dilute solutions were used, and ammonia gave a product which was insoluble in chloroform (and thus unable to react further).

The derivatives prepared from amines and phenols appeared to be stable to ordinary laboratory storage conditions when reasonably pure.

In general, our experience with the use of I as a reagent for preparing derivatives may be summarized a follows: for aliphatic alcohols—good in most cases, particularly useful with fairly unreactive alcohols; for aliphatic amines—not recommended; for phenols—good, except for very acidic phenols; for aromatic amines—good for monoamino compounds. The principal advantage of I is that reaction with water yields β-bromopropionamide which can be removed from the product by crystallization in most cases; aryl isocyanates yield diarylureas which are more difficult to remove from the product. The increase in molecular weight of an alcohol or amine upon reaction with I is 178, which compares favorably with 119 for phenyl isocyanate and 169 for naphthyl isocyanate.

## Experimental

The phenols and amines used in this work were obtained from commercial sources. Melting points were determined with a Koffler block. Analyses were performed by Dr. Weiler and Dr. Strauss, Oxford.

The method of preparation of I has been reported previously.[2]

**Preparation of Derivatives.**—A suspension of 1.0 g. (0.0056 mole) of N-bromosuccinimide, 10 ml. of chloroform (dried over calcium chloride), 0.5 ml. of allyl chloride, and a small amount (*ca.* 10 mg.) of benzoyl peroxide was refluxed for 30 min. The now-clear solution was allowed to cool to room temperature, and an approximately equimolar amount of the phenol or aniline dissolved in a few milliliters of chloroform was added. If the amine or phenol was insoluble in chloroform, it was dissolved in a few milliliters of tetrahydrofuran. A vigorous reaction ensued in most instances. The solution was cooled in an ice bath, and in many instances the product crystallized from the reaction mixture. The solid was filtered and crystallized from the solvent indicated in the table. If no solid precipitated, low boiling petroleum ether was added to precipitate the product. The solid was then crystallized from the solvent indicated in the table.

The same procedure has been used to prepare derivatives on a 50-g. scale.

To prepare the derivatives of aliphatic amines, *e.g.*, benzylamine, it was necessary to add an equimolar amount of the amine very slowly, with stirring, keeping the solution temperature below 5°. The preparation of β-bromopropionylurea (from I and ammonia) was accomplished by bubbling gaseous ammonia into the chloroform solution, from which the derivative precipitated immediately.

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# The Monoaddition of Phenylsilane to Cyclic Polyolefins[1]

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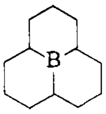
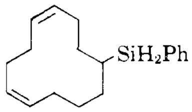
*Received November 13, 1962*

Recently several workers have reported the addition of diborane or triethylamineborane to 1,5,9-cyclododecatriene to give perhydro-9b-borphenalene (I).[2,3] It seemed possible that an analogous reaction might take place with silicon in place of boron. We have attempted to add phenylsilane to the same triolefin using benzoyl peroxide and chloroplatinic acid as catalysts. In neither case is any of the desired tricyclic silicon analog of I obtained. Chloroplatinic acid catalysis led only to polymeric material, but with benzoyl peroxide a 16% yield of 9-phenylsilyl-1,5-cyclododecadiene (II) was obtained. The monoaddition product is completely unreactive toward further addition, being recovered unchanged after seven days of heating with benzoyl peroxide catalyst. Similar results were obtained in the addition of phenylsilane to 1,5-cyclooctadiene, which led only to the monoadduct, 5-phenylsilylcyclooctene.


I



II

The reluctance of silicon to add to form the perhydrosilaphenalene ring may result in part from the large radius of the silicon atom, which would prevent the molecule from assuming a strainless configuration. However, unsuccessful attempts to cyclize 5-pentenyldichlorosilane by intramolecular Si–H addition suggest that the mechanism of silane addition may require a geometry which makes the formation of a six-membered ring unfavorable. With either chloroplatinic acid or benzoyl peroxide, 5-pentenyldichlorosilane gave none of the desired 1,1-dichlorosilacyclohexane, even though the latter compound can assume a strainless chair-like configuration.[4]

## Experimental

**9-Phenylsilyl-1,5-cyclododecadiene.**—Fifteen milliliters (0.12 mole) of phenylsilane and 22 ml. (0.12 mole) of 1,5,9-cyclododecatriene in 150 ml. of dry heptane were refluxed for 3 days during which time a total of 2.5 g. of benzoyl peroxide was added in 250 mg. increments at 6–10-hr. intervals. After cooling, the mixture was shaken with an aqueous solution 1 *N* each in ammonia and ammonium chloride in order to remove benzoic acid formed in decomposition of the peroxide. The organic layer was separated, dried, and fractionally distilled. After removal of heptane and unreacted starting materials, the only volatile product, a colorless liquid, was distilled at 114–127° (0.15 mm.); yield 5.0 g., 16%. A large residue of polymeric material was left in the flask. The product had $n^{25}$D 1.5449, $d^{26}_{4}$ 1.0197.

*Anal.* Calcd. for $C_{18}H_{26}Si$: C, 79.92; H, 9.69; Si, 10.38. Found: C, 80.15; H, 9.57; Si, 10.29.

The infrared spectrum of the product showed a very strong band at 2120 cm.$^{-1}$ (Si—H) as well as a weak doublet at 1600 cm.$^{-1}$ (C═C). The proton magnetic resonance spectrum showed a cluster of lines near $\tau = 2.8$, a sharp line at $\tau = 5.83$, and a broad unresolved band from $\tau = 8.0$ to 9.4. These resonances are assigned to phenyl, silane, and a mixture of methylene and vinylic protons, respectively; the relative integrated intensities were 5.0:1.8:20. A semiquantitative base-catalyzed hydrolysis of the substance in aqueous tetrahydrofuran yielded 1.7 moles of hydrogen per mole of compound.

**Attempted Addition Using Chloroplatinic Acid Catalyst.**—A 5.8-ml. sample (0.046 mole) of phenylsilane and 8.4 ml. (0.046 mole) of 1,5,9-cyclododecatriene and a small amount of chloroplatinic acid in isopropyl alcohol were dissolved in 50 ml. of dry heptane, and the solution was refluxed for 24 hr. The heptane

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract no. AF49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] R. Köster, *Angew. Chem.*, **69**, 684 (1957); G. Rotermund and R. Köster, *ibid.*, **74**, 329 (1962).

[3] N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 2922 (1960).

[4] R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954).

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-Phenylsilylcycloöctene.**—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).

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# Synthesis of Substituted β-Lactams

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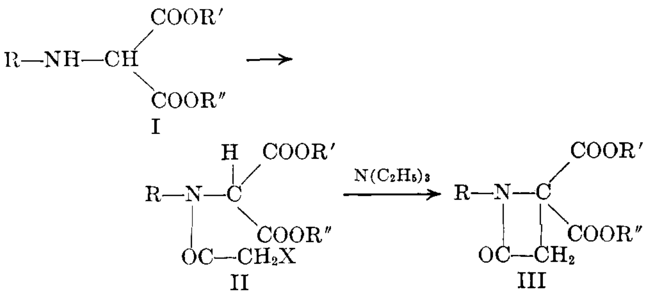
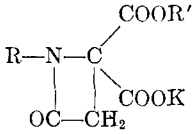
*Received October 10, 1962*

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.



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

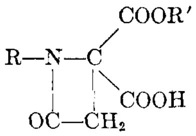
When the β-lactam III is treated with one mole of alcoholic potassium hydroxide, the potassium salt IV is obtained in quantitative yield within one hour.



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).