A General Method for the Synthesis of Amines by the Rearrangement of Allylic Trichloroacetimidates. 1,3 Transposition of Alcohol and Amine Functions

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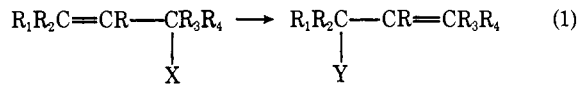
Abstract: A new synthetic method for the preparation of amines is reported (Scheme I). Allylic alcohols are condensed with trichloroacetonitrile to yield the corresponding allylic trichloroacetimidic esters (**3**). Thermolysis of **3** at 25–140 °C results in allylic rearrangement to afford the corresponding trichloroacetamide **4**. To complete the 1,3 conversion of a hydroxy to a primary amino group, the trichloroacetyl group can be removed by treatment with dilute base. Details of the application of this method to 13 varied primary, secondary, and tertiary alcohols are described. With the exception of 3-substituted 2-cyclohexen-1-ols, the overall yields are excellent. Evidence is presented to indicate that the thermal rearrangement is an operationally concerted [3,3]-sigmatropic rearrangement. Mercury(II) salts dramatically catalyze the rearrangement of trichloroacetimidic esters of 2-alken-1-ols. Rate accelerations of up to 10^{12} are obtained. A two-step iminomercuration–deoxymercuration mechanism (Scheme II) is suggested for this novel mercury(II) catalysis.

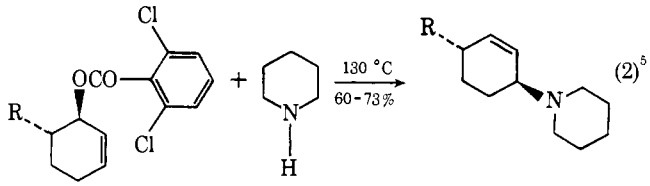
In recent years, the 1,3 interchange of allylic functionality (eq 1) has played an increasingly important role in synthetic



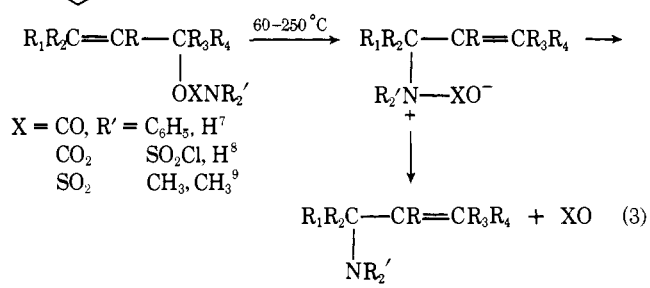
$$R_1R_2C{=}CR{-}CR_3R_4 \longrightarrow R_1R_2C(X){-}CR{=}CR_3R_4 \quad (1)$$

organic methodology.[2,3] Excellent synthetic procedures, which embody significant substrate flexibility, exist for the 1,3 conversion of oxygen functions into carbon (Claisen-type rearrangements),[3a] sulfur,[3b] and halogen[3c] functionalities. Many other such transformations have also been demonstrated[2] but their scope has not yet been fully delineated. Among these are the 1,3 conversions of sulfur functions to oxygen[3d] and nitrogen[3e] functionalities and the allylic interconversion of oxygen and nitrogen functions.[3f,g] In large part, due to their high specificity in affording only a single allylic isomer, [3,3]- and [2,3]-sigmatropic rearrangements have been particularly widely employed.

Prior to 1974 a generally useful synthetic method for the 1,3 transposition of oxygen and nitrogen functions (eq 1, X = OR, Y = NR_2) was not available. That such a method would be useful in synthesis is readily apparent when one considers how much more difficult is the introduction of an amino than a hydroxyl group into complex molecules.[4] Previously existing methods for achieving this transformation have serious limitations. The SN2′ reaction of allylic alcohol derivatives with amines is sometimes successful, but it is restricted to cases where direct displacement is precluded by steric or other factors (eq 2).[5,6] Rearrangements of the type illustrated in eq 3



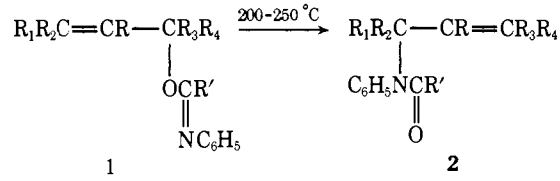
$$\text{(2)}^{5}$$



$$R_1R_2C{=}CR{-}CR_3R_4 \xrightarrow{60\text{–}250\,^\circ C} R_1R_2C(OXNR_2'){-}CR{=}CR_3R_4 \longrightarrow R_1R_2C{=}CR{-}CR_3R_4 + XO \quad (3)$$

X = CO, R′ = C_6H_5, H[7]; CO_2, SO_2Cl, H[8]; SO_2, CH_3, CH_3[9]

also affect this transformation.[7–9] The most useful of these processes is the base-catalyzed thermal rearrangement (200–240 °C) of allylic phenyl urethanes (eq 3, X = CO, R′ = C_6H_5, H) which affords the allylically transposed amine in 24–60% yield. Unfortunately, reactions of this type have some ionization (SNi) component and even in the most favorable cases afford significant amounts of the unrearranged allylic isomer.[7–9] Allylic *N*-phenylbenzimidates[10] (**1**, R′ = C_6H_5) and *N*-phenylformimidates[11] (**1**, R′ = H) are also reported to



$$R_1R_2C{=}CR{-}CR_3R_4 \xrightarrow{200\text{–}250\,^\circ C} R_1R_2C(C_6H_5NCR'{=}O){-}CR{=}CR_3R_4$$

1 **2**

rearrange at 200–250 °C to give in high yields[12] the corresponding rearranged amides **2**. The general utility of these rearrangements is, however, seriously limited by the moderate yields obtained in preparing the imidate derivative (<50% based on the allylic alcohol),[10,11] the high pyrolysis temperatures which may result in further transformations of the product amides **2**,[13] and the lack of flexibility in nitrogen substitution.

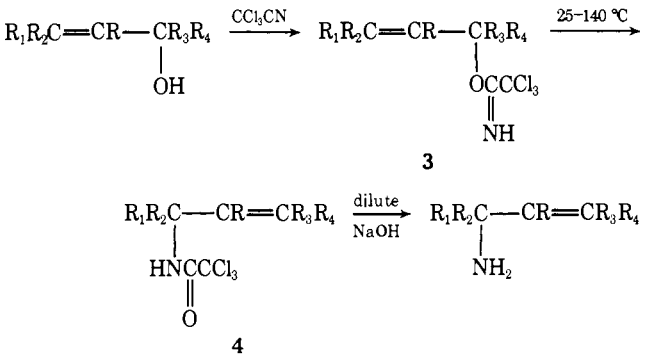
In 1974[14] we reported that the [3,3]-sigmatropic rearrangement of trichloroacetimidic[15a] esters of allylic alcohols provides a superior method for the 1,3 transposition of hydroxyl and amino functions. In this paper we present the details of our investigations of this synthetic procedure.

Results

Scheme I illustrates the sequence. The application of this method to a variety of primary, secondary, and tertiary allylic alcohols is summarized in Table I. With the exception of 3-substituted cyclohexenols, the overall isolated yields are excellent.

Preparation of Trichloroacetimidates.[16] The base-catalyzed addition of alcohols to trichloroacetonitrile was first reported by Cramer.[17,18] The procedure we have found most reproducible is to utilize the corresponding sodium or potassium alkoxide (0.1–0.2 equiv) as the catalyst and to carry out the condensation with trichloroacetonitrile at 0 °C in an ether solvent. For tertiary and many secondary alcohols, it is essential that the alcohol–alkoxide solution be added to an ether solution of trichloroacetonitrile at 0 °C (inverse addition). The reason for the higher yields obtained by this sequence is unclear. In

Scheme I. 1,3-Transposition of Hydroxyl and Amino Groups via the Rearrangement of Allylic Trichloroacetimidates



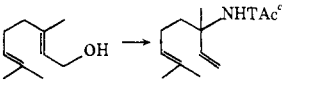
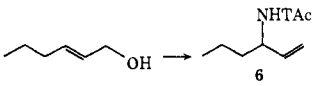
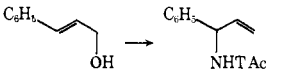
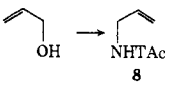
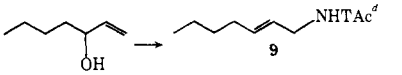
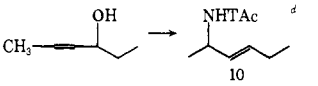
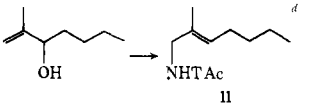
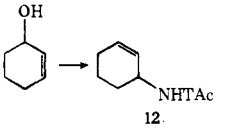
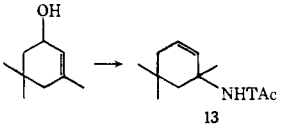
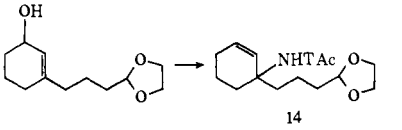
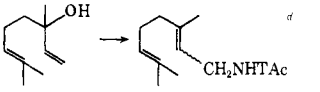
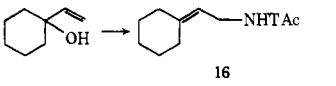
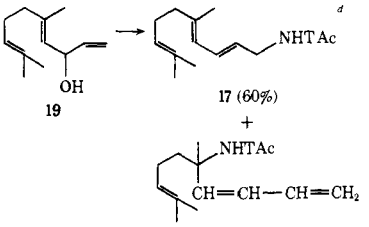
this way trichloroacetimidic esters (**3**) of a variety of primary, secondary, and tertiary alcohols have been prepared in crude yields of 80–100% without the necessity for yield optimization. In our early experiments crude imidates were generally purified by distillation (Table IV, Experimental Section); however, in more recent experiments they have been used directly without purification.

Thermal Rearrangement of Allylic Trichloroacetimidates.[19] The conditions required for the thermal rearrangement varied considerably with the structure of the imidate. Trichloroacetimidic esters of primary and secondary allylic alcohols were isomerized in refluxing xylene (140 °C; $t_{1/2} \sim 1$ h for primary esters and ~5 min for secondary esters). Tertiary imidates rearranged at a convenient rate in refluxing benzene (80 °C, $t_{1/2} \sim 1$ h). The trichloroacetimidic ester of the bisallylic alcohol **19** (Table I) underwent facile rearrangement at room temperature, and only the rearranged amides **17** and **18** were isolated when **19** was condensed with trichloroacetonitrile in the normal fashion. Overall yields were not significantly improved by purifying the trichloroacetimidic ester (Tables I and IV), and we therefore recommend that crude imidates be thermolyzed directly.

The rearrangements are totally regiospecific. In no case was a trichloroacetamide with an unrearranged carbon skeleton detected in the ^{1}H NMR spectrum of the crude thermolysis product (2% of this isomer would have easily been detected in the cases of **5, 7, 9,** and **15**).

The rearrangement of trichloroacetimidic esters of secondary allylic alcohols proceeded in a highly stereoselective manner. Amides **9** and **10** were assigned the trans configuration on the basis[21] of strong ir absorption at 965–970 cm^{-1} and the absence of absorption at 690–720 cm^{-1}. The stereochemical homogeneity of **9** was examined in detail by HPLC, and no trace of a second isomer was detected. Similarly high stereoselectivity was apparent in the formation of the trisubstituted alkene **11**. The ^{1}H NMR spectrum of the crude material showed only a single allylic methyl singlet at δ 1.62 (2% of another isomer would have been detected). Although stereochemical correlations for trisubstituted alkenes containing allylic amide substitutents have not to our knowledge been established, the observed methyl chemical shift is within the range[2c,22] expected for the *E* isomer, and such a tentative assignment is made. Thermolysis of the trichloroacetimidic ester of linalool (**21**) affords a 60:40 mixture of the geranyl and neryl amides, (*E*)- and (*Z*)-**15**. The assignment of the *E* configuration to the major isomer on the basis of the smaller chemical shift observed for its C-3 allylic methyl in the ^{1}H NMR spectrum was confirmed by the results of shift reagent experiments (see Experimental Section). Although **17** and **18** were not stereochemically homogeneous (alcohol **19** was a mixture of *E* and *Z* isomers), the disubstituted double bond in **17** is primarily trans (ir 964 cm^{-1}, absorption minimum 690–720 cm^{-1}).

Table I. 1,3 Conversion of an Alcohol to an Amide. Thermolysis of Allylic Trichloroacetimidates[a]

Conversion	Isolated yield, % Overall[b]	Thermolysis
 **5**	67–74	87–92
 **6**	72	92
 **7**	76	87
 **8**	50	63
 **9**	74	92
 **10**	74	93
 **11**	61	89
 **12**	61	79
 **13**	10–43	18–79[e]
 **14**	20	
 **21** **15** (60% E, 40% Z)	83	
 **16**	57 (67)[f]	
 **19** **17** (60%) + **18** (40%)	66	

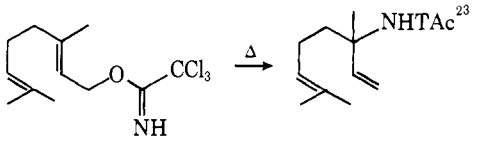
[a] Yields were maximized for **5** only. [b] From starting alcohol. [c] TAc = trichloroacetyl. [d] For discussion of stereochemistry, see text. [e] Not reproducible, see Experimental Section. [f] Based on recovered alcohol.

The results of our preliminary kinetic investigations of the thermal rearrangement of imidate **20** (eq 4) are summarized

Table II. Kinetics of the Thermal Rearrangement of the Trichloroacetimidic Ester of Geraniol (20)

Solvent	Temp, °C[a]	10^5k, s^{-1}[b]	No. of runs	Activation parameters (xylene)
Xylene	119.9	4.25 ± 0.47	7	E_a = 24.6 ± 0.5 kcal mol^{-1}
Xylene	132.3	10.8 ± 1.1	5	$\Delta H^{\ddagger}$[c] = 23.8 ± 0.5 kcal mol^{-1}[d]
Xylene	143.5	25.3 ± 1.6	5	Log A (s^{-1}) = 9.3 ± 0.3
				$\Delta S^{\ddagger}$[c] = −18.6 cal deg^{-1} mol^{-1}[e]
Nitrobenzene	132.3	55.0 ± 4.7	3	

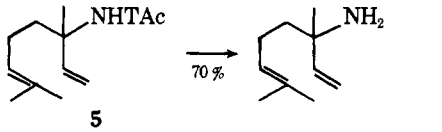
[a] ±0.1 °C. [b] Runs made following both the disappearance of imidate 20 and the appearance of amide 5 are included in this average. [c] Calculated at 132.3 °C. [d] Maximum error = 2.8 kcal/mol. [e] Maximum error = 7.2 cal deg^{-1} mol^{-1}.



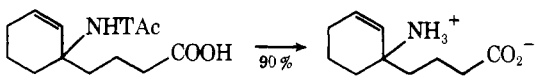
20 5 (4)

in Table II. The rearrangement was conveniently monitored in the ir by following either the appearance of the C=O band of **5** or the disappearance of the C=N band of **20**. The reactions were cleanly first order over 3 half-lives.

Removal of the Trichloroacetyl Group. To complete the 1,3 conversion of a hydroxyl to a primary amino function, the trichloroacetyl group[24] can be removed at room temperature by treatment with 3 M sodium hydroxide as is illustrated in eq 5 and 6.



5 (5)



(6)[25]

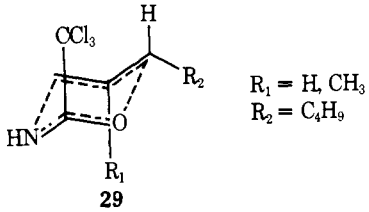
Mercury(II)-Catalyzed Rearrangement of Allylic Trichloroacetimidates. Mercury(II) salts dramatically catalyze the rearrangement of some allylic trichloroacetimidates (Table III). For example, if 0.1 equiv of mercuric trifluoroacetate (or mercuric nitrate) is added to a THF (or benzene) solution of imidate **22** in a ^1H NMR tube and the spectrum immediately recorded, only the rearranged amide **6** is observed. This should be contrasted to the thermal rearrangement of imidate **22** which requires 12 h at 140 °C. That trifluoroacetic acid was not responsible for the observed catalysis was clearly established by control experiments. For example, the addition of 0.1–0.8 equiv of trifluoracetic acid to THF solutions of imidates of **20** or **22** afforded after 5 h only a trace (<3%) of the rearranged amides **5** or **6**. As was the case with the thermal rearrangement, the mercury(II)-catalyzed rearrangement of imidates **5, 6, 7,** and **21** occurs with complete regiospecificity, since no trace (<3%) of the corresponding amide with an unrearranged carbon skeleton could be detected by ^1H NMR analysis. Several methods have been utilized to separate the mercuric catalyst from the product amide. The catalyst has been removed by chromatography on silica gel, complexation with pyridine,[26] or complexation with triphenylphosphine[27] (preferred).

As is apparent from Table III, the scope of the catalyzed reaction is very limited and is synthetically useful only for imidates derived from 2-alken-1-ols. With tertiary and some secondary imidates, the major process appeared to be an elimination reaction since considerable trichloroacetamide was isolated.

The following incidental observations were made. The mercury(II)-promoted rearrangement of imidate **20** was rapid even at −60 °C (0.3 equiv of mercuric trifluoroacetate in THF, catalyst destroyed at −60 °C with sodium borohydride) and afforded a 40% yield of amide **5** after 1 h. The mercuric trifluoroacetate-catalyzed rearrangement of **20** was, on the other hand, totally suppressed in protic solvents such as methanol or THF–water. The rearranged amide **6** was also not formed when imidate **22** was treated with aluminum chloride etherate or silver tetrafluoroborate. Such treatment in THF resulted in the disappearance of imidate **22** without the formation of any detectable amide **6**.

Discussion

Mechanism of the Thermal Rearrangement. The thermal rearrangement of allylic trichloroacetimidates (**3** → **4**) is, to the limits of detection, irreversible. This results from the large enthalpic driving force associated with the conversion of the imidate to the amide functionality.[28] Although we have not made an extensive study of the mechanism of the thermal rearrangement, its formulation as an operationally concerted pericyclic process seems appropriate. Thus by the usual mechanistic criteria an intermediate has not been detected. For example, only amides with allylically rearranged carbon skeletons were obtained from the thermal rearrangement of all the monoallylic imidates we have studied, even in cases such as the preparation of amides **7, 15,** and **16** where formation of an intermediate would have appeared particularly favorable.[3e,29] The stereoselectivity observed in the formation of substituted alkenes is similar to that observed for other [3,3]-sigmatropic rearrangements. The large preference observed for the formation of the *E* isomer of the di- and trisubstituted alkenes **9** and **11** is expected from the large steric bulk of the trichloromethyl substituent and the usual chair model for the cyclic six-centered transition state **29**.[30] The lack of



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stereoselectivity observed in the formation of **15** is also consistent with this model, and similar product ratios have been reported for the rearrangement of other linalool derivatives.[3a]

The activation parameters observed for the rearrangement of **20** ($\Delta H^{\ddagger}$ = 24 kcal/mol, $\Delta S^{\ddagger}$ = −19 eu) are typical of those observed for other [3,3]-sigmatropic rearrangements.[31a] The small increase in rate[31b] obtained upon changing solvent from xylene to nitrobenzene and the rate increase resulting from the attachment of carbocation stabilizing groups to the imidate bearing carbon suggest that there is some charge separation in the transition state **30**. A similar polarized transition state was suggested for the gas-phase rearrangement of allylic tri-

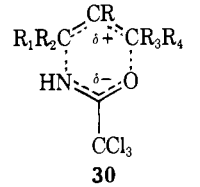

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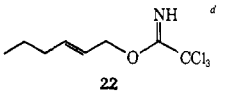
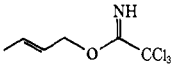
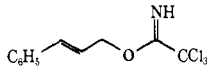
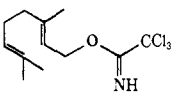
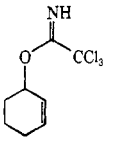
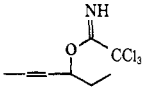
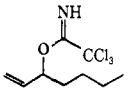
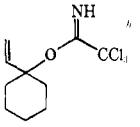
Table III. Mercuric Trifluoroacetate Catalyzed Rearrangement of Allylic Trichloroacetimidates[a]

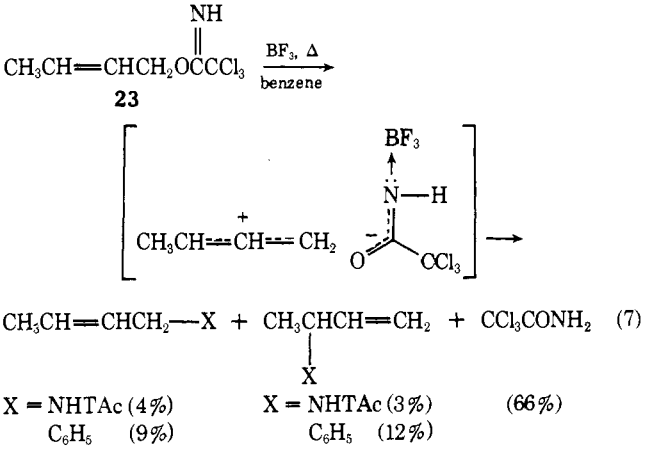
Imidate	HgX_2[b], equiv	Time, h	Amide product	Yield (%) Isolated	Yield (%) ^{1}H NMR[c]
 22	0.10	0.25	6	79	92
 23	0.20	1[e]	*i*	78	
 24	0.40	1[e]	7	45	
 20	0.20	1[f]	5	79	
	0.20	4	5	70	81
	0.30	4	5		73
 25	0.30	4	12		Tr (<5%)
 26	0.30	4	10		10[g]
 27	0.30	4	9		Tr (<6%)
 28	0.30	4	16		none (<2%)[g]

[a] In THF at 25 °C using distilled imidate samples unless otherwise noted; [imidate] = 0.2 M. [b] Mercuric trifluoroacetate. [c] Entries in this column correspond to experiments conducted under identical conditions. In all cases the reaction was quenched after 4 h with triphenylphosphine and the yields determined by NMR analysis using internal standards. [d] [Imidate] = 1.0 M. [e] The catalyst was added to 0 °C and the reaction allowed to warm to room temperature. [f] The catalyst was added at −78 °C and the reaction allowed to warm to room temperature. [g] Elimination was the major reaction. Considerable trichloroacetamide was isolated. [h] A crude sample of imidate was employed. [i] 2,2,2-Trichloro-*N*-(1-buten-3yl)acetamide.[20]

fluoroacetate esters,[32] a reaction which is a close oxygen analogue of the allylic trichloroacetimidate rearrangement.

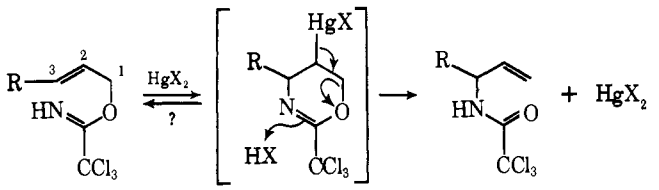
Mechanism of the Mercury(II)-Catalyzed Rearrangement. Catalysis of the rearrangement of allylic imidates by protic[3g] and Lewis acids[20] has been reported. For example, treatment of trichloroacetimidate **23** with 0.1 equiv of boron trifluoride etherate in refluxing benzene yields the mixture of products shown in eq 7.[20] A characteristic feature of these catalyzed rearrangements is the formation of mixtures of allylic isomers and Friedel-Crafts products. Ionic (SNi) mechanisms, involving ion pair intermediates such as **31**, have been suggested for these acid-catalyzed processes.[3g,20]

Our observation that mercury(II) will promote the rearrangement of trichloroacetimidic esters of 2-alken-1-ols (**20, 22, 23,** and **24**) constitutes, to our knowledge, the first report of mercuric ion catalysis of a formal [3,3]-sigmatropic rearrangement.[33] Catalysis by mercury(II) of the rearrangement of allylic imidates differs dramatically from the previously reported catalysis by acids in that mixtures of allylic isomers are *not* formed in the former process. The two-step mechanism we propose for the mercury(II)-catalyzed reaction is shown



in Scheme II. In the first step, the mercuric electrophile adds to the double bond to form a mercurinium ion (or its equivalent)[34] which is then captured intramolecularly at C-3 by the nucleophilic imino nitrogen to afford **32**.[35] Dihydrooxazine **32**

Scheme II. Iminomercuration–Deoxymercuration Mechanism



32

can then suffer cleavage of the carbon–nitrogen bond to reform the starting material or the carbon–oxygen bond to afford the rearranged amide. The later process should eventually be favored due to the thermodynamic driving force. The success of this catalyzed reaction undoubtedly derives from the fact that, in aprotic solvents, adduct formation between an olefin and mercuric trifluoroacetate is both rapid and reversible.[26,37] A related two-step mechanism has been suggested for the palladium(II)-catalyzed isomerization of allylic propionate esters.[38]

The clean regiospecificity observed for the mercury(II)-catalyzed reaction and the absence of Friedel–Crafts products (eq 7) when the reaction is conducted in benzene are consistent with the mechanism of Scheme II and incompatible with an SNi′-type mechanism. The iminomercuration–deoxymercuration mechanism also provides a convenient rationale for the limited scope of the mercury(II)-catalyzed process (Table III). Thus mercury(II) catalysis is expected to be most favorable for imidates such as **20** where addition of the imino nitrogen at C-3 is favored and less successful for imidates such as **25, 27,** and **28** where addition at C-2 is preferred.[39] In these later cases alternate reaction processes, such as the elimination reaction observed for **28**, may dominate. Evidence for the formation of C-2 adducts in the case of imidates **25** and **27** comes from experiments utilizing 1 equiv of mercuric trifluoroacetate where subsequent transformations of the intermediate adducts affords the corresponding 2-amino alcohols.[40,41]

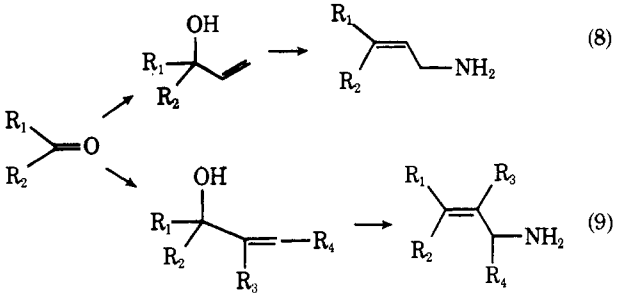
An estimate of the magnitude of the rate acceleration brought about by the mercury(II) catalyst was obtained by comparing the estimated half-life of ~70 min for the rearrangement of imidate **20** in THF at −60 °C (0.3 equiv of mercuric trifluoroacetate) with the extrapolated half-life for the thermal rearrangement (xylene solvent) at this temperature.[43] Such a comparison indicates a catalytic effect for mercury(II) of *greater than* 10^{12}.

Synthetic Applications. The method reported in this paper for the 1,3 transposition of hydroxyl and amino groups (Scheme I) is, we believe, the preferred method for achieving this transformation. Some of the important features of this sequence are (a) the overall high yields, (b) the relatively low temperatures required for the thermal rearrangement, (c) the ability of mercury(II) to catalyze the rearrangement of imidate derivatives of 2-alken-1-ols, (d) the total regiospecificity and high stereoselectivity of the process, (e) the ease of removal of the trichloroacetyl group, and (f) most importantly, the apparently broad scope of this method.

As is apparent from Table I, the rearrangement of allylic trichloroacetimidic esters of tertiary alcohols is also successful, in contrast to several other rearrangements of this type.[2a,44] The only serious limitation we have encountered is a competing elimination reaction which becomes important for trichloroacetimidic esters of 3-substituted 2-cyclohexen-1-ols. The reluctance of derivatives of such conformationally flexible alcohols to undergo [3,3]-sigmatropic rearrangements is well precedented.[44]

This method for the preparation of amines should be particularly useful for the synthesis of tertiary carbinyl amines, e.g., **5**, for which there are few alternate synthetic methods.[4] With previously existing synthetic methodology, the regiospecific synthesis of 3-amino-1-alkenes (e.g., the parent amines of **5–8**) was particularly difficult;[46] however, such compounds are readily available by the method reported here. Recently the use of this sequence in the construction of an unsaturated azaspirc ring system was reported.[25]

The combination of this 1,3 transposition of functionality with the addition of vinyl organometallics to ketones and aldehydes allows for synthetic transformations of the type shown in eq 8 and 9. In cases where the starting carbonyl component



(8)

(9)

is an aldehyde (R_2 = H), this method should stereoselectively afford the *E* isomers (R_2 = H). Such conversions have been demonstrated in the preparation of amides **11** and **16** in yields (based on the starting carbonyl compound) of over 50%.

We believe the method of amine synthesis reported in this paper is both convenient and practical. In many cases it should be the preferred method for the preparation of a variety of amines.

Experimental Section

Allylic alcohols (purity 98% or better) were purchased from Aldrich Chemical Co. or Chemical Samples Co. 1-Vinylcyclohexanol[47] and 5,9-dimethyl-1,4,8-decatrien-3-ol[48] were prepared in greater than 85% yield according to the procedure of Normant.[49] Tetrahydrofuran (THF) was distilled from benzophenone and sodium immediately prior to use. Benzene and xylene (a mixture of isomers, bp 139–143 °C) were distilled from calcium hydride. Mercuric trifluoroacetate was purchased from Aldrich Chemical Co. or prepared as described.[50] This hygroscopic salt was stored in a desiccator over potassium hydroxide, and only material melting above 163 °C was used; the anhydrous salt melts at 166–168 °C. Some samples of commercial material contain considerable water and melt as low as 100 °C. Such samples can be purified by recrystallization from trifluoroacetic acid and vacuum drying over KOH. Trichloroacetonitrile was purchased from Aldrich Chemical Co. and was distilled. The shift reagent ytterbium tris(2,2,6,6-tetramethylheptanedionate) ($Yb(dpm)_3$) was purchased from Ventron Corp. All other chemicals used were analytical reagent grade.

Microanalyses were performed by Chemalytics, Tempe, Ariz., or by Galbraith Laboratories, Knoxville, Tenn. Analyses agreed with calculated values within ±0.4% unless otherwise noted. Melting points were determined in capillary tubes with a Büchi apparatus which was calibrated with known standards.

Proton magnetic resonance (^{1}H NMR) spectra were determined at 60 MHz on a Varian 56/60 or EM360 instrument. Chemical shifts are reported as δ values in ppm relative to tetramethylsilane = 0. Coupling constants (J) are reported in Hz; abbreviations used are: s, singlet; d, doublet; t, triplet; m, complex multiplet. Infrared spectra were determined on a Perkin-Elmer Model 137 spectrophotometer. Unless otherwise indicated, short-path (bulb-to-bulb) distillations were carried out at <150 °C (<0.05 Torr) in a Kugelrohr apparatus.

All thin-layer (TLC) and preparative-layer (PLC) chromatography separations were done with E. Merck silica gel (GF and PF-254). Dry column chromatography used Woelm silica gel for dry column chromatography purchased from ICN Corp. W. R. Grace silica gel (grade 62) was used for slurry packed columns.

All reactions were run under a nitrogen atmosphere. Concentrations were done using a rotary evaporator under reduced pressure.

Preparation of Trichloroacetimidates. Representative procedures are detailed below. The inverse addition procedure is preferred for secondary and tertiary alcohols. In early experiments crude imidates were often purified by vacuum distillation, and the distilled yields and

physical properties for these materials are summarized in Table IV. In more recent studies, crude imidates have been used directly and their characterization is described individually. With the exception of low-boiling members, trichloroacetimidates are reasonably difficult to purify to analytical purity. This is particularly true of secondary and tertiary imidates which may rearrange to some extent during vacuum distillation and are often unstable (undergo elimination) upon PLC or column chromatography (silica gel or alumina). As a result of these difficulties, with but a few exceptions, analyses have not been obtained on trichloroacetimidate intermediates.

Method A. Normal Addition. (*E*)-3,7-Dimethyl-2,6-octadien-1-yl 2,2,2-Trichloroethanimidate (20)[51] (Geraniol Trichloroacetimidate). A suspension of sodium hydride [410 mg of a 57% dispersion in mineral oil (10 mmol), which had been previously washed twice with hexane] and 60 ml of anhydrous ether was treated dropwise with a solution of 15.4 g (100 mmol) of (*E*)-3-7-dimethyl-2,6-octadien-1-ol (geraniol) and 15 ml of anhydrous ether. After the evolution of hydrogen ceased (~5 min), the reaction mixture was cooled to −10 to 0 °C, and trichloroacetonitrile (10.0 ml, 14.4 g, 100 mmol) was added dropwise to the stirred solution, while the temperature was maintained below 0 °C. Addition was complete within 15 min, and the solution was allowed to warm to room temperature and was concentrated. Pentane [150 ml, containing 0.4 ml (10 mmol) of methanol] was added, the mixture shaken vigorously for 1 min, and a small amount of dark, insoluble material was removed by gravity filtration. After washing the residue two times with pentane, the combined filtrate was concentrated to give 27–29 g (90–97%) of crude **20**.

The crude imidate was sufficiently pure (~95% by ^{1}H NMR) for most purposes. It could be distilled rapidly through a short Vigreux column to give 24–28 g (80–93%) of pure **20**: bp 109–111 °C (0.1 Torr); ν_{max} (film) 3340 (NH) and 1660 cm^{-1} (C=N); ^{1}H NMR (CCl_4) 8.3 (broad s, N*H*), 5.5 (approximate t, J = 7, C-2 vinylic hydrogen), 5.1 (broad s, C-6 vinylic hydrogen), 4.77 (d, J = 7, CH_2O-(C=NH)CCl_3), 1.73 (s, CH_3), 1.66 (s, CH_3), and 1.58 ppm (s, CH_3). Anal. ($C_{12}H_{18}Cl_3NO$) C, H, N.

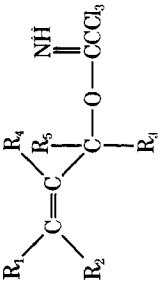
Method B. Inverse Addition. 3,7-Dimethyl-1,6-octadien-3-yl 2,2,2-Trichloroethanimidate (33) (Linalool Trichloroacetimidate). A solution of 1.54 g (10 mmol) of 3,7-dimethyl-1,6-octadien-3-ol (linalool) in 10 ml of anhydrous THF at room temperature was treated portionwise with a hexane slurry of 0.17 g (1.5 mmol) of potassium hydride (a 35% dispersion in oil, which had been previously washed twice with hexane). After stirring for 5 min, the yellow alkoxide-alcohol solution was added dropwise (double-needle transfer) to a solution of 1.0 ml (1.44 g, 10 mmol) of trichloroacetonitrile in 10 ml of anhydrous ether. The temperature during addition was maintained at −5 to 0 °C by external cooling. After stirring for 1½ h at 0 °C, the yellow solution was concentrated (temperature <25 °C); pentane [50 ml, containing 0.1 ml (2.5 mmol) of methanol] was added, the mixture shaken vigorously for 1 min, and a small amount of insoluble material was removed by filtration. Concentration afforded 2.87 g (96%) of crude, **33**, a light-yellow liquid which appeared at least 85% pure by ^{1}H NMR analysis: ν_{max} (film) 3400 (N—H, 1660 (C=N), 1290, and 1075 cm^{-1}; ^{1}H NMR (CCl_4) 8.2 (broad s, NH), 4.7–6.3 (m, CH=CH_2 and C-6 vinylic hydrogen), 1.55 (s, CH_3), and 1.67 ppm (s, two CH_3 groups).

Thermal Rearrangements. 2,2,2-Trichloro-*N*-(3,7-dimethyl-1,6-octadien-3-yl)acetamide (5). A solution of crude imidate **20** (28 g) in 300 ml of xylene was heated at reflux for 8 h. After cooling to room temperature, the dark xylene solution was filtered through a short column (4.5 cm in diameter) which was packed with silica gel (70 g) and toluene. The column was eluted with an additional 250 ml of toluene, and the combined light yellow eluent was concentrated and distilled through a short Vigreux column to give 20–22 g (67–74% for the two steps) of **5**, bp 94–97 °C (0.03 Torr), TLC (R_f 0.4, trace impurity R_f 0.7, 4:1 hexane:ethyl acetate.) The analytical sample was prepared by crystallization from hexane at −78 °C to give a colorless liquid: mp <20 °C, ν_{max} (film) 3267 and 3330 (NH), 1724 (C=O), 1503 (amide II band), 987 and 917 (CH=CH_2), and 817 cm^{-1} (C—Cl); ^{1}H NMR (CCl_4) 6.6 (broad s, NH), 5.96 (approximate d of doublets, J = 9.5 and 18.5, C-2 vinylic hydrogen), 4.9–5.3 (m, C-1 and C-6 vinylic hydrogens), 1.67 (s, CH_3), 1.60 (s, CH_3), and 1.49 ppm (s, CH_3). Anal. ($C_{12}H_{18}Cl_3NO$) C, H, Cl, N.

Similar thermolysis of a distilled sample of imidate **20** afforded pure **5** (homogeneous by TLC) in 87–92% yield after distillation through a short Vigreux column.

2,2,2-Trichloro-*N*-(1-hexen-3-yl)acetamide (6). A solution of dis-

Table IV. Yields and Physical Properties for Distilled Trichloroacetimidates[a]



Imidate	R_1	R_2	R_3	R_4	R_5	Bp, °C (Torr)	% yield	Method	Ir, ν cm^{-1}[b] N—H	C=N	Other	^{1}H NMR, δ[c] NH	H_3	H_5	Vinylic	Other
34	H	H	H	H	H	63 (5)[d]	78	A	3380	1660	1290, 1067, 985	8.3	4.77 (d, J = 5)		5.1–6.5	
23	CH_3	H	H	H	H[f]	44–45 (0.2)[e]	89	A	3450	1660	1290, 1074, 971	8.3	4.6–5.0		5.4–6.2	
22	C_3H_7	H	H	H	H	124–125 (11)	78	A	3360	1665	1300, 1078, 981	8.3	4.72 (d, J = 4)		5.3–6.2	1.76 (d, J = 7, CH_3)
27	H	H	H	H	C_4H_9	45 (0.04)	80	B	3440	1665	1290, 1070, 977	8.2	~5.3		5.0–6.2	
25	H	—(C	$H_2)_3$—	H	H	91–95 (2)	77	A	3425	1660	1282, 1078, 908	8.3	5.38		5.6–6.2	
24	C_6H_5	H	H	H	H[f]	112–115 (0.03)	87	A	3436	1660	1495, 1447, 1376, 1287, 1072, 972	8.3	4.90 (d, J = 6)		6.0–6.9	7.29 (C_6H_5)
26	CH_3	H	C_2H_5	H	H[f]	40–42 (0.02)	80	B	3420	1660	1313, 1286, 1055, 950	8.2	See vinylic		5.1–6.1	1.72 (d, J = 5, =CHCH_3)
36	CH_3	—CH_2C(CH_3)$_2$CH_2—		H	H	82–85 (0.05)	55	A	3450	1660	1284, 1076, 972	8.2	5.37		5.5–5.7	1.72, 1.03, 0.98 (s, CH_3's)
35	C_6H_{11}	CH_3	H	H	H	110–113 (0.03)	96	A	3340	1660	1290, 1075, 975	8.3	4.77 (d, J = 7)		5.5 (t, J = 7, H_2) 5.1 (br s, H_6)	1.73, 1.66, 1.58 (s, CH_3's)

[a] Distilled imidates were pure (>93%) by ^{1}H NMR. In some cases they were contaminated with up to 5% of the rearranged amide. Yields are not optimized. [b] Film. [c] In CCl_4. [d] Lit.[20] 78 °C (13 Torr). [e] Lit.[20] 86–87 °C (11 Torr). [f] A mixture of *E* and *Z* isomers.

tilled imidate **22** (254 mg, 1.03 mmol) in 10 ml of xylene was heated at reflux for 12 h, concentrated, and distilled (short path) to afford 234 mg (92%) of **6**, pure by ^{1}H NMR analysis, TLC (R_f 0.3, trace impurity R_f 0.2, 12:1 ethyl acetate: hexane). The analytical sample was prepared by PLC (benzene) and distillation (short path): ν_{max} (film) 3410 (NH), 1695 (C=O), 1510 (amide II band), 987 and 923 (CH=CH_2), and 820 cm^{-1} (C—Cl); ^{1}H NMR (CCl_4) 6.6 (broad s, NH), 5.0–6.2 (m, CH=CH_2), and 4.4 ppm (m, C*H*NHTAc). Anal. ($C_8H_{12}Cl_3NO$) C, H, Cl, N.

2,2,2-Trichloro-*N*-(1-propen-3-yl)acetamide (8). A solution of distilled imidate **34** (1.99 g, 9.83 mmol) and 25 ml of xylene was heated at reflux for 18 h, concentrated, and distilled (short path) to afford 1.78 g (89%) of **8**, contaminated with 8% of **34** (^{1}H NMR analysis). A 150-mg sample was purified by PLC (10:1 hexane:ethyl acetate) to afford 107 mg (63%) of **8**: mp 28–31 °C (lit.[20] mp 31–32 °C); ν_{max} (CCl_4) 3400 (N—H), 1727 (C=O), 1508 (amide II band), 989 and 922 cm^{-1} (CH=CH_2); ^{1}H NMR (CCl_4) 6.9 (broad s, NH), 5.0–6.3 (m, CH=CH_2), and 3.97 ppm (apparent t, J = 5.5, CH_2NHTAc).

2,2,2-Trichloro-*N*-(3-phenyl-1-penten-3-yl)acetamide (7). A solution of distilled imidate **24** (910 mg, 3.27 mmol) and 25 ml of xylene was heated at reflux for 10 h, concentrated, and purified by PLC (10:1 benzene:ethyl acetate) to afford 793 mg (87%) of **7**, a light yellow solid: mp 56–58 °C, TLC (R_f 0.6, 10:1 benzene:ethyl acetate). The analytical sample was prepared by sublimation (80 °C, 0.1 Torr): mp 58–59 °C; ν_{max} (KBr) 3257 (NH), 1689 (C=O), 1513 (amide II band), 999 and 934 cm^{-1} (CH=CH_2); ^{1}H NMR (CCl_4) 7.39 (s, C_6H_5), 5.1–6.2 (m, CH=CH_2), and 5.6 ppm (m, C*H*NHTAc). Anal. ($C_{11}H_{10}Cl_3NO$) C, H, Cl, N.

2,2,2-Trichloro-*N*-[(*E*)-2-hepten-1-yl]Acetamide (9). A solution of distilled imidate **27** (432 mg, 1.67 mmol) in 20 ml of xylene was heated at reflux for 2½ h, concentrated, and purified by dry column chromatography on silica gel (9:1 hexane:ethyl acetate) and distillation (short path) to give 399 mg (92%) of pure **9**: ν_{max} (film) 3410 (NH), 1698 (C=O), 1508 (amide II band), 967 (trans CH=CH), and 820 cm^{-1} (CCl); ^{1}H NMR (CCl_4) 7.2 (broad s, NH), 5.2–6.0 (m, CH=CH), and 3.9 ppm (apparent t, J = 5, CH_2NHTAc). Anal. ($C_9H_{14}Cl_3NO$) C, H, Cl, N.

This sample when analyzed by HPLC (2 ft μ porasil column, >6000 theoretical plates, three solvent systems) showed only a single peak.

2,2,2-Trichloro-*N*-[(*E*)-3-hexen-2-yl]acetamide (10). A solution of distilled imidate **26** (1.14 g, 4.67 mmol, a mixture of cis and trans isomers) in 25 ml of xylene was heated at reflux for 1 h, concentrated, and distilled (short path) to afford 1.06 g (93%) of pure **10**: bp 88–89 °C (0.7 Torr); TLC (R_f 0.5, benzene), ν_{max} (film) 3410 (NH), 1700 (C=O), 1508 (amide II band), 966 (trans CH=CH), and 823 cm^{-1} (CCl); ^{1}H NMR (CCl_4) 6.8 (broadened d, $J \sim 6$, NH), 5.1–6.0 (m, C*H*=C*H*), 4.2–4.6 (m, C*H*NHTAc), 1.6–2.5 (m, CH_2), 1.32 (d, J = 7, CH_3), and 1.00 ppm (t, J = 7, CH_3). Anal. ($C_8H_{12}Cl_3NO$) C, H, N.

2,2,2-Trichloro-*N*-[(*E*)-2-methyl-2-hepten-1-yl]acetamide (11). Following procedure B, 2-methyl-1-hepten-3-ol (1.28 g, 10 mmol) was condensed with trichloroacetonitrile to yield 2.64 g (97%) of the crude imidate, which appeared to be greater than 90% pure by ^{1}H NMR analysis. A 1.00-g sample in benzene was filtered through a short column packed with silica gel (3 g) and benzene to afford 0.71 g (69%) of pure 2-methyl-1-hepten-3-yl 2,2,2-trichloroethanimidate: ν_{max} (film) 3320 (NH), 1665 (C=N), 1300, and 1070 cm^{-1}; ^{1}H NMR (CCl_4) 8.2 (broad s, NH), 5.27 (t, J = 6, C*H*O(C=NH)CCl_3), 4.8–5.1 (m, =CH_2), and 1.73 ppm (broadened s, CH_3).

A 200-mg sample of the above purified imidate was dissolved in xylene and heated at reflux for 3½ h. Concentration, purification by PLC (3:1 benzene:hexane), and distillation (short path) afforded 179 mg (89%) of analytically pure **11**: TLC (R_f 0.35, 3:1 benzene:hexane); ν_{max} (film) 3320 (NH), 1710 (C=O), 1520 (amide II band), and 820 cm^{-1} (CCl); ^{1}H NMR (CCl_4) 6.8 (broad s, NH), 5.33 (t, J = 7, =CH), 3.85 (d, J = 6, CH_2NHTAc), and 1.63 ppm (s, CH_3). Anal. ($C_{10}H_{16}Cl_3NO$) C, H, N.

The isomeric purity of the product amide was at least 98% since no trace of a second vinyl methyl singlet was apparent in the ^{1}H NMR spectrum. A resolved vinyl methyl singlet 2% as intense as that of the major isomer would have been detected. The addition of sequential amounts (up to 0.5 equiv) of Yb(dpm)$_3$ also failed to resolve a second isomer.

2,2,2-Trichloro-*N*-(2-cyclohexene-1-yl)acetamide (12). A solution of distilled imidate **25** (153 mg, 0.631 mmol) and 20 ml of *o*-dichlorobenzene was heated at reflux for 1 h, concentrated, and purified by PLC (benzene) to afford 121 mg (79%) of pure **12**, 84–86 °C. The analytical sample was prepared by one recrystallization from hexane: mp 85.5–87 °C; ν_{max} (KBr) 3226 (NH), 1686 (C=O), and 1522 cm^{-1} (amide II band); ^{1}H NMR (CCl_4) 6.53 (broad s, NH), 5.4–6.2 (m, CH=CH), and 4.4 ppm (m, C*H*NHTAc). Anal. ($C_8H_{10}NOCl_3$) C, H, N.

2,2,2-Trichloro-*N*-(1,5,5-trimethyl-2-cyclohexen-1-yl)acetamide (13). A solution of distilled imidate **36** (361 mg, 1.27 mmol) in 15 ml of xylene was heated at reflux for 1 h and concentrated to afford a colorless semisolid material. Hexane (20 ml) was added and the mixture filtered to yield 93 mg (0.57 mmol) of trichloroacetamide, mp 137–139 °C (lit.[52] mp 142°). The concentrated hexane filtrate was purified by PLC (benzene) to afford 177 mg (49%) of **13**, a colorless liquid, TLC (R_f 0.5, benzene). Two additional pyrolyses of other samples of presumably comparable **36** afforded **13** in 18 and 79%. Imidate **36** is apparently very sensitive to acid-promoted ionization, which we believe to be responsible for the widely differing results observed. As examples of the extreme sensitivity of **36**, attempted filtration through silica gel resulted in extensive elimination, as did extraction of a pentane solution of **36** with dilute aqueous acetic acid. The analytical sample of amide **13** was prepared by distillation (short path): ν_{max} (film) 3330 (NH), 1705 (C=O), and 1510 cm^{-1} (amide II band); ^{1}H NMR (CCl_4) 6.6 (broad s, NH), 5.8–5.9 (m, CH=CH), 1.1–2.4 (m, 2 ring methylenes), 1.50 (s, C-1 CH_3), and 1.02 ppm (s, two C-5 CH_3 groups). Anal. ($C_{11}H_{16}Cl_3NO$) C, H, Cl, N.

2,2,2-Trichloro-*N*-[1-(4-ethylenedioxy-1-butyl)-2-cyclohexene-1-yl]acetamide (14). Following procedure B (NaH was used in place of KH), 3-(4-ethylenedioxy-1-butyl)-2-cyclohexen-1-ol[25] (23.0 g, 0.108 mol) was condensed with trichloroacetonitrile to yield 36.3 g (94%) of 3-(4-ethylenedioxy-1-butyl)-2-cyclohexen-1-yl 2,2,2-trichloroethanimidate; 90% pure by ^{1}H NMR analysis; ^{1}H NMR (CCl_4) 8.1 (s, NH), 5.5–5.8 (m, =CH), 5.34 (s, $W_{H/2}$ = 11 Hz, C*H*O-C(=NH)CCl_3), 4.73 (m, C*H*(O)O), and 3.79 ppm (m, OCH_2CH_2O).

The above imidate sample was dissolved in 1.5 l. of hexane and heated at reflux for 5 days. After cooling to 0 °C, the mixture was filtered to yield 9.5 g (58.5 mmol) of trichloroacetamide mp 136–139 °C (lit.[52] 142 °C). The concentrated filtrate was dissolved in 30 ml of hexane and allowed to crystallize at 0 °C to afford 4.85 g (13% for two steps) of the rearranged amide **14**: mp 86–89 °C; TLC (R_f 0.2, 4:1 hexane:ethyl acetate). An additional 2.61 g (7% for two steps) of **14**, mp 86–88.5 °C was obtained by dry column chromatography (4:1 hexane:ethyl acetate). The analytical sample was prepared by two recrystallizations from hexane to yield fine colorless needles: mp 90.5–91.5 °C: ν_{max} (KBr) 3200 (NH), 1701 (C=O), 1511 (amide II band), and 824 cm^{-1} (CCl); ^{1}H NMR (CCl_4) 6.28 (broad s, NH), 5.89 (s, CH=CH), 4.78 (unsymmetrical t, J = 4.5, C*H*(O)O), and 3.83 ppm (m, OCH_2CH_2O). Anal. ($C_{14}H_{20}Cl_3NO$) C, H, N.

2,2,2-Trichloro-*N*-[(*E*)- and -(*Z*)-3,7-dimethyl-2,6-octadien-1-yl]acetamide (15). A 1.15-g sample of linalool trichloroacetimidate (**33**) (preparation described above) and 40 ml of benzene was heated at reflux for 2 h, allowed to cool to room temperature, and filtered through a short column packed with 5 g of silica gel and benzene. After elution with an additional 10 ml of benzene, the eluents were concentrated to afford 1.00 g (83% for the two steps) of a 60:40 mixture of amides (*E*)-**15** and (*Z*)-**15**. Two isomers were apparent by TLC (9:1 hexane:ethyl acetate, double elution): a major isomer R_f 0.4, a minor isomer R_f 0.5, and a trace impurity R_f 0.3. The isomer ratios were conveniently determined by integration of the ^{1}H NMR spectrum after the addition of the shift reagent Yb(dpm)$_3$, which caused a larger downfield shift for the NH hydrogen of the major isomer. The analytical sample (isomer mixture) was prepared by PLC (15:1 hexane:ethyl acetate) and distillation (short path): ν_{max} (film) 3246 (NH), 1686 (C=O), and 1502 cm^{-1} (amide II band); ^{1}H NMR (CCl_4) 6.8 (broad s, NH), 4.8–5.4 (m, two =CH), and 3.90 ppm (apparent t, CH_2NHTAc). Anal. ($C_{12}H_{18}Cl_3NO5$ C, H, N.

A 78-mg sample of the isomer mixture was separated by PLC (30:1 hexane:ethyl acetate, developed four times) to afford 42 mg of the major isomer: lower R_f, methyl singlets in the ^{1}H NMR (CCl_4) at 1.72, 1.66, and 1.59 ppm, ν_{max} (CCl_4) 3437 and 1623 cm^{-1}; and 21 mg of the minor isomer: higher R_f, methyl singlets in the ^{1}H NMR (CCl_4) at 1.77, 1.69, and 1.61 ppm, ν_{max} (CCl_4) 3432 and 1621 cm^{-1}. The major isomer was assigned the *E* configuration on the basis of the smaller chemical shift observed for its C-3 methyl group (δ 1.77 vs. 1.72).[22] Consistent with this assignment were the results of shift reagent experiments conducted on the isomer mixture. The NH,

CH_2NHTAc, and C-2 vinylic hydrogens of the major isomer exhibited larger downfield shifts than the corresponding hydrogens of the minor isomer, but the C-5 vinylic hydrogen exhibited a *smaller* downfield shift than the same hydrogen of the minor isomer.

2,2,2-Trichloro-*N*-(2-cyclohexylideneethyl)acetamide (16). Following procedure B, 1-vinylcyclohexanol[47] (2.53 g, 20 mmol) was converted into 4.12 g of crude imidate **28**. The ^{1}H NMR spectrum indicated that this sample was contaminated with 15% of 1-vinylcyclohexanol. A solution of 1.13 g of this imidate sample in 30 ml of benzene was heated at reflux for 2 h and concentrated to afford 1.29 g of a colorless semisolid material. The ^{1}H NMR spectrum indicated that this sample was a 15:85 mixture of 1-vinylcyclohexanol and rearranged amide **16**. Crystallization from 4 ml of hexane afforded 764 mg (51% for the two steps, 60% based on recovered alcohol) of **16**, mp 60–63 °C. An additional 89 mg (6%) of **16**, mp 60–62 °C, was obtained by purification of the crystallization residues by PLC (9:1 hexane:ethyl acetate). The analytical sample was prepared by two recrystallizations from hexane: mp 64–65 °C; TLC (R_f 0.4, 9:1 hexane:ethyl acetate); ν_{max} (CCl_4) 3433 (NH), 1723 (C=O), and 1503 cm^{-1} (amide II band); ^{1}H NMR (CCl_4) 7.23 (broadened t, J = 5, N*H*), 5.17 (t, J = 7, =CH), and 3.9 ppm (m, CH_2NHTAc). Anal. ($C_{10}H_{14}Cl_3NO$) C, H, N.

2,2,2-Trichloro-*N*-(5,9-dimethyl-2,4,8-decatrien-1-yl)acetamide (17) and 2,2,2-Trichloro-*N*-(5,9-dimethyl-1,3,8-decatrien-5-yl)acetamide (18). Following procedure B, 5,9-dimethyl-1,4,8-decatrien-3-ol[48] (900 mg, 4.99 mmol) was condensed with trichloroacetonitrile to afford 1.522 g (94%) of a yellow liquid. The ^{1}H NMR spectrum of the crude product clearly indicated that no imidate was present (no absorption at δ 8.3) and that the crude product was a 60:40 mixture of the rearranged amides **17** and **18**.[53]

Purification of 218 mg of this isomer mixture by PLC (15:1 hexane:ethyl acetate) followed by distillation (short path) afforded 92 mg (39%) of **17**: R_f 0.25; ν_{max} (film) 3300 (NH), 1706 (C=O), 1510 (amide II band), and 964 cm^{-1} (trans CH=CH); ^{1}H NMR (CCl_4) 7.1 (broad s, NH), 4.7–6.7 (m, four vinylic hydrogens), 3.96 (apparent t, J = 5, CH_2NHTAc), 1.75 (s, CH_3), 1.63 (s, CH_3), and 1.57 ppm (s, CH_3). Anal. ($C_{14}H_{20}Cl_3NO$) C, H, N. The higher R_f fraction afforded 63 mg (27%) of **18**: R_f 0.45; ν_{max} (film) 3390 (NH), 1724 (C=O), 1508 (amide II band), 1004, and 908 cm^{-1}; ^{1}H NMR (CCl_4) 6.4 (broad s, NH), 4.8–6.4 (six vinylic hydrogens), 1.67 (s, CH_3), 1.58 (s, CH_3), and 1.52 ppm (s, CH_3). Anal. ($C_{14}H_{20}Cl_3NO$) C, H, N.

Mercury(II)-Promoted Rearrangements. 2,2,2-Trichloro-*N*-(3,7-dimethyl-1,6-octadien-3-yl)acetamide (5). A. Pyridine Quenched. A solution of distilled imidate **20** (7.47 g, 25 mmol) and 125 ml of anhydrous THF was cooled to −78 °C. A solution of mercuric trifluoroacetate (25 ml of a 0.2 M THF solution) was added dropwise over 15 min using a glass addition funnel. The resulting solution was allowed to warm to room temperature during 1 h, and pyridine (8 ml) was added to complex free mercuric ion.[26] THF and excess pyridine were removed in vacuo, ether was added, and the ether solution was washed with H_2O until the aqueous extracts gave a negative test for ionic mercury ($NaBH_4$–NaOH). Drying ($MgSO_4$) and distillation through a short Vigreux column afforded 5.93 g (79%) of pure **5**, which was identical with a sample prepared by thermal rearrangement.

B. Triphenylphosphine Quenched. A solution of distilled **20** (595 mg, 1.99 mmol) in 10 ml of anhydrous THF was treated at room temperature with 181 mg (0.424 mmol) of mercuric trifluoroacetate. After 4 h the reaction was quenched by adding 230 mg (0.88 mmol) of triphenylphosphine. The resulting solution was stirred for 5 min, a few crystals of bis(triphenylphosphine)bis(trifluoroacetato)mercury(II) (**37**) were added, followed by 15 ml of hexane. A light-gray precipitate began to form, and the mixture was stirred overnight. Filtration afforded 403 mg (67%) of **37**, mp 118–130 °C (lit.[27] 136 °C)The filtrate was concentrated and purified by dry column chromatography (4:1 hexane:ethyl acetate) to afford 421 mg (70%) of pure **5**.

2,2,2-Trichloro-*N*-(1-hexen-3-yl)acetamide (6). A solution of distilled imidate **22** (93.3 mg, 0.379 mmol) and 0.4 ml of anhydrous THF was treated at room temperature with 17.1 mg (0.040 mmol) of mercuric trifluoroacetate. A ^{1}H NMR spectrum taken immediately after addition indicated the absence of **22**. Pyridine (0.5 ml) was added and the solution was shaken for 2 min. After concentration, purification was affected by PLC (benzene) to afford 74 mg (79%) of pure **6**, identical with a sample prepared by thermal rearrangement.

2,2,2-Trichloro-*N*-(1-buten-3-yl)acetamide. A solution of distilled imidate **23** (216 mg, 1.00 mmol) in 5 ml of THF was cooled to 0 °C and treated dropwise with 2.0 ml of a 0.10 M solution of mercuric trifluoroacetate in anhydrous THF. After allowing the reaction mixture to warm to room temperature it was concentrated and purified by PLC (9:1 hexane:ethyl acetate) to afford 168 mg (78%) of pure 2,2,2-trichloro-*N*-(1-buten-3-yl)acetamide, lit.[20] bp 120–130 °C (11 Torr), identical with a sample prepared by thermal rearrangement.

2,2,2-Trichloro-*N*-(3-phenyl-1-propen-3-yl)acetamide (7). A solution of distilled imidate **24** (278 mg, 1.00 mmol) in 10 ml of THF was cooled to −78 °C and treated dropwise with 2.0 ml of a 0.20 M solution of mercuric trifluoroacetate in anhydrous THF. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was concentrated to afford a light yellow semisolid material. Analysis by ^{1}H NMR indicated that this material was a 7:3 mixture of **7** and the starting imidate **24**. Purification by PLC (9:1 benzene:ethyl acetate) yielded 125 mg (45%) of **7**, which was 90% pure by ^{1}H NMR analysis.

Mercury(II)-Catalyzed Rearrangement-Standard Reaction Conditions. A solution of 2.0 mmol of distilled imidate in 10 ml of anhydrous THF was treated at room temperature with 256 mg (0.60 mmol) of mercuric trifluoroacetate, and the resulting solution was stirred under a nitrogen atmosphere at room temperature. After 4 h the reaction was quenched by adding 346 mg (1.32 mmol, 10% excess) of triphenylphosphine. After stirring for 5 min, 15 ml of hexane and a few seed crystals of bis(triphenylphosphine)bis(trifluoroacetato)mercury(II) were added. Sometimes an immediate precipitate formed, while in others crystallization was more sluggish. After stirring for 12 h the precipitated bis(triphenylphosphine)bis(trifluoroacetato)mercury(II) was removed by filtration and the filtrate concentrated. An appropriate internal standard was added, and the yield of rearranged amide was determined by careful ^{1}H NMR integration.

Control experiments demonstrated that a THF solution of trichloroacetamide **10** and triphenylphosphine (1 equiv) was unchanged after 24 h.

Mercury(II)-Catalyzed Rearrangement of Imidate 20 at Low Temperature. A solution of 597 mg (2.00 mmol) of distilled imidate **20** and 10 ml of anhydrous THF was cooled to −60 °C. Under a stream of nitrogen 256 mg (0.60 mmol) of mercuric trifluoroacetate was quickly added and the colorless solution maintained at −60 °C. After 1 h the catalyst was destroyed[54] by adding 0.30 ml of a diglyme solution of sodium borohydride (hydride molarity = 5.6 M). The characteristic gray color of colloidal mercury was immediately apparent, and the mixture was stirred for an additional 1 h at −70 to −60 °C. After warming to room temperature, the mixture was filtered and concentrated, and a weighed amount of freshly distilled benzaldehyde was added as an internal standard. ^{1}H NMR integration of the characteristic terminal vinyl multiplet at δ 5.8–6.3 (1 H) of amide **5** vs. the benzaldehyde aldehydic hydrogen indicated that a 38–51% yield (two experiments) of **5** was obtained.

Attempted Rearrangement of Imidate 20 in Protic Solvents. A solution of 299 mg (1.00 mmol) of imidate **20** and 5 ml of methanol was cooled to −78 °C and treated dropwise with 1.5 ml of a 0.2 M solution of mercuric trifluoroacetate in THF. The reaction mixture was allowed to warm to room temperature and was concentrated. Analysis by ^{1}H NMR indicated that no imidate was present [no absorption at δ 4.77 ($CH_2OC(NH)CCl_3$)] and that only a trace (<10%) of **5** was present (characteristic terminal vinyl multiplet at δ 5.8–6.3).

Nearly identical results were obtained from a similar experiment employing mercuric acetate as the catalyst in a 1:1 mixture of THF and H_2O at 25 °C.

Attempted Rearrangement of Imidate 22 with Lewis Acid Catalysts. A. Silver Tetrafluoroborate. A solution of 112 mg (0.456 mg) of imidate **22** in 0.5 ml of deuteriochloroform was treated at room temperature with 90.2 mg of silver tetrafluoroborate (0.46 mmol). Analysis by ^{1}H NMR immediately after the addition indicated that no **22** remained [no absorption at δ 4.77, ($CH_2OC(NH)CCl_3$)]. The reaction mixture was diluted with chloroform and washed three times with a saturated aqueous solution of sodium chloride [to remove silver(I)], dried ($MgSO_4$), and concentrated. Analysis by ^{1}H NMR indicated that no (<5%) rearranged amide **6** was formed—no absorption characteristic of the terminal vinyl group at δ 5.8–6.3 was detected.

B. Aluminum Chloride Etherate. A solution of 123 mg (0.50 mmol) of imidate **22** in 2.5 ml of anhydrous benzene was treated at room temperature with 104 mg (0.50 mmol) of aluminum chloride etherate.[55] After 1 h the reaction mixture was poured onto 5 ml of 5% hy-

drochloric acid, diluted with ether, and the organic layer was separated, dried ($MgSO_4$), and concentrated. Analysis as above by ^1H NMR indicated that no imidate **22** remained and that no (<5%) rearranged amide **6** had been formed.

Removal of the Trichloroacetyl Group. 3,7-Dimethyl-1,6-octadien-3-amine (Linalylamine). A solution of 9.0 g (30 mmol) of trichloroacetamide **5**, 160 ml of 95% ethanol, and 150 ml of 6 N sodium hydroxide was stirred at room temperature for 30 h. Ether (300 ml) was added, the organic layer separated, and the aqueous layer washed twice with ether. The combined extracts were dried (Na_2CO_3), concentrated, and the semisolid residue extracted with 50 ml of boiling hexane. The hexane solution was concentrated and distilled through a short Vigreux column to yield 3.24 g (70%) of 3,7-dimethyl-1,6-octadien-3-amine: bp 58–61 °C (2.6 Torr); ν_{max} (film) 3280 and 3200 (NH), 998 and 919 ($CH{=}CH_2$); ^1H NMR (CCl_4) 5.84 (approximate d of doublets, J = 10.1 and 17.8 (C-2 vinylic hydrogen), 4.7–5.2 (m, C-1 and C-6 vinylic hydrogens), 1.63 (s, CH_3), 1.55 (s, CH_3), 1.08 (s, CH_3). Anal. ($C_{10}H_{19}N$) C, H, N.

Kinetics of the Thermal Rearrangement of Imidate 20. Standard sealed ampule techniques were utilized. To prevent catalyzed rearrangements, the ampules were washed successively with triethylamine, *N,O*-bis(trimethylsilyl)acetamide, and xylene and were dried at 150 °C. The reaction was followed by monitoring both the appearance of the C=O band [ν_{max}(xylene) 1730 cm^{-1} (ϵ 509)] and the disappearance of the C=N band [ν_{max}(xylene) 1662 cm^{-1} (ϵ 320)]. Over the concentration range utilized Beer's law was obeyed. The starting concentration of imidate **20** was 0.10–0.15 M.

The infrared measurements were made on either a Perkin-Elmer 521 or a Beckman 5A spectrophotometer. Similar rate constants were obtained with either instrument. First-order rate constants were calculated using a computer program similar to that described by Wiberg[56] in which the experimental infinity value is varied to give the best least-squares fit. Runs were rejected if this procedure changed the infinity value greater than 8%, or if the correlation coefficient was less than 0.995. All errors reported are ±1 standard deviation.

Activation parameters were calculated from the least-squares slope and intercept of a plot of ln k (s^{-1}) vs. $1/T$. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated at 132.3 °C as described.[57] The maximum error in these quantities was calculated as described by Wiberg.[58]

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(41) A third mechanism which could be considered is one in which a complex other than **32**, formed from the imidate and the mercury(II) salt, rearranges more rapidly than the free imidate itself. This type of mechanism has been suggested for several acid-catalyzed [3,3]-sigmatropic rearrangements.[42] In those cases, the acceleration was attributed to the charge induced in the substrate molecule within the catalyst–substrate complex. Such a mechanism cannot be rigorously excluded, particularly if the nature of the complex is not defined. However, we consider it less likely than the mechanism of Scheme II.
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Chlorocyanation of Barrelenes as a Route to 1-Cyanosemibullvalenes. Convenient Introduction of an Efficient π-Electron Acceptor Substituent and Its Influence on the Cope Equilibrium

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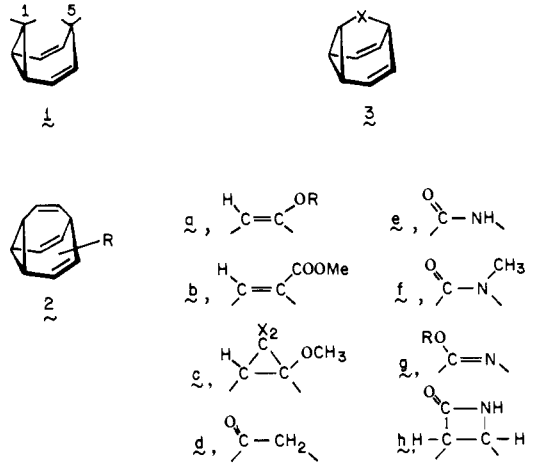
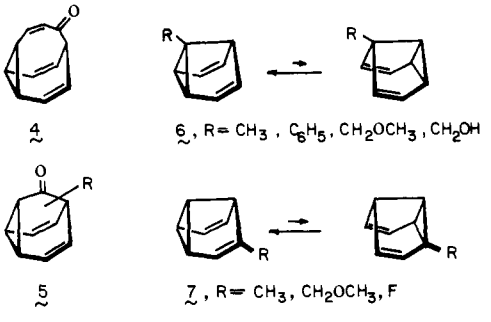
Abstract: The two-step sequence of chlorosulfonyl isocyanate addition to a barrelene followed by heating in a dimethylformamide at ca. 90° proceeds with skeletal rearrangement to a [3.2.1] bicyclic frame and introduction of cyano and chloro substituents in a 1,3 relationship. These products undergo ready dehydrohalogenation with potassium *tert*-butoxide in Me_2SO–THF solution at room temperature to give 1-cyanosemibullvalenes. By NMR and x-ray methods, the parent nitrile is shown to exist in that tautomeric form having the CN substituent bonded to the cyclopropane ring at C_1. The mono- and dibenzo analogues lack the capability for Cope rearrangement and are consequently locked into this form as well. The initially formed barrelene–CSI adducts have been characterized and certain mechanistic conclusions drawn. The structural parameters of 1(5)-cyanosemibullvalene are discussed in light of known cyclopropane bond lengths and those features peculiar to the semibullvalene derivative are summarized.

As a consequence of their fluxional character, unsymmetrically bridged homotropilidenes (**1**) can satisfy internal electronic requirements by shifting the position of structural equilibrium. Although Schröder's investigation[1] of monosubstituted bullvalenes (**2**) has indicated that such weakly



accepting and donating groups as methyl, chloro, bromo, and iodo discriminate hardly at all between the various available sites, fluorobullvalene exists chiefly (80–85%) in that form where the electronegative functionality prefers the lone sp^3-hybridized aliphatic carbon (C-5). With alkoxy and carbomethoxy substituents, the preferred orientation is that illustrated in **3a–c**.[1,2] Therefore, at the bullvalene level of homologation, a general pattern of preferential equilibration in the C-5 direction is seen. When an electron-withdrawing carbonyl group is introduced as in bullvalone (**3d**)[3] or the lactams **3e**[4] and **3f**,[5] the result is to alter the prevailing competition chiefly in the opposite direction, and this trend is maintained in the azabullvalenes **3g**[6] and β-lactam **3h**.[7]

Goldstein's more recent finding[2] that homobullvalenone **4** is characterized by preferred bonding of the carbonyl terminus to C-5 conflicts with those trends found in the lower homologues and is not easily reconciled with available theoretical assessments of electronic effects in Cope equilibria.[8,9] Because complications from larger longicyclic frameworks[10] can arise from a number of sources, the true electronic perturbational effects in **4** are conceivably not being revealed. This is not so



in the twofold degenerate barbaralone series (**5**) where methyl is recognized to prefer C-1 (K = 3.28) and deuterium C-5 (K = 0.80).[11] In those 1(5)- and 2(4)-substituted semibullvalenes (**6** and **7**, respectively) examined to date,[12b,c] the equilibria are clearly illustrative of preferential attachment to olefinic > cyclopropyl > aliphatic, irrespective of the particular substituent. With the exception of **7**-F, good agreement is found with prediction.[8,9] However, the effect of an efficient π-electron acceptor such as cyano on the very facile[13] Cope rearrangement process which operates in semibullvalenes remained to be assessed.