[CONTRIBUTION FROM THE CHEMICAL LABORATORY, IOWA STATE UNIVERSITY]

# Bromination Studies in the 5,10-Dihydrophenazasiline Series

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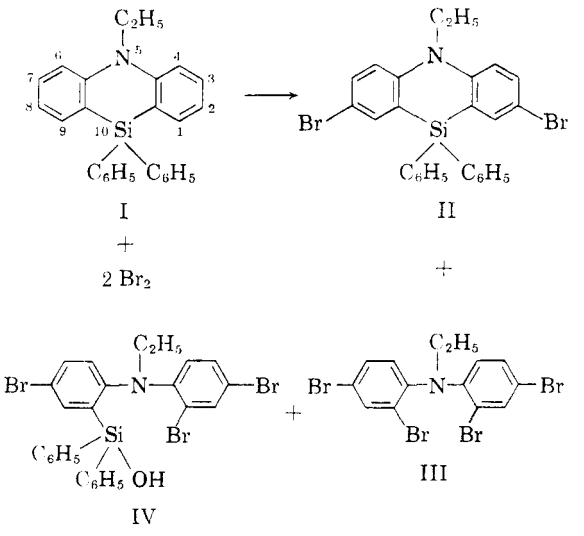
Bromination of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline under several different conditions has given 5-ethyl 2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline, 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine, and 2,2′,4,4′-tetrabromodiphenylamine. The formation of 5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by two schemes, interrelating 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline and 2,2′-dibromodi-*p*-tolylamine, is also presented.

Syntheses of bromoaryl silicon compounds have been accomplished by direct bromination, but in many cases rapid cleavage of carbon-silicon bonds occurs. Treatment of tetraphenylsilane with bromine gives bromobenzene, bromotriphenylsilane, and dibromodiphenylsilane.[1] Similarly, trimethylphenylsilane undergoes cleavage to afford good yields of bromobenzene and bromotrimethylsilane.[2] On the other hand, trichlorophenylsilane may be brominated in the presence of iron to give the corresponding 4-bromo and 2,4-dibromo compounds.[3]

In connection with our investigations in the 5,10-dihydrophenazasiline series,[4,5] 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (I) has been allowed to react with bromine under several different conditions. The addition of bromine to a carbon disulfide solution of the phenazasiline compound, cooled to −20°, gave a 21% yield of 5-ethyl - 2,8 - dibromo - 10,10 - diphenyl - 5,10-dihydrophenazasilane (II). There were also isolated small amounts of silicon-carbon cleavage products, *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine (III) and a silanol-containing compound tentatively identified as 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol (IV), in addition to a 27% recovery of starting compound I. A slightly improved yield (25%) of the 2,8-dibromo compound II was obtained, when the reaction mixture was allowed to warm to room temperature, but only 11% of the phenazasiline compound I was recovered.

When bromine was added to a cold glacial acetic acid solution of the phenazasiline compound, only small amounts of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine (III) and 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline (II) were isolated. There was also obtained a large amount of a colorless viscous oil which could not be characterized. The infrared spectrum contained large




absorption bands indicative of silanols and disiloxanes.

A reaction with excess bromine in refluxing glacial acetic acid gave only silicon-free cleavage products, *N*-ethyl-2,2′,4,4′-tetabromodiphenylamine (III) (22%) and 2,2′,4,4′-tetrabromodiphenylamine (31%).

Since acids, such as hydrobromic acid, are known to effect the cleavage of silicon-aryl bonds,[6] a reaction between 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (I) and bromine in glacial acetic acid was conducted in the presence of sodium acetate, in a effort to neutralize the hydrogen bromide as it was formed. Work-up gave a 10% yield of the tetrabromo compound III, a 4% yield of the 2,8-dibromo compound II, and a 33% yield of the silanol IV. It should be noted that a 21% recovery of starting phenazasilane compound I was also effected. None of this material had been recovered in the previously described reactions in glacial acetic acid. Thus, it appears that the hydrogen bromide is responsible, in part, for the cleavage of the silicon heterocycle.

The structure of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine (III) was verified by independent synthesis from 2,2′,4,4′-tetrabromodiphenylamine

(1) A. Ladenberg, *Ber.*, **40**, 2274 (1907).

(2) B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. D. George, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 433 (1948).

(3) A. Y. Yakubovich and G. V. Motsarev, *Zhur. Obshchei Khim.*, **23**, 412 (1953). [*Chem. Abstr.*, **48**, 3286 (1954)].

(4) H. Gilman and E. A. Zuech, *Chem. & Ind.*, 1227 (1958); *J. Am. Chem. Soc.*, **82**, 2522 (1960).

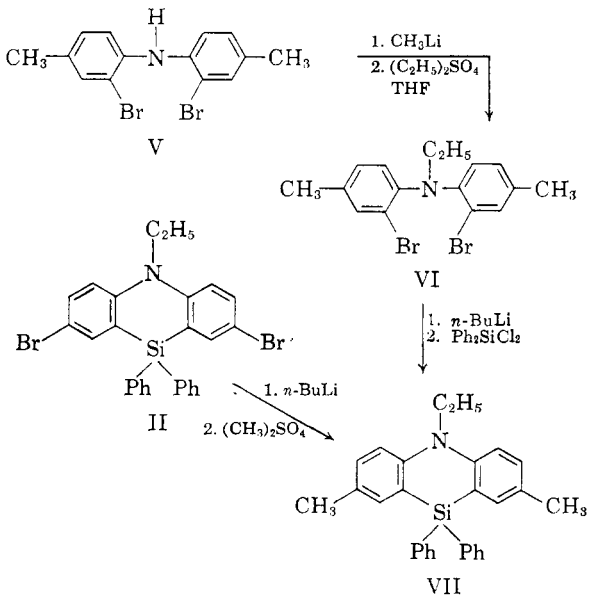
(5) H. Gilman and E. A. Zuech, *J. Org. Chem.*, in press.

(6) C. Eaborn, *J. Chem. Soc.*, 4859 (1956); F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2299 (1959).

using the *N*-alkylation procedure utilized on 2,2′-dibromodiphenylamine.[4] The tentative structure assigned to the cleavage product, 2-(*N*-ethyl-2,4-dibromoanilino) - 5 - bromophenyldiphenylsilanol (IV), was based on analytical data, on infrared spectra, and on the fact that treatment with bromine afforded a good yield of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine (III).

In a previous communication,[7] the preparation of 2,2′-dibromodi-*p*-tolylamine (V) by the direct bromination of di-*p*-tolylamine was reported. This dibromo amine derivative and 5-ethyl-2,8-dibromo - 10,10 - diphenyl - 5,10 - dihydrophenazasiline (II) were found to be interrelatable by a series of reactions, thus serving to substantiate the structures for the various compounds.

Treatment of di-*p*-tolylamine in glacial acetic acid with two molar equivalents of bromine gave a 64% yield of 2,2′-dibromodi-*p*-tolylamine (V). Compound V was then converted to the *N*-lithio intermediate upon interaction with methyllithium, and this was subsequently treated with a refluxing tetrahydrofuran solution of diethyl sulfate to give a 79% yield of *N*-ethyl-2,2′-dibromodi-*p*-tolylamine (VI).




The *N*-ethyl compound VI was transformed into the dilithium derivative by halogen-metal interconversion with *n*-butyllithium and then treated with dichlorodiphenylsilane to give a good yield of 5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline (VII). The phenazasiline compound VII was also obtained from the 2,8-dibromo compound II by treatment first with *n*-butyllithium and then with dimethyl sulfate.

(7) H. Gilman and E. A. Zuech, *J. Org. Chem.*, **24**, 1394 (1959).

## EXPERIMENTAL[8]

*Bromination of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline.* (*A*) *In carbon disulfide at −20°.* A solution of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 50 ml. of carbon disulfide, cooled to −20 ± 2°, was treated with 9.6 g. (0.06 mole) of bromine by dropwise addition over a period of 10 min. Stirring was continued for 20 min. at −20°, and then the reaction mixture was poured upon a cold solution of sodium bisulfite. Ether was added and the organic layer separated. After drying and evaporating the organic layer, the residue was chromatographed over alumina. Elution with petroleum ether (b.p. 60–70°) gave a small amount of solid, which was recrystallized three times from petroleum ether to give 0.13 g. of colorless crystals, m.p. 135–137°, identified as *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine. The infrared spectrum as a carbon disulfide solution showed absorption bands indicative of aromatic and aliphatic C—H and C—N groups. A strong band was present at 12.3 μ, characteristic of 1,2,4-trisubstituted benzene.

*Anal.* Calcd. for $C_{14}H_{11}Br_4N$: C, 32.78; H, 2.16. Found: C, 32.69, 32.59; H, 2.31, 2.34.

Further elution with petroleum ether and then with cyclohexane gave a colorless solid, m.p. 107–115°. After three recrystallizations from petroleum ether (b.p. 60–70°), there was obtained 3 03 g. (27%) of recovered 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 118–121°, which was identified by mixed melting point and by comparison of the infrared spectra. Continued elution with cyclohexane, followed by benzene, gave a colorless solid which was recrystallized twice from cyclohexane to give 4.15 g. of colorless solid, m.p. 190–198°. This material was recrystallized twice from ethyl acetate to give 3.37 g. (21%) of colorless crystals, m.p. 197–200°, identified as 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline. An additional recrystallization from ethyl acetate raised the melting point to 198–200°. The infrared spectrum of the compound in carbon disulfide exhibited a strong absorption band at 12.4 μ, indicative of 1,2,4-trisubstituted benzene. The remainder of the spectrum was similar to that of the other 5,10-dihydrophenazasilane derivative, except that the *ortho*-disubstitution band was absent.

*Anal.* Calcd. for $C_{26}H_{21}Br_2NSi$: C, 58.32; H, 3.95; N, 2.62; Si, 5.25. Found: C, 58.10, 58.32; H, 4.05, 3.87; N, 2.91, 2.97; Si, 5.34, 5.29.

The column was then eluted further with benzene and the product recrystallized twice from petroleum ether (b.p. 60–70°) to give 0.67 g. (4%) of colorless flakes, m.p. 138–141°. The analytical sample melted at 138–140°. The material has been tentatively identified as 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol. The infrared spectrum as a carbon disulfide solution had absorption bands at 2.8, 3.3, 3.4, 9.0, 12.3, and 13.5 μ, which are characteristic of the hydroxy, C—H aliphatic, C—H aromatic, silicon-phenyl, 1,2,4-trisubstituted benzene, and monosubstituted phenyl groups, respectively.

*Anal.* Calcd. for $C_{26}H_{22}Br_3NOSi$: C, 49.38; H, 3.51; N, 2.22; Si, 4.44. Found: C, 49.74, 49.90; H, 3.42, 3.37; N, 2.67, 2.49; Si, 4.54, 4.45.

Elution with other solvents gave small amounts of viscous oils which could not be further purified or identified.

Another run employing identical reaction conditions and work-up afforded 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline in a 21% yield. There was also obtained a 2% yield of 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, in addition to a 42% recovery of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline.

A slightly improved yield (25%) of the dibromo compound was obtained in a third run. The bromine addition was car-

(8) All reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen, and all melting points are uncorrected.

ried out as in the previous runs, but instead of stirring at −20° the reaction mixture was allowed to warm to room temperature, which required 20 min., before effecting hydrolysis. However, only 11% of the 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline was recovered from this run.

(*B*) *In glacial acetic acid.* A suspension of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of glacial acetic acid, cooled in an ice bath, was treated with 10.5 g. (0.065 mole) of bromine by dropwise addition over a period of 15 min. The ice-bath was removed and the reaction mixture stirred for 45 min. The orange mixture was then hydrolyzed with a dilute solution of sodium bisulfite. The aqueous solution was filtered and the yellow sticky material was taken up in ether. The ethereal solution was then worked up in the usual manner and the reaction products chromatographed as described in the previous runs. This gave 0.72 g. (5%) of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine, m.p. 135–137°, which was identified by mixed melting point and by comparison of the infrared spectra; and 0.83 g. (5%) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline. There was also obtained a large amount of a colorless viscous oil which could not be characterized. The infrared spectrum contained large absorption bands indicative of silanols and disiloxanes.

(*C*) *In refluxing glacial acetic acid.* A solution of 7.54 g. (0.02 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of glacial acetic acid, cooled in an ice-bath, was treated with 14.4 g. (0.09 mole) of bromine. After warming to room temperature, the reaction mixture was heated at reflux for 1 hr. and then hydrolyzed with a dilute solution of sodium bisulfite. The resulting solid material was filtered, air-dried, and chromatographed. Elution with petroleum ether (b.p. 60–70°) and three subsequent recrystallizations from the same solvent afforded 2.27 g. (22%) of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine, m.p. 134–137°, which was identified by mixed melting point and by comparison of the infrared spectra. Using cyclohexane as the eluant, there was obtained a colorless solid, m.p. 180–186°. This material was recrystallized twice from ethyl acetate to give 3.03 g. (31%) of colorless needles, m.p. 185–186.5°, which was identified as 2,2′,4,4′-tetrabromodiphenylamine by mixed melting point with an authentic sample.[9]

(*D*) *In glacial acetic acid in the presence of sodium acetate.* A mixture of 11.3 g. (0.03 mole) of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, 6 g. (0.073 mole) of sodium acetate, and 100 ml. of glacial acetic acid was cooled in an ice bath and treated with 10.5 g. (0.065 mole) of bromine. The ice bath was removed and the reaction mixture stirred for 45 min. After hydrolysis and the usual work-up, the reaction products were chromatographed. Elution with the various solvents in the customary manner gave 1.53 g. (10%) of *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine, m.p. 135–137°; 2.42 g. (21%) of recovered 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline; and 0.67 g. (4%) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 198–200°. Elution of the column with ethyl acetate gave 7.28 g. of colorless solid, m.p. 136–140°. Recrystallization of this material from a 5:1 mixture of petroleum ether (b.p. 60–70°) and benzene gave a crystalline solid, m.p. 156–160°. An additional recrystallization from the same solvent mixture raised the melting point to 158–160°. This material was found to be identical with 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol, which has been previously described as colorless flakes, m.p. 138–140°. When the lower melting material was taken up in petroleum ether and seeded with some of the higher melting material, the higher melting crystalline solid was obtained. However, attempts to obtain the lower melting solid by a similar process were unsuccessful affording only a recovery of the higher melting material. The infrared spectra of the two solids as carbon disulfide solutions are identical, but have small absorption differences as potassium bromide pellets.[10] A total of 6.32 g. (33%) of the material was isolated.

*N-Ethyl-2,2′,4,4′-tetrabromodiphenylamine.* A suspension of 8.9 g. (0.0183 mole) of 2,2′,4,4′-tetrabromodiphenylamine[9] in 200 ml. of ether, cooled in an ice bath, was treated with 0.027 mole of methyllithium. After stirring for 30 min., a solution of 4.2 g. (0.028 mole) of diethyl sulfate in 200 ml. of tetrahydrofuran was added. The ether was removed by distillation and the reaction mixture heated at reflux for 18 hr. After hydrolysis, ether was added and the organic layer separated. The ethereal solution was dried with sodium sulfate and evaporated, and the reaction products chromatographed. Elution with petroleum ether (b.p. 60–70°) and two subsequent recrystallizations from the same solvent gave 5.56 g. (59%) of colorless crystals, m.p. 133–136°. Another recrystallization raised the melting point to 135–137°. This material was identified as *N*-ethyl-2,2′,4,4-tetrabromodiphenylamine by mixed melting point and by comparison of the infrared spectra.

*Bromination of 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol.* Bromine (1.8 g., 0.011 mole) was added to 4.65 g. (0.0074 mole) of 2-(*N*-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol in 100 ml. of glacial acetic acid, and the reaction mixture stirred at room temperature for 1 hr. After hydrolysis with a dilute solution of sodium bisulfite, the aqueous solution was filtered. The resulting material was air-dried and chromatographed over alumina. Using petroleum ether (b.p. 60–70°) as the eluant there was obtained a colorless solid, which was recrystallized three times from petroleum ether to give 2.69 g. (71%) of colorless crystals, m.p. 133–137°. An additional recrystallization from the same solvent raised the melting point to 135–137°. The material was identified as *N*-ethyl-2,2′,4,4′-tetrabromodiphenylamine by mixed melting point.

*Bromination of di-p-tolylamine.* Bromine (16 g., 0.1 mole) was added dropwise over a period of 10 min. to a solution of 10 g. (0.051 mole) of di-*p*-tolylamine in 100 ml. of glacial acetic acid, while cooling in an ice bath. The reaction mixture was allowed to warm to room temperature, stirred for 1 hr., and then hydrolyzed with 200 ml. of a dilute solution of sodium bisulfite. The aqueous solution was cooled in an ice bath and the resulting material was filtered yielding 16.9 g. of pale blue-green solid, m.p. 40–53°. After two recrystallizations from absolute ethanol, there was obtained 11.3 g. (64%) of 2,2′-dibromodi-*p*-tolylamine, m.p. 57–59°. An additional recrystallization of a portion gave colorless needles, m.p. 57.5–59°. The infrared spectrum of the material in carbon disulfide exhibited a strong absorption band at 12.4 $\mu$, indicative of 1,2,4-trisubstituted benzene.

*Anal.* Calcd. for $C_{14}H_{13}Br_2N$: Br, 45.01; N, 3.95. Found: Br, 44.64, 44.59; N, 3.92, 3.76.

A repeat reaction employing 20 g. (0.102 mole) of di-*p*-tolylamine and 32 g. (0.2 mole) of bromine gave a 60% yield of the dibromo compound.

*N-Ethyl-2,2′-dibromodi-p-tolylamine.* An ethereal solution containing 0.031 mole of methyllithium was added to 11 g. (0.031 mole) of 2,2′-dibromodi-*p*-tolylamine in 100 ml. of ether, while cooling in an ice bath. After stirring for 45 min., this solution was treated with 6.16 g. (0.04 mole) of diethyl sulfate in 100 ml. of tetrahydrofuran. The ether was removed by distillation and the resulting tetrahydrofuran solution heated at reflux for 16 hr. After the usual work-up, the reaction products were subsequently taken up in absolute ethanol to give 10.73 g. of pale yellow needles, m.p. 104–111°. This material was recrystallized three times from absolute ethanol to give 9.33 g. (79%) of colorless needles, m.p. 109–111°.

*Anal.* Calcd. for $C_{16}H_{17}Br_2N$: C, 50.15; H, 4.47. Found: C, 50.21, 50.09; H, 4.79, 4.61.

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*5-Ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline.* (*A*) *From N-ethyl-2,2′-dibromodi-p-tolylamine.* A solution of 5.75 g. (0.015 mole) of *N*-ethyl-2,2′-dibromodi-*p*-tolylamine in 50 ml. of ether, cooled in an ice bath, was treated with 0.03 mole of *n*-butyllithium. After stirring for 30 min., a solution of 3.80 g. (0.015 mole) of dichlorodiphenylsilane in 50 ml. of ether was added and the reaction mixture heated at reflux for 17 hr. Subsequently, 30 ml. of toluene was added and the ether distilled. After refluxing the resulting solution for 2 hr., Color Test I[11] was negative. The reaction mixture was hydrolyzed with 50 ml. of water and worked up in the usual manner. The reaction products were taken up in petroleum ether (b.p. 60–70°) to give 3.76 g. of yellow solid, m.p. 147–158°. This material was taken up again in petroleum ether, treated with charcoal, and concentrated to give 3.27 g. (54%) of colorless crystals, m.p. 159–162°. The analytical sample melted at 160.5–162°.

*Anal.* Calcd. for $C_{28}H_{27}NSi$: C, 82.91; H, 6.71; Si, 6.93. Found: C, 83.23, 83.00; H, 6.89, 6.86; Si, 7.15, 7.01.

(*B*) *From 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline.* An ethereal solution of 0.023 mole of *n*-butyllithium was added to 4.0 g. (0.0075 mole) of 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline in 100 ml. of ether, while cooling in an ice bath. The reaction mixture was allowed to warm to room temperature and stirred for 45 min. A solution of 3.15 g. (0.025 mole) of freshly distilled dimethyl sulfate in 25 ml. of ether was added, and after refluxing for 2 hr. Color Test I[11] was negative. Subsequently, the usual work-up and crystallization from petroleum ether (b.p. 60–70°) gave 2.54 g. of colorless solid, m.p. 150–160°. This material was recrystallized twice from petroleum ether to give 1.89 g. (62%) of colorless crystals, m.p. 158–160°. An additional recrystallization raised the melting point to 159–161°. The material was identified as 5-ethyl-2,8-dimethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melting point and by comparison of the infrared spectra.

(11) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

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AMES, IOWA

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[CONTRIBUTION FROM THE NEW BEDFORD INSTITUTE OF TECHNOLOGY]

# Chromatographic Adsorption. V. Isomer Distributions during Methyl Mannoside and during Methyl Arabinoside Formations by the Fischer Method Using a Cation Exchange Resin as Catalyst

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Methyl mannoside and methyl arabinoside formations by the Fischer method, using a strongly acidic ion-exchange resin as catalyst, were followed by chromatographing aliquots on a starch column with butanol-pyridine-water (10:3:3 by volume). D-Mannose disappeared at a first order rate to yield, initially at first order rates, the $\alpha$- and $\beta$-methyl mannofuranosides and mannopyranosides and to reach a final equilibrium containing all four methyl mannosides after seventy-two hours. Arabinose behaved similarly to reach a final equilibrium mixture after twenty-four hours. The same final equilibrium mixtures could be formed from any of the methyl glycosides by similar treatment.

Although the Fischer method of glycoside formation has been known for a long time and a modification of this method using an ion-exchange resin as the acid catalyst for a shorter time,[1] only one quantitative study of the distribution of all four existing isomers during the course of the reaction has been attempted. This was done in paper III of this series[2] in which the isomer distribution during methyl galactoside formation was investigated using a Florex XXX adsorption column for the separations. Unfortunately only two fractions were obtained and the percentages of the four methyl galactosides had to be calculated from the optical rotations of these fractions. Since publication of this paper there has been considerable activity in the field of chromatographic and electrophoretic separations of methyl glycoside mixtures.[3-11] Most of these methods use cellulose partition columns with varied solvent combinations. The separation of the four methyl mannosides[10] has been accomplished completely enough for quantitative analysis using a cellulose powder column with butanol-pyridine-water (10:3:3 by volume) as developer. An improved separation of the methyl mannosides and also separation of the four methyl arabinosides has been obtained by

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