IR (KBr) 3333 and 3125 (NH_2), 3030 (vinyl H), 1640 (C=O), 1610 (NH_2 bend); ^1H NMR ($CDCl_3$) δ 6.00–5.40 (br, 2, $CONH_2$), 4.90 (d, 1, J = 8 Hz, C=CH), 2.00 (t, 1, J = 9 Hz, C=CCH), 1.70 (s, 6, $(CH_3)_2C$=C), 1.25 (s, 4, ring CH_3 and $CHCONH_2$), 1.10 (s, 3, ring CH_3).

***trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carbonitrile (1).** A suspension of 38.6 g (0.203 mol) of recrystallized *p*-toluenesulfonyl chloride and 22.7 g (0.135 mol) of *trans*-chrysanthemylamide in 100 mL of dry pyridine was stirred 1.25 h at room temperature.[16] The yellow-white suspension was diluted with 200 mL of water and extracted with two 150-mL portions of diethyl ether. The ether extract was washed with four 100-mL protions of saturated copper sulfate solution, dried ($MgSO_4$), and evaporated. Distillation of the resulting yellow liquid under reduced pressure gave, after separation of a 6.2-g forerun [bp 24 °C (0.2 mm)], 16.3 g (81%) of *trans*-chrysanthemic nitrile 1 as a clear, slightly pink liquid with a sweet odor: bp 54–55 °C (0.8 mm) [lit.[47] bp 107–108 °C (18 mm)]; mass spectrum: (10 eV), m/e (relative intensity) 149 (M^+, 78.4), 148 (17.2), 134 (100.0), 119 (12.1), 107 (41.9). The IR and ^1H NMR spectral properties of the product agree with the literature data.[3,46]

***cis*- and *trans*-1-Deuterio-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane-1-carbonitrile.** A solution of lithium diisopropylamide was prepared by addition of 1.55 mL of 2.39 M *n*-butyllithium in hexane to 0.38 g (3.69 mmol) of diisopropylamine in 11 mL of tetrahydrofuran at ice-bath temperature and then cooled to −78 °C. Trans nitrile 1 (0.50 g, 3.35 mmol) in 2 mL of tetrahydrofuran was then introduced by means of a syringe. After the mixture was stirred 20 min, 20 mL of deuterium oxide was added. Five minutes later, 5.0 mL of 5% hydrochloric acid was added, and the reaction mixture was warmed to room temperature and diluted with 50 mL of petroleum ether. The organic phase was separated, washed with 5% hydrochloric acid and saturated sodium chloride solution, dried ($MgSO_4$), and evaporated. Distillation of the residue afforded 0.40 g (80%) of the deuterated nitrile as a mixture of cis and trans isomers: bp 55–56 °C (0.5 mm); ^1H NMR ($CDCl_3$, 220 MHz) δ 5.05 (d, 1, J = 7 Hz, C=CH of cis), 4.84 (d, 1, J = 7 Hz, C=CH of trans), 1.89 (d, 1, J = Hz, C=CCH), 1.82 (s, 6, C=C$(CH_3)_2$ of cis), 1.74 (s, 6, C=C$(CH_3)_2$ of trans), 1.36 (s, 3, ring CH_3 of trans), 1.18 (s, 6, ring CH_3 of cis), 1.14 (s, 3, ring CH_3 of trans), 1.08 (d, ~0.4, J = 7 Hz, residual CHCN); mass spectrum (10 eV), m/e (relative intensity), 150 (M^+, 73.7), 149 (31.9), 148 (3.8), 135 (100.0), 120 (14.3), 108 (37.6). Integration of the vinyl protons indicated the ratio of cis/trans was 47:53.

***trans*- and *cis*-2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-(phenylthio)cyclopropane-1-carbonitrile (3 and 4).** A solution of lithium diisopropylamide was prepared by adding 10.8 mL of 2.75 M *n*-butyllithium in hexane to 2.99 g (29.5 mmol) of diisopropylamine in 90 mL of THF. The solution was stirred and cooled at −78 °C, and 4.002 g (26.8 mmol) of nitrile 1 was added. After 30 min, 5.88 g (26.8 mmol) of diphenyl disulfide dissolved in 10 mL of THF was added to the resulting clear yellow solution. Stirring was continued for 1.0 h at −78 °C following which 10 mL of 5% hydrochloric acid was added. The reaction mixture was warmed to room temperature, diluted with 100 mL of ether, and extracted with 10% hydrochloric acid, 15% sodium hydroxide, and saturated sodium chloride. The ether phase was dried ($MgSO_4$) and evaporated to give 6.9 g of a translucent viscous liquid. This material was purified by medium-pressure liquid chromatography on a 120 × 3.8 cm column packed with 600 g of 45–63 μm silica gel. The eluant was 6% chloroform in hexane with a flow rate of 40 mL/min, the average pressure was 180 psi,

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(44) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, (a) p 1096, (b) p 584.
(45) Bramwell, A. F.; Crombie, L.; Hemesley, P.; Pattenden, G.; Elliot, M.; Janes, N. F. *Tetrahedron* **1969**, *25*, 1727–41.
(46) Harper, S. H.; Sleep, K. C. *J. Sci. Food Agric.* **1955**, *6*, 116–20.
(47) Chen, Y.-L.; Barthel, W. F. *J. Am. Chem. Soc.* **1953**, *75*, 4287–9.

and the separation was monitored by UV absorbance at 260 nm.

The first component to elute was unreacted diphenyl disulfide: 0.467 g; mp 59–60 °C (lit.[48] mp 61 °C, mmp 59–60 °C). The second component was a yellow oil which solidified upon cooling at −15 °C. The solid (3.399 g) was recrystallized from pentane to give 1.932 g (28%) of α-phenylthio nitrile **3** as white flocculent crystals: mp 52.5–54.0 °C; IR (neat melt) 2222 (C≡N), 1587, 1575, 1488, 1449, 840, 714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.17 (br, 5, aromatic H), 5.03 (d, 1, J = 8 Hz, C=CH), 2.00 (d, 1, J = 8 Hz, C=CCH), 1.73 and 1.60 (s, 3, C=C(CH_3)$_2$), 1.40 and 1.36 (s, 3, ring CH_3); mass spectrum (70 eV), m/e (relative intensity) 257 (M^+, 7.5), 148 (100.0).

Anal. Calcd for $C_{16}H_{19}NS$: C, 74.66; H, 7.44; N, 5.44; S, 12.46. Found: C, 74.49; H, 7.35; N, 5.53; S, 12.41.

The third component (0.50 g) was obtained as a translucent oil which was induced to solidify with cooling and agitation. Recrystallization from pentane yielded 0.234 g (3.4%) of the other α-phenylthio nitrile isomer **4** as a white solid: mp 46.5–47.0 °C; IR (neat melt) 2222 (C≡N), 1587, 1481, 1445, 1381, 741, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.17 (br, 5, aromatic H), 4.97 (d, 1, J = 8 Hz, C=CH), 2.30 (d, 1, J = 8 Hz, C=CCH), 1.73 and 1.70 (s, 3, C=C(CH_3)$_2$), 1.53 and 1.27 (s, 3, ring CH_3); mass spectrum (70 eV), m/e (relative intensity) 256.9 (M^+, 7.10), 148 (100.0).

***trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-(phenylthio)cyclopropanemethanamine (5): General Procedure for Reduction of Nitriles.** A mixture of 3.339 (13.0 mmol) of *trans*-α-phenylthio nitrile **3** and 1.97 g (52.0 mmol) of lithium aluminum hydride in 50 mL of diethyl ether was heated under reflux for 1.0 h. The reaction mixture was stirred and cooled at ice-bath temperature as 1.97 mL of water, 1.97 mL of 15% sodium hydroxide solution, and 6.0 mL of water were added in succession.[44b] The precipitated salts were filtered, the filtrate was dried ($MgSO_4$), and the solvent was evaporated to give 3.084 g of a translucent oil which solidified upon cooling to −20 °C. Recrystallization from pentane gave 2.40 g (71%) of amine **5** as a white solid: mp 70.5–71.0 °C; IR (KBr) 3704–3226 (br, NH_2) 1585, 1475, 826, 735, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–7.10 (br, 5, aromatic), 5.00 (d, 1, J = Hz, C=CH), 2.81 (s, 2, CH_2—N), 1.75 and 1.67 (s, 3, C=C(CH_3)$_2$), 1.43 and 1.23 (s, 3, ring CH_3); mass spectrum (10 eV), m/e (relative intensity) 261.0 (M^+, 0.22), 84.0 (100.0).

Anal. Calcd for $C_{16}H_{23}NS$: C, 73.56; H, 8.81; N, 5.36; S, 12.26. Found: C, 73.72; H, 8.86; N, 5.50; S, 12.08.

***cis*- and *trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-hydroxycyclpropane-1-carbonitrile (6).** A solution of lithium diisopropylamide prepared from 14.75 mL of 2.00 M *n*-butyllithium in hexane and 2.99 g (29.5 mmol) of diisopropylamine in 120 mL of THF was cooled to −78 °C and stirred as a solution of 4.024 g (27.0 mmol) of chrysanthemic nitrile in 15 mL of THF was added at once. After 30 min, 15.127 g (34.9 mmol) of molybdenum perioxide–pyridine–hexamethylphosphoramide comples[19,49] was added to the clear, yellow solution of the nitrile anion. The resulting suspension was stirred at −78 °C for 0.5 h, warmed to −20 °C, and stirred for 1.0 h. A 25-mL portion of saturated aqueous sodium metabisulfite was added to the olive-green solution. The mixture was allowed to warm to room temperature, diluted with 100 mL of ether, and extracted with 5% hydrochloric acid, 5% sodium bicarbonate, and saturated sodium chloride. The organic solution was dried ($MgSO_4$) and evaporated, leaving a yellow liquid, distillation of which gave 3.325 g (75%) of cyanohydrin **6** as a clear, slightly yellow liquid: bp 105–107 °C (0.3 mm); IR (neat) 3350 (br, OH), 2225 (C≡N), 1453, 1387, 1112 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz δ 5.02 (d, 1, J = 6 Hz, C=CH of cis), 4.93 (d, 1, J = 6 Hz, C=CH of trans), 4.25–3.90 (br, 1, OH), 1.77 and 1.71 (s, 7, C=C(CH_3)$_2$ of trans and cis and C=CCH), 1.21 and 1.20 (s, 6, ring CH_3 of cis), 1.23 and 1.10 (s, 3, ring CH_3 of trans); mass spectrum (70 eV), m/e (relative intensity) 165.0 (M^+, 14.09), 150.0 (24.92), 69.0 (100.0). Integration of the vinyl protons indicated that the ratio of isomers with the nitrile cis and trans to the isobutenyl group was 18:82. This isomer ratio was unchanged during all manipulations of **6** and the compounds prepared from it.[50]

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.98; H, 9.23; N, 8.50.

***cis*- and *trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-methoxycyclopropane-1-carbonitrile (7).** Following the procedure of Merz,[51] a solution of 3.325 g (20.1 mmol) of cyanohydrin **6** and 0.5 g of tetra-*n*-butylammonium iodide in 50 mL of diethyl ether was mixed with 2.09 g (52.3 mmol) of aqueous 50% sodium hydroxide. The mixture was stirred vigorously and cooled at ice-bath temperature for 15 min, after which 3.80 g (30.1 mmol) of dimethyl sulfate was added over 5 min. The resulting suspension was stirred at ice-bath temperature for 2.5 h and at room temperature for 2.5 h. After addition of 10 mL of concentrated ammonium hydroxide, the solution was diluted with 50 mL of diethyl ether. The ether phase was washed with water, dried ($MgSO_4$), and evaporated. Distillation of the residue (3.57 g) under reduced pressure gave 3.31 g (92%) of a α-methoxy nitrile **7** as a clear, colorless liquid: bp 74–76 °C (0.2 mm); IR (neat) 2222 (C≡N), 1449 and 1379 (*gem*-dimethyl), 1220, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.90 (d, 1, J = 5 Hz, C=CH), 3.47 (s, 3, OCH_3), 1.77 and 1.73 (s, 3, C=C(CH_3)$_2$), 1.30 and 1.18 (s, 3, ring CH_3); mass spectrum (70 eV), m/e (relative intensity) 179.1 (M^+, 26.49), 164.1 (100.0).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.74; H, 9.50; N, 7.82. Found: C, 73.90; H, 9.76; N, 7.57.

***cis*- and *trans*-2,2-Dimethyl-3-(2-methyl-1-propenyl)-1-methoxycyclopropanemethanamine (8).** α-Methoxy nitrile **7** (3.115 g, 17.4 mmol) was reduced to the amine by the procedure given above for the preparation of **5**. Distillation of the product provided 2.65 g (83%) of amine **8** as a clear, colorless liquid: bp 58–59 °C (0.3 mm); IR (neat) 3500–3100 (br, NH_2), 1449, 1374, 1091, 909–820 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.93 (d, 1, J = 7 Hz, C=CH), 3.33 (s, 3, OCH_3), 2.90 (:br s, 2, CH_2N), 1.73 (br s, 7. C=C(CH_3)$_2$ and C=CCH), 1.30 and 1.10 (s, 3, ring CH_3); mass spectrum (70 eV), m/e (relative intensity) 84.0 (100.0).

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.85; H, 11.55; N, 7.80.

***cis*- and *trans*-2,2-Dimethyl-3-(2-methyl-1-propyl)-1-methoxycyclopropane-1-carbonitrile (9).** A mixture of 5.109 g (28.5 mmol) of α-methoxy nitrile **7** and 0.70 g of 5% palladium on carbon in 150 mL of absolute ethanol was hydrogenated in a Parr apparatus at 35 psi for 18 h. Filtration of the catalyst followed by evaporation of the solvent and distillation of the residue yielded 4.027 g (78%) of nitrile **9** as a clear, colorless liquid: bp 86–87 °C (0.5 mm); IR (neat) 2247 (C≡N), 1471, 1385, 1170, 1114 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz δ 3.44 (s, 3, OCH_3), 1.67 (septet, 1, J = 7 Hz, CH(CH_3)$_2$), 1.45–1.04 (br m, 3, CH_2CH), 1.23 and 1.18 (s, 3, ring CH_3), 0.98 and 0.94 (d, 3, J = 7 Hz, (CH_3)$_2$CH); mass spectrum (70 eV), m/e (relative intensity) 181.1 (M^+, 0.85), 124.0 (100.0).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.71; H, 10.64; N, 7.83.

***cis*- and *trans*-2,2-Dimethyl-3-(2-methyl-1-propyl)-1-methoxycyclopropanemethanamine (10).** The reduction of 4.027 g (22.2 mmol) of nitrile **9** was carried out by the procedure given above for the preparation of **5**. Amine **10** was obtained as a clear, colorless liquid: yield 3.67 g (89%); bp 67.5–68.5 °C (0.2 mm); IR (neat) 3704–3060 (NH_2), 1650–1550 (br), 1471, 1370, 909–769 (br); ^1H NMR ($CDCl_3$) 220 MHz δ 3.26 (s, 3, OCH_3), 2.92 and 2.70 (d, 1, J = 7 Hz, CH_2N), 1.31 (septet, 1, J = 3 Hz, (CH_3)$_2$CH), 120 and 1.01 (s, 3, ring CH_3), 0.92 and 0.89 (d, 3, J = 2 Hz, (CH_3)$_2$CH), 0.64 (t, 1, J = 5 Hz, cyclopropyl H); mass spectrum (70 eV), m/e (relative intensity), 170.0 (1.09), 58.1 (100.0).

Anal. Calcd for $C_{11}H_{23}NO$: C, 71.27; H, 12.51; N, 7.59. Found: C, 71.10; H, 12.64; N, 7.70.

2,2-Dimethyl-3-(2-methyl-1-propyl)cyclobutanone (22). A mixture of 0.515 g (3.39 mmol) of cyclobutanone **20**[30] and 0.10 g of 5% palladium on carbon in 50 mL of absolute ethanol was hydrogenated in a Parr apparatus at 30 psi of hydrogen for 20 h. Filtration of the catalyst and evaporation of the solvent left

(48) Yiannios, C. N.; Karabinos, J. V. *J. Org. Chem.* **1963**, *28*, 3246–8.

(49) Although Vedejs et al.[19b] indicate that the molybdenum peroxide complex should be kept in a refrigerator, we were able to store the reagent in a vacuum desiccator over phosphorus pentoxide at room temperature for periods as long as 3 months with no noticeable loss of reactivity.

(50) The NMR spectral data cited for the compounds prepared from **6** refer to the major isomer unless stated otherwise.

(51) Merz, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 846–7.

0.184 g (35%) of cyclobutanone **22** as a clear, colorless liquid which was purified by preparative GC on a 2.3 m × 1 cm column packed with 20% SE-30 on 60/80-Chromosorb W at 155 °C. The spectral properties of **22** are as follows: IR (neat) 1792 (C=O), 1468, 1389, 1370, 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 3.13 and 3.07 (d, 1, J = 8 Hz, CHC=O), 2.71 and 2.63 (d, 1, J = 8 Hz, CHC=O), 2.10 (m, 1, $CHCH_2C$=O), 1.65–1.22 (br m, 3, $(CH_3)_2CH$); mass spectrum (70 eV), m/e (relative intensity), 154.0 (M^+, 0.36), 112.0 (31.03), 70.0 (52.33), 69.0 (100.0), 68.0 (13.50), 57.0 (44.29), 56.0 (37.16). The mass spectrum was obtained by GC/MS using a 25 m × 0.25 mm capillary column coated with OV-101 and operated at 80 °C with a carrier-gas flow rate for 40 mL/min.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.61; H, 11.67.

6,6-Dimethyl-7-(2-methyl-1-propenyl)-1-oxa-3-azaspiro-[2.4]heptan-2-one (12). Cyanohydrin **6** (5.245 g, 31.8 mmol) was reduced to aminohydrin **11** in ether by the procedure detailed above for the preparation of **5**. The ethereal solution of **11** was stirred and combined with an ice-cold mixture prepared from a solution of 10.4 g (0.186 mol) of potassium hydroxide in 83 mL of water and 250 mL of benzene.[52] The resulting mixture was stirred and cooled at ice-bath temperature as 89.3 mL of a 12.5% solution of phosgene (9.28 g, 99.2 mmol) in benzene was added over a 15-min period. After 30 min at ice-bath temperature the phases were separated, and the benzene layer was washed with 15% sodium hydroxide solution and saturated sodium chloride. The solution was dried ($MgSO_4$), the solvent was evaporated, and the remaining yellow solid was recrystallized from pentane–benzene. The yield was 1.902 g (31%) of oxazolidone **12**, a white solid, as a mixture of isomers: mp 142–150 °C; IR (KBr) 3704–3030 (br, NH), 1818–1724 (br, C=O), 1111, 971, 855, 769, 735 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz, δ 5.56 (br s, 1, NH), 4.68 (d, 1, J = 7 Hz, C=CH), 3.54 and 3.43 (d, 2, J = 10 Hz, CH_2N), 1.75 and 1.70 (s, 3, $(CH_3)_2C$=C), 1.30 and 0.93 (s, 3, ring CH_3); mass spectrum (70 eV), m/e (relative intensity) 195.0 (M^+, 19.46), 40.9 (100.0).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.61; H, 8.76; N, 7.18.

6,6-Dimethyl-7-(2-methyl-1-propenyl)-3-nitroso-1-oxa-3-azaspiro[2.4]heptan-2-one (13). A solution of 1.865 g (9.56 mmol) of oxazolidinone **12** in 25 mL of pyridine was stirred and maintained at 10–15 °C while 2.19 mL of 4.80 M nitrosyl chloride (0.689 g, 10.5 mmol) in acetic anhydride was added.[52] After 30 min, 50 g of ice was added to the red solution, and the mixture was extracted three times with chloroform. The chloroform extracts were dried ($MgSO_4$), concentrated to a volume of 10 mL, decolorized with activated charcoal, and filtered over 15 g of silica gel. The filtrate was evaporated to leave a yellow oil which crystallized upon trituration with 10 mL of pentane and storage at −25 °C. Recrystallization from pentane afforded 1.038 g (48%) of *N*-nitrosooxazolidinone isomers **13** as a yellow solid: mp 53–62 °C; IR (KBr) 1818 (C=O) 1471, 1351, 1212, 1183, 1147, 866, 746 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz δ 4.64 (d, 1, J = 7 Hz, C=CH), 3.70 (s, 1, CH_2N), 1.75 and 1.65 (s, 3, C=$C(CH_3)_2$), 1.35 and 0.95 (s, 3, ring CH_3); mass spectrum (10 eV), m/e (relative intensity) 224.1 (M^+, 0.16), 109.1 (100.0).

Anal. Calcd for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N, 12.49. Found: C, 59.09; H, 7.28; N, 12.74.

Deamination of 5: General Deamination Procedure. A solution of 2.140 g (8.20 mmol) of amine **5** and 2.95 g (49.2 mmol) of glacial acetic acid in 5.6 mL of water was stirred at ice-bath temperature as 1.70 g (24.6 mmol) of sodium nitrite in 5.1 mL of water was added.[14] After a 1-min induction period, gas evolution began, and the solution turned green. After 45 min at ice-bath temperature, the reaction mixture was diluted with 50 mL of diethyl ether, and the aqueous layer was neutralized by addition of 5% sodium bicarbonate solution. The phases were separated, and the ether layer was washed with 10% hydrochloric acid and 15% sodium hydroxide solution. Drying ($MgSO_4$) and evaporation left 1.858 g of a yellow-green liquid which was dissolved in 50 mL of anhydrous methanol and mixed with 4.397 g (31.8 mmol) of anhydrous potassium carbonate. The resulting suspension was stirred for 16 h at room temperature, diluted with 100 mL of water, and extracted three times with ether. The combined ether extracts were washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated. The remaining orange liquid (1.53 g) was purified by column chromatography on 20 g of silica gel (145 × 20 mm) eluting with hexane first and then with dichloromethane.

The hexane eluant (300 mL) provided 0.34 g (17%) of triene **15** as a colorless liquid which was further purified by preparative gas chromatography on a 2.3 m × 1 cm column packed with 20% SE-30 on 60/80 AW Chromosorb W at 250 °C to obtain an analytical sample: IR (neat) 2000–1675 (monosubstituted aromatic pattern), 1600, 1580, 1471, 1370, 893, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.17 (br m, 5, aromatic H), 5.29 (d, 1, J = 9 Hz, $(CH_3)_2C$=CH), 5.17 (s, 1, CH=CSPh), 4.81 (s, 3, CH_3C=CH_2 and CH=CSPh), 3.68 (d, 1, J = 9 Hz, $(CH_3)_2C$=CH), 1.71 (s, 6, $(CH_3)_2C$=C), 1.52 (s, 3, CH_2=CCH_3); mass spectrum (70 eV), m/e (relative intensity) 244.0 (M^+, 60.82), 135.1 (100.0).

Anal. Calcd for $C_{16}H_{20}S$: C, 78.69; H, 8.20; S, 13.11. Found: C, 78.36; H, 8.24; S, 13.20.

The first dichloromethane fraction (200 mL) yielded 0.387 g of an orange liquid the IR and NMR spectra of which indicated that it was a 50:50 mixture of alcohol **14** and triene **15**. The second dichloromethane fraction (400 mL) gave 0.635 g (30%) of alcohol **14** as an orange liquid uncontaminated with triene. Distillation of the alcohol in a micro-Hickman apparatus under high vacuum [112 °C (7.0×10^{-4} mm)] provided an analytical sample: IR (neat) 3571–3030 (OH), 1595, 1582, 1437, 1370, 749, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.17 (br m, 5, aromatic H), 5.63 (s, 2, CH=CH), 5.27 (s, 1, CH=CSPh), 4.70 (s, 1, CH=CSPh), 1.60–1.43 (br, 1, OH), 1.31 (s, 6, $(CH_3)_2C$(OH)), 1.28 (s, 6, C=$CC(CH_3)_2$C); mass spectrum (70 eV), m/e (relative intensity) 262 (M^+, 20.4), 43.0 (100.0).

Anal. Calcd for $C_{16}H_{20}OS$: C, 73.28; H, 8.40; S, 12.20. Found: C, 73.54; H, 8.95; S, 12.19.

The overall yields of **14** and **15** are 39% and 26%, respectively, when the amount of material in the mixed fraction is included.

Deamination of 8. The amino ether **8** (0.906 g, 4.94 mmol) was deaminated according to the procedure given above for **5**. The deamination mixture was diluted with 50 mL of ether and the aqueous phase saturated with sodium bicarbonate. The ether layer was dried ($MgSO_4$) and evaporated to leave 0.863 g of a dark red liquid which was divided into two equal portions and submitted to preparative thin-layer chromatography with nitromethane as eluant. The ultraviolet light active band at R_F 0.64–0.60 was collected from each plate and gave a total of 0.177 g of material which was resubmitted to the same preparative TLC development in nitromethane. The liquid (0.103 g) recovered from the second elution was submitted to a third preparative TLC, this time utilizing 35% hexane in ether as eluant. The band at R_F 0.21–0.12, which was not UV active but stained brilliant red upon visualization with phosphomolybdic acid reagent, was collected and gave 0.0474 g of a liquid which was distilled in a Kugelrohr apparatus [oven temperature 140–150 °C (0.05 mm)] to afford 0.0428 g of a clear, yellow liquid which was assigned the structure **17** on the basis of the following data: IR (neat) 3500 (br, OH), 1553 and 1348 (s, NO_2), 1085, 983, 855 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 6.05 and 5.61 (d, 1, J = 15 Hz, *trans*-CH=CH), 5.02 and 4.04 (AB d, 1, J = 18 Hz, diastereotopic CH_2NO_2), 3.05 (s, 3, OCH_3), 1.74 (s, 6, $HOc(CH_3)_2$), 1.52 and 0.87 (s, 3, $NO_2CC(CH_3)_2$); mass spectrum (10 eV), m/e (relative intensity) 220 (1.5), 107 (33) 152 (32), 125 (46), 110 (100), 95 (92), 59 (31), 43 (28). Compound **17** thus isolated was homogeneous on analytical TLC in several solvent systems and showed only a minor (<2%) impurity upon gas chromatography.

Compounds **18–20** could be isolated by preparative gas chromatography of the crude deamination material by utilizing a 2.7 m × 1 cm column packed with 20% OV-17 on 60/80 AW Chromosorb P and operated at 145 °C. Cyclobutanone **20** had NMR and IR spectral characteristics identical with and chromatographed with an authentic sample of **20**.[30] Cyclobutanone **19** had the following spectral characteristics: IR (CCl_4) 1786 (C=O), 1464, 1379, 1253, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz δ 5.11 (d, 1, J = 7 Hz, C=CH), 3.77 (d, 1, J = 7 Hz, C=CCHC=O), 2.89 and 2.54 (d, 1, J = 13 Hz, CH_2C=O), 1.76 and 1.64 (s, 3, C=$C(CH_3)_2$), 1.44 and 1.10 (s, 3, ring CH_3). A mass spectrum of this compound was obtained by GC/MS using a 1.8 m × 0.6 cm column packed

(52) Newman, M. S.; Kutner, A. *J. Am. Chem. Soc.* **1951**, *73*, 4199–204.

with 3% OV-17 on 100/120 AW Chromosorb Q and operated at 80 °C with a flow rate of 40 mL/min: low-resolution mass spectrum (70 eV), *m/e* (relative intensity) 152 (M^+, 1.48), 137 (M − 15, 9.62), 109 (M − 43, 12.65), 96 (69. 79), 67 (81.97), 41 (100.00); high-resolution mass spectrum calculated for $C_{10}H_{16}O$ (M^+) *m/e* 152.1201, found 152.1197.

Keto alcohol **18** had the following characteristics: IR (neat) 3704–3125 (br, OH), 1701 (C=O), 1361, 1124, 980 cm^{-1}; ^1H NMR (C_6D_6) δ 5.69 and 5.47 (d, 1, J = 15 Hz, *trans*-CH=CH), 1.82 (s, 3, CH_3C=O), 1.15 (s, 6, $(CH_3)_2C(OH)$), 1.09 (s, 6, $(CH_3)_2CC$=O); mass spectrum (70 eV), *m/e* (relative intensity) 169 (M − 1, 0.21), 152 (M − 18, 2.12), 110 (20.50), 43.0 (100.0); ^{13}C NMR ($CDCl_3$) δ 138.0 and 131.0 (C=C), 70.7 (COH), 49.7 ($(CH_3)_2CC$=O), 29.8 ($(CH_3)_2$), 25.4 (CH_3C=O), 24.1 ($(CH_3)_2$.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.23; H, 10.82.

When the proton NMR of **18** was performed in $CDCl_3$, the signal for the vinyl protons collapsed to a singlet at δ 5.22.

Deamination of 0.4117 g of **8** as described above gave 0.3385 g of crude product to which 0.0240 g of *p*-dichlorobenzene was added as an internal standard for NMR analysis. Integration of the singlet at δ 3.05, arising from the methoxyl group of **17**, vs. the singlet of the internal standard at δ 7.27 indicated the yield of **17** to be 20%.

Deamination of 0.309 g of **8** as described above provided a sample for GC yield analysis to which 0.0512 g of pulegone was added as an internal standard. Gas chromatographic analysis was perfomed by utilizing a 3.6 m × 0.3 cm column packed with 3% OV-17 on 100/120 Chromosorb Q and operated with an initial column temperature of 105 °C maintained for 1 min followed by a programmed temperature increase of 3 °C/min to a final temperature of 118 °C which was maintained for 3 min. Compounds **20**, **19**, and **18** and the internal standard eluted in that order, and the peak areas integrated vs. the internal standard indicated yields of 3%, 7%, and 8%, respectively.

Deamination of 10. The amino ether **10** (0.81 g, 4.38 mmol) was deaminated, and the product was hydrolyzed according to the procedure given for **5**. The hydrolysate (0.421 g) was purified by column chromatography on 40 g of silica gel (320 × 25 mm) by using the following stepwise elution gradient (volume of eluant in milliliters, hexane–dichloromethane ratio): 400, 100:0; 400, 90:10; 200, 80:20; 200, 60:40; 200, 20:80. Cyclobutanones **21** and **22** (140 mg, 21%) eluted together as a clear, colorless liquid which was distilled in a Kugelrohr apparatus [140 °C oven temperature (0.5 mm)]: IR (neat) 1786 (C=O), 1471, 1379, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 3.13 and 3.07 (d, 1, J = 8 Hz, CHC=O of **22**), 2.98–2.78 (br m, 2, CH(CO)CH of **21**) 2.71 and 2.63 (d, 1, J = 8 Hz, CHC=O of **22**), 2.55 and 2.48 (d, 1, J = 2 Hz, $(CH_3)_2C$-CHC=O of **21**), 2.10 (br m, 1, $CHCH_2C$=O of **22**), 1.41 and 1.10 (s, 3 ring CH_3 of **21**), 1.17 and 1.07 (s, 3, ring CH_3 of **22**). Integration of the protons α to the carbonyl of **21** and **22** indicated that the ratio of these two isomers was 60:40.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.91; H, 11.78.

In another run, 0.50 g (2.70 mmol) of amino ether **10** was deaminated, and the hydrolysis step was omitted. Workup gave 0.343 g (83%) of a clear, faintly yellow liquid, the NMR and IR spectra of which showed no significant difference from that of the purified mixture of **21** and **22**. Integration of the geminal ring methyl groups of each isomer based on line height in the NMR spectra of the crude product gave a **21**/**22** ratio of 60:40.

Isomers **21** and **22** in the purified product mixture were analyzed by GC/MS using a 25 m × 0.25 mm capillary column coated with OV-101 and operated at 80 °C with a flow rate of 40 mL/min. The minor isomer cochromatographed with an authentic sample of **22**, and the ratio of **21** to **22** as determined by integration of the completely resolved peaks was 62:38. The mass spectral characteristics of the isomers are as follows: **21** (70 eV), *m/e* (relative intensity) 154 (M^+, 0.40), 112 (34.77), 98 (14.02), 79 (27.84), 69 (100.0), 56 (42.44), 55 (88.64), 42 (4.90); **22** (70 eV), *m/e* (relative intensity) 154 (M^+, 0.36), 112 (31.03), 70 (52.33), 69 (100.0), 56 (37.16), 55 (16.12), 42 (21.52).

Hydrolysis of *N*-Nitrosooxazolidone 13. To a mechanically stirred, viscous, yellow solution of 0.496 g (2.21 mmol) of **13** in 16 mL of 1,2-dimethoxyethane and 4 mL of water saturated with 13.77 g of lithium nitrate was added 0.215 g (5.38 mmol) of sodium hydroxide in 0.25 mL of water.[21] The resulting mixture, which foamed extensively, was stirred for 1.0 h, diluted with 50 g of ice and 25 mL of water, and extracted three times with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated. The remaining orange-yellow oil (0.430 g) was purified by chromatography on 30 g of silica gel (220 × 20 mm) with the following stepwise elution gradient (volume of eluant in milliliters, hexane–diethyl ether ratio): 250, 95:5; 250, 80:20; 250, 50:50; 500, 0:100. Compounds **24**, **20**, and **19** eluted as a mixture which weighted 74.3 mg (22%). The three components were separated by preparative gas chromatography on a 2.7 m × 1 cm column packed with 20% OV-17 on 60/80 Chromosorb P and operated at 110 °C. The areas of the three peaks were in the ratio 21:40:28, respectively.[53] The major component cochromatographed with and had NMR and IR spectral characteristics identical to authentic sample of cyclobutanone of **20**.[30]

The first component, **24**, had the following spectral properties: IR (CCl_4), 1724 (C=O), 1449, 1379, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) 220 MHz, δ 5.39 (d, 1, J = 8 Hz, $(CH_3)_2C$=CH), 4.84 (s, 2, C=CH_2) 3.82 (d, 1, J = 8 Hz, $CHCOCH_3$), 2.03 (s, 3, CH_3C=O), 1.77, 1.66, 1.62 (s, 3, C=CCH_3). A mass spectrum of this compound was obtained by GC/MS using a 1.8 m × 0.6 cm column packed with 3% OV-17 on 100/120 Chromosorb Q and operated at 80 °C with a flow rate of 40 mL/min: low-resolution mass spectrum (70 eV), *m/e* (relative intensity) 152 (M^+, 11.08), 137 (M − 15, 2.23), 110 (M − 43, 10.70), 109 (90.72), 81 (27.99), 67 (100.0), 43 (96.37); high-resolution mass spectrum calculated for $C_{10}H_{16}O$ (M^+) *m/e* 152.1201, found 152.1204.

The third component, cyclobutanone **19**, had spectral properties as previously described.

Eluting later from the silica gel column was 86.9 mg (23%) of **18**, the properties of which have been previously detailed.

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Registry No. **1**, 61057-36-1; *cis*-**2**, 78715-29-4; *trans*-**2**, 78715-30-7; **3**, 78715-31-8; **4**, 78715-32-9; **5**, 78715-33-0; *cis*-**6**, 78715-34-1; *trans*-**6**, 78715-35-2; *cis*-**7**, 78715-36-3; *trans*-**7**, 78715-37-4; *cis*-**8**, 78715-38-5; *trans*-**8**, 78715-39-6; *cis*-**9**, 78715-40-9; *trans*-**9**, 78715-41-0; *cis*-**10**, 78715-42-1; *trans*-**10**, 78715-43-2; **11**, 78715-44-3; **12**, 78739-29-4; **13**, 78715-45-4; **14**, 78715-46-5; **15**, 78715-47-6; **17**, 78715-48-7; **18**, 78715-49-8; **19**, 78715-50-1; **20**, 38086-97-4; **21**, 78715-51-2; **22**, 78715-52-3; **24**, 78715-53-4; *tert*-amyl *trans*-chrysanthemate, 78715-54-5; *trans*-chrysanthemic acid, 827-90-7; *trans*-chrysanthemoyl chloride, 51348-74-4; *trans*-chrysanthemamide, 78779-89-2.

(53) A fourth unidentified component comprised the remaining 11%.