suspension was added a solution of 9.93 g. (0.05 mole) of bromotrichloromethane in 50 ml. of cyclohexene. The suspension was stirred at room temperature for 60 hr. Ice was added, and the organic layer was separated and concentrated. The residual oil was shown by vapor phase chromatography to contain about 1% (based on the amount of bromotrichloromethane consumed) of 7,7-dichlorononcarane (I), identified by comparison of the retention time with that of an authentic sample. The aqueous solution did not give a Prussian blue test for cyanide ion. From the oil was recovered 6.36 g. (64%) of bromotrichloromethane. Some of this starting material was probably lost during the work-up.

Treatment of Chloroamine with Potassium Amide.—To a stirred solution of 0.05 mole of potassium amide in 150 ml. of liquid ammonia was added an ethereal solution of 0.018 mole of chloroamine.[12] The ammonia was allowed to evaporate and water was added. A portion of the aqueous solution was acidified with acetic acid, and benzaldehyde was added. The mixture developed a gray turbidity, but no weighable amount of solid was collected.

Reaction of Chloroform with Potassium Amide.—To a solution of 0.075 mole of potassium amide in 150 ml. of liquid ammonia was added an ethereal solution of 2.25 g. (0.019 mole) of chloroform. A vigorous reaction took place. The ammonia was evaporated, and the residue was dissolved in water. The yield of cyanide ion[10] was 0.017 mole (93%).

(12) G. H. Coleman and C. R. Hauser, *J. Am. Chem. Soc.* **50**, 1193 (1928).

Action of Tertiary Amines and Phosphines upon Alkyl β-Bromopropionylcarbamates

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The recent report of Johnson and Schweitzer[1] concerning the dehydrobromination of alkyl or aryl β-bromopropionylcarbamates and ureas prompts us to disclose some similar results from a synthetic rather than a kinetic approach to the problem.

When β-bromopropionylcarbamates, made by the reaction of alcohols with β-bromopropionyl isocyanate,[2,3] are allowed to react with a variety of tertiary amines, the products (Table I) indicate that the reaction can proceed in two different ways (equations 1 and 2).

$$\mathrm{R'_3\overset{+}{N}CH_2CH_2CONHCOOR,\ Br^-} \quad (1)$$

$$\mathrm{BrCH_2CH_2CONHCOOR + R'_3N} \begin{cases} \uparrow \\ \downarrow \end{cases}$$

$$\mathrm{CH_2{=}CHCONHCOOR + R'_3N{\cdot}HBr} \quad (2)$$

When R is *n*-octadecyl, dried pyridine leads to the quaternary salt (equation 1). Quaternization also takes place in pyridine which has not been specially dried, but under these conditions hydrolysis of the ester group also results (equation 3). With triphenylphosphine and tri-*n*-butylphosphine, the quaternization reaction

$$\mathrm{BrCH_2CH_2CONHCOOR + C_5H_5N \xrightarrow{H_2O} C_5N_5\overset{+}{N}CH_2CH_2CONH_2,\ Br^- + CO_2 + ROH} \quad (3)$$

also takes place. However, in all other cases studied, the elimination reaction (equation 2) predominated as the reasonably high yield of products indicates. The reactions proceed in the same manner when R is ethyl or cholesteryl rather than octadecyl.

TABLE I

RESULTS OF REACTION OF ALKYL β-BROMOPROPIONYLCARBAMATES WITH TERTIARY AMINES AND PHOSPHINES

R	Base	Reaction	Quaternary salt	% Yield acrylylcarbamate	% Yield amine hydrobromide
C_2H_5	C_5H_5N	1	68		
n-$C_{18}H_{37}$	C_5H_5N[a]	1	62		
Cholesteryl	C_5H_5N	3	84[b]		
n-$C_{18}H_{37}$	C_5H_5N	3	76		
n-$C_{18}H_{37}$	$(C_6H_5)_3P$	1	60		
n-$C_{18}H_{37}$	$(n\text{-}C_4H_9)_3P$	1	42		
n-$C_{18}H_{37}$	$(C_2H_5)_3N$	2		84	95
n-$C_{18}H_{37}$	$(n\text{-}C_4H_9)_3N$	2		92	
n-$C_{18}H_{37}$	N-Ethylpiperidine	2		85	
n-$C_{18}H_{37}$	[c] (1 equiv.)	2			56 (di-HBr)
n-$C_{18}H_{37}$	[c] (2 equiv.)	2			42 (mono-HBr)
Cholesteryl	$(n\text{-}C_4H_9)_3N$	2		79	
C_2H_5	$(C_2H_5)_3N$	2		79	75

[a] Dried with and distilled from calcium hydride. [b] Cholesterol was also isolated in 68% yield. [c] 1,4-Diazabicyclo[2.2.2]octane.

The pK_a values of pyridine, tri-*n*-butylamine, and triethylamine are 5.23, 9.93, and 10.78.[4] The results indicate, therefore, that the course of reaction as well as the rate of the elimination reaction[1] is strongly dependent upon the base strength of the amine.

Treatment of octadecyl β-bromopropionylcarbamate with excess dry pyridine gave 1-(3,5-dioxo-6-oxa-4-azatetracosyl)pyridinium bromide in 62% yield. When the reaction was run in acetonitrile using only one equivalent of pyridine, a 74% yield of the quaternary bromide resulted. When pyridine hydrobromide and octadecyl acrylcarbamate were allowed to react in acetonitrile under identical conditions, a 62% yield of the quaternary bromide resulted. Owing to the small difference between these yields, we are unable to choose (as were Johnson and Schweitzer[1]) between displacement and elimination–addition mechanisms for the quaternization of the β-bromopropionylcarbamates.

Experimental[5]

Materials.—Sodium tetraphenylboron was obtained from K and K Laboratories, tri-*n*-butylphosphine from Westvaco Mineral Products Division of Food Machinery and Chemical Corp., hydrogen bromide from the Matheson Co., Inc., and 1,4-diazabicyclo[2.2.2]octane from Houdry Process Corp. All other materials were Eastman organic chemicals. "Dried" pyridine was refluxed for 2 hr. with and distilled from calcium hydride.

I. Quaternizations. 1-(3,5-Dioxo-6-oxa-4-azaoctyl)pyridinium Tetraphenylboride.—A solution of 5.00 g. (0.0223 mole) of ethyl β-bromopropionylcarbamate,[3] 1.77 g. (0.0223 mole) of pyridine, and 50 ml. of acetonitrile was refluxed for 15 hr., cooled

(1) H. W. Johnson, Jr., and M. Schweitzer, *J. Org. Chem.*, **26**, 3666 (1961).
(2) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); H. W. Johnson, Jr., and D. E. Bublitz, *ibid.*, **80**, 3150 (1958).
(3) H. W. Johnson, Jr., H. A. Kreyssler, and H. L. Needles, *J. Org. Chem.*, **25**, 279 (1960).
(4) M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *J. Am. Chem. Soc.*, **76**, 3983 (1954).
(5) Melting points were determined on a Fisher–Johns apparatus, unless otherwise noted, and are corrected.

slightly, and then concentrated on a steam bath under water-pump vacuum. The residual oil was cooled, taken up in 50 ml. of distilled water, and the solution added dropwise during 10 min., with mechanical stirring, to a solution of 8.6 g. (0.025 mole) of sodium tetraphenylboron in 100 ml. of distilled water. The mixture was stirred for 10 min. after the addition was complete. The precipitated solid was filtered, washed with distilled water, and air-dried to give 11.3 g. (93.2%) of white solid product. Upon gradual heating, the solid turned, with effervescence, to a cloudy oil from 150 to 154°, gradually resolidified from 155 to 165°, and then melted to a yellow oil from 173–190°.

Anal. Calcd. for $C_{35}H_{35}BN_2O_3$: C, 77.5; H, 6.46; N, 5.13. Found: C, 77.7; H, 6.4; N, 4.7.

Recrystallization from 200 ml. of ethyl acetate gave 8.17 g. (67.6%) of pale yellow crystals, m.p. 158–160° dec. On further heating, it resolidified and melted again from 171–179°. Found: C, 77.7; H, 6.5.

One gram of the product was heated to 165° for 5 min., cooled, and recrystallized from dimethylformamide–acetonitrile to give 0.7 g. of white needles, m.p. 175–181°. The infrared spectrum of this material was identical with that of an authentic sample of pyridinium tetraphenylboride (made by mixing pyridine hydrochloride with sodium tetraphenylboron in water). A mixture melting point showed no depression.

Anal. Calcd. for $C_{29}H_{28}BN$: C, 87.2; H, 6.52; N, 3.51. Found: C, 85.9; H, 6.6; N, 4.5.

1-(3,5-Dioxo-6-oxa-4-azatetracosyl)pyridinium Bromide. A.—A solution of 10.0 g. (0.0223 mole) of octadecyl β-bromopropionylcarbamate[3] and 100 ml. of dried pyridine was refluxed for 15 hr., cooled, and the precipitated solid filtered, sucked dry, and recrystallized twice from 100-ml. portions of dioxane to give 7.3 g. (62%) of white crystals, m.p. 130–131°.

Anal. Calcd. for $C_{27}H_{47}BrN_2O_3$: C, 61.5; H, 8.90; Br, 15.2; N, 5.31. Found: C, 61.3; H, 9.2; Br, 15.2; N, 5.2.

B. A solution of 9.6 g. (0.021 mole) of octadecyl β-bromopropionylcarbamate,[3] 1.7 g. (0.021 mole) of pyridine, and 50 ml. of acetonitrile was treated as in A to give 8.2 g. (74%) of product, m.p. 131–132°. The same product was obtained in 62% yield by refluxing octadecyl acrylylcarbamate with one equivalent of pyridine hydrobromide in acetonitrile for 15 hr.

2-Carbamoylethylpyridinium Bromide.—In experiment A the use of pyridine, which had not been dried, gave a 76% yield of colorless crystals, m.p. 198–200°, not improved by recrystallization from ethanol.

Anal. Calcd. for $C_8H_{11}BrN_2O$: C, 41.6; H, 4.76; Br, 34.7; N, 12.1. Found: C, 42.1; H, 4.9; Br, 34.3; N, 11.7.

The same product was obtained in 84% yield by similar treatment of cholesteryl 3-β-bromopropionylcarbamate.[3] Concentration of the filtrate and recrystallization of the gummy residue from ethanol gave a 68% recovery of cholesterol, identified by m.m.p. and infrared spectrum.

1-(3,5-Dioxo-6-oxa-4-azatetracosyl)triphenylphosphonium Bromide.—Substitution of triphenylphosphine for pyridine in procedure B gave, after two recrystallizations from ethyl acetate, 9.3 g. (60%) of colorless crystals, m.p. 99–102°.

Anal. Calcd. for $C_{40}H_{57}BrNO_3P$: C, 67.6; H, 8.03; Br, 11.3; N, 1.97; P, 4.36. Found: C, 66.9; H, 8.3; Br, 11.5; N, 1.8; P, 4.1.

1-(3,5-Dioxo-6-oxa-4-azatetracosyl)tri-*n*-butylphosphonium Bromide.—Substitution of tri-*n*-butylphosphine for pyridine in procedure B gave 6.1 g. (42%) of colorless needles, m.p. 88.5–89.5°.

Anal. Calcd. for $C_{34}H_{69}BrNO_3P$: C, 63.0; H, 10.6; Br, 12.3; N, 2.15; P, 4.76. Found: C, 62.7; H, 10.4; Br, 12.6; N, 2.3; P, 4.6.

II. Eliminations. Octadecyl Acrylylcarbamate.—A solution of 6.44 g. (0.0143 mole) of octadecyl β-bromopropionylcarbamate,[3] 1.45 g. (0.0143 mole) of triethylamine and 65 ml. of acetonitrile was refluxed overnight, filtered while hot, and the filtrate was allowed to cool to room temperature. The solid was filtered, washed with acetonitrile, and air-dried to give 4.38 g. (83.6%) of white crystals, m.p. 88–89°.

Anal. Calcd. for $C_{22}H_{41}NO_3$: C, 72.0; H, 11.2; N, 3.82. Found: C, 71.8; H, 11.4; N, 3.5.

The acetonitrile filtrate was concentrated on a steam bath under water-pump vacuum to give 2.48 g. (95.3%) of triethylamine hydrobromide.

Anal. Calcd. for $C_6H_{16}BrN$: C, 39.6; H, 8.80; Br, 44.0; N, 7.70. Found: C, 39.7; H, 8.7; Br, 44.0; N, 7.8.

Similar treatment of 10.0 g. (0.0223 mole) portions of octadecyl β-bromopropionylcarbamate with 4.1 g. (0.022 mole) of tri-*n*-butylamine and with 2.52 g. (0.0223 mole) of N-ethylpiperidine gave octadecyl acrylylcarbamate in 92% and 85% yields, respectively. When 2.50 g. (0.0223 mole) of 1,4-diazabicyclo-[2.2.2]octane was used, 1.8 g. (42%) of the amine monohydrobromide, purified by boiling in dioxane and recrystallizing from ethanol, was obtained. It decomposed upon heating, starting at 270°.

Anal. Calcd. for $C_6H_{13}BrN_2$: C, 37.3; H, 6.74; Br, 41.3; N, 14.5. Found: C, 37.4; H, 6.9; Br, 40.0; N, 14.5.

Use of 1.26 g. (0.0112 mole) of 1,4-diazabicyclo[2.2.2]octane gave 1.7 g. (56%) of the amine dihydrobromide, m.p. 290–300° dec., after two recrystallizations from dimethylformamide.

Anal. Calcd. for $C_6H_{14}Br_2N_2$: C, 26.3; H, 5.11; Br, 58.4; N, 10.2. Found: C, 27.9; H, 5.3; Br, 56.2; N, 10.4.

Cholesteryl 3-Acrylylcarbamate.—Similar treatment of cholesteryl 3-β-bromopropionylcarbamate with one equivalent of tri-*n*-butylamine gave a 79% yield of colorless powder, m.p. 200–202°, not improved by recrystallization from dimethylformamide.

Anal. Calcd. for $C_{31}H_{49}NO_3$: C, 77.0; H, 10.1; N, 2.9. Found: C, 77.4; H, 10.3; N, 2.9.

Ethyl Acrylylcarbamate.—Similar treatment of ethyl β-bromopropionylcarbamate with one equivalent of triethylamine gave a 75% yield of triethylamine hydrobromide. Work-up of the filtrate gave, after recrystallization from 1:1 benzene–ligroin (b.p. 66–75°), a 79% yield of colorless crystals, m.p. 80–82°.

Anal. Calcd. for $C_6H_9NO_3$: C, 50.3; H, 6.30; N, 9.78. Found: C, 50.6; H, 6.4; N, 9.8.

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Ring Enlargement Reactions of Bicyclo[2.2.1]-heptane Derivatives

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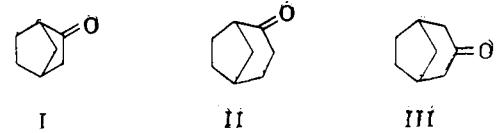
Utilization of bicyclo[2.2.1]heptane derivatives as precursors for the synthesis of bicyclo[3.2.1]octane derivatives is of interest owing to the availability of the former and the lack of general syntheses of the latter. Two potential ring expansion reactions of norbornyl derivatives have been investigated in this study, namely, the reaction of diazomethane with norcamphor(I) and solvolysis of 2-*exo*- and *endo*-hydroxymethylnorbornyl tosylates (IV).

Reaction of equimolar quantities of norcamphor (I) and diazomethane led to a complex mixture which contained five major components. Three of them were shown by gas chromatography to be norcamphor, bicyclo[3.2.1]octanone-2 (II), and bicyclo[3.2.1]octanone-3 (III). The last two peaks were very likely



I II III

(1) Abstracted in part from the B. S. thesis of R. J. T., Rutgers, 1962.