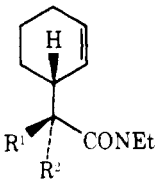

7, $R^1 = CH_3$; $R^2 = H$
8, $R^1 = H$; $R^2 = CH_3$

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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Curtius Conversion of Acids to Amines under Neutral Conditions via an Anthrylmethyl Carbamate

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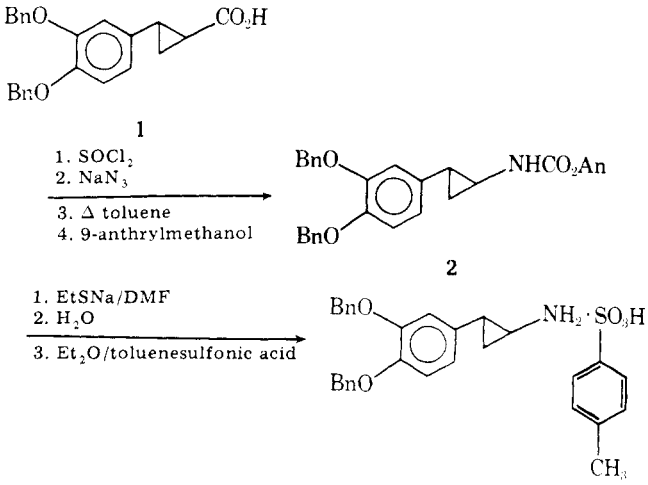
In the course of our synthesis of certain phenylcyclopropylamine systems,[1] it became necessary to develop a method for converting an acid function to an amine[2] under neutral conditions.[3] In addition, the desire to retain benzyl ether functionality precluded typical catalytic hydrogenolysis of a 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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appear to alter the selectivity for preferential attack of the anthryl system and allows for more convenient in situ generation of the nucleophilic species.[6] Similarly, the use of diphenylphosphoryl azide[7] in the conversion of acid **1** to carbamate **2** simplifies the procedure, but in this case, yields of carbamate are slightly lowered (~50%).

Experimental Section[8]

9'-Anthrylmethyl (±)-(*E*)-2-(3,4-Dibenzyloxyphenyl)cyclopropylcarbamate (2). A solution of 3.0 g (0.008 mol) of acid **1** in 15 mL of toluene and 15 mL of thionyl chloride was stirred at room temperature for 4 h. The reaction medium was then evaporated under reduced pressure leaving the acid chloride as an oil (IR γ_{max} 1775 cm^{-1}). The oil was taken up in 30 mL of acetone, cooled to 0–2 °C, and treated dropwise with 3 g (0.046 mol) of sodium azide in 15 mL of water. After the addition, the mixture was stirred for 1 h gradually attaining room temperature and then 25 mL of water was added and the mixture extracted with toluene (2 × 70 mL). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure leaving the acyl azide as an oil. The oil was taken up in toluene and maintained at ~90 °C until bubbling ceased (1–4 h) and an IR indicated absence of the characteristic acyl azide absorptions (2140 and 1705 cm^{-1}). 9-Anthracenemethanol (1.7 g, 0.008 mol) was then added and heating at ~90 °C continued (24–48 h) until an IR indicated absence of the isocyanate absorption (2280 cm^{-1}) and maximal carbamate carbonyl absorption (1700 cm^{-1}). As the mixture attained room temperature, yellow crystals were produced which were collected and recrystallized from toluene to finally provide 2.9 g (64%) of yellow crystals: mp 166–167 °C; IR (KBr disk) 1680 cm^{-1}; NMR ($CDCl_3$) δ 6.1 (S, 3, $-CH_2An$ and $-NHCO_2-$ the latter of which disappears upon addition of CD_3OD and Et_3N). Anal. Calcd for $C_{39}H_{33}NO_4$: C, 80.80; H, 5.74; N, 2.42. Found: C, 80.54; H, 5.77; N, 2.34.

(±)-(*E*)-2-(3,4-Dibenzyloxyphenyl)cyclopropylamine Tosylate (3). To a mixture of 0.13 g (0.003 mol) of 57% sodium hydride in 5 mL of DMF under N_2 at room temperature was added 0.22 mL (0.003 mol) of ethanethiol in 1 mL of DMF. When the solution was clear (~15 min), 1.45 g (0.0025 mol) of carbamate **2** in 20 mL of DMF was added quickly via syringe. The resulting red-colored solution was stirred for 30 min and then dumped into 100 mL of water/25 mL of crushed ice. The resulting milky suspension was extracted with ether (3 × 100 mL), adding potassium carbonate to the aqueous phase during the first extraction. The combined ethereal extracts were washed with water (2 × 50 mL), dried over K_2CO_3, and concentrated to ~50 mL. To this phase was then added 0.475 g (0.0025 mol) of *p*-toluenesulfonic acid monohydrate dissolved in 25 mL of ether. Yellow crystals were obtained after standing at room temperature. Recrystallization was effected from ethanol–ether (1:1) and provided 0.95 g (74%) of yellow crystals: mp 163–164 °C; NMR ($CDCl_3$) δ 8.1 (broad S, 3, $-NH_3^+$, disappears upon addition of CD_3OD). Anal. Calcd for $C_{30}H_{31}NO_5S$: C, 69.63; H, 6.00; N, 2.71. Found: C, 69.83; H, 6.36; N, 2.62.

Registry No.—**1**, 68708-15-6; **2**, 68708-16-7; **3**, 68708-18-9; 9-anthracenemethanol, 1468-95-7.

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Selective Monomer/Dimer Formation in a Many-Membered Crown Ether Lactone Synthesis

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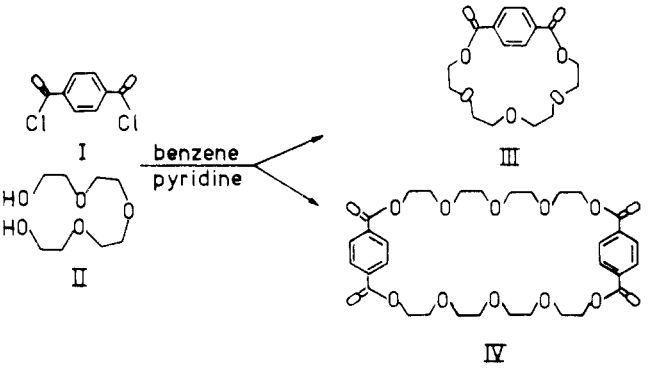
The existence of the monomeric terephthalic acid ester III,[1] which we synthesized in 1977, was recently questioned[2] since its melting point was similar to that of the dimeric tetralactone IV. In this communication, we give unequivocal



proof of the existence of both cycles and describe their syntheses in detail.

Reaction of terephthalic acid dichloride I with tetraethylene glycol II under high dilution conditions gave, in contrast to other reports,[2] the monomeric lactone III as well as the dimeric cyclic ester IV. The monomer/dimer ratio may be influenced by variation of the reaction conditions; reaction in more concentrated solution yields only the dimeric ester IV apart from polycondensed material, while more diluted conditions lead to the monomer ester III as main product besides polymeric material and some dimer product.

It is, in fact, a peculiarity of these cyclic compounds that the melting point of dimer IV (96 °C) is almost identical with that of monomer III (98–99 °C). While III forms large, colorless crystals (*n*-heptane/petroleum ether), IV always crystallized as a colorless powder (*n*-heptane).

By osmometric molecular weight determination we found a molecular weight of 632 for the dimer IV and 322 for the monomer III. Mass spectra show molecular ion peaks M^+ at *m/e* 648 for the dimer and at *m/e* 324 for the monomer. High-resolution mass spectra confirm the molecular formulas $C_{32}H_{40}O_{14}$ and $C_{16}H_{20}O_7$, respectively. The ^1H NMR spectra of III and IV (Figure 1) are significantly different. While the spectrum of the dimer shows a splitting into two multiplets and one singlet for the CH_2 protons lying α,β and γ,δ to the ester oxygen (α, 4.5 ppm; β, 3.8 ppm; γ, 3.65 ppm), the signals due to the γ- and δ-CH_2 protons of the monomer are further split so that a total of four multiplets results: α, 4.5 ppm; β, 3.65 ppm; γ, 3.35 ppm; δ, 2.85 ppm. The strong highfield shift of the bridge protons clearly indicates the presence of the *monomeric* ester since the γ and δ protons come close to the aromatic nucleus and are, therefore, expected to show signals at higher field strength as is known for other paracyclophanes.[3,4]

The ligand IV yields a 1:2 complex with NaSCN, mp 174–176.5 °C, formerly ascribed to III.[1] With pure III, only unstoichiometric salt-containing material could be isolated up to now.

Experimental Section

Melting points were taken on a Kofler Mikroskopheiztisch and are uncorrected. NMR spectra were recorded on a Bruker EM-390

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