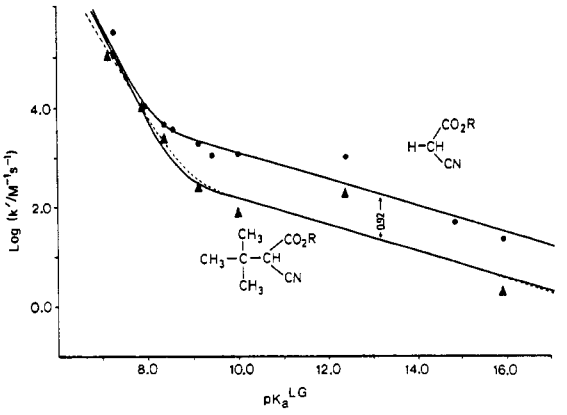
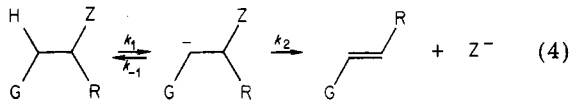


Figure 2. Plots of log k' (M^{-1} s^{-1}) vs. pK_a of the conjugate acid of the leaving group (pK_a^{LG}) for the esters 1 and 2. For ester 2, the slopes of the solid line are identical with the slopes drawn for 1 and the broken line represents the best fit.

Results and Discussion

Plots of log k_{pl} vs. pK_a of the conjugate acid of the leaving group (pK_a^{LG}) for the esters 1 and 2 are provided in Figure 1. The slopes of the plots are large and negative for the E1cb hydrolysis of the esters with good leaving groups and small and positive for the $B_{AC}2$ hydrolysis of the esters with more strongly basic leaving groups.[11,13] The values of k_{pl} for the $B_{AC}2$ hydrolysis of esters 2 are seen to be ~20 times *larger* than for esters 1. As this is an unexpected finding, we have explored the hydrolysis of 1 and 2 at pH $\ll$ pK_a^{CH}, where hydrolysis rates are proportional to the hydroxide concentration. The so-determined second-order rate constants are shown in the Brønsted-type plot of Figure 2. Inspection of Figure 2 reveals that the $B_{AC}2$ hydrolysis rate constants for esters 2 are approximately 8 times smaller than for esters 1. This finding would be anticipated on the basis of the steric bulk of the *tert*-butyl substituent α to the ester group in esters 2. Since the plateau rate of the $B_{AC}2$ reaction is given by the equation $k_{pl} = k_2K_w/K_a^{CH}$, it follows that any change in pK_a^{CH} of esters 2 compared to 1 (i.e., ΔpK_a^{CH}) is given by the equation $\Delta pK_a^{CH} = (\Delta \log k_{pl}) - (\Delta \log k_2)$, implying $\Delta pK_a^{CH} \simeq 2$. The increase in k_{pl} for the $B_{AC}2$ reaction on *tert*-butylation is then due to the accompanying increase in pK_a^{CH} by 2 units which is much larger than the magnitude of decrease in log k_2.

The rate constant for the departure step (k_1 of eq 2) of the E1cB reaction is increased by a factor of approximately 70 by *tert*-butylation of the α-carbon atom as is anticipated by the steric acceleration in dissociative reactions. This finding is in striking contrast to the deductions of Stirling et al.[9] Their conclusion was reached by examination of values of k_2/k_{-1} (eq 4) in the region pH $\ll$ pK_a^{CH} with the



(4)

assumption that k_{-1} was constant and at the diffusion-controlled limit.[14] From our observation that pK_a^{CH} is changed by 2 units on substitution of the α-hydrogen of 1 with the bulky *tert*-butyl group, it is possible that k_{-1} in eq 4 also is sensitive to steric effects of substituents and in the same manner as k_2.[15] This discussion may be supported by our observation that the second-order rate constants k' (at pH $\ll$ pK_a^{CH}) for the E1cB reaction are apparently insensitive to the steric effect.

Finally it must be noted that one should be careful in using steric effects as a criterion for distinguishing $B_{AC}2$ from E1cB mechanisms. The plateau rates of both the $B_{AC}2$ and E1cB reactions may be increased by a bulky substituent, and the pH-dependent rate can be insensitive to steric effects even though the rate of the departure step is increased in the E1cB reaction by the bulky substituent.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

Registry No. **1a**, 105-56-6; **1b**, 27827-83-4; **1c**, 6131-48-2; **1d**, 80256-96-8; **1e**, 80256-94-6; **1f**, 80256-93-5; **1g**, 80256-92-4; **2a**, 21954-81-4; **2b**, 86834-63-1; **2c**, 86834-64-2; **2d**, 86834-65-3; **2e**, 86834-66-4; **2f**, 86834-67-5; **2g**, 86834-68-6; $POCl_3$, 10025-87-3; ethyl 2-cyano-3-methylbutanoate, 3213-49-8; methylmagnesium iodide, 917-64-6; 2-cyano-3,3-dimethylbutanoic acid, 22426-28-4; cyanoacetic acid, 372-09-8; *p*-cyanophenol, 767-00-0; *p*-nitrophenol, 100-02-7.

(13) Alborz, M.; Douglas, K. T. *J. Chem. Soc., Chem. Commun.* **1980**, 728.

(14) It must be noted that for E1cB ester hydrolysis, the rate constant of departure of leaving group k_2 of eq 2 can be measured directly while for E1cB alkene formation only the rate ratio k_2/k_{-1} can be empirically determined.

(15) On the other hand, the conclusions of Stirling and co-workers may be quite valid, in which case, the difference in the sensitivities to steric effects in the departure of the leaving groups of E1cB alkene formation and ketene formation may be sought in the positions of the transition states as suggested by the standard free energies for the two elimination reactions. In the case of alkene formation (eq 3) an unstable carbanion yields a stable alkene; the transition state should be early, and the steric strain in the carbanion would be minimally *released* in the transition state. In contrast, the E1cB ester hydrolysis proceeds from a carbanion of greater stability than the ketene product and the release of strain should be fully felt in the late transition state. The observation of the insensitivity of second-order rate constants k' to the steric effect also reminds us of Williams and Douglas' early conclusion[16] that "the insensitivity of substituted azides to steric effects is consistent with the E1cB mechanism". Their conclusion was made on the basis of the data of Matier et. al.[17] for a series of azides ($RNHSO_2N_2$). As the azides have high pK_a values, only k' values (second-order rate constants) were determined.[18]

(16) Williams, A.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1727.

(17) Matier, W. L.; Comer, W. T.; Reitchman, D. *J. Med. Chem.* **1972**, *15*, 538.

(18) See also: Casida, J. E.; Augustinsson, K. B.; Jonsson, G. *J. Econ. Entomol.* **1960**, *53*, 205.

Bis(methoxycarbonyl)sulfur Diimide, a Convenient Reagent for the Allylic Amination of Alkenes

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Received February 8, 1983

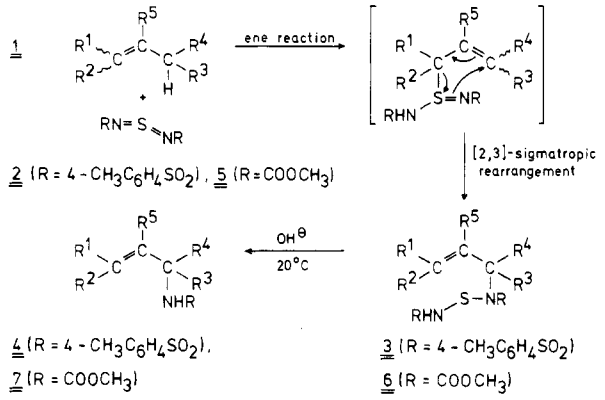
Despite the growing interest in this class of compounds, not many highly regio- and stereoselective procedures for the synthesis of primary 2-alkenylamines from easily accessible starting materials like alkenes are known to date. Simple examples may be laboriously prepared by allylic halogenation of an alkene and subsequent treatment with ammonia. However, the halogenation step is seldom selective enough;[1] the scope of this method is strictly limited.

Some years ago, we discovered ditosylsulfur diimide (2) to be a highly reactive enophile, converting a wide variety of alkenes (1) into *N*-(2-alkenyl)sulfinamidines under mild

(1) See for example: Stroh, R. "Methoden der organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1962; Vol. V/3, pp 585-592, 800, 805, 806; Roedig, A. 1960, Vol. V/4, pp 221-233.

0022-3263/83/1948-3561$01.50/0

Scheme I



2 (R = 4-$CH_3C_6H_4SO_2$), 5 (R = $COOCH_3$)

4 (R = 4-$CH_3C_6H_4SO_2$), 7 (R = $COOCH_3$)

3 (R = 4-$CH_3C_6H_4SO_2$), 6 (R = $COOCH_3$)

conditions.[2] As a rule, these ene products spontaneously undergo a [2,3]-sigmatropic rearrangement to afford *N*-(2-alkenyl)diamino sulfanes **3** (Scheme I). Particularly remarkable is the pronounced selectivity of product formation in these cases, as documented by many examples. From the results of our investigations[3] the following conclusions can be drawn. (i) Whenever possible, the C=C bond of the diaminosulfanes **3** is exclusively *E* configurated, regardless of the configuration of the starting alkene. (ii) When an 1,2-disubstituted alkene is employed, usually only the weaker C–H bond is cleaved (C–H bond dissociation energy: $CH_3 > CH_2R > CHRR'$). (iii) In the case of trisubstituted alkenes the H abstraction exclusively occurs on the disubstituted side of the C=C bond.

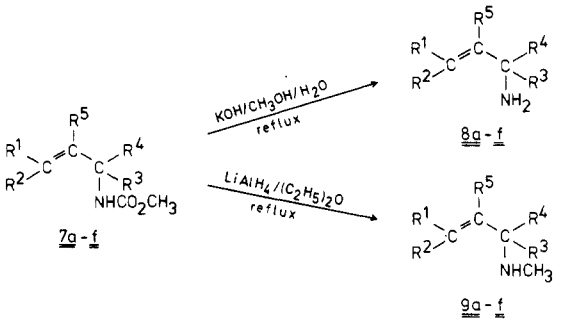
As for 1,1-disubstituted alkenes, the selectivities are not that pronounced, although one of the possible regioisomers sometimes is predominant by far.

The reaction sequence depicted in Scheme I is equivalent to the replacement of an allylic hydrogen atom of the starting alkene by a nitrogen functionality. Sharpless[4a] has used it in his gabaculin synthesis, for example. As he has pointed out, the conversion of the diamino sulfanes **3** into the free amines unfortunately meets with difficulties in most cases. While the N–S–N bond is readily cleaved by a multitude of reagents[3] the resulting tosyl amides **4** are very difficult to solvolyze; harsh and inconvenient conditions and/or sophisticated reagents have to be employed for this purpose.[4a] Another method of selective allylic amination comparable with that described above used a selenium diimide.[4b]

To overcome this difficulty, we replaced **2** by bis(methoxycarbonyl)sulfur diimide (**5**). Although **5** is less reactive than **2**, it undergoes ene reaction at ambient temperatures or below with many alkenes that are not too electron poor. The selectivity in such cases is as high as in reactions with **2**. The ene products spontaneously rearrange to the diamino sulfanes **6** which in turn may be transformed into the carbamates **7**, e.g., by treatment with hydroxide at room temperature.

The main advantage of the use of **5** compared to that of **2** lies in the ease of degradation of the product **7** to free amines. Just heating the **7** in alkaline solution gives the corresponding primary amine **8**. Moreover, reduction with $LiAlH_4$[5] leads to the (2-alkenyl)methylamines **9** in excellent yields (Scheme II).

Scheme II



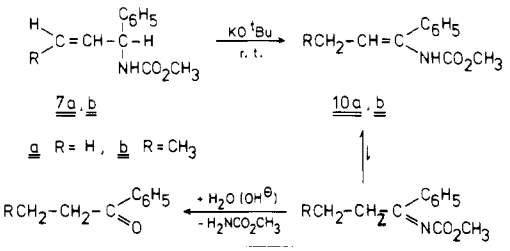
7a-f

8a-f

9a-f

7, 8, 9	R^1	R^2	R^3	R^4	R^5
a	H	H	H	C_6H_5	H
b	H	CH_3	H	C_6H_5	H
c	H	H	CH_3	C_6H_5	H
d	CH_3	H	CH_3	H	H
e	H	$(-CH_2-)_3$		H	H
f	CH_3	H	H	H	CH_3

Scheme III



7a, b

a R = H, b R = CH_3

10a, b

As **5** (in contrast to **2**) is a liquid, less reactive alkenes (e.g., 2-bromopropene) may be brought to reaction without solvent. Furthermore, the whole reaction sequence leading to the compounds **7** may be performed conveniently as a one pot procedure. The yield of the pure carbamate is usually around 50%; the solvolysis or reduction step proceeds almost quantitatively. Remarkably, the alkene **1b** (which yields only decomposition products with **2**) constitutes an exception to the general selectivity rules in one respect. Here, independently of the configuration of the starting alkene, a mixture of (*E*)- and (*Z*)-**6b** is obtained, from which the surprisingly prevailing (by a factor of about 4) *Z* isomer may be easily separated at the carbamate stage by fractional crystallization.

The carbamates stemming from the 3-phenylalkenes **1a** and **1b** are converted into the corresponding 1-alkenylcarbamates **10a** and **10b** by treatment with KO-*t*-Bu (Scheme III). This base-catalyzed isomerization probably is the reason for the formation of 1-phenyl-1-propanone or -1-butanone, respectively, as side products during the degradation of **7a** and **7b** with hydroxide. Whereas the latter ketone is only a (easily removable) byproduct (<-10%), the former one is the main product (>75%), even under optimized conditions. However, its formation may be avoided by employing Me_3SiI as the degrading agent.[6] Thus, the amine **8a** is obtained in excellent yield.

Experimental Section

All reactions except the degradation of the diamino sulfanes **6** into the carbamates **7** and the conversion of the latter into the amines **8** must be carried out under anhydrous conditions. Chloroform was dried according to standard procedures, distilled

(2) Schönberger, N.; Kresze, G. *Justus Liebigs Ann. Chem.* **1975**, 1725.
(3) Bussas, R.; Kresze, G. *Liebigs Ann. Chem.* **1980**, 629.
(4) (a) Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1448. (b) Sharpless, K. B.; Hori, T.; Tunesdale, L. K.; Dietrich, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 269.
(5) (a) Wessely, F.; Swoboda, W. *Monatsh. Chem.* **1951**, *82*, 621. (b) Dannley, R. L.; Lukin, M.; Shapiro, J. *J. Org. Chem.* **1955**, *20*, 92.
(6) (a) Jung, M. E.; Lyster, M. A. *J. Chem. Soc., Chem. Commun.* **1978**, 315. (b) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

Table I. Yields, Reaction Conditions, and Physical Constants of Compounds 7[a,b]

compd[a]	yield, %	reaction time,[c] h	mp,[d] °C, or bp, °C/mbar
7a	58	36	70/0.01
7b	51	20	93
7c	25	120	76/0.01
7d	53	8	71/7
7e	51	60	88/3
7f	59	6	75/3
7g[e]	45	240	78/0.01

[a] All compounds showed characteristic IR absorption bands at 3450, 1725 (C=O), and 3350 cm^{-1} (NH) in CCl_4 solution. [b] ^1H NMR data (δ) for 7a 3.65 (s, 3, CH_3O), 5.0-5.5 (m, 4, CH_2=, CHN, NH), 5.8-6.3 (m, 1, CH=), 7.3 ("s", 5, C_6H_5). For 7b: 1.6-1.8 (m, 3, CH_3), 3.67 (s, 3, CH_3O), 5.0-5.8 (m, 4, 2CH=, CHN, NH), 7.3 ("s", 5, C_6H_5). For 7c: 1.75 (s, 3, CH_3), 3.58 (s, 3, CH_3O), 5.0-5.4 (m, 3, H_2C=, NH), 6.1-6.6 (m, 1, CH=), 7.2-7.6 (m, 5, C_6H_5). For 7d: 1.20 (d, 3, J = 6.5 Hz, H_3CC), 1.68 ("d", 3, J = 5 Hz; $H_3CC\leqslant$), 3.67 (s, 3, CH_3O), 3.9-4.5 (m, 1, CHN), 4.7-5.2 (m, 1, NH), 5.3-5.9 (m, 2, 2CH=). For 7e: 1.3-2.2 (m, 6, $(CH_2)_3$), 3.68 (s, 3, CH_3O), 4.0-4.4 (m, 1, CHN), 4.7-5.4 (m, 1, NH), 5.5-6.0 (m, 2, 2CH=). For 7f: 1.60 (d, 3, J = 5 Hz, CH_3CH=), 1.65 (s, 3, $CH_3C\leqslant$), 3.67 (s, 3, CH_3O), 3.73 (s, 2, CH_2N), 4.9-5.7 (m, 2, CH=, NH). For 7g: 3.68 (s, 3, CH_3O), 4.02 (d, 2, J = 6.5 Hz, CH_2N), 4.5-5.8 (s, 1, NH), 5.55 ("s", 1, CH=), 5.83 ("s", 1, CH=). ^{13}C NMR data (δ) for 7a: 52.1 (q), 57.1 (d), 115.5 (t), 126.9 (d), 127.5 (d), 128.6 (d), 137.8 (d); 140.8 (s), 156.4 (s). For 7b: 17.7 (q), 52.0 (q), 56.7 (d), 126.8 (d), 127.2 (d), 127.4 (d), 128.5 (d), 131.0 (d), 141.7 (s), 156.3 (s). For 7c: 26.6 (q), 51.6 (q), 59.2 (d), 113.3 (t), 125.5 (d), 126.8 (d), (d), 128.2 (d), 142.3 (d), 144.9 (s), 155.2 (s). For 7d: 17.6 (q), 21.1 (q), 48.4 (t), 51.8 (q), 125.1 (d), 133.0 (d), 156.4 (s). For 7e: 19.7 (t), 24.8 (t), 29.8 (t), 46.4 (d), 51.9 (q), 128.0 (d), 130.6 (d), 156.4 (s). For 7f: 13.2 (q), 14.0 (q), 48.6 (t), 52.0 (q), 120.4 (d), 132.8 (s), 157.3 (s). For 7g: 48.9 (t), 52.4 (q), 117.0 (t), 130.1 (s), 156.9 (s). [c] For the conversion 1 → 6. [d] All carbamates except 7b have low melting points (−10 to +25 °C). [e] Starting alkene was 2-bromopropene.

and stored over molecular sieve (400 pm, activated). IR spectra were recorded on a Perkin-Elmer 257 spectrometer. NMR spectra were measured in $CDCl_3/Me_4Si$ solution with a Varian A 60 (^1H NMR) or a JEOL JNM-FX 90 (^{13}C NMR) spectrometer.

Materials. All alkenes employed in this work are commercially available compounds.

Bis(methoxycarbonyl)sulfur Diimide (5).[7] *N,N*-Dichlorocarbamate[8] (144 g, 1.0 mol), pyridine (~0.5 mL) and SCl_2 (~5 g, freshly distilled) are placed in a flask and stirred at 50–60 °C until a vigorous evolution of Cl_2 sets in (~5-10 min). Thereupon the heating is removed, and the remainder of the required SCl_2 (totaling 52 g, 0.5 mol) is added at such a rate that a rapid evolution of chlorine is maintained and the temperature of the reaction mixture does not exceed 35 °C for more than a short interval. After the end of addition, the mixture is heated at 60 °C under reduced pressure (15 mbar) for 10 min. Volatile material is further removed at 20 °C/0.01 mbar (1 h). The moisture-sensitive, yellow oil thus obtained is pure enough for preparative purposes, and distillation is not required. The yield of crude material is almost quantitative. The product is best stored for extended periods protected from light at −78 °C; ^1H NMR ($CDCl_3$) δ 3.88 (s).

General Procedure for the Preparation of Methyl *N*-(2-Alkenyl)carbamates 7. The corresponding alkene 1 (0.1 mol) is slowly dropped into a stirred solution of bis(methoxycarbonyl)sulfur diimide 5 (17.8 g, 0.1 mol) in 15 mL of dry chloroform at 0 °C. In the case of less reactive alkenes, e.g., 2-bromopropene, the reaction is preferentially carried out under neat circumstances. After completion of addition, stirring is continued at ambient temperature for the period indicated in Table I. The subsequent removal of the solvent at 30 °C (15 mbar) is followed by treatment of the crude diamino sulfane 6 with a solution of KOH (14 g, 0.25 mol) in 180 mL of methanol for 3 h at 20 °C. The resultant mixture is filtered (if a precipitate has occured during the degradation process), concentrated on a rotating evaporator at 40 °C, and dissolved in 250 mL of ether and 100 mL of water. The mostly dark brown ethereal layer, after being washed with water (4 × 100 mL), is treated with charcoal and finally dried over anhydrous Na_2SO_4. Removal of the solvent yields the crude product (usually as an oil), which is advantageously purified by distillation under reduced pressure (see Table I). Purification of **7b** is achieved by recrystallization from dichloromethane/pentane (1:4).

Table II. Yields, Reaction Conditions, and Boiling Points of Compounds 8[a,b]

compd	yield, %	reaction time,[c] h	bp °C/mbar (lit. bp)	method
8a	22	3	75/7 (57/0.09)[10]	B
8b	75	30	81/3	B
8c	78	48	66/3	B
8d	69	24	100/1013	A
8e	83	24	139/1013 (137-138/1013)[11]	A
8f	76	24	108/1013	A

[a] All compounds showed two characteristic ν(NH) absorptions between 3380 and 3250 cm^{-1} in their IR spectra (film). [b] ^1H NMR data (δ) for 8a: 1.60 (s, 2, NH_2), 4.53 ("d", 1, J = 6 Hz, CHN), 5.0-5.5 (m, 2, H_2C=), 5.8-6.4 (m, 1, CH=), 7.4 ("s", 5, C_6H_5). For 8b: 1.45 (s, 2, NH_2), 1.68 ("d", 3, J = 5 Hz, CH_3), 4.4-4.6 (m, 1, CHN), 5.5-5.8 (m, 2, 2CH=), 7.3 ("s", 5, C_6H_5). For 8c: 1.57 (s, 5, CH_3, NH_2), 5.0-5.4 (m, 2, CH_2=), 6.0-6.4 (m, 1, CH=), 7.2-7.6 (m, 5, C_6H_5). For 8d: 1.13 (d, 3, J = 6.5 Hz, CH_3C), 1.45 (s, 2, NH_2), 1.67 ("d", 3, J = 5 Hz, $CH_3C\leqslant$), 3.2-3.7 (m, 1, CHN), 5.3-5.8 (m, 2, 2CH=). For 8e: 1.27 (s, 2, NH_2), 1.3-2.2 (m, 6, $(CH_2)_3$), 3.2-3.6 (m, 1, CHN), 5.72 ("s", 2, 2CH=). For 8f: 1.20 (s, 2, NH_2), 1.60 (d, 3, J = 5 Hz, CH_3), 1.65 (s, 3, CH_3), 3.20 (s, 2, CH_2N), 5.42 ("q", 1, J = 5 Hz, CH=). ^{13}C NMR data (δ) for 8a: 58.3 (d), 113.5 (t), 126.6 (d), 127.0 (d), 128.4 (d), 142.3 (d), 144.4 (s). For 8b: 17.7 (q), 57.8 (d), 124.8 (d), 126.4 (d), 126.8 (d), 128.4 (d), 135.5 (d), 145.2 (s). For 8c: 29.8 (q), 56.4 (s), 110.7 (t), 125.4 (d), 126.4 (d), 128.1 (d), 147.2 (d), 147.6 (s). For 8d: 17.6 (q), 24.1 (q), 49.1 (t), 123.2 (d), 137.7 (d). For 8e: 20.3 (t), 25.1 (t), 33.7 (t), 47.0 (d), 127.9 (d), 132.7 (d). For 8f: 13.1 (q), 14.2 (q), 50.1 (t), 118.0 (d), 137.3 (s). [c] For the conversion 7 → 8.

General Procedure for the Preparation of 2-Alkenylamines 8. A mixture consisting of the corresponding methyl *N*-(2-alkenyl)carbamate 7 (0.1 mol), KOH (28 g, 0.5 mol), 70 mL of methanol, and 50 mL of water is refluxed for the period indicated in Table II. The workup depends on the boiling point of the amine.

Method A (bp <200 °C). The solution is cooled to ambient temperature, acidified with diluted hydrochloric acid, and concentrated on a rotating evaporator at 60 °C. The residue is made alkaline by addition of 30 mL of aqueous KOH, and the resultant emulsion is extracted with ether (2 × 50 mL). Drying of the combined ethereal solutions with anhydrous Na_2SO_4 is followed by fractionated distillation.

Method B (bp >200 °C). Methanol is removed from the mixture on a rotating evaporator at ambient temperature, and the resulting emulsion is extracted with ether (2 × 50 mL). The further workup is analogous to that described for method A. The ketones formed during the preparation of **8a** and **8b** are separated by acidification of the amine/ketone mixture with hydrochloric acid and subsequent evaporation of the ketone under reduced pressure (0.01 mbar) at 50 °C. Yields, physical constants, and spectroscopic data for products 8 are compiled in Table II.

(7) A similar procedure has been previously reported for the preparation of millimolar amounts of 5: Levchenko, E. S.; Balon, Y. G.; Kirsanov, A. V. *Zh. Org. Khim.* **1967**, *3*, 2083.
(8) Foglia, T. A.; Swern, D. *J. Org. Chem.* **1966**, *31*, 3625.

Table III. Yields, Boiling Points, and Spectroscopic Data of Compounds 9[a,b]

compd	yield, %	bp, °C/mbar (lit. bp)
9a	82	80/7
9b	85	77/3
9c	79	74/2
9d	71	106/1013
9e	80	97/180 (44-46/15)[12]
9f	78	115/1013

[a] All compounds displayed a broad IR absorption between 3350 and 3250 cm^{-1} (film). [b] ^1H NMR data (δ) for 9a: 1.33 (br s, 1, NH), 2.38 (s, 3, CH_3N), 4.08 (d, 1, J = 7 Hz, CHN), 5.0-5.4 (m, 2, H_2C=), 5.7-6.3 (m, 1, HC=), 7.3 ("s", 5, C_6H_5). For 9b: 1.27 (br s, 1, NH), 1.6-1.7 (m, 3, CH_3), 2.32 (s, 3, CH_3N), 3.9-4.1 (m, 1, CHN), 5.5-5.8 (m, 2, 2CH=), 7.3 ("s", 5, C_6H_5). For 9c: 1.30 (br s, 1, NH), 1.50 (s, 3, CH_3), 2.25 (s, 3, CH_3N), 5.0-5.4 (m, 2, CH_2=), 5.8-6.3 (m, 1, CH=), 7.2-7.6 (m, 5, C_6H_5). For 9d: 1.00 (br s, 1, NH), 1.10 (d, 3, J = 6.5 Hz, CH_3C), 1.68 ("d", 3, J = 5 Hz, $CH_3C{\leqslant}$), 2.33 (s, 3, CH_3N), 2.8-3.3 (m, 1, CHN), 5.0-5.6 (m, 2, 2HC=). For 9e: 0.93 (br s, 1, NH), 1.3-2.2 (m, 6, $(CH_2)_3$), 2.43 (s, 3, CH_3N), 2.9-3.1 (m, 1, CHN), 5.75 ("s", 2, 2HC=). For 9f: 1.00 (br s, 1, NH), 1.60 (d, 3, J = 5 Hz, CH_3CH), 1.65 (s, 3, $CH_3C{\leqslant}$), 2.38 (s, 3, CH_3N), 3.12 (s, 2, CH_2N), 5.2-5.7 (m, 1, CH=). ^{13}C NMR data (δ) for 9a: 34.3 (q), 68.1 (d), 114.8 (t), 127.0 (d), 127.2 (d), 128.4 (d), 140.8 (d), 142.5 (s). For 9b: 17.7 (q), 34.3 (q), 67.5 (d), 126.0 (d), 126.9 (d), 127.1 (d), 128.4 (d), 134.2 (d), 143.5 (d). For 9c: 25.1 (q), 29.5 (q), 60.6 (s), 112.9 (t), 126.3 (d), 126.5 (d), 128.0 (d), 144.6 (d), 146.0 (s). For 9d: 17.7 (q), 21.8 (q), 34.0 (q), 57.8 (t), 125.3 (d), 135.5 (d). For 9e: 20.3 (t), 25.5 (t), 29.2 (t), 33.6 (q), 54.7 (d), 128.6 (d), 129.9 (d). For 9f: 13.2 (q), 14.4 (q), 35.8 (q), 60.1 (t), 120.2 (d), 134.3 (s).

Conversion of 7a into 8a by Iodotrimethylsilane. A solution of **7a** (6.5 g, 33 mmol), sodium iodide (14.0 g, 93 mmol), and iodotrimethylsilane (7.7 g, 71 mmol) in 70 mL of CH_3CN is refluxed under anhydrous conditions for 24 h. Thereupon, the mixture is chilled and acidified with 6 mL of concentrated hydrochloric acid. Volatile material is then removed on a rotating evaporator at ambient temperature. After being made alkaline with aqueous potassium hydroxide, the resultant emulsion is extracted with ether (3 × 50 mL). The combined ethereal extracts are washed successively with $Na_2S_2O_3$ solution and water, dried over anhydrous Na_2SO_4, and finally concentrated in vacuo. The product is purified by distillation to yield 3.6 g (81%).

General Procedure for the Preparation of 2-Alkenylmethylamines 9. A solution of the corresponding **7** (0.1 mol) in 75 mL of dry ether is slowly added to a stirred suspension of $LiAlH_4$ (5.7 g, 0.15 mol) in 150 mL of ether. After completion of addition the mixture is refluxed for 4 h. Thereupon, excess $LiAlH_4$ is carefully quenched with water (quenching with ethyl acetate would afford a tertiary amine[9]), followed by filtration of the resultant inorganic salts. The filtrate is dried over anhydrous Na_2SO_4 and fractionated by distillation. Yields, physical constants, and spectroscopic data for products **9** are given in Table III. All compounds **7-9** gave satisfactory combustion analytical data.

Methyl *N*-(1-Phenyl-1-propenyl)carbamate (10a). Compound **7a** (3.0 g, 16 mmol), KO-*t*-Bu (2.5 g, 22 mmol), and catalytic amounts of dibenzo-18-crown-6 in 50 mL of dry ether are stirred for 60 h at ambient temperature. Thereupon, undissolved material is collected by filtration, and the filter cake is suspended in 50 mL of ether and dissolved by addition of 50 mL of water. The organic layer is rapidly separated, washed with water (3 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo (15 mbar). The residue is recrystallized from CH_2Cl_2/pentane (1:4) to yield 1.9 g (63%) of white needles: mp 72 °C; ^1H NMR ($CDCl_3$) δ 1.78 (d, 3, J = 7 Hz, CH_3CH), 3.67 (s, 3, CH_3O), 5.85 (q, 1, J = 7 Hz, CH=), 6.2 (br s, 1, NH), 7.2-7.7 (m, 5, C_6H_5). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.96; H, 6.98; N, 6.97.

Methyl *N*-(1-phenyl-1-butenyl)carbamate (10b) was obtained from **7b** (1.7 g, 8.3 mmol), potassium *tert*-butoxide (3.0 g, 27 mmol), and dibenzo-18-crown-6 in 40 mL of dry ether as described for **10a**. In this case, however, not the filter cake but the filtrate is subjected to further workup: yield 0.9 g (53%); mp 43 °C; ^1H NMR ($CDCl_3$) δ 1.08 (t, 3, J = 7 Hz, CH_3CH_2), 2.23 (quint, 2, J = 7 Hz, CH_2), 3.70 (s, 3, CH_3O), 5.73 (t, 1, J = 7 Hz, CH=), 7.2-7.6 (m, 5, C_6H_5). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.36; N, 6.82. Found: C, 70.05; H, 7.42; N, 6.65.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, Frankfurt am Main. We are grateful to the late Prof. Kwart, Newark, DE, for many helpful discussions about ene reactions and his advice concerning this publication as well as others.

Registry No. **1a**, 300-57-2; **1b**, 1560-06-1; **1c**, 934-10-1; **1d**, 109-68-2; **1e**, 110-83-8; **1f**, 513-35-9; **1g**, 557-93-7; **5**, 16762-82-6; **7a**, 86766-60-1; **7b**, 86766-61-2; **7c**, 86766-62-3; **7d**, 86766-63-4; **7e**, 86766-64-5; **7f**, 86766-65-6; **7g**, 86766-66-7; **8a**, 4393-21-9; **8b**, 4393-18-4; **8c**, 86766-67-8; **8d**, 86766-68-9; **8e**, 1541-25-9; **8f**, 86766-69-0; **9a**, 86766-70-3; **9b**, 86766-71-4; **9c**, 86766-72-5; **9d**, 86766-73-6; **9e**, 86766-74-7; **9f**, 86766-75-8; **10a**, 86766-76-9; **10b**, 86766-77-0; SCl_2, 10545-99-0; methyl *N*,*N*-dichlorocarbamate, 16487-46-0; iodotrimethylsilane, 16029-98-4.

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Identification of Configurational Isomers of Fluorochloridone

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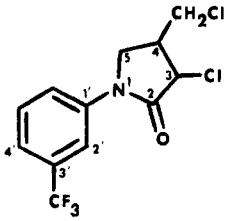
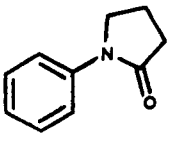
Received January 31, 1983

The experimental herbicide Fluorochloridone[1] (3-chloro-4-(chloromethyl)-1-[3-(trifluoromethyl)phenyl]-2-pyrrolidinone) was reported[2] to reduce chlorophyll production in corn. This compound can exist as both a cis and a trans isomer. These isomers were separated, and the configuration of each isomer was determined. Initial structural assignments were unsuccessful due to ambiguous results obtained in ^1H and ^{13}C NMR studies. X-ray crystallographic studies of the major isomer (**1a**) subsequently allowed its assignment as the trans isomer.



1a (trans)
1b (cis)



2

Proton NMR. The proton NMR parameters for **1a** and **1b** are listed in Table I. The chloromethyl group of **1a** exhibited a doublet with a coupling constant of 5.4 Hz whereas that of **1b** exhibited a multiplet. The ring proton H3 of **1a** showed a doublet at 4.48 ppm with a coupling constant of 8.82 Hz and that of **1b** a double at 4.55 ppm

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