This result is, however, entirely consistent with our calculations, which, as we have pointed out, predict that it should be much harder to trap the ketene intermediate (**3b**) from **5** than that (**3a**) from **4**. The heat of formation of the transition state for dissociation of **3b** (into **7**) is lower by 7 kcal/mol than that for its formation from **2b**, whereas in the case of **3a**, both transition states are similar in energy. This difference is not unexpected because alkyl substituents stabilize carbenes. The conversion of **3b** to **7** should therefore be more facile than that of **3a** to **6**.

It would be of interest to try further trapping experiments under conditions where loss of thermal excitation might be expected to occur more readily than in our case. For example it should be possible to codeposit carbon atoms and **5** in a dilute argon matrix and then allow them to react by warming the matrix until it softens or melts.

Summary and Conclusions

The MNDO calculations reported here seem to suggest rather strongly that the deoxygenation of carbonyl compounds to carbenes by atomic carbon takes place by addition of carbon to the CO bond rather than by a direct electrophilic attack on oxygen, as has been commonly believed. The initial adduct, an oxiranylidene, rearranges to a ketene which undergoes decarbonylation by a "hot molecule" reaction, the necessary energy being provided by the extreme exothermicity of the two previous steps. When arc-generated carbon atoms reacted with cold butanal, the intermediate ketene could be identified in the products by hydration to butyric acid.

Experimental Section

Reaction of Chemically Generated Carbon Atoms with 4 and 5. 5-Diazotetrazole (**8**) was prepared as described previously,[17,18] and ~0.1 mmol was coated as a thin film on the walls of a 500-mL round-bottom flask. The flask was evacuated and 100 mm of gaseous carbonyl compound was admitted. The flask was closed and **8** was decomposed by immersing it in a 100 °C oil bath for 5 min. The flask was then opened on a vacuum line and the contents analyzed. The products were analyzed by pumping them through traps at −78 °C and −115 °C into a U-tube containing activated charcoal at −196 °C. The C_4 hydrocarbons, contained in the −115 °C trap, were analyzed by gas chromotography (GC) on a 20-ft 20% dimethylsulfolane (DMS) on a 40/60 firebrick column. The activated charcoal trap contained carbon monoxide which was analyzed by GC on a 16-ft 13× molecular sieve column.

Decomposition of **8** (~0.1 mmol) in the presence of an excess of **4** yielded carbon monoxide (3.1×10^{-2} mmol), 1-butene (7.2×10^{-4} mmol), methylcyclopropane (4.8×10^{-4} mmol), (*E*)-2-butene (1.05×10^{-4} mmol), and (*Z*)-2-butene (5.5×10^{-5} mmol). The pyrolysis of **8** (~0.1 mmol) in the presence of an excess of **5** yielded carbon monoxide (8.3×10^{-2} mmol), 1-butene (2.12×10^{-5} mmol), methylcyclopropane (1.6×10^{-4} mmol), (*E*)-2-butene (3.0×10^{-4} mmol), and (*Z*)-2-butene (1.61×10^{-4} mmol).

The above experiments were repeated, the flasks being immersed in liquid nitrogen immediately after pyrolysis. Transfer of either water or methanol to the cold flasks followed by warming to room temperature did not result in amounts of either esters or carboxylic acids detectable by mass spectrometry. Similar results were obtained upon decomposition of **8** in the presence of an excess of methanol and an excess of **4** or **5**.

Reaction of Arc-Generated Carbon with 4 or 5. Trapping of Ketene Intermediates. An apparatus, similar to that described by Skell and co-workers,[20] was used to generate carbon atoms. An intermittent arc was struck by passing a current of 100 A (AC) between two graphite electrodes. The carbonyl compound (**4** or **5**, 113 mmol) was introduced as a vapor and deposited on liquid N_2 cooled walls where it reacted with the carbon atoms. In a typical reaction, 0.5 g (41 mmol) of carbon was lost from the electrodes. However, some carbon was physically removed from the electrodes making a determination of the amount of carbon that was actually vaporized difficult. After the carbonyl compound had been added to the reaction, the arc was turned off and 10 mL of water was added. The reactor was warmed to room temperature and the volatile contents were pumped into traps at −78 °C and −196 °C. The reactor was opened, 10 mL of 5% $NaHCO_3$ was added, and the resultant solution was washed with ether. The $NaHCO_3$ solution was acidified with HCl and extracted with ether. In the case of **4**, evaporation of the ether yielded pentanoic acid (1.35×10^{-2} mmol by NMR), identified by comparing its spectral properties with those of an authentic sample. Analysis of the contents of the −196 °C trap by GLC showed that the yield of 1-butene in this experiment was 3.92×10^{-2} mmol.

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Thermal Rearrangements of Propargylic Trichloroacetimidates. Synthesis of (Trichloroacetamido)-1,3-dienes and -1,2-dienes

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Abstract: A new method for preparing (acylamino)-1,3-dienes is reported (Scheme I). Propargylic alcohols are condensed with trichloroacetonitrile to yield trichloroacetimidates **1**, which rearrange upon solution thermolysis to afford, depending on the structure of **1**, 1-(trichloroacetamido)-1,3-dienes (**3**), 2-(trichloroacetamido)-1,3-dienes (**4**), or 1-(trichloroacetamido)-1,2-dienes (**2**). The preparation of twelve 1-(trichloroacetamido)-1,3-dienes (Table I), three 2-(trichloroacetamido)-1,3-dienes, and five 1-(trichloroacetamido)-1,2-dienes is reported. Overall yields of 1,3-dienes from the starting propargylic alcohols range from 12 to 80%. More highly substituted 1,3-dienes are obtained in higher yields. The rearrangement is highly stereoselective and affords exclusively the (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-diene isomer. In some cases the corresponding (1*E*,3*E*)-1-(trichloroacetamido)-1,3-diene could be prepared by base-catalyzed equilibration of the kinetic isomer. Several experiments which define important energetic and mechanistic details of isomer interconversions in this series are described, and a detailed mechanism for the thermal conversion of a propargylic trichloroacetimidate to a (trichloroacetamido)-1,3-diene is proposed (Scheme III).

Recent studies in our laboratory have demonstrated that the thermal [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates is a superior method for the 1,3-transposition of alcohol and amine functionality (eq 1).[2,3] In order to further

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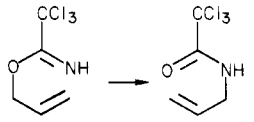


(1)

exploit the exothermic[4] imidate → amide functional group isomerization for the synthesis of organonitrogen compounds, we have extended these studies to propargylic trichloroacetimidates (Scheme I), where [3,3]-sigmatropic rearrangement should afford initially an *N*-allenamide (**2**).

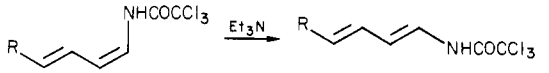
In this paper we present the details of our investigations of propargylic trichloroacetimidate thermal rearrangements.[2,5] To our knowledge, this study constitutes the first report of the rich thermal chemistry of propargylic imidates.[6] In particular, our studies have resulted in a general stereoselective synthesis of (*Z*)-1-(trichloroacetamido)-1,3-dienes (**3**), as well as the preparation of a limited number of (*E*)-1-(trichloroacetamido)-1,3-dienes, 2-(trichloroacetamido)-1,3-dienes (**4**), and 1-(trichloroacetamido)-1,2-dienes (**2**). These studies moreover define many of the energetic and mechanistic details of isomer interconversions in this series. The important use of reactive (trichloroacetamido)-1,3-dienes for Diels–Alder synthesis of nitrogen-functionalized cyclohexanes is described in the accompanying manuscript.[7]

Results

Preparation of 1-(Trichloroacetamido)-1,3-dienes.[8] Propargylic trichloroacetimidates were prepared by base-catalyzed addition of propargylic alcohols and trichloroacetonitrile.[9] The standard procedure we have described in detail previously[3b] gave trichloroacetimidic esters of secondary propargylic alcohols in excellent yields, without the necessity for yield optimization (Table I). However, this procedure afforded the trichloroacetimidic ester of the tertiary alcohol, 1-ethynylcyclohexanol, in low yield, and attempts to optimize this conversion met with only moderate success.[10]

Thermal rearrangements of secondary and tertiary propargylic trichloroacetimidates were conveniently carried out in dilute (0.15–0.03 M) refluxing xylene and gave crystalline (*Z*)-1-(trichloroacetamido)-1,3-dienes in moderate to excellent yields (Table I). For the preparation of the less substituted (and consequently more reactive and less stable) dienes by this procedure, it was essential that the rearrangement be accomplished under dilute conditions. For example, the yield of (acylamino)butadiene **17** fell to 13% when the thermal rearrangement of imidate **5** was carried out at a concentration of 0.15 M rather than 0.03 M. The structures for dienes **17**–**28** follow from (a) trichloroacetamido carbonyl absorptions near 1700 cm^{-1} in the infrared spectra, (b) vinylic protons between δ 5.1 and 6.9 in the ^1H NMR spectra, (c) four vinylic carbons between δ 115 and 150 in the ^{13}C NMR spectra, and (d) elemental compositions.

As shown in Table I, the major diene products produced in this rearrangement have the 1*Z*,3*E* stereochemistry. Isomerization of (*Z*)-1-(trichloroacetamido)-1,3-butadiene (**17**) to the more stable *E* isomer **29** was readily accomplished (73%) with triethylamine catalysis in refluxing xylene (an 85:15 equilibrium



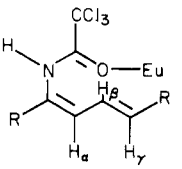
17, R = H
18, R = CH_3

29, R = H
30, R = CH_3

mixture of **29**:**17** was reached after ~1 h, Et_3N = 0.4 M). In a similar fashion, (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-pentadiene (**18**) was converted to the more stable 1*E*,3*E* isomer **30** in 63% yield. However, (*Z*)-1-(trichloroacetamido)-1,3-dienes with an alkyl substitutent at C-1 (e.g., diene **24**) were not isomerized under these conditions.

Stereochemical assignments for the 1-(trichloroacetamido)-1,3-butadienes **17** and **29** follow from ^1H NMR coupling constants measured at 220–300 MHz (**17**, $J_{1,2}$ = 10.0 Hz; **29**, $J_{1,2}$ = 13.7 Hz),[11-13] and ^{13}C NMR spectra which show the expected upfield shifts[14,15] for carbons 1–3 of the (*Z*)-isomer **17**. The stereochemistry of 1-(trichloroacetamido)-1,3-dienes **18**, **19**, **20**, and **30** also follow directly from ^{13}C NMR spectra. For example, both **18** and **30** show similar absorptions for an *E* vinylic methyl group[14] at ~18 ppm, while the upfield shifts for carbons 1–3 of **18** unambiguously establish the 1*Z*,3*E* configuration for this isomer and the 1*E*,3*E* configuration for the more stable isomer **30**. Similar arguments[10] allow the 1*Z*,3*E* and 1*Z* configurations to be assigned to dienes **19** and **20** and also allow the 3,4 double bond in dienes **24** and **28** to be assigned the 3*E* configuration.

Since only a single isomer was available for the 1-(trichloroacetamido)-1,3-dienes with alkyl or aryl substitution at carbon 1, ^{13}C NMR spectra were not useful in establishing the 1,2 double bond stereochemistry. However, lanthanide-induced ^1H NMR shift experiments allowed these assignments to be made for dienes **21**, **24**, and **28**. It is known that lanthanides complex with amides preferentially at the carbonyl oxygen[16] and that secondary amides generally adopt trans-amide conformations.[17] Thus, the anticipated structures for the europium complexes of a (1*Z*,3*E*)- and (1*E*,3*E*)-1-(trichloroacetamido)-1,3-diene should be as illustrated in structures **31** and **32**. The unique feature of the (1*Z*)-diene



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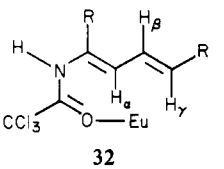

32

complex is that the europium atom is closer to H_β than H_α, and thus a larger induced shift is expected for the central vinylic hydrogen H_β of the 1*Z* isomer. This is precisely what is observed for dienes **21**, **24**, and **28**. For example, **21** showed induced shifts with Eu(dpm)$_3$ of 1.4 (H_β), 0.8 (H_α), and 0.2 (H_γ) ppm (mol/mol). The shifted spectrum also allowed the coupling constants for H_β ($J_{\alpha\beta}$ = 10.3 Hz, $J_{\beta\gamma}$ = 14.3 Hz) to be determined, which, although caution must be exercised in interpreting coupling constants measured in this way,[18] are consistent with the *E* configuration for the 3,4 double bond. The 1*Z* stereochemistry for dienes **22**, **23**, **25**, and **26** was not directly determined but was assigned by analogy with the other compounds in this series.

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(14) Cf. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757. Couperus, P. A.; Clague, A. D. H.; Van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426.
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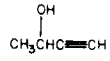
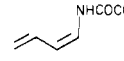
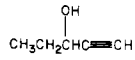
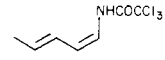
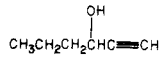
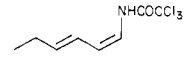
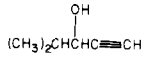
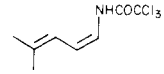
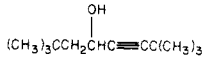
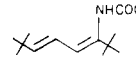
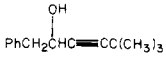
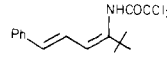
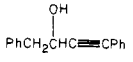
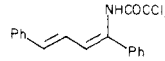
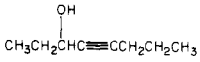
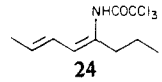
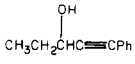
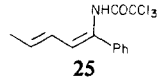
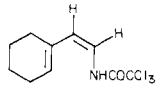
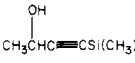
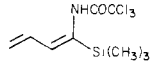
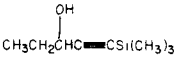
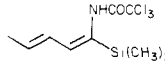
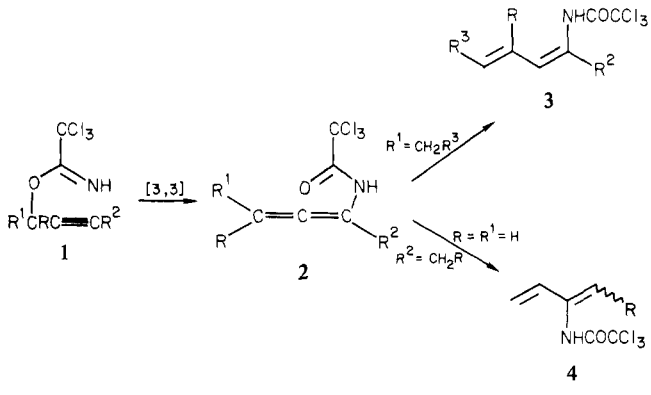
(16) Beaute, C.f Wolkowski, Z. W.; Thoai, N. *J. Chem. Soc. D.* **1971**, 700.
(17) Cf. Hallam, H. E.; Jones, C. M. *J. Mol. Struct.* **1970**, *5*, 1.
(18) Sievers, R. E. "Nuclear Magnetic Resonance Shift Reagents"; Academic Press: New York, 1973.

Table I. Preparation of 1-(Trichloroacetamido)-1,3-dienes from Propargylic Alcohols

starting alcohol	trichloroacetimidate, bp °C (pressure, mm), % yield[a]	1-(trichloroacetamido)-1,3-diene structure	% yield[a]
	5, 62–64 (3.3), 85	 **17**	38
	6, 74–80 (3.7), 86	 **18**	51
	7, 43–47 (0.005), 84	 **19**	66
	8, 75 (0.015), 80	 **20**	27
	9, 86–94 (0.1), 81	 **21**	92
	10, 155 (0.1), 88	 **22**	68
	11,[b] 60	 **23**	55
	12, 80 (0.015), 80	 **24**	86
	13, 126–129 (0.2), 60	 **25**	80
	14,[b] 38	 **26**	83
	15, 65–70 (0.005), 78	 **27**	29
	16, 100–110 (0.4), 81	 **28**	63

[a] Isolated yield of pure (>95%) product. In most cases no attempt was made to optimize yields. [b] Purified by column chromatography.

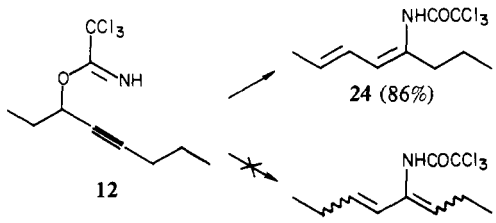
Scheme I



The magnitude of the 1*Z* stereoselectivity of the propargylic imidate rearrangement was examined in detail for the preparation of dienes **17** and **18** for which the corresponding *E* isomers were also available. Quantitative high-performance LC analysis demonstrated that the (*Z*)- and (*E*)-butadienes **17** and **29** were formed in refluxing xylene from imidate **5** in a kinetically controlled ratio of 98:2 (±0.2), respectively. Similar quantitative analysis of the crude thermolysis mixture formed under identical conditions from imidate **6** failed to reveal a trace of the (1*E*,3*E*)-pentadiene **30** by high-performance LC (2% detection limit) or ^{13}C NMR (1.5% detection limit) analysis. That the high 1*Z* stereoselectivity in the formation of diene **17** did not result from selective destruction of the more reactive 1*E* isomer under the thermolysis conditions was demonstrated by carrying out the rearrangement of imidate **5** in the presence of the (*E*)-diene **29**. Thus, thermolysis (5 h, refluxing xylene) of a mixture of imidate **5** (0.19 mmol, 0.032 M) and (*E*)-diene **29** (0.054 mmol) afforded (high-performance LC analysis) a mixture of the (*Z*)-diene **17** (0.099 mmol) and the (*E*)-diene **29** (0.049 mmol, 87% recovery). The thermal rearrangment of imidate **5** at 140 °C was considerably less stereoselective when *p*-dioxane was employed as the solvent. This decreased stereoselectivity could be shown to result from isomerization of the (*Z*)-diene **17** to the (*E*)-diene **29** under these thermolysis conditions, since the (*Z*)-diene **17** was converted to a 62:38 mixture of **17** and **29** when heated at 140 °C for 5 h in dioxane.

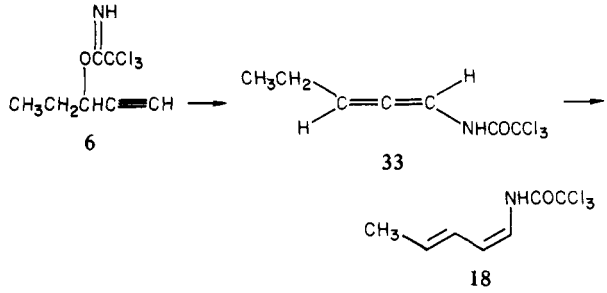
An interesting situation arises in the thermolysis of an imidate such as **12**, where formation of a 1,3-diene with the trichloroacetamido group at either the 1- or 2-position is possible (eq 2). In this example and in all related cases, only the (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-diene was isolated.

Isolation of 1-(Trichloroacetamido)-1,2-diene[8] Intermediates. When the thermolysis of imidate **6** was monitored by high-per-



(2)

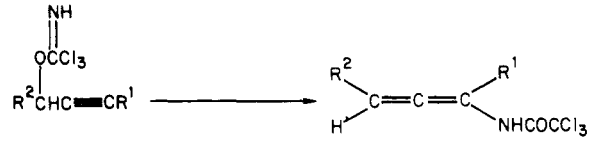
formance LC, the buildup and subsequent decay of an intermediate (Figure 1) was clearly apparent. Termination of this reaction after 1.1 h (refluxing xylene, ~1.5 half-lives) allowed this intermediate, 1-(trichloroacetamido)-1,2-pentadiene (**33**, mp 69–70 °C), to be isolated in 16% yield (eq 3).[5b] The structural assignment for



(3)

1,2-diene **33** follows from (a) the IR spectrum which showed a very weak C=C=C stretch at 1976 cm^{-1}, (b) the ^{13}C NMR spectrum which showed a resonance for the central allenic carbon at δ 195.9, and (c) extensive ^1H NMR homonuclear decoupling experiments (see Experimental Section). When 1,2-diene **33** (0.03 M) was subsequently heated at 140 °C in xylene, the (1*Z*,3*E*)-diene **18** was formed stereoselectively (**18**:**30** = 97:3 ± 3, high-performance LC analysis) in 65% yield.

The crystalline 1-(trichloroacetamido)-1,2-dienes **34–37** were



8	R^1 = H, R^2 = $CH(CH_3)_2$	34
38	R^1 = H, R^2 = H	35
39	R^1 = H, R^2 = $C(CH_3)_3$	36
40	R^1 = R^2 = $C(CH_3)_3$	37

similarly isolated from thermolyses of the corresponding propargylic trichloroacetamidates in yields of 14–19%. Purification of these allenamides was attended with substantial losses, and the crude yields (^1H NMR or high-performance LC analysis) were somewhat higher. Subsequent tautomerization to a 1,3-diene is not possible for 1,2-dienes **35–37**.

Isolation of α,β-Unsaturated Acylimines. The thermal rearrangement of the *di-tert*-butylpropargylic imidate **40** was examined in detail. When **40** (0.10 M) was thermolyzed in refluxing xylene and the progress of the rearrangement was monitored by ^1H NMR analysis of concentrated reaction aliquots, the 1,2-diene **37** was observed to increase to a maximum of ~25% at 3 h and decrease thereafter. The formation of two other products (**41** and **42**) (Table II), which showed characteristic AB quartets in the ^1H NMR, was clearly apparent. Unfortunately, we were unable to separate these materials by GC, preparative TLC, high-performance LC, or selective hydrolysis (vide infra). Compounds **41** and **42** could be obtained as a 3:1 mixture[19] by preparative GC, and much of ^{13}C and ^1H NMR of these compounds was determined from this mixture. The characterization of the major product as the trans-α,β-unsaturated acylimine **41** follows convincingly from the NMR data (Table II) which are strikingly similar to those of the related enone **43**.[20] In particular, **41** shows an AB quartet

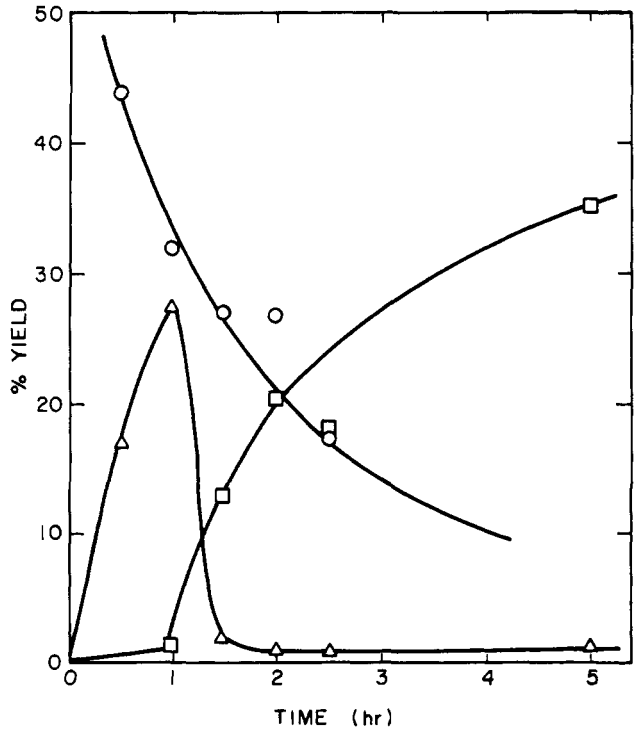
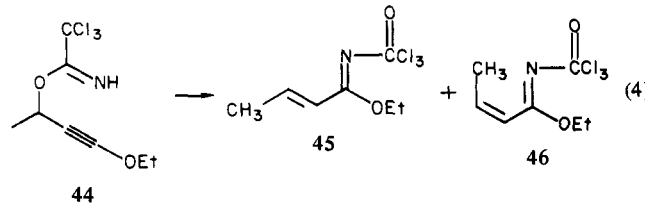


Figure 1. Time course of the thermolysis of trichloroacetimidate **6** in refluxing xylene: imidate **6** (○); 1,2-diene **33** (△); 1,3-diene **18** (□).

(J = 16.0 Hz) for the vinylic protons H_4 (δ 6.10) and H_5 (δ 6.48) in the ^1H NMR spectrum and characteristic doublets in the off-resonance ^{13}C NMR spectrum for the vinylic carbons C_4 and C_5 at 118.9 and 155.4 ppm, respectively. The ^{13}C NMR absorptions at 179.8 and 170.6 ppm appear resonable for the imine and acyl carbons of the acylimine group (both are downfield of the carbonyl carbon of a trichloroacetamide), although close model compounds are not available. The structure of the minor product cannot be assigned with comparable certainty. This material is tentatively characterized as the 6*H*-1,3-oxazine **42** on mechanistic grounds (**42** would be formed from **41** by electrocyclic ring closure) and limited spectral characterization. This material shows a characteristic AB quartet (J = 3.4 Hz), assigned to hydrogens H_5 (δ 5.00) and H_6 (δ 4.68) of **42**, in the ^1H NMR spectrum, and two characteristic doublet absorptions in the off-resonance ^{13}C NMR spectrum, assigned to C_5 and C_6, at 86.0 and 101.2 ppm. Further confirmation of the structure of acylimine **41** was obtained by hydrolysis of a 3:1 mixture of **41** and **42** at room temperature with dilute HCl to give *trans*-2,2,6,6-tetramethyl-4-hepten-3-one[20] (**43**, Table II) in 71% yield and trichloroacetamide in 97% yield. Under these conditions, **41** and **42** were transformed at similar rates; however the mass balance obtained in this reaction was not sufficient to establish with certainty that the trans-enone **43** was formed from both materials.

In an attempt to prepare 1-ethoxy-1-(trichloroacetamido)-1,3-butadiene, the thermal rearrangement of the reactive[21] ethoxy imidate **44** was investigated. Thermolysis of **44** in refluxing hexane



(4)

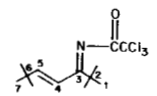
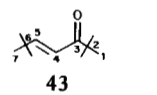
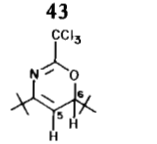
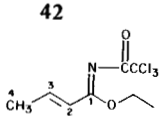
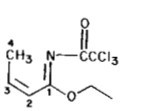
(69 °C) for 6 h afforded the (*E*)- and (*Z*)-α,β-unsaturated acyl

(19) We were unable to separate the mixture of **41** and **42** on 3% SP 2401, 3% SP 2100, 10% SP 2330, or 10% carbowax. Attempted purification of a 1:1 mixture of **41** and **42** by preparative GC (3% SP 2100, 180 °C) gave a single peak and resulted in the isolation of a 3:1 mixture of **41** and **42**.

(20) Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, **92**, 2783–2799.

(21) *Caution*!! Attempted vacuum distillation of **44** at ~100 °C resulted in a mild explosion, since the highly exothermic [3,3]-sigmatropic rearrangement occurred under these conditions.

Table II. NMR Data for Compounds **41–43, 45,** and **46**

compd	^{13}C NMR[a] C_1	C_2	C_3	C_4	C_5	C_6	C_7	other	^{1}H NMR[b]
 **41**	28.7 (q)	40.5 (s)	179.8 (s)	118.9 (d)	155.4 (d)	34.4 (s)	27.7 (s)	170.6 (s, C=O) 93.6 (s, CCl_3)	6.10 (C_4 H, $J_{4,5}$ = 16 Hz) 6.48 (C_5 H)
 **43**	28.9	43.1	204.6	119.1	157.2	33.8	26.4		6.20 (C_4 H, $J_{4,5}$ = 15.5 Hz[20]) 6.74 (C_5 H)
 **42**					101.2 (d)	86.0 (d)		37.3 (s, CMe_3) 35.5 (s, CMe_3) 24.4 (q, CH_3)	4.68 (C_5 H, $J_{5,6}$ = 3.4 Hz) 5.00 (C_6 H)
 **45**	163.9	119.5	144.8	18.5				170.2 (C=O) 94.8 (CCl_3) 64.4 (CH_2) 13.9 (CH_3)	6.06 (C_2 H), 1.93 (=CCH_3) 6.99 (C_3 H, $J_{2,3}$ = 14.9 Hz)
 **46**	165.2	118.1	144.0	16.4				169.9 (C=O) 94.0 (CCl_3) 64.7 (CH_2) 14.1 (CH_3)	5.97 (C_2 H), 2.07 (=CCH_3) 6.27 (C_3 H, $J_{2,3}$ = 11.6 Hz)

[a] In $CDCl_3$, chemical shifts are given in ppm from internal Me_4Si; multiplicities observed in off-resonance spectra are in parentheses. [b] In $CDCl_3$; chemical shifts are given in ppm from internal Me_4Si.

Scheme II

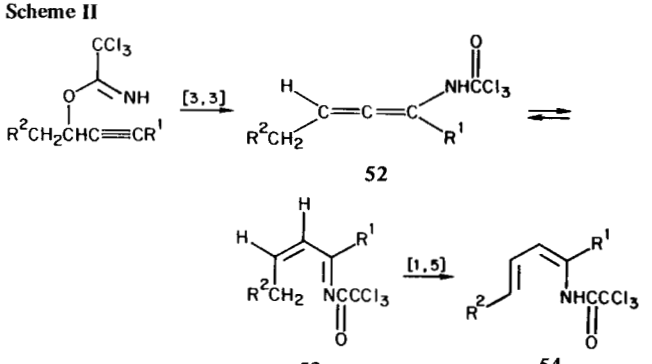
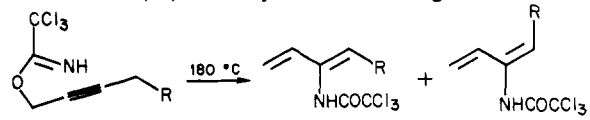


Table III

imidate	pyrolysis conditions temp, °C time, h	high-performance LC analysis eluant	(1*Z*)-diene *k'*	%	(1*E*)-diene *k'*	%
5	140, 5	92:8 hexane–ethyl acetate	0.5	98.0	0.8	2.0
5	140, 5		0.5	97.9	0.8	2.1
6	137, 5	97.5:2.5 hexane–ethyl acetate	1.1	100	2.1	none detected
6	137, 5		1.1	100	2.1	none detected

imidates **45** and **46** (84:16 ratio) in 84% yield after distillation. Acyl imidates **45** and **46** were separated by preparative high-performance LC, and their structures were unambiguously assigned on the basis of NMR spectra (Table II). The *E* stereochemistry of the major isomer **45** follows from the magnitude of the vinylic coupling constant ($J_{2,3}$ = 15.3 Hz), the upfield chemical shift of the vinylic methyl[22a] group in the ^{1}H NMR spectrum, and the downfield position[14] of this group in the ^{13}C NMR spectrum. Acylimines **45** and **46** were recovered unchanged when heated at 140 °C for 24 h or at 80 °C for 8 h in the presence of triethylamine.

Preparation of 2-(Trichloroacetamido)-1,3-dienes. Dienes with the trichloroacetamido substituent at an internal diene carbon can be prepared by propargylic trichloroacetimidate rearrangement only in cases where the formation of a 1-(trichloroacetamido)-1,3-diene is not possible. Solution thermolysis of the trichloroacetimidic ester (**47**) of 2-butyn-1-ol in refluxing *o*-dichlorobenzene



47, R = H
49, R = n-C_4H_9

48, R = H
50, R = n-C_4H_9

51, R = n-C_4H_9

(0.008 M) gave 2-(trichloroacetamido)-1,3-butadiene (**48**) (mp 27–30 °C) in 14% yield. The low yield reflects the reactivity of diene **48** and its attendant instability under the solution thermolysis conditions. The more highly substituted, and consequently more stable, 3-(trichloroacetamido)-1,3-octadienes **50** and **51** were formed in a ratio of 3:1 (74% yield) from the rearrangement of trichloroacetimidate **49** in refluxing *o*-dichlorobenzene for 2 h. The (*Z*)- and (*E*)-dienes **50** and **51** were easily separated by preparative high-performance LC and their stereochemical assignments follow directly from ^{1}H and ^{13}C NMR spectra. Thus the (*E*)-diene **51** shows absorptions at 129.3 and 129.0 ppm for the vinylic carbons C_2 and C_4, while these carbons of the (*Z*)-diene **50** are observed at 134.3 and 133.5 ppm. The upfield shift of vinylic carbons 2 and 4 in diene **51** is consistent[14] with the cis relationship of the vinyl and butyl groups in this isomer. These assignments are confirmed by the 300-MHz ^{1}H NMR spectra which show long-range coupling (J = 1.7 Hz) for the C_1 and C_4 vinylic hydrogens of isomer **51**. Preparatively useful amounts of the crystalline (*Z*)-diene **50** (mp 40 °C) can be obtained, since the (*E*)-diene **51** can be equilibrated with **50** in the presence of triethylamine at 110 °C.

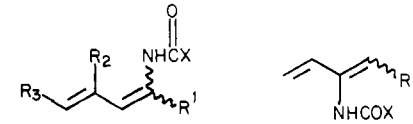
Discussion

Although thermal rearrangements of allylic imidates have been investigated in some detail in our laboratory[2,3] and elsewhere,[23] the rich thermal chemistry of propargylic imidates has not to our knowledge been described previously.[6] Thermal reorganization of many other heteroatom-containing 1-en-5-yne systems (e.g., aryl propargyl ethers[24]) are however, well-known.[25,26]

Mechanism. The results described here allow many aspects of the thermal conversion of a propargylic trichloroacetimidate to a (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-diene to be detailed (Scheme II). The conversion is initiated by a [3,3]-sigmatropic rearrangement to give the 1,2-diene amide **52**, which subsequently undergoes tautomeric reorganization to yield the more stable 1,3-diene amide **54**. The high kinetic preference which is observed for forming the 1,3-diene with the *Z* configuration about the 1,2-double bond may be rationalized by invoking the cis-α,β-unsaturated *N*-acylimine **53** as an intermediate in this tautomeric conversion. The cis-α,β-unsaturated *N*-acylimine **53** either is the highly favored kinetic tautomer of **52** (preferential protonation at C_2 cis to the C_3 hydrogen[27]) or is in rapid equilibrium with the corresponding trans isomer.[28]

The mechanism of Scheme II is supported by our isolation of the 1,2-diene amide **33** and the demonstration that it was rapidly and stereoselectively converted to the (1*Z*,3*E*)-diene amide **18** (eq 3) under the solution thermolysis conditions. Although the α,β-unsaturated acylimine intermediate **53** has not been isolated or detected in a thermal rearrangement which produces a 1,3-diene amide product, the trans-α,β-unsaturated *N*-acylimine **41** (Table II) was formed when final tautomerization to give a 1,3-diene was precluded by *tert*-butyl substitution. The closely related cis- and trans-α,β-unsaturated acylimidates **45** and **46** were also isolated in high yield from thermal rearrangement of the 1-ethoxyimidate **44**, in which case the stability of the acylimine tautomer presumably derives from the directly conjugated imidate oxygen. When a heteroatom at carbon 1 is not present, acylimine **53** would be expected[29] to be considerably less stable than the 1,3-diene amide **54**. The stereoselective formation of the (1*Z*,3*E*)-diene stereoisomer **54** by suprafacial [1,5]-sigmatropic hydrogen migration[30] of **53** is well precedented, since the closely related tautomerization of *cis*-1,3-hexadiene affords (2*Z*,4*E*)-2,4-hexadiene with high stereoselectivity.[31]

Synthesis Applications. A large variety of (1*Z*,3*E*)-1-(trichloroacetamido)-1,3-dienes (Table I) and a limited number of 2-(trichloroacetamido)-1,3-dienes can be prepared from the solution thermolysis of propargylic trichloroacetimidates. Overall yields from the starting propargylic alcohols range from 12 to 80%. More highly substituted dienes are obtained in higher yields, which reflects the greater stability of these dienes under the solution thermolysis conditions. (Trichloroacetamido)-1,3-dienes represented by structures **55** and **56** (X = CCl_3) should be available



55, (*Z*)-NHCOX
57, (*E*)-NHCOX

56

by this procedure. Moreover, the related (1*E*,3*E*)-1-(trichloroacetamido)-1,3-dienes **57** (X = CCl_3) should be generally available from the base-catalyzed isomerization of those (1*Z*)-dienes **55** which have R^1 = H. The propargylic trichloroacetimidate rearrangement also provides the only general synthesis[5b] of *N*-allenamides.

The preparation of (acylamino)-1,3-dienes by alternate procedures has been described. For example, base-catalyzed rearrangement of 2-(4-nitrophenyl)-4,7-dihydro-1,3-oxazepine has been reported[32] to yield *cis*-1-(4-nitrobenzamido)-1,3-butadiene (**55**, $R^1 = R^2 = R^3$ = H, X = 4-NO_2Ph), and the preparation of 2-acetamido- and 2-benzamido-1,3-butadiene from gas-phase thermolysis of 2-amino-3-butyne has been claimed in a patent disclosure.[33] The (1*E*)-dienes **57** with heteroatom acyl substituents (X = OR, SR, NR_2) are generally available in good yields from 1,3-dienoic acids under the Curtius[34] and Hoffman[35] rear-

(22) (a) Reference 12, pp 223–225. (b) Reference 12, pp 341–342.
(23) For a recent review see: McCarty, C. G.; Garner, L. A. In "The Chemistry of Amidines and Imidates", Patai, S., Ed.; Wiley: New York, 1975; Chapter 4.
(24) Cf. Zsindely, J.; Schmid, H. *Helv. Chim. Acta* **1968**, *51*, 1510. Trahanovsky, W. S.; Mullen, P. W. *J. Am. Chem. Soc.* **1972**, *94*, 5911.
(25) Some examples are summarized in recent reviews: Rhoads, S. J.; Raukins, N. R. *Org. React.* **1975**, *22*, 1. Bennett, G. B. *Synthesis* **1977**, 589.
(26) A number of relevant examples are summarized in ref 10.
(27) Cf. Meyer, E. F.; Burwell, R. L. *J. Am. Chem. Soc.* **1963**, *85*, 2881.
(28) The kinetic implications of these possibilities are developed in more detail in ref 10.
(29) Kiefer, H. *Synthesis* **1972**, 39. Oppolzer, W. Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 593. Oppolzer, W.; Bieber, L.; Francotte, E. *Tetrahedron Lett.* **1979**, 981.
(30) Roth, W. R.; König, J.; Stein, K. *Chem. Ber.* **1970**, *103*, 426.
(31) Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* **1966**, 1701. Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103.
(32) Heine, H. W.; Mente, P. G. *J. Org. Chem.* **1971**, *36*, 3078.
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rangement conditions, and a general synthesis of the related *trans*-*N*-alkyl-*N*-acyl-1-amino-1,3-dienes from enal precursors has also been described.[29] Since good alternate procedures exist for preparing the (*E*)-diene amides **57**,[29,34,35] the propargylic imidate rearrangement should be of greatest synthetic value for the preparation of the 2-(acylamino)-1,3-dienes **56** and the (1*Z*)-1,3-dienes **55**. For the preparation of diene amides of these latter types, the propargylic trichloroacetamidate procedure is clearly the method of choice.

Experimental Section[36]

Preparation of Trichloroacetimidates. Propargylic trichloroacetimidates were prepared by using the inverse addition procedure we have described previously.[3b] A representative procedure is detailed below. Infrared and NMR data for the propargylic trichloroacetimidates prepared in this study are summarized in the supplementary material. Freshly distilled propargylic trichloroacetimidates, like allylic trichloroacetimidates,[3b] undergo partial decomposition within hours (or days) at 25 °C and should be used directly. For this reason, elemental analyses were not obtained on trichloroacetimidate intermediates.

1-Methyl-2-propynyl 2,2,2-Trichloroethanimidate (5). A rapidly stirred solution of 3.04 g (43.4 mmol) of 3-butyn-2-ol and 34 mL of anhydrous THF was treated at room temperature in one portion with a hexane slurry of 0.51 g (4.4 mmol) of potassium hydride (a 35% dispersion in oil, which had been previously washed twice with hexane). After the mixture was stirred for 5 min, the yellow alcohol–alkoxide solution was added dropwise (double-needle transfer) over 90 min to a solution of 4.72 mL (47 mmol) of freshly distilled trichloroacetonitrile and 16 mL of anhydrous THF. The temperature during addition was maintained at −5 to +4 °C by external cooling. The resulting dark brown reaction mixture was stirred at 0 °C for 1.5 h and then concentrated to afford a dark oil. Pentane (50 mL, containing 5 drops of methanol) was added, and a small amount of dark, insoluble material was removed by vacuum filtration by using a small pad of Celite filter aid in a medium frit sintered-glass funnel. Concentration and short-path distillation gave 7.93 g (85%) of **5** (>95% pure by ^{1}H NMR): bp 62–64 °C (3.3 mm); IR (film) 3340 (NH), 2123 (C≡C), 1667 (C=N), 1279, 1070, 794 cm^{-1} (CCl_3); ^{1}H NMR ($CDCl_3$) δ 8.5 (br s, NH), 5.5 (d of q, J = 2, 6 Hz, CHOR), 2.55 (d, J = 2 Hz, C≡CH), 1.62 (d, J = 6 Hz, CH_3).

Preparation of (1*Z*)-1-(Trichloroacetamido)-1,3-dienes from the Thermal Rearrangement of Propargylic Trichloroacetimidates. (*Z*)-2,2,2-Trichloro-*N*-(1,3-butadienyl)acetamide (17). A solution of imidate **5** (1.06 g, 5.0 mmol), 17.5 mg of 4-*tert*-butyl catechol, and 165 mL of dry xylene was degassed[38] and heated at reflux under a nitrogen atmosphere for 5 h. The solution was then concentrated to afford a light yellow oil, which was dissolved in a small amount of 10:1 hexane–ethyl acetate and introduced onto a nylon column[37] (30 mm) containing 70 g of silica gel (Grace grade 62, preequilibrated with 10% by weight of eluant). The column was developed with 9:1 hexane–ethyl acetate, and the UV detectable band (R_f 0.42–0.50) was extracted with 100 mL of ethyl acetate. Concentration gave 465 mg of a semisolid, which was sublimed (50 °C (0.03 mm) to give 374 mg (35%) of the slightly yellow diene **17** (mp 86–87 °C, >95% pure by ^{1}H NMR). The analytical sample was prepared by preparative TLC (9:1 hexane–ethyl acetate) followed by sublimation (40 °C (0.003 mm)): mp 88–88.5 °C; IR (CCl_4) 3367 (NH), 1736 (C=O), 1669, 1497, 1263, 916 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.5 (br s, NH), 6.60 (apparent t, J = 9.5 Hz, C_1 H), 6.43 (ddd, J = 16.5, 10.0, 10.0 Hz, C_3 H), 5.70 (dd, J = 10.0, 10.0 Hz, C_2 H), 5.38 (d, J = 16.5 Hz, cis C_4 H), 5.28 (d, J = 10.0 Hz, trans-C_4 H); ^{13}C NMR ($CDCl_3$) δ 158.8 (C=O), 128.1 (C_3), 120.5 (C_1), 119.6 (C_4), 115.4 (C_2), 92.2 (CCl_3); mass spectrum, m/e (relative percent, 5% cutoff) 217 (9), 215 (28), 213 (30), 180 (9), 178 (13), 137 (8), 119 (11), 117 (11), 112 (6), 110 (10), 96 (85), 84 (7), 82 (12), 78 (36), 70 (5) 69 (10), 68 (100); mol wt ($C_7H_8Cl_3NO$ requires 212.951) 212.951. Anal. Calcd for $C_7H_8Cl_3NO$: C, 33.60; H, 2.82; N, 6.53. Found: C, 33.36; H, 2.97; N, 6.40.

(1*Z*,3*E*)-2,2,2-Trichloro-*N*-(1,3-pentadienyl)acetamide (18). A solution of 2.30 g (10.0 mmol) of freshly distilled imidate **6** and 340 mL of dry xylene was heated at reflux for 5.5 h and concentrated, and the residue was purified by chromatography (silica gel, 95:5 hexane–ethyl acetate) to afford 1.17 g (51%) of diene **18**. The analytical sample was prepared by preparative TLC (two elutions with 9:1 hexane–ethyl acetate) followed by sublimation (40 °C (0.02 mm)): mp 103–104 °C (sealed, evacuated capillary); IR (KBr) 3300 (NH), 1712 (C=O), 1691, 1624, 1518, 1256, 973, 837, 653 cm^{-1}; ^{1}H NMR ($CDCl_3$), 8.7 (br apparent d, NH), 5.1–6.8 (m, 4 vinylic H), 1.76 (d, J = 5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) 158.6 (C=O), 132.4 (C_4), 122.8 (C_3), 118.0 (C_1), 115.4 (C_2), 92.4 (CCl_3), 18.5 (CH_3); mass spectrum, m/e (relative percent, 5% cutoff) 231 (16), 229 (54), 227 (56), 194 (12), 192 (19), 151 (6), 149 (15), 119 (5), 117 (5), 110 (59), 92 (13), 84 (7), 83 (14), 82 (100), 81 (11), 80 (15), 77 (5), 67 (54), 6(12), 65 (13); mol wt ($C_7H_8Cl_3NO$ requires 226.967) 226.965. Anal. Calcd for $C_7H_8Cl_3NO$: C, 36.79; H, 3.53; N, 6.13. Found: C, 37.06; H, 3.69; N, 6.14.

(1*Z*,3*E*)-2,2,2-Trichloro-*N*-(1,3-hexadienyl)acetamide (19). A solution of 2.43 g (10.0 mmol) of freshly distilled imidate **7** and 330 mL of dry xylene was heated at reflux 8 h and concentrated, and the residue was purified by chromatography (silica gel, 95:5 hexane–ethyl acetate) to afford 1.56 g of diene **19** (>95% pure by ^{13}C NMR). Recrystallization from hexanes at −78 °C (3 times) produced a pure sample of **19**, which was sufficiently unstable such that a correct combustion analysis could not be obtained: mp 49–50 °C; IR (KBr) 3314 (NH), 1693 (C=O), 1503, 834 cm^{-1} (CCl_3); ^{1}H NMR ($CDCl_3$) δ 8.1–8.7 (br d, NH), 5.2–6.7 (m, 4 vinylic H), 1.9–2.5 (m, CH_2), 1.06 (t, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 158.6 (C=O), 139.2 (C_4), 120.6 (C_3), 118.2 (C_1), 115.5 (C_2), 92.3 (CCl_3), 26.1 (CH_2), 13.4 (CH_3).

(1*Z*)-2,2,2-Trichloro-*N*-(4-methyl-1,3-pentadienyl)acetamide (20). A solution of 2.46 g (10.1 mmol) of imidate **8** and 330 mL of dry xylene was heated at reflux under nitrogen for 5 h and concentrated, and the residue was purified by bulb-to-bulb distillation to give 1.58 g of a light yellow oil. This oil contained diene **20** (42%), allene **34** (38%), and xylene by ^{1}H NMR analysis. The yield of **20** was thus 27%. Separation of **20** and **34** was achieved only with difficulty, as diene **20** was unusually labile during silica gel chromatography. Crystallization of 0.51 g of the distilled oil from hexane at −78 °C afforded 0.14 g of light yellow **20** (88% pure by ^{1}H NMR). A second recrystallization from hexane at −78 °C afforded white crystalline **20**: mp 53.5–56 °C (sealed, evacuated capillary); IR (KBr) 3310 (NH), 1690 (C=O), 1618, 1500, 1267, 1233, 1072, 846, 816 cm^{-1} (CCl_3); ^{1}H NMR ($CDCl_3$) δ 8.0–8.7 (br apparent d, NH), 5.3–6.7 (m, 3 vinylic H), 1.83 (s, CH_3), 1.77 (s, CH_3); ^{13}C NMR ($CDCl_3$) 158.4 (C=O), 138.7 (C_4), 117.8 (C_1*), 116.4 (C_3*), 112.0 (C_2), 92.2 (CCl_3), 26.2 ((*E*)-CH_3), 18.4 ((*Z*)-CH_3). This diene was not stable for more than a few hours at room temperature, and a combustion analysis was not attempted.

(3*Z*,5*E*)-2,2,2-Trichloro-*N*-(2,2,7,7-tetramethyl-3,5-octadien-3-yl)-acetamide (21). A solution of 2.46 g (7.5 mmol) of imidate **9** and 50 mL of dry xylene was heated at reflux for 3.5 h and concentrated to afford 2.25 g (92%) of nearly pure **21** (mp 129–135 °C). The analytical sample was prepared by preparative TLC (silica gel, benzene) followed by sublimation (90 °C (0.12 mm)): mp 142–143 °C; IR (KBr) 3279 (NH), 1709 (C=O), 1497, 824 cm^{-1} (CCl_3); ^{1}H NMR ($CDCl_3$) δ 7.4 (br s, NH), 5.7–6.3 (m, 3 vinylic H), 1.14 (s, CH_3), 1.02 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 159.9 (C=O), 148.7 (C_4), 138.0 (C_1), 123.9 (C_2), 120.0 (C_3), 93.5 (CCl_3) 36.9, 33.7, 29.5, 28.2. Anal. Calcd for $C_{14}H_{22}Cl_3NO$: C, 51.47; H, 6.79; N, 4.29. Found: C, 51.79; H, 6.61; N, 4.25. Addition of 0.2–0.8 equiv of europium tris(2,2,6,6-tetramethylheptanedionate) ($Eu(dpm)_3$) to a $CDCl_3$ solution of **21** resulted in the following shifts [ppm shift (mol of $Eu(dpm)_3$/mol of **21**)]: 1.4 (H_5), 0.8 (H_4), 0.4 (H_1), 0.2 (H_6), <0.1 (H_8).

(3*Z*,5*E*)-2,2,2-Trichloro-*N*-(2,2-dimethyl-6-phenyl-3,5-hexadien-3-yl)acetamide (22). A solution of 0.69 g (2.0 mmol) of freshly distilled imidate **10** and 13 mL of dry xylene was heated to reflux for 8 h, con-

(36) Propargylic alcohols (purity >98%) were purchased from Aldrich Chemical Co. or Chemical Samples Co. or were prepared[10] in good yield from the reaction of aldehydes or ketones with 1-lithio-1-alkynes (from *n*-BuLi) in THF at −78 to +25 °C. Trichloroacetonitrile (Aldrich) was distilled immediately prior to use. Xylene (a mixture of isomers) and toluene were distilled from CaH_2. ^{1}H NMR spectra were determined with Varian EM 360, Bruker WH-90, or Varian WR-300 spectrometer. ^{13}C NMR spectra were determined at 22.62 MHz with a Bruker WH-90 spectrometer. ^{1}H and ^{13}C NMR shifts are reported as δ values in parts per million relative to internal tetramethylsilane. ^{13}C NMR assignments were consistent with off-resonance decoupled spectra, and assignments marked with an asterisk may be reversed. Coupling constants (J) are reported in hertz, and they refer to apparent multiplicities and not true coupling constants; abbreviations used are as follows: s, singlet; d, doublet; t, triplet; m, complex multiplet. Infrared spectra were determined with a Perkin-Elmer Model 283 or a Perkin-Elmer Model 137 spectrophotometer. Electron-impact (70 eV) mass spectra were determined with a Du Pont 21-498 B double-focusing spectrometer at the Caltech Analytical Facility. Chemical ionization mass spectra were determined on a Finnigan GC/MS/DS. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or Chemalytics, Inc., Tempe, Ariz. Analytical and preparative TLC were determined on E. Merck silica gel (GF-254). Dry column chromatography[37] 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. High-performance LC were obtained with Waters components, including a 6000-A pump, U6K injector, and R401 differential refractometer. All reactions were run under a nitrogen atmosphere,[38] and concentrations were done by using a rotary evaporator under reduced pressure.

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centrated, and recrystallized once from hexane to afford 0.40 g (55%) of diene **22** as off-white crystals (mp 115–118 °C). Dry column chromatography[37] of the mother liquors (silica gel, 9:1 hexane–ethyl acetate) gave an additional 89 mg (13%) of pure **22**. The analytical sample was prepared by sublimation (97 °C (0.001 mm)) followed by recrystallization from hexane: mp 121–122 °C; IR (KBr) 3290 (NH), 1707 (C=O), 1497, 1241, 818, 746 cm^{-1}; ^1H NMR ($CDCl_3$) 7.6 (br s, NH), 7.26 (apparent s, C_6H_5), 6.1–6.8 (m, 3 vinylic H), 1.16 (s, CH_3). Anal. Calcd for $C_{16}H_{18}Cl_3NO$: C, 55.43; H, 5.23; N, 4.04. Found: C, 55.51; H, 5.22; N, 4.12.

(1*Z*,3*E*)-2,2,2-Trichloro-*N*-(1,4-diphenyl-1,3-butadienyl)acetamide (23). A solution of 1.90 g (5.2 mmol) of imidate **11** and 30 mL of dry xylene was heated at reflux for 9 h and concentrated, and the residue was purified by dry column chromatography[37] (silica gel, 9:1 hexane–ethyl acetate) to give 1.06 g (56%) of diene **23** (mp 139–142 °C). Recrystallization once from hexane–benzene and twice from hexane–methylene chloride afforded the analytical sample: mp 145–146 °C; IR (KBr) 3245 (NH), 1696 (C=O), 1493, 1245, 955, 814, 763, 740, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (br s, NH), 7.36 (br apparent s, C_6H_5), 6.6–6.9 (m, 3 vinylic H). Anal. Calcd for $C_{18}H_{14}Cl_3NO$: C, 58.96; H, 3.85; N, 3.82. Found: C, 58.86; H, 3.84; N, 3.81.

(2*E*,4*Z*)-2,2,2-Trichloro-*N*-(2,4-octadien-5-yl)acetamide (24). A solution of 5.41 g (20.0 mmol) of imidate **12** and 670 mL of dry xylene was heated at reflux for 5 h and concentrated, and the residue was purified by filtration through a plug of silica gel (hexane) and bulb-to-bulb distillation (85 °C (0.015 mm)) to give 4.63 g (86%) of **24** (>95% pure by ^1H NMR). The analytical sample was obtained by two recrystallizations from hexane at −78 °C: mp 57–58 °C; IR (KBr) 3310 (NH), 1704 (C=O), 1490, 1236, 962, 818 cm^{-1} (CCl_3); ^1H NMR ($CDCl_3$) δ 7.7 (br s, NH), 5.7–6.1 (m, 3 vinylic H), 2.42 (t, J = 7 Hz, $CH_3CH_2CH_2$), 1.79 (d, J = 5.6 Hz, =CHCH_3), 1.48 (m, $CH_3CH_2CH_2CH_2$), 0.92 (t, J = 7 Hz, $CH_3CH_2CH_2CH_2$); ^{13}C NMR ($CDCl_3$) δ 159.2 (C=O), 131.4 (C_1), 130.6 (C_4), 124.8 (C_2), 122.8 (C_3), 92.8 (CCl_3), 35.7, 20.4, 18.2 ((*Z*)-CH_3), 13.3. Anal. Calcd for $C_{10}H_{14}Cl_3NO$: C, 44.38; H, 5.21; N, 5.18. Found: C, 44.56; H, 5.26; N, 5.27.

Addition of europium tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionate) [Eu(fod)$_3$] to a $CDCl_3$ solution of **24** resulted in a shift for the central vinylic hydrogen of 1.26 ppm (mol of Eu(fod)$_3$/mol of **24**). Neither of the other two vinylic hydrogens experienced shifts of more than 0.7 ppm (mol of Eu(fod)$_3$/mol of **24**).

2,2,2-Trichloro-*N*-(1-phenyl-1,3-pentadien-1-yl)acetamide (25). A solution of 7.41 g (24.3 mmol) of imidate **13** and 75 mL of *o*-dichlorobenzene was heated at reflux for 35 min, and the resulting dark solution was filtered through a short silica gel column (toluene) to give 6.97 g of a yellow liquid which was ~70% pure diene **25** (^1H NMR analysis, doublet at δ 1.83). A 200-mg sample of this material was purified by preparative TLC (97:3 hexane–ethyl acetate) to afford 96 mg (45%) of crystalline **25**, mp 103–115 °C. A comparable sample was recrystallized twice for 80% enthanol to afford an analytical specimen of diene **25**: mp 129–130 °C; IR (KBr) 3290 (NH), 1710 (C=O), 820 cm^{-1} (CCl_3); ^1H NMR (CCl_4) δ 7.8 (br s, NH), 7.23 (apparent s, C_6H_5), 5.5–6.6 (m, 3 vinylic H), 1.83 (d, J = 5.6 Hz, =CHCH_3). Anal. Calcd for $C_{13}H_{12}Cl_3NO$: C, 51.26; H, 3.97. Found: C, 51.14; H, 4.04.

(*Z*)-2,2,2-Trichloro-*N*-[2-(cyclohexen-1-yl)ethenyl]acetamide (26). A solution of 1.22 g of a mixture of imidate **14** (90%) and 1-ethynylcyclohexanol (10%) (4.7 mmol of **14**) in 150 mL of dry xylene was heated at reflux for 1 h and concentrated, and the residue was purified by chromatography (silica gel, hexane) to give 0.91 g (83%) of **26** (>95% pure by ^1H NMR and ^{13}C NMR), a colorless oil: IR (film) 3450 (NH), 1730 (C=O), 1645, 1497, 1274, 816 (CCl_3), 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.1 (br apparent d, NH), 6.67 (t, J = 10 Hz, ring =CH), 5.92 (m, =C*H*NH), 5.35 (d, J = 11 Hz, C*H*=CHNH), 2.2 (m, allylic CH_2); ^{13}C NMR ($CDCl_3$) δ 158.2 (C=O), 133.3 (C_3), 128.7 (C_4), 118.3 (C_2*), 117.7 (C_1*), 92.3 (CCl_3), 28.7, 25.5, 22.5, 21.6.

(1*E*)-2,2,2-Trichloro-*N*-[1-(trimethylsilyl)-1,3-butadienyl]acetamide (27). A solution of 4.00 g (14.0 mmol) of imidate **15**, 50 mg of 4-*tert*-butylcatechol, and 280 mL of xylene was degassed[38] and heated at reflux for 18 h and concentrated, and the residue was purified by preparative high-performance LC (porasil, 99:1 hexane–ether) to afford 1.17 g (29%) of pure diene **27**. The analytical sample was prepared by recrystallization from hexane at −78 °C followed by sublimation (100 °C (10 mm)): mp 60.5–62 °C; IR (CCl_4) 3420 (NH), 1730 (C=O), 1622, 1575, 1495, 1252, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9 (br s, NH), 6.50 (ddd, J = 16, 10, 11 Hz, C_3 H), 6.11 (d, J = 11 Hz, C_2 H), 5.44 (dd, J = 16, 1.1 Hz, cis-C_4 H), 5.30 (dd, J = 10, 1.1 Hz, trans-C_4 H); ^{13}C NMR ($CDCl_3$) δ 159.5 (C=O), 137.7 (C_1), 131.2 (C_3*), 128.9 (C_2*), 120.9 (C_4), 92.8 (CCl_3), −0.6 (CH_3Si). Anal. Calcd for $C_9H_{14}Cl_3NOSi$: C, 37.72; H, 4.92; N, 4.87. Found: C, 37.63; H, 4.94; N, 4.84.

Addition of 0.07–0.4 equiv of Eu(fod)$_3$ to a $CDCl_3$ solution of **27** resulted in the following shifts [ppm (mol of Eu(fod)$_3$/mol of **27**)]: 1.1 (C_3H), 0.5 (C_2H), 1.0 (NH).

(1*E*,3*E*)-2,2,2-Trichloro-*N*-[1-(trimethylsilyl)-1,3-pentadienyl]acetamide (28). A solution of 2.0 g (6.7 mmol) of imidate **16**, 50 mg of 4-*tert*-butylcatechol, and 130 mL of xylene was degassed,[38] heated at reflux for 27 h, and concentrated, and the residue was purified by chromatography (silica gel, 98:2 hexane–$CHCl_3$) to afford 1.26 g (63%) of crystalline diene **28**, mp 66–68 °C. The analytical sample was prepared by sublimation (60 °C (0.15 mm)): mp 66–68 °C; IR (CCl_4) 3415 (NH), 1726 (C=O), 1490, 960, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0 (br s, NH), 6.2–5.8 (m, 3 vinylic H), 1.84 (d, J = 5.7 Hz, =CHCH_3), 0.23 (s, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 159.5 (C=O), 134.5 (C_1), 134.1 (C_3*), 131.6 (C_4*), 124.0 (C_2), 93.0 (CCl_3), 19.2 ((*Z*)-CH_3), 0.6 (CH_3Si). Anal. Calcd for $C_{10}H_{16}Cl_3NOSi$: C, 39.95; H, 5.36; N, 4.66. Found: C, 39.80; H, 5.49; N, 4.72.

Isomerization of (*Z*)-Diene 17 with Triethylamine. Preparation of (*E*)-2,2,2-Trichloro-*N*-(1,3-butadienyl)acetamide (29). A solution of 1.51 g (7.0 mmol) of diene **17**, 3.5 mL of triethylamine, and 70 mL of *p*-dioxane was heated at reflux under nitrogen for 1.0 h. Concentration afforded an oil which was adsorbed onto 5 g of silica gel and layered onto a nylon column[37] (50 mm) packed with 200 g of silica gel. The column was developed with 9:1 hexane–ethyl acetate, and the UV-visible band was divided into two parts. The first part (R_f 0.48–0.61) gave 405 mg (27%) of diene **29** (pure by TLC). The second part (R_f 0.61–0.75) gave 858 mg of an 81:19 mixture of **29** and **17**, respectively (high-performance LC analysis). The total yield of diene **29** was thus 1.10 g (73%). Further purification of 216 mg of this latter mixture was accomplished by preparative TLC (silica gel, two elutions with 95:5 hexane–ethyl acetate) to afford 136 mg of **29**, which was sublimed (40 °C/0.005 mm) to afford an analytical sample of **29**: mp 91–93 °C (sealed, evacuated capillary); IR (CCl_4) 3430 (NH), 1731 (C=O), 1660, 1506, 1274, 1212, 996, 899, 843 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 8.2 (br s, NH), 6.87 (dd, J = 10.8, 13.7 Hz, C_1 H), 6.34 (apparent d of t, J = 10.8, 16.9, 10.4 Hz, C_3 H), 6.10 (dd, J = 13.7, 10.8 Hz, C_2 H), 5.22 (d, J = 16.9 Hz, cis-C_4 H), 5.12 (d, J = 10.4 Hz, trans-C_4 H); ^{13}C NMR (CCl_3) δ 159.1 (C=O), 133.4 (C_3), 124.4 (C_1), 118.6 (C_2), 117.3 (C_4), 92.0 (CCl_3); mass spectrum, *m/e* (relative percent, 5% cutoff) 217 (18), 215 (50), 213 (53), 181 (11), 180 (5), 179 (18), 138 (8), 136 (15), 119 (6), 117 (7), 114 (5), 112 (5), 110 (8), 99 (5), 97 (8), 96 (100), 88 (5), 85 (7), 82 (6), 78 (13), 71 (6), 69 (18), 68 (79), 67 (15); mol wt ($C_6H_6Cl_3NO$ requires 212.951) 212.949. Anal. Calcd for $C_6H_6Cl_3NO$: C, 33.60; H, 2.82; N, 6.53. Found: C, 33.42; H, 2.83; N, 6.47.

Isomerization of the (1*Z*)-Diene 18. Preparation of (1*E*,3*E*)-2,2,2-Trichloro-*N*-(1,3-pentadienyl)acetamide (30). A solution of 1.61 g (7.0 mmol) of diene **18**, 3.5 mL of triethylamine, and 70 mL of *p*-dioxane was heated at reflux for 2.5 h. Concentration in vacuo then afforded an oil which was adsorbed onto 4 g of silica gel (Grace 62) and layered onto a nylon column[37] (50 mm) packed with silica gel. The column was developed with 9:1 hexane–ethyl acetate, and the UV-visible band was divided into two parts. The first part (R_f 0.32–0.54) afforded 74 mg (5%) of **30** (>95% pure by TLC). The second part (R_f 0.54–0.74) afforded 1.29 g of a 75:25 mixture of **30** and **18**, respectively. The total yield of diene **30** was thus 1.04 g (65%). Further purification of 220 mg of this latter mixture was accomplished by preparative TLC (silica gel, two elutions with 95:5 hexane–ethyl acetate) to afford 125 mg of **30**, which was sublimed (40 °C (0.005 mm)) to afford an analytical sample: mp 105–106 °C (sealed, evacuated capillary); ^1H NMR ($CDCl_3$) δ 8.2 (br s, NH), 5.4–7.1 (m, 4 vinylic H), 1.74 (d, J = 5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 158.7 (C=O), 129.9 (C_4), 127.9 (C_3), 121.9 (C_1), 118.6 (C_2), 92.2 (CCl_3), 18.2 ((E)-CH_3). Anal. Calcd. for $C_7H_8Cl_3NO$: C, 36.79; H, 3.53; N, 6.13. Found: C, 36.59; H, 3.60; N, 6.06.

Quantitative Determinations of Stereoselectivity. Reaction mixtures were concentrated, the residue was filtered through a short plug of silica gel (CH_2Cl_2), a weighed amount of *p*-dinitrobenzene (internal standard) was added, and the mixture was analyzed by high-performance LC [30 cm × 40 mm μ-Porasil column, refractive index (RI) detector]. The RI detector response was calibrated[10] by analyzing weighed amounts of *p*-dinitrobenzene and dienes **17**, **18**, **29**, and **30**. Results are summarized in Table III.

Isolation of 1-(Trichloroacetamido)-1,2-dienes. 2,2,2-Trichloro-*N*-(1,2-pentadienyl)acetamide (33). A solution of 4.57 g (20.0 mmol) of imidate **6** and 670 mL dry xylene was heated at reflux for 1.1 h. Concentration and purification of the residue by a combination of column chromatography (silica gel, 9:1 hexane–ethyl acetate), preparative TLC (four elutions, 95:5 hexane–ethyl acetate), and sublimation (30 °C (0.005 mm)) afforded 0.725 g (16%) of the 1,2-diene **33**: mp 69–70 °C (sealed, evacuated capillary); IR (CCl_4) 3439 (NH), 1976 (C=C=C, v weak), 1728 (C=O), 1520, 818 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.6 (br s, NH), 6.83 (m, C_1 H), 5.89 (apparent q, C_3 H), 2.16 (m, CH_2), 1.07 (t,

J = 7.4 Hz, CH_3); ^1H homonuclear decoupling experiments allowed the following constants to be determined: δ 6.83 (J = 2.0, 6.0, 9.7 Hz), 5.89 (J = 5.8, 6.0), 2.16 (J = 2.0, 5.8, 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 195.9 (C=*C*=C), 159.0 (C=O), 105.8 (C_1), 94.4 (C_3) 92.1 (CCl_3), 23.0 (CH_2), 12.8 (CH_3); mass spectrum, m/e (relative intensity, 6% cutoff) 231 (8), 229 (24), 227 (25), 214 (12), 212 (12), 196 (10), 195 (6), 194 (63), 193 (10), 192 (100), 179 (20), 178 (8), 177 (30), 176 (9), 119 (14), 117 (14), 112 (7), 110 (13), 84 (7), 83 (7), 82 (41), 81 (6), 80 (11), 67 (78), 66 (15), 65 (19); mol wt ($C_7H_8Cl_3NO$ requires 226.967) 226.968.

2,2,2-Trichloro-*N*-(4-methyl-1,2-pentadienyl)acetamide (34). A solution of 0.514 g (2.12 mmol) of imidate **8** and 70 mL of dry xylene was heated at reflux for 1.75 h and concentrated, and the residue was purified by preparative TLC (two elutions 95:5 hexane–ethyl acetate) and sublimation (40 °C (0.015 mm)) to afford 80 mg (16%) of the 1,2-diene **34**: mp 63–65.5 °C; IR (CCl_4) 3439 (NH), 1974 (C=C=C), 1730 (C=O), 1209, 841, 672 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.56 (br s, NH), 6.83 (ddd, J = 2.8, 6.2, 9.7 Hz, NHC*H*), 5.83 (apparent t, NHCH=C=C*H*), 2.39 (m, $CHMe_2$), 1.07 (d, J = 6.7 Hz, CH_3); ^1H homonuclear decoupling experiments allowed the following coupling constants to be determined: δ 5.83 (J = 6.0, 6.2 Hz), 2.39 (J = 2.8, 6.0, 6.7 Hz); mass spectrum, m/e (relative percent, 10% cutoff) 245 (16), 243 (51), 241 (55), 228 (27), 226 (29), 210 (10), 208 (63), 207 (12), 206 (100), 193 (20), 192 (13), 191 (27), 190 (15), 164 (11), 127 (12), 124 (16), 119 (16), 117 (16), 110 (12), 96 (55), 94 (15), 83 (11), 82 (10), 81 (59), 80 (53), 79 (37), 77 (11), 69 (10), 67 (10), 65 (10); mol wt ($C_8H_{10}Cl_3NO$ requires 240.983) 240.986.

2,2,2-Trichloro-*N*-(1,2-propadienyl)acetamide (35). A solution of 5.0 g (24.9 mmol) of imidate **38** and 750 mL of dry xylene was degassed[38] and heated at reflux for 4.5 h and concentrated, and the residue was purifieed by chromatography (silica gel, 95:5–90:10 hexane–ethyl acetate) and sublimation (60 °C (0.5 mm)) to afford 550 mg (11%) of 1,2-diene **35**: mp 70–71 °C; IR (CCl_4) 3440 (NH), 1965 (C=C=C, very weak), 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 7.9 (br s, NH), 6.86 (dt, J = 6.3, 11 Hz, =CHN), 5.44 (d, J = 6.3 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ 202.7 (C=*C*=C), 159.0 (C=O), 94.0 (=CHN), 92.0 (CCl_3), 87.3 ($=CH_2$). Anal. Calcd for $C_5H_4Cl_3NO$: C, 29.96; H, 2.01; N, 6.99. Found: C, 30.12; H, 2.04; N, 6.96.

2,2,2-Trichloro-*N*-(4,4-dimethyl-1,2-pentadienyl)acetamide (36). A solution of 259 mg (1.0 mmol) of imidate **39** and 15 mL of dry xylene was heated at reflux for 1 h and concentrated, and the residue was purified by preparative TLC (98:2 hexane–ethyl acetate) and recrystallization from cold hexane to afford 48 mg (18%) of pure 1,2-diene **36**: mp 90–91 °C; IR (CCl_4) 3440 (NH), 1970 (C=C=C, very weak), 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 7.5 (br s, NH), 6.84 (dd, J = 5.9, 9.6 Hz, C_1 H), 5.81 (d, J = 5.9 Hz, C_3 H), 1.09 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 193.2 (C=*C*=C), 158.9 (C=O), 115.5 (C_1), 95.1 (C_3), 92.0 (CCl_3), 33.4 (*C*CH_3), 29.7 (CH_3). Anal. Calcd for $C_9H_{12}Cl_3NO$: C, 42.13; H, 4.71; N, 5.46. Found: C, 42.02; H, 4.68; N, 5.38.

2,2,2-Trichloro-*N*-(2,2,6,6-tetramethyl-3,4-heptadienyl)acetamide (37). A solution of 1.00 g (3.19 mmol) of imidate **40** and 32 mL of dry xylene was heated at reflux for 3 h and concentrated. Purification of the residue by preparative TLC (3 elutions, 99:1 hexane–ethyl acetate) gave 82 mg of 2,2,6,6-tetramethyl-4-hepten-3-one (**43**)[20] and 140 mg (14%) of 1,2-diene **37**: mp 59–60 °C (after recrystallization from hexane); IR (CCl_4) 3440 (N-H), 1965 (C=C=C, very weak), 1730 cm^{-1} (C=O); ^1H NMR (δ, $CDCl_3$) 7.3 (br s, NH), 5.66 (d, J = 2 Hz, =CH), 1.12 (s, CH_3), 1.06 (s, CH_3); ^{13}C NMR 193.5 (C=*C*=C), 158.8 (C=O), 113.4 (=CNR), 112.2 (=CHR), 93.3 (CCl_3), 34.2 (CMe_3), 33.1 (CMe_3), 29.7 (CH_3), 28.5 (CH_3). Anal. Calcd for $C_{13}H_{20}Cl_3NO$: C, 49.94; H, 6.45; N, 4.48. Found: C, 50.00; H, 6.57; N, 4.39.

Isolation of Acylimine 41 and Isomer 42 from the Thermal Rearrangement of Propargylic Trichloroacetimidate 40. A solution of imidate **40** (376 mg, 1.20 mmol), 10 mg of 4-*tert*-butylcatechol, and 12 mL of dry xylene was degassed[38] and heated at reflux for 18 h. Concentration afforded a ~1:1 mixture of **41** and **42** which was purified by preparative GC (180 °C, SP2100) to give a 3:1 mixture of **41** and **42**: IR (CCl_4) 1710 (C=O), 1650 (C=N), 1634 cm^{-1} (C=C). The ^1H and ^{13}C NMR of this mixture are summarized in Table II.

Hydrolysis of a Mixture of 41 and 42. Isolation of 2,2,6,6-Tetramethyl-4-hepten-3-one (43) and Trichloroacetamide. A 3:1 mixture of **40** and **41** (279 mg, 0.892 mmol, isolated by preparative GC) and 15 mL of THF was treated with 0.5 mL of 1% HCl, and the resulting solution was stirred at room temperature for 2.5 h. Concentration and purification of the residue by chromatography on silica gel (ethyl acetate) gave 107 mg (71%) of chromatographically pure *trans*-enone **43**. Sublimation (55 °C (1 atm)) gave crystalline **43**, mp 43–43.5 °C, which was identical (mixture melting point, ^1H NMR, ^{13}C NMR, IR) with an authentic sample prepared by the procedure of House.[20] Further elution with methanol gave 140 mg (97%) of trichloroacetamide, mp 140–141 °C after recrystallization from chloroform (lit.[39] mp 142 °C).

Ethyl *N*-(Trichloroacetyl)-2-(*E*)-butenimidate (45) and Ethyl *N*-(Trichloroacetyl)-2-(*Z*)-butenimidate (46). A solution of the crude trichloroacetimidate formed from 4.11 g (36.1 mmol) of 1-ethoxy-1-butyn-3-ol, and 180 mL of hexane was heated at reflux for 6 h. *Caution! This imidate rearranges explosively when heated as the neat liquid.*[21] Concentration and distillation (bp 60–65 °C (0.015 mm)) of the residue gave 7.85 g (84%) of a 84:16 mixture (high-performance LC analysis) of acylimidates **45** and **46**, respectively. These isomers were separated by preparative high-performance LC (porasil, 99:1 hexane–ether). *E* isomer **45**: IR (CCl_4) 1742 (C=O), 1711 (C=N), 1660 and 1608 (C=C), 1375, 1041 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 6.99 (dq, J = 14.9, 6.9 Hz, CH_3CH=), 6.06 (dq, J = 14.9, 1.5 Hz, CH_3CH=C*H*), 4.34 (q, J = 7.1 Hz, OCH_2), 1.93 (dd, J = 6.9, 1.5 Hz, *C*H_3CH=), 1.39 (t, J = 7.1 Hz, CH_2CH_3); mass spectrum (isobutane CI), m/e relative percent, 5% cutoff) 262 (33), 260 (95), 258 (100), 140 (6). Anal. Calcd for $C_8H_{10}Cl_3NO_2$: C, 37.17; H, 3.90; N, 5.42. Found: C, 37.27; H, 3.90; N, 5.37.

Z isomer **46**: ^1H NMR ($CDCl_3$) δ 6.27 (dq, J = 11.6, 6.8 Hz, CH_3CH=), 5.97 (dq, J = 11.6, 1.5 Hz, CH_3CH=C*H*), 4.32 (q, J = 7.1 Hz, OCH_2), 2.07 (dd, J = 6.8, 1.5 Hz, *C*H_3CH=), 1.38 (t, J = 7.1 Hz, CH_2CH_3).

2,2,2-Trichloro-*N*-(1,3-butadien-2-yl)acetamide (48). A solution of 804 mg (3.75 mmol) of imidate **47**, 80 mg of 4-*tert*-butylcatechol, and 500 mL of *o*-dichlorobenzene was heated at reflux for 50 min, and the *o*-dichlorobenzene was removed by distillation (~45 °C (0.02 mm)). Purification of the residue by dry column chromatography[37] (silica gel, 9:1 hexane–ethyl acetate) gave 110 mg (14%) of chromatographically pure diene **48** and 177 mg (22%) of recovered imidate **47**. An analytical sample of **48** was prepared by preparative TLC (silica gel, 2:1 chloroform–hexane) and crystallization from hexane at −20 °C: mp 27–30 °C; IR (KBr) 3257 (NH), 1718 (C=O), 1522, 822 cm^{-1}; ^1H NMR (CCl_4) δ 7.8 (br s, NH), 6.20 (dd, J = 10, 17 Hz, CH_2=C*H*-), 5.9 (apparent s, one C_1 H), 4.8–5.5 (m, vinylic H); mass spectrum, m/e (relative percent, 15% cutoff) 217 (8), 215 (22), 213 (22), 210 (17), 180 (72), 178 (100), 97 (28), 96 (94), 95 (28), 85 (56), 83 (78), 72 (16), 71 (36), 69 (39), 67 (16); mol wt ($C_6H_6Cl_3NO$ requires 212.9515) 212.9513.

(*Z*)- and (*E*)-2,2,2-Trichloro-*N*-(1,3-octadien-3-yl)acetamide (50) and (51). A solution of imidate **49** (3.34 g, 12.3 mmol), 10 mg of 4-*tert*-butylcatechol, and 250 mL of *o*-dichlorobenzene was degassed[38] and heated at reflux for 2.2 h. Concentration (~45 °C (0.01 mm)) and filtration of the residue through a short silica gel column (94:6 hexane–ethyl acetate) gave 2.46 g (74%) of a 3:1 mixture (high-performance LC analysis) of dienes **50** and **51**. Separation of this mixture by preparative high-performance LC (porasil 99:1 hexane–ethyl acetate) afforded 566 mg (17%) of the pure (*E*)-diene **51** (k' = 3.9) and 1.08 g (32%) of the pure (*Z*)-diene **50** (k' =2.2). Crystallization from hexane–ether at −78 °C afforded an analytical sample of **50**: mp 38–40 °C; IR (CCl_4) 3360 (NH), 1730 (C=O), 920 cm^{-1}; ^1H NMR (300 MHz, CCl_4) δ 7.24 (br s, NH), 6.27 (dd, J = 16.7, 10.5 Hz, CH_2=C*H*-), 5.60 (t, J = 7.4 Hz, CH_2CH=), 5.14 (d, J = 16.7 Hz, cis-C_1 H), 5.03 (d, J = 10.4 Hz, *trans*-C_1 H), 2.07 (apparent t, $J \approx$ 7.5 Hz), 1.1–1.7 (m), 0.92 (t, J = 7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) 160.0 (s, C=O), 134.3 (d, C_2 or C_4), 133.5 (d, C_2 or C_4), 131.0 (s, C_3), 112.5 (t, C_1), 93.0 (s, CCl_4), 30.7 (t, C_5), 27.4 (t, C_6), 22.4 (t, C_7), 13.8 (q, CH_3). Anal. Calcd for $C_{10}H_{14}Cl_3NO$: C, 44.39; H, 5.21. Found: C, 44.19; H, 5.38.

An analytical sample of **51** was prepared by bulb-to-bulb distillation (bath temperature 60–100 °C (0.003 mm)): IR (CCl_4) 3358 (NH), 1730 (C=O), 918 cm^{-1}; ^1H NMR (300 MHz, CCl_4) δ 7.43 (broad s, NH), 6.57 (dd, J = 16.8, 10.6 Hz, CH_2=C*H*), 6.09 (br t, J = 7.8 Hz, CH_2CH=), 5.24 (d, J = 10.6 Hz, cis-C_1 H), 5.18 (dd, J = 16.8, 1.7 Hz, trans-C_1 H), 2.25 (apparent t, $J \approx$ 7.5 Hz, CH_2CH=), 1.1–1.7 (m), 0.92 (t, J = 7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 160.2 (s, C=O), 129.7 (s, C_3), 129.3 (d, C_2 or C_4), 129.0 (d, C_2 or C_4), 113.7 (t, C_1), 93.3 (s, CCl_3), 31.5 (t, C_5), 26.7 (t, C_6), 22.2 (t, C_7), 13.8 (q, CH_3). Anal. Calcd for $C_{10}H_{14}Cl_3NO$: C, 44.39; H, 5.21; N, 5.17. Found: C, 44.37; H, 5.26; N, 5.03.

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Supplementary Material Available: The boiling points and IR and NMR data for compounds **6–12**, **14–16**, **38–40**, **44**, **47**, and **49** (4 pages). Ordering information is given on any current masthead page.

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