calomel electrode. Proton nuclear magnetic resonance spectra were recorded on a Bruker WP-80 instrument in deuteriochloroform solution. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane.

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(14) Table I, footnote *d*.

Stereochemical Control of the Ynamine–Claisen Rearrangement

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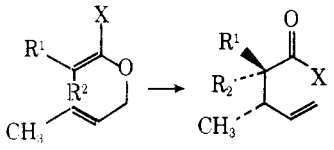
The Claisen rearrangement of carboxylic acid derivatives, proceeding via the ketene acetal tautomers **1**, has gained prominence as a means of introducing adjacent chiral centers in acyclic compounds in a stereoselective manner.[1] For example, the condensation of crotyl alcohol with 1-(diethylamino)-1-ethoxypropene[2] in refluxing xylene affords predominantly the erythro rearrangement product **2a** via the (*Z*)-ketene *N,O*-acetal **1a** in a reaction first developed by



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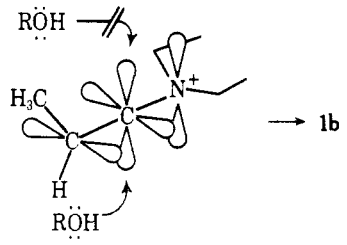
a, $R^1 = H$, $R^2 = CH_3$, $X = NEt_2$; b, $R^1 = CH_3$, $R^2 = H$, $X = NEt_2$; c, $R^1 = H$, $R^2 = CH_3$, $X = OSiR_3$; d, $R^1 = CH_3$, $R^2 = H$, $X = OSiR_3$

Eschenmoser.[3] In a more general procedure, Ireland has shown that either the *E* (**1c**) or *Z* (**1d**) enol trialkylsilyl ethers of allylic esters can be generated selectively as desired, giving the erythro (**2c**) or threo (**2d**) rearrangement products, respectively.[4] The condensation of crotyl alcohol with 1-(diethylamino)propyne also leads to a ketene *N,O*-acetal, and to a rearranged product;[5] however, a study of the stereochemistry of this reaction has not been reported.

A reasonable step in the ynamine–Claisen rearrangement is the addition of the alcohol (or alkoxide) to the keteniminium intermediate **3**. Because the alcohol must approach this intermediate in the plane of the carbon–carbon double bond, we reasoned that steric interference by the methyl group would favor formation of the (*E*)-ketene *N,O*-acetal **1b**, as



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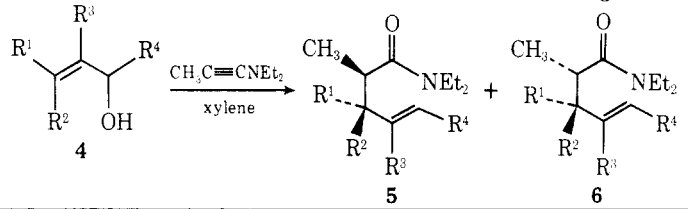
depicted. Rearrangement of this kinetically formed *E* isomer to the threo product **2b** would be a useful complement to the Eschenmoser procedure.

The reaction of crotyl alcohol with 1-(diethylamino)propyne at room temperature in benzene with catalysis by boron trifluoride etherate gives a better than 20:1 ratio of stereoisomeric products, favoring the *same* isomer (**2a**) as does the Eschenmoser reaction. Apparently, in the presence of a Lewis acid, equilibration of the initially formed adduct to the thermodynamically favored *Z* stereoisomer (**1a**) takes place before rearrangement. Similar high stereoselectivity is observed with a variety of allylic alcohols, as shown in Table I.[6]

On the other hand, equilibration of the ketene *N,O*-acetals can be avoided, and rearranged products arising from the *E* isomer (e.g., **1b**) can be obtained by adding the alcohol slowly to a refluxing solution of the ynamine in xylene. Under these conditions, in the absence of acid and with a low concentration of alcohol at all times, equilibration is slowed and rearrangement occurs predominantly via the kinetically formed (*E*)-ketene *N,O*-acetal. This reversal of stereoselectivity with choice of rearrangement conditions is observed for all of the acyclic allylic alcohols examined (see Table I). Moreover, in some instances the stereoselectivity of the uncatalyzed, thermal rearrangement is quite good. Poorer stereoselectivity is observed if the alcohol is added to the ynamine all at once, suggesting that isomerization may be proceeding via the amide acetal (by addition, then elimination, of a second molecule of alcohol).

2-Cyclohexenol reacts with the ynamine in refluxing xylene to give a 10:1 ratio of rearranged products **7** and **8** in 64% yield. The BF_3-catalyzed reaction results in dehydration only;[5] however, the condensation of this alcohol with 1-ethoxy-1-(diethylamino)propene affords a 50:50 mixture of **7** and **8**. The fact that the (*Z*)-ketene *N,O*-acetal, formed in the latter reaction, leads to a mixture of products while the intermediate in the neutral ynamine reaction gives essentially a single isomer is further confirmation that this intermediate has the *E* geometry. The major isomer formed in the ynamine–Claisen rearrangement is **7**, and it must arise via a boat-like transition state. The rearrangement of the (*E*)-ketene *N,O*-acetal may

Table I. Stereocontrol of the Ynamine–Claisen Rearrangement



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entry	R^1	R^2	R^3	R^4	ratio[a] of **5/6** (yield,[b] %) catalyzed by BF_3-Et_2O, 25 °C	ratio[a] of **5/6** (yield,[b] %) slow addition of alcohol, 140 °C
a	CH_3	H	H	H	1:20 (44)	2:1 (62)
b	H	CH_3	H	H	1:5 (37)	2.5:1 (74)
c	CH_3	H	CH_3	H	1:10 (50)	10:1 (56)
d	CH_3	H	H	CH_3	1:3 (19)	4:1 (38)
e	Ph	H	H	H	1:10 (60)	2:1 (61)

[a] Lower limit, determined by ^{13}C NMR. [b] Isolated yield of distilled material.

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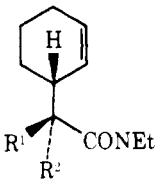

7, $R^1 = CH_3$; $R^2 = H$
8, $R^1 = H$; $R^2 = CH_3$

indeed be stereospecific since a small amount of the (*Z*)-ketene *N,O*-acetal may be responsible for the traces of **8** observed. The proof of the stereochemistry of **7** and **8**, along with further stereochemical studies of the Claisen rearrangements of cyclohexenyl systems, will be presented elsewhere.[8]

Experimental Section

1-(Diethylamino)propyne was purchased from Tridom-Fluka and used as obtained. The allylic alcohols were prepared by standard routes or obtained commercially. All of the alcohols, reaction solvents, and reagents were distilled. All new compounds gave satisfactory combustion analyses (C, ±0.36%, H, ±0.17%, N, ±0.18%) after purification by preparative VPC (SE-30). Representative procedures are given for both of the reaction conditions.

***erythro-N,N*-Diethyl-2,3-dimethyl-4-pentenamide (2a) (BF_3-Catalyzed Addition).** To a solution of 0.38 g (5.2 mmol) of *trans*-crotyl alcohol and 0.67 g (6.0 mmol) of 1-(diethylamino)propyne in 5 mL of benzene was added two drops of BF_3 etherate, with stirring, and the mixture was kept at 25 °C. After 4 days, the mixture was washed with 1 N HCl, dried (Na_2CO_3), concentrated, and chromatographed (silica gel; eluted with ether/hexane, 70:30) to give 0.42 g (44% yield) of the rearranged amide **2a**: ^1H NMR δ 0.85–1.35 (m, 12), 2.5 (m, 2), 3.4 (two q, 4), 5.0–5.6 (m, 3, vinyl); ^{13}C NMR δ 12.8, 14.7, 16.4, 18.7 ($-CH_3$), 40.3, 40.5, 41.7, 41.8 (>CH– and $-CH_2-$), 114.9 ($=CH_2$), 141.8 (=CH–), 175.1 (C=O); IR (film) 1635 cm^{-1} (C=O).

***threo-N,N*-Diethyl-2,3-dimethyl-4-pentenamide (2b) (Uncatalyzed Reaction).** A solution of 0.32 g (4.5 mmol) of *trans*-crotyl alcohol in 7 mL of xylene was added by syringe pump to a refluxing solution of 0.64 g (5.8 mmol) of 1-(diethylamino)propyne in 25 mL of xylene over 18 h. After another day at reflux, the mixture was cooled, washed with 1 N HCl, and dried (Na_2CO_3), and the xylene was removed by distillation. The crude product was chromatographed (silica gel; eluted with ether/hexane, 70:30) to give 0.51 g (62% yield) of the amides **2a** and **2b** as a 1:2 mixture: ^{13}C NMR (major isomer) δ 12.5, 14.4, 14.8, 15.7 ($-CH_3$), 40.1, 40.4, 41.5, 41.6 (>CH– and $-CH_2-$), 113.2 ($=CH_2$), 141.8 (=CH–), 174.6 (C=O).

***erythro-N,N*-Diethyl-2-(2-cyclohexenyl)propionamide (7).** A solution of 2.0 g (20 mmol) of 2-cyclohexenol in 5 mL of xylene was added by syringe pump to a refluxing solution of 2.26 g (20 mmol) of 1-(diethylamino)propyne in 45 mL of xylene over a period of 20 h. After 2 h more, the xylene was evaporated at reduced pressure and 2.6 g (62% yield) of rearranged amide **7** was isolated by bulb-to-bulb distillation (~60 °C (0.02 torr)): ^1H NMR δ 1.0–1.4 (m, 9), 1.5–2.2 (m, 5), 2.3–2.6 (m, 3), 3.05–3.65 (m, 4), 5.3–5.8 (m, 2); ^{13}C NMR δ 12.7, 14.5, 15.2 ($-CH_3$), 21.0, 24.85, 25.8, 38.2, 40.1, 40.2, 41.7 ($-CH_2-$ and >CH–), 127.4, 129.7 (=CH–), 175.05 (C=O). Minor peaks in the ^{13}C NMR spectrum at δ 25.0, 27.4, 38.1, 39.8, 128.1, and 128.4 were due to isomer **8**, as shown by ^{13}C NMR of a 50:50 mixture of **7** and **8** produced on condensation of 2-cyclohexenol with 1-ethoxy-1-(diethylamino)-propene.[8]

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Registry No.—**4a**, 504-61-0; **4b**, 4088-60-2; **4c**, 497-02-9; **4d**, 3899-34-1; **4e**, 4407-36-7; **5a**, 68813-19-4; **5b**, 68813-20-7; **5c**, 68813-21-8; **5d**, 68813-22-9; **5e**, 68813-23-0; **6c**, 68813-24-1; **6d**, 68813-25-2; **6e**, 68813-26-3; **7**, 68813-27-4; **8**, 68813-28-5; 1-(diethylamino)propyne, 4231-35-0; 2-cyclohexenol, 822-67-3.

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(7) Cf. M. Barbieux and R. H. Martin, *Tetrahedron Lett.*, 2919 (1965).
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Curtius Conversion of Acids to Amines under Neutral Conditions via an Anthrylmethyl Carbamate

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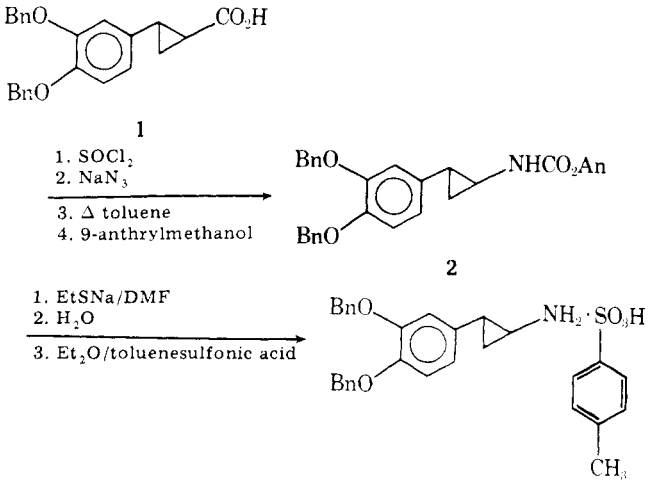
In the course of our synthesis of certain phenylcyclopropylamine systems,[1] it became necessary to develop a method for converting an acid function to an amine[2] under neutral conditions.[3] In addition, the desire to retain benzyl ether functionality precluded typical catalytic hydrogenolysis of a benzylcarbamate intermediate. Recently, 9-anthrylmethoxycarbonyl has been described as a protecting group for amines.[4] Although stable to various acids and bases, this group



Bn = benzyl, An = 9-anthrylmethyl

can be efficiently removed by treatment with the sodium salt of methyl mercaptan under neutral conditions. Thus, owing to the unique electrophilic character of the 9-anthrylmethyl group,[5] this intermediate was exploited in the Curtius conversion of the benzyl ether containing cyclopropyl acid **1** to its amine **3** in approximately 50% overall yield. This approach to the Curtius conversion should be of general utility for systems which cannot tolerate acidic media and possess additional functionality susceptible to catalytic hydrogenolysis.

The use of ethanethiol, rather than methanethiol,[4] does not

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