(95% EtOH) λ_{max} 228 nm (log ϵ 4.44), 261 (4.37), 291 (3.91), 434 (4.04); high-resolution mass spectral mol wt calcd for $C_{20}H_{14}O_5$ 334.0841, found 334.0837.

2-Acetyl-2-acetoxy-5,7-dihydroxy-1*H*-3,4-dihydronaphthacene-6,11-dione (7,11-Dideoxy-9-*O*-acetylcarminomycinone, 20). To a solution of acetylenic alcohol **19** (0.100 g, 0.30 mmol) in ethyl acetate (180 mL) was added mercuric acetate (1.00 g, 3.10 mmol). The resulting orange suspension was stirred overnight under nitrogen. Hydrogen sulfide gas was then bubbled through the mixture for 7 min, with formation of a black precipitate which was removed by filtration through Celite. The filtrate was washed sequentially with saturated sodium bicarbonate solution, water, and brine, dried over Na_2SO_4, and concentrated by rotary evaporation. Preparative layer chromatography (elution with 3% methanol–dichloromethane) gave acetate **20**: 0.103 g (85%); mp 238–240 °C (from pentane-chloroform); orange powder; ^{1}H NMR (FT-100, $CDCl_3$) δ 2.06 (s, 3 H), 2.14–2.39 (m, 2 H), 2.20 (s, 3 H), 2.94 (m, 2 H), 3.21 (AB q, 1 H, J = 18 Hz), 3.49 (AB q, 1 H, J = 18 Hz), 7.29 (dd, 1 H, J = 7, 2 Hz), 7.60 (s, 1 H), 7.67 (t, 1 H, J = 7 Hz), 7.83 (dd, 1 H, J = 7, 2 Hz), 12.10 (s, 1 H), 12.48 (s, 1 H); IR (CH_2Cl_2) 3050, 1740, 1725, 1670, 1625, 1260 cm^{-1}; mass spectrum, *m/e* (relative intensity) 394 ($M^{+}\cdot$), 334 (100), 309, 291; UV (95% EtOH) λ_{max} 228 nm (log ϵ 4.50), 261 (4.42), 290 (3.94), 432 (4.06).

(±)-11-Deoxycarminomycinone (22). Nitrogen was bubbled through a mixture of acetate **20** (0.025 g, 0.065 mmol) in carbon tetrachloride (100 mL) for 15 min. After the solution had been heated to reflux, bromine (0.1 M in CCl_4, 1.0 mL, 1.0 mmol) and 2,2′-azobis(2-methylpropionitrile) (AIBN, 0.003 g) were added, and the solution was heated at reflux under nitrogen flow for 20 min. When analytical TLC (SiO_2, 3% methanol–dichloromethane) showed the presence of starting material, additional aliquots of bromine solution (1.0 mL) and AIBN (0.003 g) were added, and reflux was continued for 20 min. The mixture was then washed with sodium bisulfite solution and brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The residue was stirred with THF (25 mL) and saturated sodium bicarbonate solution (25 mL) for 1 h. After acidification with oxalic acid, the aqueous layer was extracted twice with chloroform, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. Preparative layer chromatography of the residue (SiO_2, 3% methanol–dichloromethane) gave 9-*O*-acetyl-11-deoxycarminomycinone (**21**; 0.010 g, 38%) plus a mixture of **21** and the 7-epi isomer (0.005 g). Spectra data for **21**: ^{1}H NMR (FT-400, $CDCl_3$) δ 2.03 (s, 3 H), 2.25 (s, 3 H), 2.34 (dd, 1 H, J = 15, 6.4 Hz), 2.86 (dt, 1 H, J = 15, 2 Hz), 3.11 (d, 1 H, J = 18 Hz), 3.16 (d, 1 H, J = 4.4 Hz), 3.29 (dd, 1 H, J = 18, 2 Hz), 5.28 (m, 1 H, $\upsilon_{1/2}$ = 14 Hz), 7.33 (dd, 1 H, J = 8, 1.5 Hz), 7.66 (s, 1 H), 7.76 (t, 1 H, J = 8 Hz), 7.85 (dd, 1 H, J = 8, 1.5 Hz), 12.02 (s, 1 H), 12.77 (s, 1 H); mass spectrum, *m/e* (relative intensity) 350, 332 (100), 317, 289, 279 (no $M^{+}\cdot$).

To a solution of acetate **21** (0.010 g, 0.024 mmol) in methanol (35 mL) under nitrogen was added saturated aqueous potassium carbonate solution (0.3 mL). After 2 h at 25 °C, the red solution was acidified with aqueous oxalic acid and partitioned between water and chloroform. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated by rotary evaporation. Preparative layer chromatography of the combined reaction mixtures (from 0.015 g of **21**; 3.5% methanol–dichloromethane) gave (±)-11-deoxycarminomycinone (**22**; 0.005 g, 37%) along with an unidentified yellow solid (0.006 g). Spectral data for **22**: ^{1}H NMR (FT-400, $CDCl_3$) δ 2.21 (dd, 1 H, J = 14, 5 Hz), 2.38 (dt, 1 H, J = 14, 2 Hz), 2.43 (s, 3 H), 3.02 (dd, 1 H, J = 20, 2 Hz), 3.29 (d, 1 H, J = 20 Hz), 3.65 (m, 1 H), 4.59 (s, 1 H), 5.36 (br t, 1 H, $\upsilon_{1/2}$ = 12 Hz), 7.32 (d, 1 H, J = 8 Hz), 7.67 (s, 1 H), 7.71 (t, 1 H, J = 8 Hz), 7.85 (d, 1 H, J = 8 Hz), 12.04 (s, 1 H), 12.75 (s, 1 H); IR (KBr) 1710, 1675, 1625, 1280 cm^{-1}; mass spectrum, *m/e* (relative intensity) 368 ($M^{+}\cdot$), 350, 332, 307 (100), 279; UV (95% EtOH) λ_{max} 228 nm (log ϵ 4.33), 259 (4.15), 286 (3.76), 433 (3.80); high-resolution mass spectral mol wt calcd for $C_{20}H_{16}O_7$ 368.0896, found 368.0908.

Acknowledgment. We are grateful to Professor Federico Arcamone (Farmitalia Carlo-Erba) and to Dr. Jean-Pierre Gesson (University of Poitiers) for providing valuable references samples and thank Mr. J. Rizzi for helpful discussions. Partial support of this work by Grant CA 11326 from the National Cancer Institute, USPHS, is grateful acknowledged.

Registry No. **4**, 32940-15-1; **5**, 32940-19-5; **7**, 77305-93-2; **8**, 77305-94-3; **9**, 77305-95-4; **10**, 77305-96-5; **11**, 77305-97-6; **12**, 77305-98-7; **13**, 77305-99-8; (±)-**14**, 77306-00-4; **15**, 77306-01-5; **16**, 77306-02-6; **17**, 77306-03-7; **18**, 77219-83-1; (±)-**19**, 77306-04-8; (±)-**20**, 77306-05-9; (±)-**21**, 77306-06-0; (±)-**22**, 77397-59-2.

Formation of Olefins in the Pyrolysis of N,N-Disubstituted Carbamates[1]

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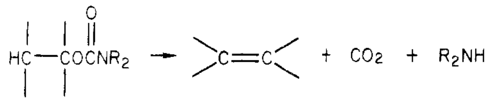
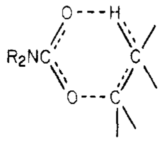
Received October 7, 1980

N,N-Disubstituted carbamates have been shown[2-8] to give alkenes, amine, and carbon dioxide upon heating.



Kinetic studies[3b,4,6-8] indicate first-order decomposition of such carbamates and support a concerted mechanism with a transition state such as that given below. This mechanism predicts a stereospecific syn elimination and the exclusive formation of terminal olefins from carbamates of primary alcohols. We have confirmed these predictions in the pyrolysis of *N,N*-dimethyl- and *N,N*-diphenylcarbamates. We have also established reaction conditions appropriate for the utilization of this reaction in the synthesis of olefins.



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[1] This work was supported by National Science Foundation Grant GY-5578 and by a grant from the Research and Scholarly Development Committee of Grand Valley State Colleges.

[2] A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, 31, 688 (1953).

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[4] E. Dyer and R. E. Read, *J. Org. Chem.*, **26**, 4388 (1961).

[5] E. Dyer and R. J. Hammond, *J. Polym. Sci.*, **2**, 1 (1964).

[6] (a) N. J. Daly and F. Ziolkowski, *Aust. J. Chem.*, **24**, 2541 (1971); (b) N. J. Daly and F. Ziolkowski, *J. Chem. Soc., Chem. Commun.*, 911 (1972); (c) N. J. Daly, G. M. Heweston, and F. Ziolkowski, *Aust. J. Chem.*, **26**, 1259 (1973).

[7] (a) H. Kwart and J. Slutsky, *J. Chem. Soc., Chem. Commun.*, 552 (1972); H. Kwart and J. Slutsky, *ibid.*, 1182 (1972).

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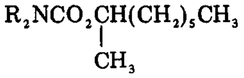
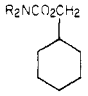
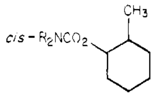
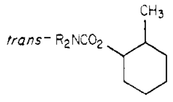
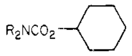
Table I. Synthesis of Carbamates from Alcohols and Carbamyl Chlorides

product[a]		% yield[b]	bp, °C (mmHg)	mp, °C
$R_2NCO_2(CH_2)_7CH_3$	**1a**, R = Me	86	124-125 (14)	
	1b, R = Ph	80		39.5-41
 $R_2NCO_2CH(CH_2)_5CH_3$ with CH_3	**2a**, R = Me	73	121-124 (18)	
	2b, R = Ph	75	159-163 (0.2)	
	**3a**, R = Me	85	126 (12)	
	3b, R = Ph	76		119-120
	**4a**, R = Me	55	121-122 (13)	
	4b, R = Ph	62		79-80
	**5a**, R = Me	76	119 (22)	
	5b, R = Ph	64		104.5-105.5
	**6a**, R = Me	60	104-106 (13)	
	6b, R = Ph	88[c]		126.5-127

[a] All compounds gave satisfactory elemental analyses except **2b** which was a heat-sensitive liquid which could not be purified for analysis. Its structure is supported by the following spectral data: IR (neat) 1705 cm^{-1}; NMR (CCl_4) δ 0.88 (m, CH_3), 1.18 (s, CH_3CO), 1.05-1.7 (br, $(CH_2)_5$), 4.85 (m, CHO), 7.20 (s, C_6H_5). [b] Based upon alcohol except **6b**. [c] Based upon carbamyl chloride.

Table II. Pyrolysis of Carbamates

carbamate	pyrolysis temp, °C	N_2 flow rate, mL/min	olefin yield, %	products (% yield)
1a	375	3	48	1-octene (>99)
1b	420	8	81	1-octene (>99)
2a	380	6	80	1-octene (47), *cis*-2-octene (23), *trans*-2-octene (30)
2b	440	8	82	1-octene (49), *cis*-2-octene (14), *trans*-2-octene (37)
3a	370[a]	25	80	methylenecyclohexane (99.7)
3b	400	8	49	methylenecyclohexane (98)
4a	320[a]	25	75	3-methylcyclohexene (>99)
4b	375	8	92	3-methylcyclohexene (>99)
5a	480	8	96	1-methylcyclohexene (55), 3-methylcyclohexene (45)
5b	390	8	69	1-methylcyclohexene (55), 3-methylcyclohexene (45)
6a	500	6	80	cyclohexene
6b	400	8	96	cyclohexene

[a] Recycled.

Carbamates were synthesized in good yield by the reaction of alcohols with *N*,*N*-dimethylcarbamyl chloride or *N*,*N*-diphenylcarbamyl chloride in refluxing pyridine. Results are summarized in Table I.

$$R_2NC(O)Cl + R'OH \xrightarrow{\text{pyridine}} R_2NCO_2R'$$

$$R = Me, Ph$$

Pyrolyses were accomplished by introducing the carbamate under a slow stream of nitrogen to a tube packed with glass helices heated in a tube furnace. Furnace temperatures of 375–480 °C with nitrogen flow rates of 6–8 mL/min converted most of the carbamates to olefins in good yield. Some of the *N*,*N*-dimethylcarbamates required temperatures greater than 500 °C for complete reaction and under these conditions olefinic products were extensively isomerized. Isomerization could be avoided by employing lower reaction temperatures, but at the expense of lower yields. However, satisfactory yields were obtained at lower temperatures by continuously recycling unreacted carbamate.[9] In general, the *N*,*N*-diphenylcarbamates reacted more readily than the *N*,*N*-dimethylcarbamates, permitting a higher flow rate and/or a lower reaction temperature for the former. Results of pyrolyses are summarized in Table II.

The *N*,*N*-dimethylcarbamates decompose to give olefin, dimethylamine, and carbon dioxide upon heating. The latter two products, however, react to give a carbamate salt.[10] This compound is a liquid at room temperature

$$2(CH_3)_2NH + CO_2 \rightarrow \underset{\mathbf{2}}{(CH_3)_2NCO_2^-H_2N(CH_3)_2^+}$$

and it codistills with olefins. Purification of olefinic products requires treatment with dilute acid followed by drying and distillation. Since diphenylamine does not react with carbon dioxide under the reaction conditions employed, olefins from pyrolysis of *N*,*N*-diphenylcarbamates can be distilled directly from the amine byproduct.

In order to establish the steric requirement for carbamate pyrolysis, we studied the carbamates of *cis*- and *trans*-2-methylcyclohexanol (**4a**, **4b**, **5a**, and **5b**). As expected, the *trans*-carbamates **5a** and **5b** gave two olefins; 1-methylcyclohexene was the predominant product. In the *cis*-carbamates **4a** and **4b**, on the other hand, a syn elimination can give only one product. In fact, both carbamates gave 3-methylcyclohexene exclusively. Since a cyclic transition state requires a syn elimination, these results

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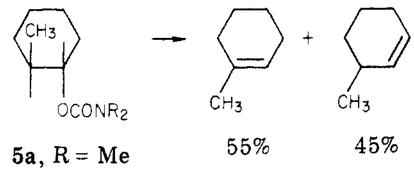
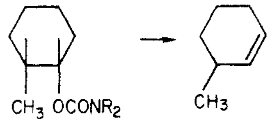
(9) See K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovic, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

(10) F. Fichter and B. Becker, *Chem. Ber.*, **44**, 3481 (1911).

support the proposed mechanism.

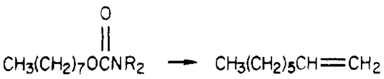


5a, R = Me
b, R = Ph



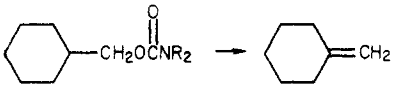
4a, R = Me
b, R = Ph

Further support for a concerted mechanism comes from the observation that carbamates of primary alcohols give terminal olefins of high purity. Thus the 1-octyl carbamates **1a** and **1b** give 1-octene with no trace of isomeric products and the cyclohexylmethyl carbamates **3a** and **3b** give methylenecyclohexane in 98% purity or better. The 2-octyl carbamates **2a** and **2b**, on the other hand, give a mixture of 1-octene and 2-octene, with the latter predominating.



$$CH_3(CH_2)_7O\overset{O}{\overset{\|}{C}}NR_2 \longrightarrow CH_3(CH_2)_5CH{=}CH_2$$

1a, R = Me
b, R = Ph



3a, R = Me
b, R = Ph

Finally, this study shows that carbamate pyrolysis is similar to acetate pyrolysis both in terms of reaction conditions and product distribution[11] and that it is capable of the same degree of selectivity. Since *N*,*N*-dimethylcarbamates react at very nearly the same rate as acetates,[6b] they probably offer no advantage in the synthesis of olefins. *N*,*N*-Diphenylcarbamates, on the other hand, react more readily than acetates and hence can be pyrolyzed at lower temperatures. DePuy and King[11c] state that a pyrolysis temperature of 500–525 °C is most convenient for secondary and tertiary acetates; we employed temperatures of 375–440 °C for *N*,*N*-diphenylcarbamates. These carbamates should thus be preferable to acetates which require high reaction temperatures, and especially to primary acetates which must be recycled for good yields. While 1-octyl acetate is reported[11d] to require two passes at 500–515 °C to give 63.5% of olefin and 1-heptyl acetate gives only a 56% yield of olefin at 540 °C, carbamate **1b** reacts at 420 °C to give an 81% yield of olefin.

Experimental Section

Melting points were obtained on a Büchi melting-point apparatus and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 700 or a Beckman IR8 spectrophotometer. VPC analyses of olefins were performed on a Varian Aerograph 200 using the following columns: 3 ft × 0.25 in. triethylene glycol saturated with $AgNO_3$ on Chromosorb P; 6 ft × 0.25 in. 10% Apiezon P on Chromosorb P; 5 ft × 0.25 in. 20% SE-30 on Chromosorb P. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Carbamates. (a) *N*,*N*-Dimethylcarbamates. A 4–8 M solution of the alcohol in dry pyridine was heated to reflux with a 20% excess of *N*,*N*-dimethylcarbamyl chloride (possible carcinogen, Aldrich). After 22–47 h, ice–water was added and the mixture was extracted with ether. The ether extracts were washed with 2 M HCl and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was distilled at reduced pressure.

(b) *N*,*N*-Diphenylcarbamates. A 4 M solution of the alcohol in dry pyridine was heated to reflux with a 10% excess of *N*,*N*-diphenylcarbamyl chloride (Aldrich). After 16–96 h, a small amount of water was added to hydrolyze excess carbamyl chloride. The mixture was stirred a few minutes, then more water was added, and the mixture was extracted with ether or methylene chloride. The organic layer was dried with anhydrous $MgSO_4$ and decolorized with carbon. After evaporation of the solvent, the product was recrystallized from 95% ethanol.

Pyrolysis of Carbamates. Pyrolyses were performed in a 15 × 400 mm Vycor tube packed with a 350-mm bed of glass helices and heated in a tube furnace. Liquid carbamates were added dropwise to the top of the tube and solid carbamates were added in small portions from a flask connected to the tube with rubber tubing. Two receivers were employed, the first cooled in ice and the second cooled with dry ice. A flow of nitrogen was maintained through the apparatus during the course of the pyrolysis.

For carbamates which required high temperatures for complete reaction, using the procedure above, a recycling apparatus adapted from that of Johnson[9] was employed. In this apparatus the carbamate was heated to boiling in a flask at the bottom of the pyrolysis tube and was swept into the tube by a stream of nitrogen at 25 mL/min. A Vigreux column at the top of the tube separated products from unreacted starting material. The former were collected in cold traps and the latter was returned to the boiling flask through a side arm.

The products from the *N*,*N*-dimethylcarbamates were treated with 2 M HCl followed by removal of the water layer and drying over anhydrous $CaCl_2$. The olefinic products were distilled at reduced pressure. Olefins from the *N*,*N*-diphenylcarbamates were distilled directly from the reaction mixture at reduced pressure.

Products were separated by preparative VPC if necessary and identified by comparison of infrared spectra with those of authentic samples.

Registry No. 1a, 54565-65-0; **1b**, 77287-42-4; **2a**, 77287-43-5; **2b**, 77287-44-6; **3a**, 77287-45-7; **3b**, 77287-46-8; **4a**, 77287-47-9; **4b**, 77287-48-0; **5a**, 77287-49-1; **5b**, 77287-50-4; **6a**, 7541-19-7; **6b**, 77287-51-5; *N*,*N*-dimethylcarbamyl chloride, 79-44-7; *N*,*N*-diphenylcarbamyl chloride, 83-01-2; 1-octanol, 111-87-5; 2-octanol, 123-96-6; cyclohexanemethanol, 100-49-2; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; cyclohexanol, 108-93-0; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; methylenecyclohexane, 1192-37-6; 3-methylcyclohexene, 591-48-0; 1-methylcyclohexene, 591-49-1; cyclohexene, 110-83-8.

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[11] (a) D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, 81, 643 (1959); (b) E. Earl Royals, *J. Org. Chem.*, **23**, 1822 (1958); (c) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960); (d) B. A. Kazanskii, A. L. Liberman, A. F. Plate, M. I. Rosengart, and G. A. Tarasova, *J. Gen. Chem. (USSR)*, 17, 1503 (1947); *Chem. Abstr.*, **42**, 2225 (1948).

Phenyl-Substituted Cyclopropylidenemethyl and 1-Cyclobutenyl Cations in the Gas Phase. Unusual Course of Homopropargyl Rearrangement[1]

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Received December 29, 1980

Whereas the existence of vinyl cations as intermediates in solvolysis reactions or electrophilic additions to allenyl or triple bonds in solution is now well established,[2] related

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[1] Mass spectroscopic investigation of acetylenic compounds. 26. For part 25 see: Wagner, W.; Levsen, K.; Zummack, W.; Schwarz, H. *Org. Mass Spectrom.*, in press.

0022-3263/81/1946-2806$01.25/0