

maxima of 950 at 257.5 μ and 210 at 367.5 μ ; in 0.1 *N* hydrochloric acid the maxima were 605 at 267.5 μ and 237 at 322.5 μ .

4-(N-[2-Amino-4-hydroxy-6-pteridyl]-methyl)-amino)-3-bromobenzenearsonic Acid (VII).—Using the general procedure 115 g. of 3-bromoarsanilic acid, 200 g. of I and 225 g. of II gave 300 g. of crude product.

The crude product was dissolved in 18 l. of a 0.1 *N* sodium hydroxide solution at 75° and treated with calcium chloride and zinc chloride as described for compound V. The filtrate was adjusted to pH 2.0 and cooled; yield 22.0 g. The product was partially dissolved in 100 cc. of concentrated hydrochloric acid and then added to a liter of warm water. The material completely dissolved and quickly crystallized out again; yield 7.5 g.

A portion of this material (0.5 g.) was slurried in 10 cc. of 6 *N* hydrochloric acid. The compound dissolved and recrystallized immediately. The product was collected (0.3 g.) and redissolved in 10 cc. of water by adding several drops of ammonium hydroxide. This was mixed with an equal volume of concentrated hydrochloric acid, clarified with Norite and cooled to give a crystalline product.

Anal. Calcd. for $C_{13}H_{12}AsBrN_6O_4 \cdot HCl \cdot H_2O$: C, 29.7; H, 2.85; N, 16.0; Br, 15.2; Cl, 6.75; As, 14.3. Found: C, 29.6; H, 3.46; N, 15.9; Br, 15.0; Cl, 6.66; As, 15.0.

2-(N-[(2-Amino-4-hydroxy-6-pteridyl)-methyl]-amino)-benzenearsonic Acid (VIII).—Using the general procedure 104 g. of 2-aminobenzenearsonic acid, 230 g. of I and 250 g. of II gave 217 g. of crude product.

The crude product was suspended in one l. of water and dissolved by adding 10 *N* sodium hydroxide (about 250 cc.). This was clarified with Norite and then mixed with 1200 cc. of a 10 *N* sodium hydroxide solution. After cooling for two days at 5° the product was collected, redissolved in water (total volume 1100 cc.) and clarified with Norite. To this was added 1100 cc. of a 10 *N* sodium hydroxide solution and the solution was cooled overnight. The crystalline product was collected and recrystallized two more times in the same manner using 850 cc. of water, Norite and 850 cc. of 10 *N* sodium hydroxide each time. The crystalline sodium salt was then collected and added in portions to 100 cc. of cold concentrated hydrochloric acid. The sodium salt changed to the free acid and precipitated. This was diluted to one l. with water, cooled and the product collected, washed with water, acetone and ether and dried; yield 26.5 g.

For purposes of analysis a small sample was recrystallized twice as the sodium salt and then converted to the free acid.

Anal. Calcd. for $C_{13}H_{13}AsN_6O_4$: C, 39.8; H, 3.32; N, 21.4; As, 19.1. Found: C, 39.7; H, 3.81; N, 21.4; As, 19.7.

In 0.1 *N* sodium hydroxide VIII showed *E* (1%, 1 cm.) maxima of 805 at 255 μ and 229 at 367.5 μ ; in 0.1 *N* hydrochloric acid the maxima were 492 at 247.5 μ and 304 at 322.5 μ .

4-(N-[(2,4-Diamino-6-pteridyl)-methyl]-amino)-benzenearsonic Acid (IX).—Using the general procedure 109 g. of arsanilic acid, 190 g. of 2,4,5,6-tetraaminopyrimidine sulfate and 218 g. of II gave 160 g. of crude product.

A portion of this product (58 g.) was dissolved in 11 l. of a 0.1 *N* sodium hydroxide solution at 70° and a small amount of insoluble black impurity was filtered off. The filtrate was warmed to 70°, treated with 100 cc. of a 30% calcium chloride solution and filtered. To the filtrate was added slowly enough of a 50% zinc chloride solution to bring the solution to pH 6.9. This was cooled and the product collected. This zinc salt was dissolved in approximately 1800 cc. of an 0.8 *N* hydrochloric acid solution at 80° and clarified with 50 g. of Norite. Upon cooling the filtrate the product crystallized; yield 1.85 g.

A portion of this material (400 mg.) was recrystallized from 100 cc. of 0.1 *N* hydrochloric acid; yield 200 mg. This was dissolved in 100 cc. of warm water containing 2 cc. of 1.0 *N* sodium bicarbonate solution, filtered and 40 cc. of a 0.1 *N* hydrochloric acid solution was added to the filtrate; yield of crystalline product 150 mg.

Anal. Calcd. for $C_{13}H_{14}AsN_7O_3$: C, 39.9; H, 3.58; N, 25.0. Found: C, 39.8; H, 4.24; N, 25.3.

In 0.1 *N* sodium hydroxide IX showed *E* (1%, 1 cm.) maxima of 990 at 257.5 μ and 205 at 372.5 μ ; in 0.1 *N* hydrochloric acid the maxima were 680 at 267.5 μ and 275 at 337.5 μ .

Acknowledgment.—The authors are indebted to Mr. Louis Brancone and staff for the microanalyses and to Anne de Grunigen for the ultraviolet determinations.

LEDERLE LABORATORIES DIVISION
AMERICAN CYANAMID CO.
PEARL RIVER, N. Y.

Nitration of the Tolytriethylsilanes

BY ROBERT A. BENKESER AND HERBERT LANDESMAN

RECEIVED OCTOBER 28, 1953

Recently¹ it was shown that copper nitrate can be used to nitrate phenyltrimethylsilane and that in this reaction the trimethylsilyl group functions as a very weak ortho-para director. It became of interest to determine whether the copper nitrate reagent could be used to nitrate substituted phenyltrialkylsilanes since in many of these compounds the tendency for cleavage of the trialkylsilyl group is more pronounced² than with the unsubstituted phenyl. The isomeric tolyltriethylsilanes were accordingly chosen for this study. It was hoped that in addition to the above information some conclusions might be reached concerning the directive effects of the triethylsilyl group compared to the methyl.

Nitration of *o*-tolyltriethylsilane resulted in a 50% yield of mononitrosilanes from which was identified 2-methyl-5-nitrotriethylsilane. The proof of structure of this isomer was accomplished by reduction to the amine, acetylation, and then cleavage of the triethylsilyl group with hydrogen chloride to yield *p*-acetotoluide. It seems likely that some 2-methyl-3-nitrotriethylsilane would also be formed in this reaction but we were unable to establish this definitely.

Nitration of *m*-tolyltriethylsilane resulted in a 74% yield of mononitrosilanes from which were identified 3-methyl-4-nitrophenyltriethylsilane and 2-nitro-5-methyltriethylsilane. The structure of the former was established by cleavage of the corresponding acetylated amine with iodine to form 5-iodo-2-acetaminotoluene. Treatment of the acetylated amine derived from 2-nitro-5-methyltriethylsilane yielded *p*-acetotoluide thus constituting a structure proof.

Nitration of *p*-tolyltriethylsilane gave a 60% yield of 4-methyl-3-nitrophenyltriethylsilane, since treatment of the corresponding amine with hydrogen chloride gave *o*-toluidine.

From the nitro isomers which were obtained it is quite apparent that the methyl group and *not* the triethylsilyl group is the dominating factor in determining the orientation. Thus in every case the incoming nitro group entered ortho or para to the methyl group even though in some instances this position was *meta* to the triethylsilyl while in others it was *ortho* or *para*. In addition the data tend to indicate (although admittedly the proof is on a less firm basis) the triethylsilyl group to be a weak ortho-para director like the trimethylsilyl. Thus the highest yield of nitrosilane isomers was

(1) R. A. Benkeser and P. E. Brumfield, *THIS JOURNAL*, **73**, 4770 (1951).

(2) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 4528 (1953).

obtained with *m*-tolyltriethylsilane. In this compound (but not in the ortho or para isomers) the directive influence of both the methyl and triethylsilyl groups (assuming the latter is ortho-para directing) reinforce one another which may account for the higher yield of product.

Experimental

***o*-Tolyltriethylsilane.**—A solution of *o*-tolyllithium prepared from 83.5 g. (0.5 mole) of *o*-bromotoluene and 7.0 g. (1 g. atom) of lithium was added to 83.6 g. of triethylchlorosilane (90% pure). The mixture was stirred until a negative Color Test I was obtained, then poured onto ice. The ether layer was separated, dried and evaporated. The residue was distilled through a Claisen head to give 76 g. (74%) of *o*-tolyltriethylsilane, b.p. 71–72° at 0.5 mm., d_{20}^4 0.906, n_D^{20} 1.5132, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.4.

***m*-Tolyltriethylsilane:** prepared from *m*-tolyllithium and triethylchlorosilane in 0.5-mole quantity as described above: yield 74 g. (72%), b.p. 63–64° at 0.5 mm., d_{20}^4 0.8905, n_D^{20} 1.5030, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.6.

***p*-Tolyltriethylsilane:** prepared from *p*-tolyllithium and triethylchlorosilane in 0.5-mole quantity as described for the ortho isomer: yield 65 g. (65%), b.p. 68–69° at 0.5 mm., d_{20}^4 0.888, n_D^{20} 1.5025, MR_{calcd} 68.6, MR_{found} 68.5.

Anal. Calcd. for $C_{13}H_{22}Si$: Si, 13.6. Found: Si, 13.3.

2-Methyl-5-nitrophenyltriethylsilane.—To a nitrating mixture from 32.7 g. (0.27 equiv.) of copper nitrate trihydrate and 175 cc. of acetic anhydride was added 46 g. (0.223 mole) of *o*-tolyltriethylsilane, keeping the temperature at 30° during the addition. The mixture was then heated to 40° for 8 hours. It was then hydrolyzed by pouring onto cracked ice and was neutralized with ammonium hydroxide. The mixture was then extracted with four 200-cc. portions of ether and the extracts were combined. The ethereal solution was dried and evaporated, and the residual oil fractionated in a Todd column to give 8 g. (27%) of triethylsilanol and a small amount of *o*-nitrotoluene. A fraction boiling between 129–142° at 3 mm. was collected and a portion of this solidified. This solid when crystallized from pentane amounted to 8 g. and melted 40–41°.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 11.0.

The total yield of mononitrosilanes in this run was 28 g. (50%).

2-Methyl-5-aminophenyltriethylsilane.—A mixture of 8.3 g. (0.033 mole) of 2-methyl-5-nitrophenyltriethylsilane in 50 cc. of ethanol was reduced in a Parr low-pressure hydrogenator with a Raney nickel catalyst. The product was distilled through a Claisen head at 123° at 2.5 mm. A yield of 7 g. (94%) was obtained, n_D^{20} 1.5430, d_{20}^4 0.9570, MR_{calcd} 73.0, MR_{found} 72.9.

Anal. Calcd. for $C_{13}H_{23}NSi$: Si, 12.7. Found: Si, 13.0.

The acetyl derivative melted at 105° after crystallization from 90–100° petroleum ether.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.5.

Structure Proof of 2-Methyl-5-aminophenyltriethylsilane.—Hydrogen chloride was passed through a solution of 6.4 g. (0.029 mole) of the amine in 100 cc. of ethanol for 4 hours. The solution was evaporated and the residue was dissolved in water. Solid potassium hydroxide was added until the solution was basic and the mixture was then extracted with ether. The ether extract was evaporated and the acetyl derivative of the residue was prepared in the usual manner. There was obtained 1.3 g. (30%) of *p*-acetotoluide (mixed m.p.) melting at 151–153°.

Nitration of *m*-Tolyltriethylsilane.—The reaction was carried out as described above for the ortho isomer. Distillation through a Todd column gave 1.3 g. of triethylsilanol, 3.7 g. (12%) of *m*-nitrotoluene and 41 g. (74%) of mononitrated silanes. A cut (18.6 g.) boiling at 135–136° at 1 mm. was collected. The refractive index (n_D^{20}) varied from 1.5299 to 1.5307. The density of the cut with an index of refraction of 1.5303 was 1.029; MR_{calcd} 74.9, MR_{found} 75.4.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 11.0.

Reduction of Nitrated *m*-Tolyltriethylsilanes.—The cut boiling at 135–136° at 1 mm. was reduced catalytically in the same fashion as described above and the product was distilled through a Todd column. Two cuts were collected, the one (A) boiling at 110–126° at 3 mm. with n_D^{20} varying from 1.5362–1.5383, and the other (B) 126–130° at 3 mm. with n_D^{20} varying from 1.5382–1.5385; d_{20}^4 0.944.

Anal. (Cut B) Calcd. for $C_{13}H_{23}NSi$: Si, 12.7. Found: Si, 13.1.

Cut (A) gave a mixture of acetylated amines from which 2-acetamino-5-methylphenyltriethylsilane melting at 124–125° was obtained after two crystallizations from 90–100° petroleum ether.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.8.

Cleavage of the above compound with hydrogen chloride gave 30% *p*-acetotoluide. Cut (B) gave only one acetyl derivative melting at 66–67°. This was shown (see below) to be 3-methyl-4-acetaminophenyltriethylsilane.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.9.

Structure Proof of 3-Methyl-4-aminophenyltriethylsilane.—Seven grams (0.27 mole) of iodine was added to 3.0 g. (0.014 mole) of the aminosilane obtained from cut (B) above. The solution immediately became very hot and tar formation was noted. The mixture was heated on a steam-bath for 3 hours, hydrolyzed and extracted with ether. The ether extract was washed with thiosulfate and evaporated. The acetyl derivative was prepared from the residue in the usual manner. Recrystallized from petroleum ether, it melted at 167–168° and did not depress the melting point of authentic 5-iodo-2-acetaminotoluene.³

4-Methyl-3-nitrophenyltriethylsilane.—Nitration of *p*-tolyltriethylsilane was accomplished as described for the ortho isomer. Distillation through a Todd column gave 8.7 g. of triethylsilanol, 10.7 g. (26%) of solid *p*-nitrotoluene and 46 g. (60%) of material boiling at 140° at 1 mm., n_D^{20} 1.5268, d_{20}^4 1.0277, MR_{calcd} 74.9, MR_{found} 75.1.

Anal. Calcd. for $C_{13}H_{21}O_2NSi$: Si, 11.1. Found: Si, 10.7.

4-Methyl-3-aminophenyltriethylsilane.—The amine was prepared in 95% yield from the nitro compound by catalytic reduction as described above. The boiling point was 109° at 0.5 mm., n_D^{20} 1.5350, d_{20}^4 0.944, MR_{calcd} 73.0, MR_{found} 73.0.

Anal. Calcd. for $C_{13}H_{23}NSi$: Si, 12.6. Found: Si, 12.9.

The acetyl derivative melted at 65–66°.

Anal. Calcd. for $C_{15}H_{25}ONSi$: Si, 10.6. Found: Si, 10.8.

When the free amine was treated with hydrogen chloride as described above a 68% yield of *o*-acetotoluide was obtained melting at 109–110°. This did not depress the melting point of an authentic sample.

(3) H. L. Wheeler and L. M. Liddle, *Am. Chem. J.*, **42**, 502 (1909).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

The Reaction of Phenyllithium with Diphenylketene¹

BY JOHN A. BEEL AND EDWARD VEJVODA

RECEIVED AUGUST 14, 1953

The addition of Grignard reagents to diphenylketene was first investigated by Staudinger² who suggested that the reaction proceeded *via* addition to the ethylenic double bond. In the reaction between phenylmagnesium bromide and diphenylketene, Staudinger obtained diphenylacetophenone (II) (equation 1) which tautomerized to form triphenylvinyl alcohol (IV).

(1) This paper was presented in part before the Colorado-Wyoming Academy of Science, Denver, Colorado, April 27, 1951.

(2) H. Staudinger, *Ann.*, **356**, 122 (1907).