= 5.9 Hz, $J_{6(5),4} = J_{6(5),7(7')} = J_{6(5),7'(7)}$ = 2.1 Hz, 1 H, 6(5)-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.79, 14.2 (t, C-1, C-2), 23.6 (s, C-3), 42.6 (t, C-7), 56.4 (d, C-4), 113.9 (t, C-9), 131.1, 133.8, 139.7 (d, C-5, C-6, C-8); GC-MS (70 eV) m/e 120 (3, M^+), 105 (22), 93 (7), 92 (84), 91 (100), 79 (16), 78 (7), 77 (18), 66 (6), 65 (14), 63 (5), 53 (6), 51 (10), 44 (7), 41 (9), 39 (21). Capillary GC conditions for GC-MS analysis: 30 m SE 30 column; helium gas flow of 1.0 kp/cm^2; oven, injector, and interface temperatures of 50, 180, and 175 °C; t_R = 10.5 min.

Dispiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane-6',1''-cyclopropane) (2c). A sample of 470 mg (3.21 mmol) of 2c was pyrolyzed as earlier at 540 °C (17 Torr) to afford 150 mg (41%) of a complex mixture, which consisted of at least seven dozen components, as established by capillary GC. When a sample of 365 mg (2.50 mmol) of 2c was pyrolyzed at 510 °C (17 Torr), 195 mg (53%) of a complex mixture of more than three dozen components was detected, while pyrolysis of 390 mg (2.67 mmol) of 2c at 480 °C (17 Torr) led to recovery of 370 mg (95%) starting tricycloheptane.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support and Dr. H. Idstein for the GC-MS analyses.

Synthesis of α-Halocinnamate Esters via Solvolytic Rearrangement of Trichloroallyl Alcohols

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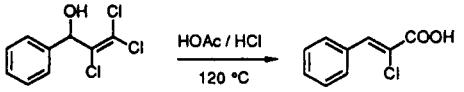
Aryl trichlorovinyl ketones undergo regioselective reduction to the corresponding carbinols with sodium borohydride in alcoholic solvents and are transformed to the (*Z*)-α-chlorocinnamate ester derivatives via an acid-catalyzed allylic rearrangement. Michael addition of ammonia to these ester derivatives affords *cis*- and/or *trans*-aziridine amides. The facile rearrangement allows the synthesis of *d,l*-phenylalanine derived from perchloroethylene and toluene.

Introduction

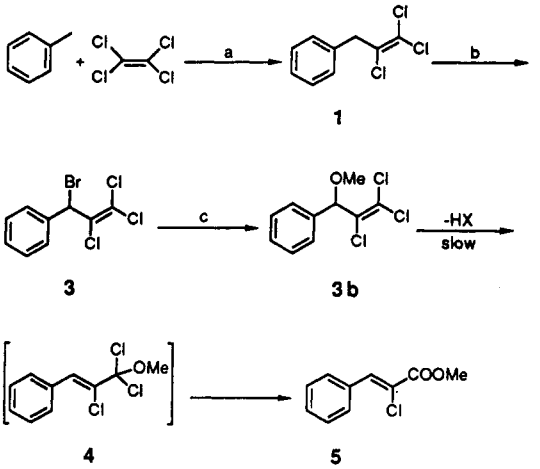
During the course of our investigations into the use of perchloroethylene as an inexpensive, commodity precursor to halogenated dienes and new, flame retardant epoxides,[1] we noted its potential as a two-carbon annelating agent for the benzyl radical (Scheme I), resulting in the formation of 1.[2] The trichlorovinyl group has served as a valuable precursor to substituted acetylenes[3] and other compounds of agricultural interest.[4] In addition, the similar oxidation state of 1 and phenylalanine prompted us to consider simple approaches to the selective hydrolysis of the trichlorovinyl group of this substrate; however, no practical methods for this transformation have been reported.[5] A related hydrolysis involving an acid-catalyzed rearrangement of 1-hydroxy-1-phenyl-2,3,3-trichloro-2-propene (2) to α-chlorocinnamic acid in low yield has been described by Zakharkin and co-workers.[6]



(1)

2 2b

Scheme I[a]



[a] Key: a Cl_2 initiator, 625 °C quartz hot tube; b, Br_2, CCl_4, AIBN; c, MeOH, H_2SO_4, 105 °C.

Since α-halocinnamate esters are useful in the preparation of aziridines,[7] optically active α-halo esters,[8] amino acids,[9] and other heterocyclic systems,[10] facilitation of this

(1) (a) Kruper, W. J., Dow Chemical Co. U.S. Patent 4,668,832, 1987. (b) Pawloski, C. E.; Kruper, W. J., Dow Chemical Co. U.S. Patent 4,668,710, 1987.

(2) Schemerling, L.; West, J. P. *J. Am. Chem. Soc.* **1953**, *75*, 6098-6104.

(3) Liese, T.; Splellstaben, G.; de Meijere, J. *Tetrahedron Lett.* **1982**, *23*, 3241-44.

(4) (a) Gajewski, R. P.; Jackson, J. L.; Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B. *J. Org. Chem.* **1989**, *54*, 3311-3317. (b) Hackett, A. G.; Kotyk, J. J.; Fujiwara, H.; Logusch, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 3669-3671.

(5) The acid-catalyzed addition of vinylidene chloride to tertiary carbocations occurs with hydrolysis to afford the tertiary alkylacetic acids and esters: (a) Randriamahefa, S.; DesChamps, P.; Gallo, R.; Grangette, H. *Synthesis* **1985**, *5*, 493-495. (b) Bott, K.; Helman, H. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 870-874. The analogous reaction with trichloroethylene or substituted trichloroethylenes is considerably more difficult and has its limitations: Bott, K. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 171-178.

(6) Zakharkin, L. I. *Acad. Sci. U.S.S.R.; Bull. Div. Chem. Sci.* **1956**, 303-310. The difficulty encountered in the rearrangement of (trichlorovinyl)carbinols of α-haloalkenoic acids has also been observed by others: Pochat, F.; Levas, E. *Bull. Chem. Soc. Fr.* **1972**, *10*, 3846-3855. In contrast to this observation, there are recent reports of facile, low temperature, acid-catalyzed rearrangement of the analogous (trifluorovinyl)carbinol (see refs 14 and 15).

(7) (a) Chari, R. U. J.; Wemple, J. *Tetrahedron Lett.* **1979**, *2*, 111-114. (b) Nakamura, I.; Harada, K. *Heterocycles* **1978**, *9*, 473-480. (c) Lown, J. W.; Itoh, J.; Ono, N. *Can. J. Chem.* **1973**, *51*, 856-859. (d) Woller, P. B., Cromwell, N. H. *J. Org. Chem.* **1970**, *35*, 892-898. (e) Fanta, P. E. In *Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1968; Part A, pp 535-537 and references therein.

(8) Servi, S. *Synthesis*, **1990**, *1*, 1-25.

(9) (a) McDonald, I. A.; Lacoste, J.; Bey, P.; Wagner, M.; Zreida, M.; Palfreyman, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 3354-3356. (b) For the original, low-yield synthesis of phenylalanine that was based upon hydrogenolysis of 2-carboxy-3-phenylaziridine (presumed to be the enamine), see: Yakawa, H.; Kimura, S. *Nippon Kagaku Zasshi* **1955**, *78*, 454-458.

0022-3263/91/1956-3323$02.50/0

difficult rearrangement could be of practical advantage over existing methods[11] for their synthesis. This report describes a highly selective and economical method for promoting the rearrangement of 2 and related derivatives to the corresponding α-chloro ester.[12] The scope of this reaction has also been extended to a number of aryl trichlorovinyl ketones that can be conveniently synthesized from trichloroacryloyl chloride 6 with use of conventional Friedel–Crafts chemistry. The stereochemical aspects of aziridine formation using these cinnamate derivatives as Michael acceptors for ammonia has also been examined and has provided a commodity-based route to racemic phenylalanine.

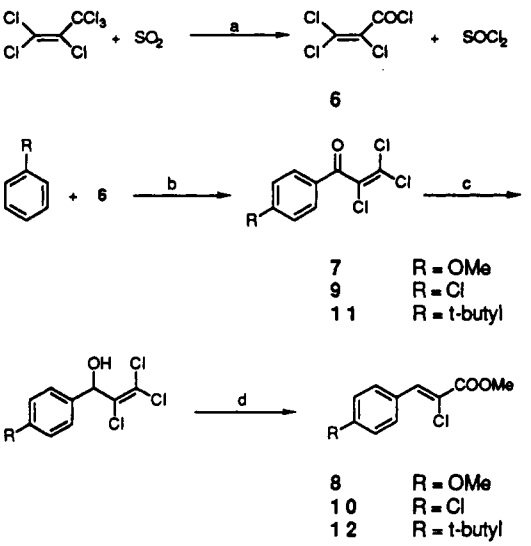
Results and Discussion

Ample precedent exists for the addition of a number of stabilized, carbon-based radicals to halogenated olefins such as perchloroethylene and trichloroethylene.[2,13] Unfortunately, the majority of these radical additions have been conducted in solution phase and suffer from low conversion, which is due to short, radical-propagation chain length. In contrast to solution-phase radical annelations,[2] we observed that the high-temperature, gas-phase condensation of toluene with perchloroethylene in a quartz hot tube afforded 3-phenyl-1,1,2-trichloro-1-propene (1) in good yield. Under similar gas-phase condensation conditions, carbinyl radicals derived from ethanol and methanol were also condensed with perchloroethylene. Free-radical bromination of 1 using bromine in carbon tetrachloride afforded only the unrearranged bromide 3 in nearly quantitative yield.

When bromide 3 was subjected to reflux in a solution of concentrated sulfuric acid–methanol (60:40), complete allylic rearrangement to methyl ester 4 occurred within 90 min accompanied by vigorous evolution of gas. Gas chromatographic analysis at the onset of reaction revealed a rapidly formed intermediate **3b** evolving from 3, which slowly converted to the rearranged ester under these conditions.

Both bromide 3 and its intermediate solvolysis product **3b** appeared to be free of any rearranged allylic isomers (e.g., 5) as indicated by broad-band, proton-decoupled ^{13}C NMR spectroscopy and infrared analysis. This observation is dramatically different from the behavior of trifluorovinyl-substituted allylic alcohols[14] and halides,[15] which undergo rapid allylic rearrangement under acidic conditions at low temperatures. It would therefore appear that an unrearranged carbocation derived from solvolysis of 3 must undergo rate-determining rearrangement to cinnamate ester 5. Under the conditions accompanying the rearrangement of 3 to 5, the observation of masked ester precursor 4 would not be expected on the basis of the acid

Scheme II[a]



[a] Key: a, 5 mol % $AlCl_3$, 80 °C; b, $AlCl_3$, CH_2Cl_2, 0 °C; c, $NaBH_4$, EtOH; d, 60% H_2SO_4 in MEOH, 105 °C.

lability of the CCl_2OMe group.[5a,b] Rapid internal collapse (S_Ni) of this group with liberation of methyl chloride and subsequent solvolysis of the acid chloride to 5 would provide a mechanism that is consistent with these results.

In order to extend the possibilities of the rearrangement, we explored the potential for Friedel–Crafts acylation of several substituted arenes using trichloroacryloyl chloride 6, which could be prepared from the sulfur dioxide mediated halogen exchange of commercially available perchloropropylene (Scheme II).[16]

A number of substituted arenes were acylated with stoichiometric quantities of 6 and anhydrous aluminum chloride in methylene chloride (0–5 °C) to give the corresponding trichlorovinyl ketones (Table I) in good yield with excellent para selectivity. In particular, there was little or no evidence of any ortho acylation products that derived from acylation of chlorobenzene or *tert*-butylbenzene as shown by capillary VPC and NMR analysis. The acylation of anisole with 6 under these conditions did give rise to some ortho-substituted product that could be separated from the predominate (86%) para isomer by flash chromatography or basic extraction.[17]

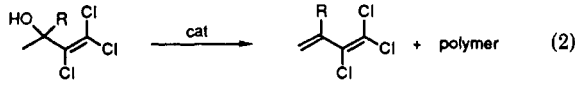
Transformation of these ketones to the desired α-chlorocinnamate in a single-pot operation would require regioselective reduction of the carbonyl group followed by the acid-catalyzed rearrangement. Thus, treatment of ethanolic solutions of ketones 7–10 with 2 equiv of sodium borohydride at room temperature resulted in rapid reduction to the corresponding (trichlorovinyl)carbinol. Under these conditions, there was no detectable evidence of olefin reduction. After the reduction was judged to be complete by TLC or VPC analysis, the crude carbinol was subjected to rearrangement conditions following the addition of sulfuric acid. This treatment allowed for the isolation of the *Z* stereoisomer of the cinnamate as its ethyl ester. The corresponding methyl esters were made by removal of ethanol from the crude reduction product and conducting the rearrangement in methanol–sulfuric acid. Despite the apparent harshness of the rearrangement

(10) Marsura, A.; Luuduc, C.; Gellon, G. *Synthesis* **1985**, *5*, 537–541.
(11) When commercially available, 3-substituted 2-alkenoic acids may be esterified, dihalogenated, and dehydrohalogenated (3-step, 2-3-pot process) to afford the unsaturated α-halo ester. For examples, see ref 5 and: Hudlicky, T.; Radesca, L.; Luna, H.; Anderson, F. E. *J. Org. Chem.* **1986**, *51*, 4746–4748.
(12) Kruper, W. J., Dow Chemical Co. U.S. Patent 4,727,181, 1988.
(13) (a) Matsuda, T.; Yumoto, T. *Bull Chem. Soc. Jpn.* **1967**, *40*, 1991–1992. (b) Matsuda, T. U.S. Patent 3,364,268, **1968**. (c) Nikishin, G. I.; Dyusenow, M. I.; Somov *Akad. Nautz. SSSR Ser. Khim.* **1966**, 2115–2119. (d) Hewertson, W.; Holland, D.; Milner, D. J. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1062–1064.
(14) (a) Tarrant, P.; Johncock, P.; Savory, J. *J. Org. Chem.* **1963**, *28*, 839–43. (b) Gillet, J. P.; Sauvetre, R.; Normant, J. F. *Synthesis* **1986**, 355–360. (c) For the allylic rearrangement of the [(trifluorovinyl)-phenyl]carbinol analogue of 3, see: Dolbier, W. R., Jr.; Gray, T. A.; Ohnishi, K. *Synthesis* **1987**, 956–958.
(15) Matsuo, N.; Kende, A. S. *J. Org. Chem.* **1988**, *53*, 2304–2308.
(16) (a) Rondesvedt, C. S. *J. Org. Chem.* **1976**, *22*, 3569–75. (b) Doorenbos, H. E.; Toner, D. D.; Calhoun, L. G., Dow Chemical Co. U.S. Patent 3,875,226, 1975.
(17) Quantitative demethylation of anisole was observed in the ortho acylation product. The resulting phenolic compound could be extracted into dilute sodium hydroxide.

conditions, the resulting esters were frequently found to be pure enough to conduct subsequent Michael chemistry without complication.

A number of acidic catalysts other than sulfuric acid were screened as candidates to promote these rearrangements, including alcoholic mixtures of phosphoric, trifluoroacetic, and triflic acids. None of these media as well as the known azeotropic boiling mixture of hydrogen chloride–acetic acid (Table I) were found to be as effective in catalyzing the rearrangement. Polymer supported catalysts such as sulfonated polystyrene beads (Dowex MSC-1 or Nafion membrane) were likewise ineffective. The slower reaction rate observed in the conversion of 3 to the corresponding acid using aqueous sulfuric acid may be ascribed to the low solubility of the starting material. Cosolvents were restricted in this study to water, methanol, and ethanol due to concerns about solvent stability in the presence of strong acid.

The rearrangement is limited to alcohols which do not bear β hydrogens capable of elimination, unlike trifluorovinyl analogues.[14,15] Trichlorobutenols 13 and previously unknown[18] 15 were noted to dehydrate to form the diene as the predominate product.



(2)

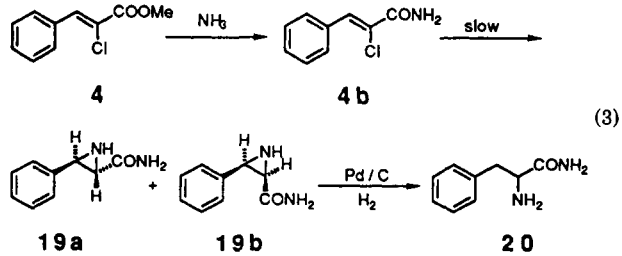
13 R=H 14

15 R=Phenyl 16

Respective dienes 14 and 16 formed rapidly as insoluble oils under the conditions prescribed for the cinnamate formation (within 5 min at 105 °C), and their lack of solubility may account for further difficulties in solvolysis and rearrangement.

Michael Addition and Aziridine Formation. The majority of examples of amine additions to α-halocinnamate esters refer to bromo derivatives, and there are few reported examples of chloro esters as Michael acceptors.[7] It was therefore of interest to differentiate the reactivity of α-chloro- and α-bromocinnamate esters with regard to Gabriel amine additions.

When chlorocinnamate 4 was subjected to direct aminolysis in liquid ammonia, a nearly quantitative yield of aziridine amides **19a** and **19b** was obtained that could be easily separated by flash chromatography. Catalytic reduction of the isomer mixture over a palladium/carbon catalyst in methanol afforded exclusively *d,l*-phenylalanine amide **20**. The hydrogenolysis of aziridine **19b** has previously been described.[9b] Under the conditions of ammonia addition, aminolysis of the ester leading to the chlorocinnamide **4b** *always* preceded aziridine formation. Good isolated yields for several other, new aziridine amides were obtained under these conditions (Table II).



(3)

(18) Oxidation of 13 in methylene chloride using pyridinium chlorochromate afforded the corresponding ketone **13b**. Treatment of this ketone with excess phenylmagnesium bromide in ether exclusively provided the 1,2-addition product **15**.

The assigned stereochemistry of aziridine products was based upon the cis (J = 4.5–6.5 Hz) or trans (J = 1.7–2.5 Hz) vicinal coupling constants observed in the separated products.[19] In all cases, NMR spectra of the products characterized were inconsistent with an isomeric enamine structure. Although there are reports of stereospecific aziridine formation under these conditions,[7b,c] it appears that cis/trans mixtures more often predominate and the stereochemical outcome is unpredictably dependent upon conditions of temperature, solvent, and substrate.

Treatment of 4 with anhydrous ammonia in solutions of methanol or dimethyl sulfoxide[7a] at room temperature resulted in the immediate formation of dark purple solutions. Aziridine ester **24** formation was noted under these conditions (Table II), and some ester aminolysis to **4b** was experienced. Under the same conditions, *colorless* solutions of dihydrodibromocinnamate **23**, an α-bromocinnamate precursor, underwent smooth conversion to a mixture of aziridine methyl esters **24** within 24 h at 25 °C. Aminolysis of the ester group in **23** did not exceed 15% when the solution was kept cool (0–5 °C) during the initial ammonia addition. It is also evident from these results that if aminolysis of the ester occurs, subsequent Michael addition is considerably slower. Thus, when cinnamide **4b** was subjected to these conditions, no aziridine amides **19** were observed to form within 24 h. Hydrogenolysis of the mixture of the isomers of **24** afforded *d,l*-phenylalanine methyl ester **25**.

It is tempting to suggest that the stronger electron-withdrawing effect of the α-chloro group increases the potential for electron transfer from ammonia with the subsequent formation of a nonreactive, ammonia/cinnamate charge-transfer complex.[20] Whatever the cause, bromocinnamate esters appear to be better candidates than their chloro analogues for aziridine ester formation under these conditions.

Conclusion

A number of stabilized carbon radicals, including carbinyl and benzyl radical, may be annelated with perchloroethylene to give substituted trichloroethylenes such as 1 in a continuous gas-phase process. Bromination of 1 followed by an acid-catalyzed, allylic rearrangement using sulfuric acid in methanol afforded the (*Z*)-α-chlorocinnamate methyl ester 4. Ammonia addition to 4 and reduction of the intermediate aziridine afforded *d,l*-phenylalanine amide in 75% overall yield from distilled 1. The process for the rearrangement has been extended to substituted arenes through Friedel–Crafts acylation with trichloroacryloyl chloride 6. The resulting ketones undergo regioselective reduction to the corresponding carbinols with sodium borohydride in alcoholic solvents and may be transformed to the (*Z*)-α-chlorocinnamate ester derivative through the analogous rearrangement in a single-pot operation.

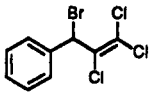
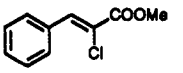
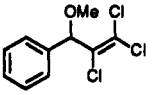
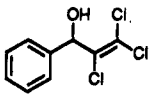
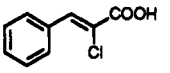
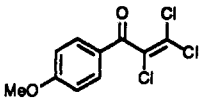
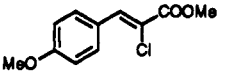
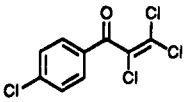
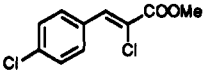
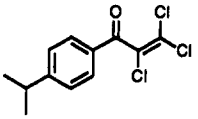
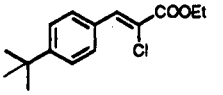
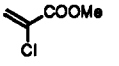
Experimental Section

Mass spectra were obtained on a Finnigan 3500 Series mass spectrometer operated at 70 eV in the EI positive-ion mode. ^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q or Varian VXR-300 spectrometer. Infrared spectra (IR) were recorded on a Nicolet SSX FT/IR or Beckman Acculab instrument. VPC analyses were conducted on a Hewlett-Packard Model 5890 gas

(19) Batterham, T. J. *NMR Spectra of Simple Heterocycles*; John Wiley and Sons: New York, 1973; pp 137–140.

(20) The formation of charge-transfer complexes between amines and other electron-deficient olefins has been reviewed: Butufei, O. *Rev. Chim.* 1980, *31*, 140–142.

Table I. Acid-Catalyzed Rearrangement of Selected Trichlorovinyl Alcohols to α-Halo-α,β-unsaturated Esters

alcohol/ketone	% yield[a] acylation	% para selectivity	solvent/catalyst[b]	time	product	% yield[c]
 3			$MeOH/H_2SO_4$	90 min	 5	97
3			$MeOH/H_2SO_4$	10 min	 3b	99
 2			HCl[d]/HOAc	4 h	 2b	4
2			H_2O/H_2SO_4	14 h	2b	88
2			$MeOH/H_2SO_4$	20 min	5	98
 7	84	87	MeOH[e]/H_2SO_4	7 min	 8	99
 9	75	>98	MeOH[e]/H_2SO_4	45 min	 10	92
 11	80	95	$EtOH/H_2SO_4$	20 min	 12	85
 17			$MeOH/H_2SO_4$	4 h	 18	74

[a] Isolated yield of isomerically pure ketone. [b] Acid:alcohol = 60:40; pot temperature of 100–108 °C. [c] Isolated yield of distilled or flash-chromatographed ester (Z:E > 95:5). [d] Constant boiling azeotrope as in reference 4a. [e] Sodium borohydride reduction procedure B. [f] Sodium borohydride reduction procedure A.

chromatograph equipped with a Megabore column for on-column injection. Elemental analyses are reported for the major chromatographed product without further purification unless noted and were determined on a Perkin-Elmer 2400 CHN analyzer. All samples were vacuum dried (50–60 °C (10^{-1} mm)) overnight immediately prior to analysis.

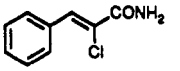
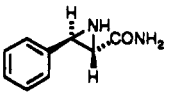
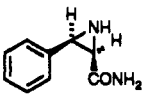
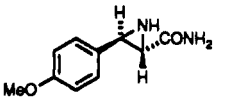
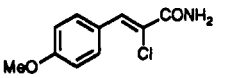
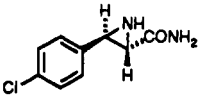
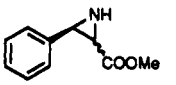
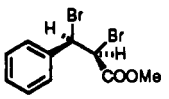
All solvents employed were Fisher HPLC-grade materials that were used without further purification. All preparative chromatography of organic compounds was performed with use of the flash chromatography (Merck Grade 60, 230–400 mesh silica gel, 60A, Aldrich Chemical Co.) and commercially available Analtech silica plates (250 micron, Analtech Inc.).

Caution: All acylations and rearrangement reactions must be conducted in a *well ventilated* fume hood, and provisions should be made for trapping and neutralizing hydrogen halide gases that are evolved. It should be emphasized that the rearrangement conditions will produce dialkyl sulfates, so that the aqueous workup procedure should also be performed in an adequately ventilated fume hood with appropriate safety equipment (gloves and goggles).

Respresentative Gas-Phase Free-Radical Condensation of Perchloroethylene and Toluene to 1,1,2-Trichloro-3-phenylpropene (1). A solution of toluene (227 g, 2.46 mol) and perchloroethylene (137 g, 0.824 mol) was passed dropwise (0.73 g min^{-1}) into a preheated zone and through a vertically mounted 16 × 1 in. quartz tube containing a $^1/_4$-in. thermowell (lengthwise) by use of a calibrated Altex (110A) HPLC pump. The quartz tube was maintained at 650 °C using a K-type LFE-230 controller and a 750-W multiple unit tube furnace (Basic Pro. Corp.). An argon (5 mL/min) and 1% chlorine in helium (58 mL/min) stream (back-pressure = 10 psig) was maintained throughout the course of the addition via calibrated rotameters. With a reactor volume of 80 mL, the residence time was 10 s, assuming ideal gas law behavior. The reactor effluent was cooled by use of an 18-in. Allyln condenser and was collected in a round-bottomed flask immersed in dry ice. The resultant gas was passed through a water percolator to scrub out residual hydrogen chloride. The brownish liquid was stripped of unreacted starting material by rotary evaporation, and the highers were short-path distilled (bp 67–68 °C (0.15 mm) (lit.[2] bp 89–91 °C (1.8 mm))) to afford 1 (37.0 g, 0.167 mol), which was readily separated from product upon distillation: ^1H NMR ($CDCl_3$) δ 7.23 (s, 5 H), 3.85 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 135.6, 131.6 (CCl_2), 128.8, 128.6, 127.3, 118.4 (vinyl CCl), 42.0 (CH_2); MS (70 eV) parent manifold 220–224 (18), base peak 149.

Ethanol/Perchloroethylene Condensation to 3,4,4-Trichloro-2-hydroxy-3-butene (13). A solution of ethanol (422 g, 9.15 mol) and perchloroethylene 506 g, 3.85 mol) was metered as described through the hot tube (575 °C at 0.49 g min^{-1}). The brownish liquid (892 g, 96% mass recovery) was stripped of unreacted perchloroethylene/ethanol by rotary evaporation, leaving a crude product that was vacuum distilled (bp 57 °C (0.6 mm) (lit.[13a] bp 86 °C (15 mm))) to afford 3,4,4-trichlorobuten-2-ol (13) (133 g, 0.76 mol), which was approximately 3% 4,4-dichloro-3-buten-2-ol as noted by VPC and GC/MS analysis: ^1H

Table II. Aziridines Derived from α-Halocinnamate Esters

cinnamate ester	solvent/amine	temp (°C)	time (h)	product	% yield[a]
4	NH_3	65	3	 **4b**	65
4	NH_3	65	17	 **19a**	56
				 **19b**	28
8	NH_3	65	17	 **21**	43
				 **8b**	15
10	NH_3	65	24	 **22**	84
4	NH_3/DMSO	25	48	 **24**	75[b]
				4b	25
 **23**	NH_3/H_2O	25[c]	120	**19a**	37[d]
23	NH_3/DMSO	25[c]	24	**24**	70

[a] Isolated yield of purified aziridine after flash chromatographic purification. [b] Ratio of products by ^1H NMR. [c] Cooled to 0 °C during ammonia addition. [d] See ref 9a.

NMR ($CDCl_3$) δ 4.98 (q, 1 H, J = 6.2 Hz), 2.45 (s, 1 H, OH), 1.32 (d, 3 H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 135.8, 118.1, 67.0, 20.7; MS (70 eV) m/e (I) parent 173/175 (12/12), 43 (100).

2,3,3-Trichloro-2-propen-1-ol (17). A solution of methanol (337 g, 10.5 mol) and perchloroethylene (582 g, 3.51 mol) was metered through the hot tube (600 °C at 0.50 g/min). The crude condensate (904 g, 98% material balance) was stripped of unreacted material and distilled (bp 54–55 °C (0.2 mm)) via a short-path apparatus to give product 17 of greater than 98% VPC purity (94 g, 0.58 mol): IR (neat) 3340, 2940, 2880, 1600, 1238, 1119, 1042, 920, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (s, 2 H), 3.18 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 131.4, 120.4, 63.0.

3-Bromo-1,1,2-trichloro-3-phenylpropene (3). 1,1,2-Trichloro-3-phenylpropene 2 (54.4 g, 0.25 mol) and AIBN (100 mg) were dissolved in 400 mL of carbon tetrachloride under nitrogen. The solution was stirred, heated to 65 °C, and irradiated with a sunlamp as bromine (42 g, 0.26 mol) dissolved in 100 mL of carbon tetrachloride was added dropwise over a 2-h period. At the end of this period, solvent was removed, whereupon *meso*-1,2-dibromo-1,2-diphenylethane precipitated and was filtered, washed, and dried (700 mg, 2.7 mmol): mp 239–240 °C (lit.[20] mp 237 °C). The crude product was vacuum distilled (bp 96–100 °C (0.10 mm)) to afford light yellow bromide 3 (69.5 g, 0.232 mol) in 93% yield. A center cut of the main fraction provided an analytical sample: ^1H NMR ($CDCl_3$) δ 7.1–7.6 (m, 5 H), 6.49 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 136.0, 132.8 (CCl_2), 128.9, 128, 128.1, 120.3 (CCl), 50.1 (CHBr). Anal. Calcd for $C_9H_6BrCl_3$: C, 35.99; H, 2.02. Found: C, 36.30; H, 2.08.

Rearrangement/Solvolysis of 3 to (*Z*)-Methyl 3-Phenyl-1,1,2-trichloropropenoate (4) and 1,1,2-Trichloro-3-methoxy-3-phenylpropene (3b). Freshly distilled bromide 3 (5.00 g, 16.67 mmol) was added to a solution of 98% concentrated sulfuric acid (8 mL) and methanol (10 mL) and was stirred vigorously under nitrogen at mild reflux (pot temperature of 100–107 °C) for 80 min. During this interval, gas evolution through the nitrogen bubbler was vigorous. The light yellow mixture was cautiously poured into 60 mL of water and stirred for 30 min, and the organic material was extracted with methylene chloride (40 mL). The organic layer was washed with 2 × 30 mL portions of water and dried over magnesium sulfate, and the solvent was removed by rotary evaporation. Light yellow ester 4 (3.24 g, 16.5 mmol) was obtained in 98% yield (bp 92–95 °C (0.2 mm) (lit.[21] bp 108–109 °C (0.5 mm))) and was used directly in the aminolysis reaction: ^1H NMR ($CDCl_3$) δ 7.80 (s, 1 H, vinyl), 7.55–7.7 (2 H, m, meta), 7.1–7.4 (m, 3 H, ortho/para), 3.82 (s, 3 H, methyl ester); ^{13}C NMR ($CDCl_3$) δ 163.9 (CO_2Me), 137.2, 127.8, (CCl), 130.7, 130.2, 128.6, 122.1 (vinyl CH), 53.4 (CH_3); MS (70 eV) m/e (I) 196/198 (18/6, parent), 102 (100).

Bromide 3 (2.00 g, 6.68 mmol) was refluxed in 10% concentrated sulfuric acid in methanol for 7 h as previously. The organic phase was washed with water (20 mL), dried over magnesium sulfate,

(21) Liebermann, G. *Chem. Ber.* **1910**, *43*, 1543–1547.

and filtered, and solvent was removed on a rotary evaporator to give **3b** (1.64 g, 6.53 mmol). Analysis by VPC (6 ft × $^1/_8$ in. nickel with 5% OV 221 on 80/100 mesh Anachrom Q, 180 °C isothermal) indicated this material to be greater than 97% methyl ether **3b**: ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 5 H), 5.55 (s, 1 H, methine), 3.40 (s, 3 H, methyl); ^{13}C NMR ($CDCl_3$) δ 137.5, 133.5 (CCl_2), 128.4, 128.39, 126.2, 120.7 (CCl), 80.4 (CHOMe), 56.8 (OCH_3); MS (70 eV) *m/e* (*I*) 250, 252, 254 (0.1, parent manifold), 121 (100). Anal. Calcd for $C_{10}H_9OCl_3$: C, 47.75; H, 3.61. Found: C, 47.81; H, 3.54.

2,3,3-Trichloropropenoyl Chloride (6). Perchloropropene (124.4 g, 0.50 mol) and anhydrous aluminum chloride (2.3 g, 3.80 mmol) were placed in a 300 mL 316 stainless steel autoclave equipped with an overhead stirrer. The reactor was cooled in a dry ice–acetone bath and evacuated (10^{-1} mm), and sulfur dioxide (106 g, 1.5 mol) was transferred to the vessel through a needle valve from an attached cylinder. The vessel was sealed and heated to 90 °C with stirring for 48 h. The vessel was cooled and slowly vented of excess sulfur dioxide to a caustic scrubber. The contents were distilled to give thionyl chloride (50 g, 0.42 mol) in 84% yield and a higher boiling fraction (bp 65 °C (20 mm)) of pure acid chloride **6**[16] (82.5 g, 0.427 mol) in 85% yield.

General Acylation Procedure Using Trichloropropenoyl Chloride 6 and Anisole: Synthesis of 1-(4-Methoxyphenyl)-2,3,3-trichloro-1-oxopropene (7). A mixture of acid chloride **6** (9.00 g, 46.2 mmol) and anisole (5.00 g, 46.2 mmol) was added dropwise to a stirred solution of methylene chloride (20 mL) and anhydrous aluminum chloride (6.47 g, 48.5 mmol) under a nitrogen atmosphere while the temperature was maintained at 0–5 °C during the course of the addition. The stirred slurry was allowed to warm to room temperature with continued stirring overnight as hydrogen chloride gas was liberated. The dark red slurry was then poured into 50 g of crushed ice and diluted with 50 mL of 1 N hydrochloric acid. The yellow solution was extracted with 100 mL of methylene chloride, and this organic phase was washed with 2 × 50 mL portions of 1 N hydrochloric acid and 2 × 50 mL portions of water. The organic phase was dried over magnesium sulfate and filtered, and solvent was reduced on a rotary evaporator to give 12.0 g of yellow oil that was a mixture of para-substituted ketone **7** (R_f = 0.56 in 10% ethyl acetate–hexane) and its demethoxylated, ortho isomer **7b** (R_f = 0.75). The para–ortho selectivity ratio was 87:13 as determined by capillary VPC analysis. The products could be preparatively separated by flash chromatography (5% ethyl acetate in hexane); however, basic extraction of **7b** from methylene chloride (100 mL) with 2 × 50 mL portions of 10% sodium hydroxide provided pure para isomer **7** (10.3 g, 38.8 mmol) in 84% isolated yield as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 2 H, *J* = 7.8 Hz)), 6.84 (2 H, d, *J* = 7.8 Hz), 3.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ IR (neat NaCl) 2840, 1720, 1598(s), 1570, 1510, 1320, 1170, 1030 cm^{-1}. Anal. Calcd for $C_{10}H_7O_2Cl_3$: C, 45.24; H, 2.66. Found: C, 45.34; H, 2.75.

Regiospecific Reduction of 7 to 1-(4-Methoxyphenyl)-2,3,3-trichloro-1-hydroxy-2-propene (7c). Ketone **7** (3.00 g, 11.3 mmol) was dissolved in 10 mL of absolute ethanol, and sodium borohydride (200 mg, 5.28 mmol) was added to the stirred solution. An immediate color change from light yellow to clear was noted, and TLC analysis revealed conversion of starting material (R_f = 0.56 in 10% ethyl acetate in hexane) to a single product **7c** (R_f = 0.30). Solvent was evaporated and the clear oil was dissolved in methylene chloride and filtered through a short plug of flash silica gel. Solvent removal afforded alcohol **7c** (2.99 g, 11.2 mmol) in 99% yield: ^{1}H NMR ($CDCl_3$) δ 7.30 (d, 2 H, *J* = 7.8 Hz), 6.70 (2 H, d, *J* = 7.8 Hz), 5.90 (d, 1 H, *J* = 4.0 Hz), 2.85 (d, 1 H, *J* = 4.0 Hz), 3.73 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.5, 134.6, 130.9, 127.0, 121.0, 119.3, 113.9, 71.5, 55.3; IR (neat NaCl) 3400, 3000 (s), 2840 (s), 1610 (s), 1590, 1510, 1250, 1170, 1110, 1040 cm^{-1}. Anal. Calcd for $C_{10}H_9O_2Cl_3$: C, 44.89; H, 3.39. Found: C, 44.95; H, 3.60.

1-(4-Chlorophenyl)-2,3,3-trichloro-1-oxopropene (9). Following the coaddition procedure outlined for anisole using **6**, ketone **9** was obtained in 75% isolated yield as a single positional isomer (capillary VPC) of analytical purity after short-path distillation (bp 95 °C (0.1 mm) as a clear oil): ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 2 H, *J* = 8.0 Hz), 7.45 (2 H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 185.6, 141.6, 132.5, 129.5, 124.6, 123.7; IR (neat NaCl) 2920, 1690, 1590, 1490, 1410, 1265, 1105, 1025 cm^{-1}. Anal. Calcd for $C_9H_4OCl_4$: C, 40.05; H, 1.49. Found: C, 40.38; H, 1.55.

1-(4-*tert*-Butylphenyl)-2,3,3-trichloro-1-oxopropene (11). Ketone **11** was obtained in 93% yield (crude) and was found to contain traces of the ortho isomer of **11** (capillary VPC). The compound was isolated free of this impurity by flash chromatography with 5% ethyl acetate in hexane, providing material that was analytically pure as a light yellow oil (R_f = 0.70 in 10% ethyl acetate in hexane): ^{1}H NMR ($CDCl_3$) δ 7.88 (d, 2 H, *J* = 8.5 Hz), 7.55 (2 H, d, *J* = 8.5 Hz), 1.36 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 187.0, 159.4, 130.6, 130.1, 126.3, 125.3, 122.9, 35.2, 30.8; IR (neat NaCl) 2920, 1690, 1590, 1490, 1410, 1265, 1105, 1025 cm^{-1}. Anal. Calcd for $C_{13}H_{13}OCl_3$: C, 53.55; H, 4.49. Found: C, 53.60; H, 4.56.

General One-Pot Reduction/Rearrangement Procedure for Trichlorovinyl Ketones 7–11. Ketone (10.0 mmol) was dissolved in 10 mL of ethanol and treated with sodium borohydride (5.0 mmol, 2.0 equiv) as detailed previously for the isolation and structural characterization of **7c** (procedure A). After the reaction was judged complete by TLC (usually 1–2 min after addition), concentrated sulfuric acid (8 mL) was cautiously added to the solution in a well-ventilated fume hood. The flask was then outfitted with a reflux condenser and was brought to reflux (internal pot temperature = 100–105 °C) for the specified period of time (generally 10 min after the cessation of vigorous gas evolution) under a nitrogen atmosphere.

An alternative procedure (procedure B) was developed for the direct synthesis of methyl esters, which involved removal of ethanol in vacuo after reduction of the ketone. Methanol–sulfuric acid catalyst was then added to the crude carbinol as noted in the rearrangement of compound **3** to **4**. The aqueous quench and workup was identical with that specified previously in the conversion of **3** to **4**.

(*Z*)-Methyl 3-(4-Methoxyphenyl)-2-chloropropenoate (8). Ester **8** was obtained (procedure B) from ketone **7** as a pale yellow oil that crystallized on standing: mp 68–70 °C (lit.[22] mp 67–70 °C); ^{1}H NMR ($CDCl_3$) δ 7.83 (s, 1 H), 7.81 (d, 2 H, *J* = 8.7 Hz), 6.80 (2 H, d, *J* = 8.7 Hz), 3.86 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 161.1, 136.7, 132.6, 125.4, 119.0, 113.9, 55.2, 53.0.

(*Z*)-Methyl 3-(4-Chlorophenyl)-2-chloropropenoate (10). Ester **10** was obtained (procedure B) from ketone **9** as a clear oil that crystallized on standing. An analytical sample was prepared by sublimation: mp 78–80 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 1 H), 7.65 (d, 2 H, *J* = 8.4 Hz), 7.30 (2 H, d, *J* = 8.7 Hz), 3.82 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.5, 136.1, 135.8, 131.6, 131.3, 128.8, 119.0, 113.9, 55.2, 53.0. Anal. Calcd for $C_{10}H_8O_2Cl_2$: C, 51.98; H, 3.49. Found: C, 52.10; H, 3.63.

(*Z*)-Ethyl 3-(4-*tert*-Butylphenyl)-2-chloropropenoate (12). Ester **12** was obtained (procedure A) from crude ketone **11** as a pale yellow oil in 93% yield. The crude ester (830 mg) was applied to a 1 × 6 in. flash silica column that was eluted with carbon tetrachloride (R_f = 0.53 in 10% ethyl acetate in hexane; visualized with phosphomolybdic acid) to obtain 620 mg of analytically pure **12** as a colorless oil, which was free of any ortho positional isomer: ^{1}H NMR ($CDCl_3$) δ 7.89 (s, 1 H), 7.81 (d, 2 H, *J* = 7.1 Hz), 7.45 (d, 2 H, *J* = 7.1 Hz), 4.35 (q, 2 H, *J* = 7.1 Hz), 1.36 (t, 3 H, 7.1 Hz), 1.34 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 163.9, 154.0, 137.0, 130.8, 130.3, 128.7, 125.7, 121.4, 62.4, 34.7, 30.9, 14.0. Anal. Calcd for $C_{15}H_{19}O_2Cl$: C, 67.54; H, 7.18. Found: C, 67.49; H, 7.09.

Methyl 2-Chloropropenoate (18). Alcohol **17** was used in the rearrangement procedure to produce **18**, whose spectral properties were in accord with those previously reported.[23] The crude product was found to contain approximately 12 area % of 1,1,2,3-tetrachloropropene as determined by VPC and GC/MS analysis.

Aziridine Formation: *cis*- and *trans*-2-Phenylaziridine-3-carboxylic Acid Amides (19a,b). Methyl 2-chloro-3-phenylpropenoate (**4**; 10.0 g, 51.0 mmol) was placed in a 300-mL stainless steel autoclave equipped with an overhead stirrer. The autoclave was sealed, evacuated (1 mm), and cooled in a dry ice–acetone bath. Anhydrous ammonia (40 g) was condensed into the bomb, and the vessel was allowed to slowly warm to room temperature. The vessel was placed in a pressure cubicle and heated to 65 °C with vigorous stirring for 17 h. The vessel was cooled and vented, and an analytical sample revealed 95% azridines and **19a** and **19b** (1:2 ratio) by ^{1}H NMR analysis.

(22) Stoermer, G.; Kirchner, R. *Chem. Ber.* **1920**, *53*, 1289–1294.
(23) Higa, T.; Krubsack, A. J. *J. Org. Chem.* **1976**, *41*, 3399–3403.

The remaining light tan solid was dissolved in 50 mL of hot chloroform and filtered. Ammonium chloride (2.68 g, 50.1 mmol dry) was obtained, and to the hot solution of crude aziridines was added hot hexane (~20 mL) dropwise. The solution was allowed to cool and stand for several hours and was then refrigerated overnight. The cold crystalline mass was filtered and washed sparingly with cold hexane/chloroform (30:70). Aziridines **19a** and **19b** were obtained (7.0 g, 43.2 mmol) in 84% recrystallized yield in a 1:2 ratio of cis to trans isomers. Pure *trans*-**19b** was obtained by flash chromatography (ethyl acetate) of the mixture (R_f = 0.36 in ethyl acetate): mp 134.5–136 °C; ^{1}H NMR ($CDCl_3$) δ 2.42 (d, 1 H, J = 1.9 Hz), 2.01 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.2 ($CONH_2$) 138.1, 128.5, 127.7, 125.9, 40.5, 39.8 (CH); IR ($CDCl_3$ on NaCl plates) 3517, 3408, 3014, 1685, 1567, 1433, 1286, 779, 736, 699 cm^{-1}; MS (70 eV) m/e (I) 162 (0.6 (M^+)), 117 (100). Anal. Calcd for $C_9H_{10}N_2O$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.54; H, 6.31; N, 17.13.

Pure *cis*-**19a** was obtained by chromatography (R_f = 0.19 in ethyl acetate) as well: mp 179–180 °C (lit.[9b] mp 179–180 °C); ^{1}H NMR (DMSO-d_6) δ 7.26 (s, 5 H), 6.70 (s, 2 H, broad amide), 3.31 (s, 1 H), 3.22 (d, 1 H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6) δ 169.8 ($CONH_2$), 136.7, 127.9, 127.6, 126.7, 38.5, 37.9; MS (70 eV) m/e (I) 162 (1 (M^+)), 117 (100). Anal. Calcd for $C_9H_{10}N_2O$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.80; H, 6.15; N, 17.31.

Treatment of ester **4** with ammonia for 1 h at 65 °C provided no aziridine and only (*Z*)-2-chloro-3-phenylpropenoic acid amide (**4b**) (R_f = 0.62 in ethyl acetate): mp 119–120.5 °C (lit.[24] mp 121–122 °C).

Reduction of Aziridines (19,b). A 2:1 isomer mixture of **19a–19b** (3.1 g, 19.1 mmol) was dissolved in 25 mL of methanol, and 400 mg of 5% palladium on carbon (Strem Chemical Co.) was added to this solution. The mixture was hydrogenated in a stirred 40-mL stainless steel bomb for 14 h at 60 °C (800 psig). The catalyst was filtered through Celite, and the solvent was removed, affording 3.1 g of crude *d,l*-phenylalanine amide **20**, which contained 10% starting material (NMR). The latter was washed away with cold chloroform: mp 234–237 °C of HCl salt (lit.[24] mp 234–235 °C); ^{1}H NMR (DMSO-d_6) δ 7.20 (s, 5 H), 2.0–3.5 (m, 7 H); ^{13}C NMR (DMSO-d_6) δ 176.0, 136.4, 129.6, 128.4, 126.5, 55.9, 40.6; MS (70 eV) m/e (I) 165 (0.2 (M^+)), 120 (100).

***trans*-2-(4-Methoxyphenyl)aziridine-3-carboxylic Acid Amide (21) and (*Z*)-2-Chloro-3-(4-methoxyphenyl)propenoic Acid Amide (8b).** Under the conditions used in the preparation of **19**, ester **8** (1.40 g, 6.18 mmol) was heated in liquid ammonia (15 g) for 17 h. The crude dark product was extracted into 30 mL of chloroform and filtered to remove ammonium chloride. The solvent was removed, and the dark residue was dissolved in a minimum amount of ethyl acetate and applied to a 0.5 × 3.5 in. flash gel column that had been eluted with ethyl acetate. The first compound eluted from the column was **8b** as a crystalline, white solid of analytical purity (220 mg, 1.04 mmol, R_f = 0.64 in ethyl acetate) in 17% yield: mp 148.5–150 °C (from chloroform); ^{1}H NMR ($CDCl_3$) δ 7.78 (s, 1 H), 7.70 (d, 2 H, J = 8.3 Hz), 6.80 (d, 2 H, J = 8.3 Hz), 6.5 (broad s, 2 H), 3.79 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 160.9, 134.2, 132.4, 125.6, 120.2, 114.0, 55.3; MS (70 eV) m/e (I) 211/213 (80/25 (M^+)), 175 (100), 159 (64), 132 (55). Anal. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62. Found: C, 56.49; H, 4.73; N, 6.63.

Further elution of the column provided *trans*-aziridine **21** (500 mg, 2.61 mmol, R_f = 0.19 in ethyl acetate) in 42% yield: mp 128–129 °C; ^{1}H NMR (D_2O) δ 7.21 (d, 2 H, J = 8.7 Hz), 6.95 (d, 2 H, J = 8.7 Hz), 3.81 (s, 3 H), 3.18 (d, 1 H, J = 1.5 Hz), 2.71 (d, 1 H, J = 1.5 Hz), 2.01 (s, 1 H); ^{13}C NMR (D_2O) δ 176.5, 161.5, 132.4, 130.1, 116.6, 57.5, 55.0, 41.1; MS (70 eV) m/e (I) 192 (10.0 (M^+)), 175 (8.0), 147 (100), 132 (40), 120, (37). Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.50. Found: C, 62.19; H, 6.18; N, 14.35.

***trans*-2-(4-Chlorophenyl)aziridine-3-carboxylic Acid Amide (22).** Under the conditions used in the preparation of **19**, ester **10** (3.00 g, 1.30 mmol) was heated in liquid ammonia (25 g) for 24 h. Venting of ammonia afforded a cream colored solid that was triturated with 70 mL of water and filtered. The moist cake was washed with 20 mL of cold (–20 to –30 °C) acetone and air dried to give exclusively the trans isomer of aziridine **22** (2.2 g, 1.11 mmol) in 86% yield (R_f = 0.29 in ethyl acetate): mp 173.5–174.5 °C (methanol as white needles); ^{1}H NMR (10% methanol-d_4 in $CDCl_3$) δ 7.30 (d, 2 H, J = 6.4 Hz), 7.21 (d, 2 H, J = 6.4 Hz), 2.48 (d, 1 H, J = 2.4 Hz), 2.14 (d, 1 H, J = 2.4 Hz); ^{13}C NMR (10% methanol-d_4 in $CDCl_3$) δ 172.1, 136.6, 133.5, 128.6, 127.6, 39.7, 38.5; ^{1}H NMR (DMSO-d_6) δ 7.60 (broad s, 2 H, amide), 7.30 (center of overlapped dd, 4 H). Anal. Calcd for $C_9H_9N_2OCl$: C, 54.97; H, 4.61; N, 14.25. Found: C, 54.93; H, 4.62; N, 14.09.

Methyl 2-Phenylaziridine-3-carboxylate (24). Erythro dibromide **23**[7c,9b] (mp 114–115 °C, 15.0 g, 46.6 mmol) was dissolved under nitrogen in dry DMSO (100 mL, dried over 4A sieves) and was cooled in an ice bath. Anhydrous ammonia was bubbled through the solution at a rate such that the temperature did not exceed 5 °C, and the solution was then allowed to warm to room temperature with stirring for 24 h. Workup was performed by adding 100 mL of water to the solution and extracting with 2 × 100 mL portions of methylene chloride. The combined organic phase was then extracted with 2 × 100 mL portions of water and dried over magnesium sulfate, and the solvent was removed to give 6.6 g of aziridine **24** isomers as a clear oil that solidified upon standing in vacuo. ^{1}H NMR analysis of the material showed it to be a mixture of aziridine methyl esters of unspecified stereochemistry (ratio of methyl esters 2:1 at δ 3.4 and 3.7), which also contained 10–15% of the α-halo ester (vinyl H at δ 8.34). The latter material was structurally confirmed in the mixture by mass spectral analysis (m/e at 242/244 for M^+). Attempts to purify this material by flash chromatography were unsuccessful: MS (70 eV) m/e (I) 177 (5.0 (M^+)), 176 (26, ($M - H$)$^+$), 161 (53), 146 (45), 129 (31), 117 (100), 102 (61).

To further confirm the aziridine structures, the crude mixture of **24** (2.01 g, 10.2 mmol corr) was dissolved in 50 mL of methanol containing 150 mg of 10% palladium on carbon and was hydrogenolyzed with use of a Parr shaker hydrogenator (50 psig of hydrogen at 25 °C for 1 h with theoretical uptake of approximately 1 equiv of hydrogen). Catalyst filtration through Celite and solvent removal gave 2.11 g of clear liquid that was vacuum distilled (93–97 °C (0.2 mm)) through a short-path still apparatus to give 1.5 g of *d,l*-phenylalanine methyl ester **25** in 82% yield: mp 158–159 °C of HCl salt (lit[25] mp 158–159 °C); ^{1}H NMR ($CDCl_3$) δ 7.10 (s, 5 H), 3.60 (s, 3 H), 2.2–3.1 (m, 3 H), 1.35 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 175.2, 137.1, 129.0, 128.3, 126.6, 55.6, 51.7, 41.0; MS (70 eV) m/e (I) 180 (38 ($M + H$)$^+$), 179 (11, (M^+)), 149 (14), 120 (63), 88 (100).

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Supplementary Material Available: Experimental procedures and data for compounds **13–16** and spectra for compounds **15** and **17** (5 pages). Ordering information is given on any current masthead page.

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