and unchanged phenylsilane were removed under vacuum. Upon fractional distillation of the residue 7.0 ml. (83%) of the triene was recovered, leaving a small amount of a discolored glassy polymer which did not dissolve in hot benzene.

5-Phenylsilylcyclooctene.—This compound was prepared from 7.0 ml. (0.057 mole) of phenylsilane and 7.0 ml. (0.057 mole) of 1,5-cyclooctadiene in 100 ml. of heptane, following the method described above for 9-phenylsilyl-1,5-cyclododecadiene. A total of 1.5 g. of benzoyl peroxide was added in small increments during 3 days of refluxing. The desired product was again the only volatile substance to be isolated; it distilled at 67–69° (0.025 mm.). The yield was 3.5 g. (25%); n^{25}_{D} 1.5380, d^{25}_{4} 0.9818.

Anal. Calcd. for $C_{14}H_{20}Si$: C, 77.77; H, 9.26. Found: C, 77.55; H, 9.26.

The substance liberated hydrogen when treated with alcoholic potassium hydroxide and the infrared spectrum showed an intense Si—H stretching band at 2110 cm.$^{-1}$. The proton n.m.r. spectrum consisted of a number of lines around $\tau = 2.9$ (aromatic H), a sharp doublet at $\tau = 5.8$ (silanic H), a diffuse line at $\tau = 7.85$ (vinylic H), and a complex group centered at $\tau = 8.8$ (methylenic H). The relative integrated intensities were 5:2:2:12, in good agreement with the proposed structure.

5-Pentenyldichlorosilane and Attempted Cyclization.—The compound was prepared from 5-pentenylmagnesium bromide and trichlorosilane in tetrahydrofuran. After separation of the organic material from the magnesium salts, it was fractionally distilled. It proved difficult to separate the silane from a hydrocarbon by product, and the desired product was isolated in only 13% yield, boiling at 65–66° (28 mm.). The infrared spectrum showed bands characteristic of Si—H, Si—C, Si—Cl, and C═C.

Anal. Calcd. for $C_5H_{10}SiCl_2$: Cl, 41.7. Found: Cl, 40.5.

Intramolecular cyclization was attempted under several conditions using either chloroplatinic acid or acetyl peroxide catalysts. The majority of the product in every case was a polymeric residue, perhaps resulting from linear polymerization of the 5-pentenyldichlorosilane. Any volatile products were characterized by exhaustive methylation with methyl Grignard reagent followed by gas chromatography. None of the desired cyclopentamethylenedimethylsilane[5] was isolated in any of the reactions.

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[5] A. Bygden, *Ber.*, **48**, 1236 (1915); R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

Synthesis of Substituted β-Lactams

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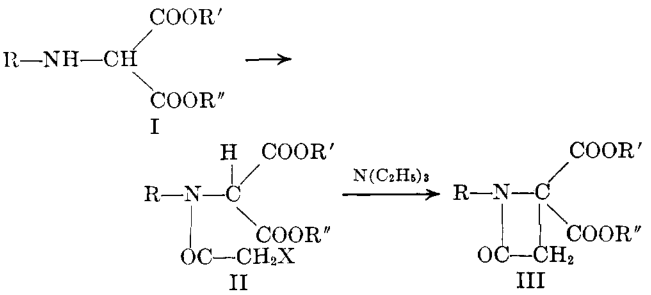
A novel method for the synthesis of substituted β-lactams III has been developed by Sheehan and Bose[1] in which the amide linkage is formed first and the four-membered β-lactam ring is then made by establishing carbon–carbon bond according to the following scheme.



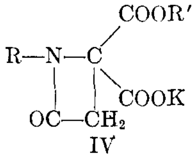
I

II

III

Further work has shown that the cyclization to β-lactam proceeds in high yield and that the reaction is a general one.[2]

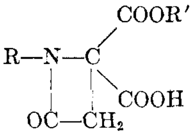
When the β-lactam III is treated with one mole of alcoholic potassium hydroxide, the potassium salt IV is obtained in quantitative yield within one hour.



IV

In order to compare the rate of intramolecular displacement reaction leading to cyclization of the amidomalonate II and the rate of ester hydrolysis in presence of potassium hydroxide, a set of two experiments was carried out. In the first experiment the amidomalonate II was treated with one mole of alcoholic potassium hydroxide and in the other it was treated with two moles of potassium hydroxide. There was an instantaneous precipitation of potassium chloride in both the cases and the potassium chloride from the first reaction mixture was filtered out within five minutes. The yield of potassium chloride was quantitative (based on silver chloride). The alcoholic solution was acidified with acetic acid. The product from this reaction was β-lactam III in more than 96% yield.

The second reaction mixture was allowed to stand at room temperature for one hour. The potassium salt on acidification with concentrated hydrochloric acid gave the monoacid V in about 95% yield.



V

The acylation of substituted aminomalonates I to the amidomalonates II have been carried out under nonbasic condition[3] with a halo acid and phosphorus trichloride. Bose and his co-workers[4] have shown that the β-lactams III can be obtained in one step in about three days when the aminomalonate I is treated with α-haloacyl halide and excess of triethylamine at room temperature.

Additional work has now shown that the conversion of a substituted aminomalonate I to the β-lactam III as well as to the corresponding monoacid V can be carried out in one operation. The β-lactams III are

TABLE I

R	R′	R″	M.p., °C./n^{30}_{D}	Yield, %
C_6H_5	C_2H_5	C_2H_5	38–39	88
C_6H_5	C_2H_5	H	101–103	79
p-Cl-C_6H_4	C_2H_5	C_2H_5	1.5260	88
p-Cl-C_6H_4	C_2H_5	H	118–120	80
p-Br-C_6H_4	C_2H_5	C_2H_5	1.5393	84
p-Br-C_6H_4	C_2H_5	H	89–91	77
p-$CH_3C_6H_4$	C_2H_5	C_2H_5	90–91	85
p-$CH_3C_6H_4$	C_2H_5	H	169–170 dec.	76
$C_{10}H_7$	C_2H_5	C_2H_5	75–76	90
$C_{10}H_7$	C_2H_5	H	181–182 dec.	88

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[1] J. C. Sheehan and A. K. Bose, *J. Am. Chem. Soc.*, **72**, 5158 (1950).

[2] J. C. Sheehan and A. K. Bose, *ibid.*, **73**, 1761 (1951).

[3] A. K. Bose, *J. Ind. Chem. Soc.*, **31**, 108 (1954).

[4] A. K. Bose, M. S. Manhas, and B. N. Ghosh Mazumdar, *J. Org. Chem.*, **27**, 1458 (1962).

TABLE II

EFFECT OF TEMPERATURE, PRESSURE, AND TIME

S. no.	Substance	Solvent	Temp., °C.	Press.	Time	Yield, %	M.p., °C.
(1)	p-$ClC_6H_4NH_2$	Benzene	30	760 mm.	24 hr.	. . .	
(2)	p-$ClC_6H_4NH_2$	Benzene	30	760 mm.	21 days	55	
(3)	p-$ClC_6H_4NH_2$	Acetone	30	760 mm.	24 hr.	. . .	
(4)	p-$ClC_6H_4NH_2$	Ethanol	30	760 mm.	24 hr.	. . .	
(5)	p-$ClC_6H_4NH_2$	Benzene	80	760 mm.	8 hr.	5	
(6)	Aniline	Benzene	30	760 mm.	24 hr.	67	
(7)	Aniline	Benzene	80	760 mm.	3 hr.	30	
(8)	Aniline	Benzene	80	760 mm.	8 hr.	67	
(9)	Aniline	. . .	60–70	760 mm.	1 hr.	62	
(10)	Aniline	. . .	60–70	760 mm.	1.5 hr.	69	
(11)	Aniline	. . .	60–70	760 mm.	8 hr.	70	
(12)	Aniline	. . .	60–70	100 mm.	8 hr.	78	
(13)	Aniline	. . .	60–70	60 mm.	8 hr.	85	
(14)	Aniline	. . .	60–70	40 mm.	8 hr.	100	44–45
(15)	p-$ClC_6H_4NH_2$	. . .	60–70	40 mm.	8 hr.	98	91–92
(16)	p-$ClC_6H_4NH_2$	. . .	60–70	30 mm.	8 hr.	98	
(17)	p-$BrC_6H_4NH_2$	. . .	60–70	40 mm.	8 hr.	98	92–93
(18)	p-$CH_3C_6H_4NH_2$	. . .	60–70	40 mm.	8 hr.	96	55–56
(19)	$C_{10}H_nNH_2$	. . .	60–70	40 mm.	8 hr.	100	86–87

obtained in more than 80% yield within a few minutes and the acids V in about 80% yield in about an hour. The substituted aminomalonates were heated with 1.2–1.5 moles of chloroacetyl chloride to about 80° for five minutes. Alcohol was then added to destroy the excess of the acid halide. When the reaction mixture was treated with 2.5 moles of alcoholic potassium hydroxide and worked up after five minutes, the product was β-lactam III, and, when it was treated with 3.5–4 moles of potassium hydroxide and worked up after forty-five minutes, the product was the mono-acid V.

The preparation of several β-lactams by this one-step method is summerized in Table I.

The substituted aminomalonates I have been synthesised[5] by treating a benzene solution of the amine with diethyl bromomalonate. The usual yield of the product is about 70%. The p-haloanilines and β-naphthylamine, however, did not react with bromomalonate under the above condition. The p-haloanilines resisted condensation in alcohol solution even at the reflux temperature.

It has now been shown that all the aminomalonates mentioned above can be obtained in more than 95% yield if the amines are treated with the bromomalonate under slightly reduced pressure (40 mm.) at about 70° for eight hours. The effect of temperature, pressure, and time is summerized in Table II.

Experimental[6]

A typical procedure for the one-step synthesis of β-lactams of type III is described.

1-*p*-Tolyl-4,4′-dicarbethoxyazetidin-2-one.—A 2.65-g. sample of p-toluidinomalonate was taken in a small dry conical flask, plugged with cotton wool. To it was added 1.0 ml. of chloroacetyl chloride and the reaction mixture was heated with occasional shaking to about 80° for 5 min. A 10–15-ml. portion of absolute alcohol was then added and the solution was cooled to room temperature. A thick precipitate of potassium chloride was obtained on the addition of 1.5 g. of potassium hydroxide in alcohol solution. The mixture was allowed to stand for 4–5 min. and then filtered. The filtrate was acidified with glacial acetic acid and the solvent was removed under reduced pressure. The residue was taken up in ether and washed several times with water. After drying the ether layer over anhydrous magnesium sulfate, the solvent was removed under reduced pressure when a semisolid mass was obtained. This solidified on scratching. Recrystallization from cyclohexane afforded 2.6 g. (85%) of colorless needles, m.p. 90–91°. No depression in melting point was observed in mixture melting point determination with an authentic sample.

Anal. Calcd. for $C_{16}H_{19}O_5N$: C, 62.59; H, 6.23; N, 4.59. Found: C, 63.22; H, 6.40; N, 4.42.

A typical procedure for the synthesis of β-lactam V is illustrated.

1-*p*-Bromophenyl-4-carboxy-4′-carbethoxyazetidin-2-one.—A 3.30-g. sample of p-bromoanilinomalonate was treated with 1.0 ml. of chloroacetyl chloride and 10–15 ml. of absolute alcohol in the manner mentioned above. To the cooled solution was added 2.2 g. of potassium hydroxide in alcohol solution. The reaction mixture was allowed to stand for about 45 min. Ether was added to precipitate the potassium salt completely. The salt was taken in water and the solution was acidified with concentrated hydrochloric acid, when an oil separated which solidified on scratching. In some cases the oil had to be taken up in ether and after usual operations the solid mass was obtained. Recrystallization from ether petroleum ether mixture afforded 2.64 g. of crystalline solid, m.p. 89–91° (77%). No depression in melting point was observed in mixture melting point determination with an authentic sample.

Anal. Calcd. for $C_{13}H_{12}O_5N\,Br$: C, 45.61; H, 3.51; N, 4.09. Found: C, 45.39; H, 3.82; N, 4.26.

A typical synthesis of substituted anilinomalonates I is given below.

Diethyl *p*-Chloroanilinomalonate.—A mixture of 25.5 g. of p-chloroaniline and 23.9 g. of diethyl bromomalonate was taken in a 100-ml. round bottom flask fitted with a two-way stop cock and was evacuated to 40 mm. The reaction mixture was then kept in an oven maintained at 60–70° for 8 hr. The solid cake was powdered and extracted several times with ether. The crude p-chloroanilinomalonate, obtained on the removal of the solvent, was recrystallized from petroleum ether; yield, 28.0 g. (98%); m.p. 91–92°. The yield of p-chloroaniline hydrobromide was 20.8 g. (100%).

Anal. Calcd. for $C_{13}H_{16}O_4NCl$: C, 54.64; H, 5.60; N, 4.90. Found: C, 54.52; H, 5.71; N, 4.82.

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[5] A. K. Bose, B. N. Ghosh Mazumdar, and B. G. Chatterjee, *J. Am. Chem. Soc.*, **82**, 2382 (1960).

[6] All melting points are uncorrected.