[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Dechlorination of Some Chloronitropicolines

BY HENRY E. BAUMGARTEN, HELEN CHIEN-FAN SU AND ARTHUR L. KRIEGER

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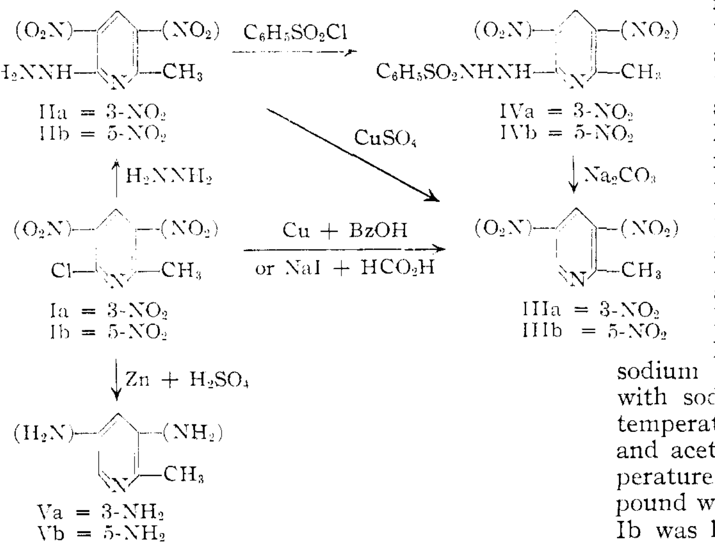
6-Chloro-3-nitro-2-picoline and 6-chloro-5-nitro-2-picoline have been subjected to three different dechlorination procedures (in addition to the one reported previously[1]) in the synthesis of 3- and 5-nitro-2-picoline, of which dechlorination by treatment with finely divided copper in an organic acid solvent at an elevated temperature appears to be the most satisfactory. Reductive dechlorination of the same chloro compounds with zinc and sulfuric acid has yielded 3- and 5-amino-2-picoline, respectively. 3-Nitro-4-picoline has been prepared by the dechlorination of a mixture of 2-chloro-3-nitro-4-picoline and 2-chloro-5-nitro-2-picoline.

In an earlier communication[1] we reported the synthesis of 3-nitro-2-picoline (IIIa) and 5-nitro-2-picoline (IIIb) by a procedure involving as the principal yield determining step the dechlorination of 6-chloro-3-nitro-2-picoline (Ia) and 6-chloro-5-nitro-2-picoline (Ib), respectively, by conversion of the chloro compounds into the corresponding hydrazino compounds (IIa and IIb) and oxidation of the latter to the dechlorinated derivatives with copper sulfate in dilute acetic acid. The need for a considerable supply of IIIa and its reduction product, 3-amino-2-picoline (Va), has led us to examine other procedures for the dechlorination. The procedures examined are outlined in the flow sheet.



McFadyen and Stevens[2] have reported the dechlorination of 2,4-dinitrochlorobenzene and picryl chloride by successive treatment with hydrazine and benzenesulfonyl chloride and decomposition of the arylbenzenesulfonhydrazide with potassium carbonate. The procedure has since been applied to heterocyclic aryl halides with varying success.[3-6] Albert and Royer[4] have introduced a useful and time-saving modification in which an aryl-*p*-toluenesulfonhydrazide is prepared directly from the aryl chloride and *p*-toluenesulfonhydrazide and then decomposed with sodium carbonate.

The reaction of IIa with benzenesulfonyl chloride in pyridine solution gave 2-methyl-3-nitro-6-(benzenesulfonhydrazino)-pyridine (IVa) in 57% yield and decomposition of the latter with aqueous sodium carbonate gave IIIa in 21% yield. By a similar sequence IIb was converted into 2-methyl-5-nitro-6-(benzenesulfonhydrazino)-pyridine (IVb) in 62% yield and the latter was decomposed to IIIb in 36% yield. The modification of Albert and Royer[4] could not be applied to the dechlorination of Ia, which failed to react with *p*-toluenesulfonhydrazide.

Blatt and Tristram[7] have reported the dechlorination of picryl chloride and several heterocyclic aryl halides by treatment with sodium iodide and formic or acetic acid. When Ia was treated with sodium iodide and acetic acid in acetone solution at room temperature for 24 hours or with sodium iodide in acetic acid at the reflux temperature for 5 hours, it was recovered unchanged from the reaction mixture. When Ia was heated with sodium iodide in formic acid for 7 hours on the steam-bath, hydrolysis took place and 65% of 6-hydroxy-3-nitro-2-picoline was obtained together with a small amount of recovered chloro compound. No IIIa was obtained in any of these experiments. When Ib was treated with sodium iodide in acetone at room temperature, with sodium iodide in acetic acid at the reflux temperature for 5 hours, or with sodium iodide and acetic acid in acetone solution at room temperature or at 80° for 4 days, the chloro compound was recovered unchanged. However, when Ib was heated with sodium iodide in formic acid on the steam-bath for 6 hours, a 25% yield of IIIb was obtained together with a larger amount of the hydrolysis product, 6-hydroxy-5-nitro-2-picoline. As was pointed out in the earlier report,[1] the chlorine atom in Ib is apparently more reactive than that in Ia.

Smith[8,9] has reported the dechlorination of several nitroaryl chlorides by heating with copper powder in molten benzoic acid or in caproic acid. Brown[10] has shown that the Smith dechlorination may be used in the preparation of 5-nitro-3-picoline. Dechlorination of Ia using copper powder

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(1) H. E. Baumgarten and H. C. Su, THIS JOURNAL, **74**, 3828 (1952).

(2) J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(3) M. J. S. Dewar, *ibid.*, 619 (1944).

(4) A. Albert and R. Royer, *ibid.*, 1148 (1949).

(5) J. S. Morley, *ibid.*, 1971 (1951).

(6) E. J. Alford and K. Schofield, *ibid.*, 609 (1953).

(7) A. H. Blatt and E. W. Tristram, THIS JOURNAL, **74**, 6273 (1952).

(8) W. T. Smith, Jr., *ibid.*, **71**, 2855 (1949).

(9) W. T. Smith, Jr., and L. Campanaro, *ibid.*, **75**, 3602 (1953).

(10) E. V. Brown, Abstracts of Papers Presented at the Los Angeles, Calif., Meeting of the American Chemical Society, March 15-19, 1953, p. 11M.

and benzoic acid at 160–180° gave under proper conditions a yield of 27–45% of IIIa. In the dechlorination of Ia the temperature of the reaction mixture was found to be more important than the nature of the copper, the order of addition of reactants, etc. When the temperature was below 160°, dechlorination did not take place. When the temperature rose above 180°, side reactions occurred which greatly decreased the yield of IIIa (even down to no yield). The dechlorination of Ib by the same procedure gave IIIb in 38% yield, and the dechlorination appeared to be less sensitive to temperature changes although temperature control was, of course, desirable for maximum yields. The lesser sensitivity of Ib to the reaction temperature relative to that of Ia may also be attributed to the greater reactivity of the chlorine atom in Ib.

The over-all yields of IIIa and IIIb (based on Ia and Ib) for the various methods of dechlorination are given in Table I.

TABLE I

OVER-ALL YIELDS OF IIIa AND IIIb

Procedure	Yield of IIIa, %	Yield of IIIb %
Baumgarten–Su[1]	12	44[a]
McFadyen–Stevens	12	22
Blatt–Tristram	0	25
Smith	45	38

[a] Originally reported as 38%. The higher yield has been obtained by omission of the purification of IIa before oxidation.

From the table it appears that the method of choice for IIIa is the Smith dechlorination and for IIIb is the earlier procedure from this Laboratory. However, based on considerations of time and number of manipulations required, the actual method of choice in this Laboratory for the preparation of both IIIa and IIIb has been that of Smith.

The synthesis of 3-nitro-4-picoline was first described by Koenigs and Fulde[11] and later by Bremer.[12] Although these multi-step syntheses have been used in recent investigations[10,13] with some success, we have preferred to prepare this compound by a route similar to that used for IIIa and IIIb.

Nitration of 2-amino-4-picoline and thermal rearrangement of the intermediate nitramine, which was not isolated, gave a mixture of 2-amino-3-nitro-4-picoline and 2-amino-5-nitro-4-picoline in 86% yield. The principal time-consuming step in the preparation of IIIa and IIIb[1] was the lengthy steam distillation required to separate the isomeric aminonitropicolines. In the present synthesis no such separation was required, for both isomers led to the same ultimate product.[14] Diazotization of the mixed nitroaminopicolines gave a mixture of 2-hydroxy-3-nitro-4-picoline and 2-hydroxy-5-nitro-4-picoline in 66% yield, and the latter was converted with phosphorus pentachloride into a mixture of 2-chloro-nitro-4-picoline and 2-chloro-5-nitro-4-picoline in 63% yield. The dechlorination of the mixed chloro compounds with copper and benzoic acid proceeded smoothly at 150° to give 3-nitro-4-picoline in 33–45% yield. Glacial acetic acid could be substituted for benzoic acid in this dechlorination with no apparent lowering of the yield. The over-all yield of 3-nitro-4-picoline was only 10–13%; however, the starting material is readily available and the length of time required for the whole sequence is not great.

Parker and Shive[15] have reported the preparation of 5-amino-2-picoline (Vb) by the hydrogenation of Ib at atmospheric pressure in the presence of both platinum oxide and palladium on barium carbonate catalysts and the preparation of Va by a somewhat more elaborate route. In order to carry out the preparations on a somewhat larger scale than that permitted by the usual low pressure hydrogenation apparatus, the procedure of Binz and Schickh[16] for the synthesis of 3-aminopyridine was adapted to the preparation of Va and Vb. Thus, Ia was reduced with zinc dust and dilute sulfuric acid to Va in 50% yield and Ib was reduced under the same conditions to Vb in 39% yield.

Experimental

Dechlorination of 6-Chloro-3-nitro-2-picoline (Ia). (a) Procedure of McFadyen and Stevens.—To a stirred, well-cooled solution of 2 g. (0.012 mole) of 6-hydrazino-3-nitro-2-picoline[1] in 10 ml. of pyridine was added slowly 1.5 ml. of benzenesulfonyl chloride. After two hours the brown solution was poured into a mixture of ice and hydrochloric acid, and the pale yellow precipitate was filtered off and washed with dilute hydrochloric acid and with water. After recrystallization from ethanol, the yield of **2-methyl-3-nitro-6-(benzenesulfonhydrazino)-pyridine (IVa)** was 2.1 g. (57%), m.p. 193–195°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4S$: C, 46.75; H, 3.93; N, 18.17. Found: C, 46.79; H, 3.91; N, 18.32.

A 0.5-g. (0.0016 mole) portion of the 2-methyl-3-nitro-6-(benzenesulfonylhydrazino)-pyridine was added in small portions to a solution of 5.7 g. of sodium carbonate in 57 ml. of water at 90°. Heating was continued for 15 minutes after addition was complete and then the mixture was refluxed for an additional 45 minutes. The cooled solution was extracted with ether and the ethereal solution was dried over magnesium sulfate. By removal of the ether, 3-nitro-2-picoline (IIIa) could be obtained as a yellow oil. However, the free base was found to decompose rather rapidly on standing, so to avoid air oxidation or self-oxidation, the 3-nitro-2-picoline was converted into its hydrochloride salt by passing hydrogen chloride through the dry ethereal solution. The resultant 3-nitro-2-picoline hydrochloride, m.p. 164–166°, weighed 0.06 g. (21%).

(b) Procedure of Blatt and Tristram.—A mixture of 6.9 g. (0.04 mole) of 6-chloro-3-nitro-2-picoline[1] in 20 ml. of formic acid and 15 g. (0.095 mole) of sodium iodide in 50 ml. of formic acid was heated on the steam-bath for 7 hours. The mixture was poured into a solution of 5 g. of sodium bisulfite in 280 ml. of water. After the solution had been cooled in an ice-bath and filtered, 4.4 g. of a pale yellow solid, m.p. 225–230°, was obtained. The solid did not depress the melting point of 6-hydroxy-3-nitro-2-picoline.[1] The filtrate was made slightly basic with 6 *N* sodium hydroxide and concentrated to a small volume, giving 0.7 g. (10%) of recovered 6-chloro-3-nitro-2-picoline.

(c) Procedure of Smith.—To a mixture of 21 g. (0.17 mole) of molten benzoic acid and 15 g. of copper powder (Baker purified, activated as described by Kleiderer and Adams[17,18]) in a three-necked flask provided with a mercury-

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(11) E. Koenigs and A. Fulde, *Ber.*, **60**, 2106 (1927).

(12) O. Bremer, *Ann.*, **529**, 290 (1937).

(13) For application of this procedure to IIIb see W. Gruber and K. Schlogl, *Monatsh.*, **80**, 499 (1949); **81**, 473 (1950).

(14) For a description of the nitration of 2-amino-4-picoline in which the nitramine is isolated and the isomeric nitroaminopicolines are separated by steam distillation, see O. Seide, *Ber.*, **57**, 791 (1924).

(15) E. D. Parker and W. Shive, THIS JOURNAL, **69**, 63 (1947).

(16) A. Binz and O. v. Schickh, *Ber.*, **68B**, 320 (1935).

(17) E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4225 (1933).

(18) The necessity for such activation was not established; it was merely a routine precaution. In some experiments very old (5 to 10 years) samples of copper gave results equal to those with activated copper.

sealed stirrer, thermometer reaching into the reaction mixture and reflux condenser and heated on a wire gauze by a burner was added 10.4 g. (0.06 mole) of 6-chloro-3-nitro-2-picoline in small portions with vigorous stirring at a temperature of 160–180°. After the chloro compound had been added, the mixture was kept at the same temperature with stirring for 10 minutes. The mixture was allowed to solidify and a solution of 15 g. of sodium carbonate in 80 ml. of water was added. The alkaline mixture was steam distilled until the distillate came over clear. The distillate was extracted with ether and the ethereal solution was dried over magnesium sulfate. By passing hydrogen chloride through the filtered solution and filtering off the precipitated salt, 3.35 g. (33%) of 3-nitro-2-picoline hydrochloride, m.p. 165–166°, was obtained. Evaporation of the filtrate to dryness left 0.62 g. (6%) of recovered 6-chloro-3-nitro-2-picoline.

In some experiments the residue from the steam distillation was filtered, and the filtrate was extracted with ether. After the extracts had been dried over magnesium sulfate and dry hydrogen chloride had been passed into the solution, up to 5% of 3-nitro-2-picoline hydrochloride could be obtained.

In other experiments the total yield of 3-nitro-2-picoline (as the hydrochloride) varied from 27–45%.

Several experiments were carried out in which the reaction mixture was heated in an oil-bath. Under these conditions it was difficult to control the temperature inside the flask, and temperatures above 200° with consequent loss of product were noted. On the other hand if the temperature fell below 160°, most of the chloro compound was recovered during the steam distillation.

Dechlorination of 6-Chloro-5-nitro-2-picoline (Ib). (a) **Procedure of McFadyen and Stevens.—2-Methyl-5-nitro-6-(benzenesulfonhydrazino)-pyridine (IVb)** was prepared by the same procedure as that described above for 2-methyl-3-nitro-6-(benzenesulfonhydrazino)-pyridine. After recrystallization from ethanol a total yield of 62% of yellow needles, m.p. 139–142°, was obtained.

Anal. Calcd. for $C_{12}H_{12}N_4O_4S$: C, 46.76; H, 3.93; N, 18.17. Found: C, 46.84; H, 3.93; N, 18.12.

The decomposition of the 2-methyl-5-nitro-6-(benzenesulfonhydrazino)-pyridine was carried out exactly as described above for 2-methyl-3-nitro-6-(benzenesulfonhydrazino)-pyridine except that the product, 5-nitro-2-picoline (IIIb), was isolated by evaporation of the ether extracts without conversion into the hydrochloride. 5-Nitro-2-picoline appeared to be quite stable as the free base. After recrystallization from petroleum ether the product, m.p. 106.5–108°, was obtained in 38% yield.

(b) **Procedure of Blatt and Tristram.**—A mixture of 0.9 g. (0.005 mole) of 6-chloro-5-nitro-2-picoline[1] in 4 ml. of formic acid and 3 g. (0.019 mole) of sodium iodide in 12 ml. of formic acid was heated on the steam-bath for 6 hours. The mixture was poured into a solution of 1 g. of sodium bisulfite in 40 ml. of water. No precipitate formed. The solution was cooled in an ice-bath and was made slightly basic with 6 *N* sodium hydroxide. A yellow-brown solid was collected by filtration, which, after recrystallization from petroleum ether (using charcoal), gave white needles of 5-nitro-2-picoline, m.p. 105–106°. The yield was 0.18 g. (25%).

After concentrating the filtrate to a small volume, 0.22 g. of a bright yellow precipitate was obtained. The yellow solid did not melt below 330°. Upon ignition, it left an alkaline ash. Elementary analysis indicated that the solid was probably the dihydrate of the sodium salt of 6-hydroxy-5-nitro-2-picoline.[1]

Anal. Calcd. for $C_6H_9N_2O_5Na$: C, 33.97; H, 4.28; N, 13.21. Found: C, 33.83; H, 3.79; N, 12.96.

The yellow solid was dissolved in water and the solution was neutralized with formic acid and evaporated on the steam-bath to a small volume. On cooling a light brown solid separated which, when recrystallized from water, melted at 221–223° and which did not depress the m.p. of an authentic sample of 6-hydroxy-5-nitro-2-picoline.[1]

Anal. Calcd. for $C_6H_6N_2O_3$: C, 46.76; H, 3.93. Found: C, 46.77; H, 4.31.

(c) **Procedure of Smith.**—The dechlorination of 6-chloro-5-nitro-2-picoline was carried out as described above for 6-chloro-3-nitro-2-picoline. After recrystallization from petroleum ether, 5-nitro-2-picoline, m.p. 106–107°, was obtained as white leaflets in 38% yield.

3-Amino-2-picoline (Va).—To a mixture of 9 g. (0.05 mole) of 6-chloro-3-nitro-2-picoline, 400 ml. of water and 60 ml. of concentrated sulfuric acid was added 20 g. of zinc dust. After an initial vigorous reaction, the mixture was refluxed for 8 hours. The cooled solution was made slightly basic with sodium hydroxide, the precipitate which formed was filtered off and the filtrate was extracted with benzene. After treating the benzene extracts with charcoal, the benzene was evaporated to a small volume and filtered. The white solid, 3-amino-2-picoline, 2.8 g. (50%), melted at 112–114°. A mixed melting point with a sample of 3-amino-2-picoline prepared by the method of Baumgarten and Dornow[19] was not depressed.

5-Amino-2-picoline (Vb) was prepared from 6-chloro-5-nitro-2-picoline by the same procedure as that described above for 3-amino-2-picoline. 5-Amino-2-picoline was obtained as an almost colorless solid, m.p. 94–96° (lit.[10] m.p. 95–96.5°). In this preparation chloroform could be used advantageously instead of benzene for the extraction of the product. The yield, after recrystallization from benzene, was 39%.

3- and 5-Nitro-2-amino-4-picoline.—Through the third opening of a 2-l., three-necked flask fitted with a stirrer and condenser and cooled in ice, 130 g. (1.2 moles) of solid 2-amino-4-picoline was added slowly to 1140 g. (620 ml.) of concentrated sulfuric acid. A dropping funnel was fitted to the flask and, with cooling and mechanical stirring, 129 g. (92 ml.) of concentrated nitric acid was added dropwise in such a manner that the temperature did not rise above 10°. The nitration mixture was allowed to stand at room temperature overnight. The mixture was stirred vigorously for 1 hour at room temperature and then warmed slowly on the steam-bath to about 95° and kept at that temperature for 2 hours to complete rearrangement of the nitramine (II). The cooled solution was poured onto ice and made basic with concentrated ammonium hydroxide solution. The filtered product, after drying, weighed 157 g. (86%). The drying could be omitted as described below.

3- and 5-Nitro-2-hydroxy-4-picoline.—A 63-g. (0.41 mole) quantity of the crude mixed nitro-2-amino-4-picolines was added to a solution of 129 g. (70 ml.) of concentrated sulfuric acid in 1 l. of water. If any of the nitramine had not been completely rearranged in the previous step and remained undissolved in the sulfuric acid solution, it was filtered off. A solution of 40 g. (0.58 mole) of sodium nitrite in 120 ml. of water was added dropwise with cooling and stirring, keeping the temperature of the reaction mixture below 10°. After the addition the mixture was stirred for one hour at the low temperature and filtered while still cold. The crude 3- and 5-nitro-2-hydroxy-4-picoline mixture, when dry, weighed 42 g. (66%).

It was not necessary to dry the crude 3- and 5-nitro-2-amino-4-picolines before the diazotization. The over-all yield on the two steps combined, based on the 2-amino-4-picoline, was 55–65% when the drying process was omitted.

3- and 5-Nitro-2-chloro-4-picoline.—A mixture of 91.5 g. (0.60 mole) of the crude, dry mixed 3- and 5-nitro-2-hydroxy-4-picolines and 165 g. (0.79 mole) of phosphorus pentachloride in a 1-l. round-bottomed flask was heated in an oil-bath held at 110–120° for 4 hours. The cooled mixture was poured onto ice to hydrolyze the excess phosphorus pentachloride. The chloro compound was steam distilled from the acid hydrolysis mixture and the distillate was extracted with ether. The ethereal solution was dried over magnesium sulfate and the ether was removed on the steam-bath. Distillation of the residue under reduced pressure gave 61.2 g. (60%) of mixed 3- and 5-nitro-2-chloro-4-picoline, b.p. 145–155° (30 mm.).

The steam distillation step could be omitted by separating the dark oily lower layer from the hydrolysis of the excess phosphorus pentachloride and distilling it under reduced pressure after drying over magnesium sulfate. This distillation had to be performed with caution and, when the distillation was complete, air was not allowed to enter the distillation set-up until the flask had been cooled to room temperature. A rather serious explosion occurred in one experiment in which air was admitted to the system while the distillation flask was still hot. The yield by this alternate procedure was 58–63%.

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(19) (a) P. Baumgarten and A. Dornow, *Ber.*, **72B**, 563 (1939); (b) A. Dornow, *ibid.*, **73B**, 78 (1940).

3-Nitro-4-picoline.—A mixture of 6.88 g. (0.04 mole) of the crude mixed 3- and 5-nitro-2-chloro-4-picoline and 13.4 g. (0.11 mole) of benzoic acid was placed in a 500-ml., three-necked flask fitted with a condenser, stirrer and thermometer. The reaction mixture was heated over a wire gauze by a burner to 150°. The burner was removed and 10 g. (0.16 mole) of copper powder (Baker purified) was added in small portions so that the temperature was maintained between 150-160°. After about half of the copper had been added, the temperature began to drop. The rest of the copper was added and heat was applied to keep the temperature at 150° for 15 minutes. The set-up was rearranged for steam distillation and, after the mixture had cooled, 50 ml. of 20% sodium carbonate solution was added slowly. The carbon dioxide produced in this neutralization was liberated only very slowly and the flask had to be heated cautiously with the burner until the evolution of gas was complete. Steam was passed into the mixture until about 300 ml. of distillate had been collected. The distillate was extracted with two 100-ml. portions of ether, the ethereal solution was dried over magnesium sulfate and the 3-nitro-4-picoline was precipitated as the hydrochloride by passing dry hydrogen chloride into the filtered solution. The yield of 3-nitro-4-picoline hydrochloride, m.p. 176-177°, was 3.07 g. (44%). The free base, 3-nitro-4-picoline, could be obtained quantitatively from the hydrochloride by neutralization with alkali. For storage purposes the hydrochloride was found to be much more stable than the free base, which, when pure, is a yellow oil that darkens rapidly on standing.

This reaction could be carried out using glacial acetic acid in place of benzoic acid. Such a procedure had the advantage of giving a liquid reaction mixture that was more readily neutralized when the reaction was complete. The yields obtained using acetic acid were often as good as those with benzoic acid, but the benzoic acid method was found to be more reliable. The dechlorination with benzoic acid was run using ten times the above amounts in a 1-l. vessel. The yield was 32%.

LINCOLN 8, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Friedel-Crafts Acylations with Trimethylsilylbenzoyl Chlorides

BY ROBERT A. BENKESER AND HENRY R. KRYSIAK

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Successful acylations of toluene with *m*- and *p*-trimethylsilylbenzoyl chlorides and aluminum chloride have been accomplished. Similarly, anisole has been acylated with *p*-trimethylsilylbenzoyl chloride in the presence of stannic chloride. The corresponding trimethylsilyl phenyl ketones were obtained in fair to good yields, as the principal reaction products. No apparent cleavage of the trimethylsilyl group was detected under the reaction conditions employed. *o*-Trimethylsilylbenzoyl chloride, when reacting under Friedel-Crafts conditions with anisole and with toluene, gave resinous materials as principal products. Structure proofs for all the silicon-containing ketones are described.

Attempts to carry out Friedel-Crafts reactions involving aromatic silicon compounds have met with little success or have resulted in fairly low yields. Thus, the attempted alkylation of diphenyldichlorosilane in the presence of anhydrous aluminum chloride yielded silicon tetrachloride, phenyltrichlorosilane, and ethyl derivatives of benzene.[1] The principal reaction of tetraphenylsilane in chloroform with aluminum chloride is that of cleavage, resulting in an 80% yield of silicon tetrachloride.[1] Similarly, tetrabenzylsilane under these conditions yields silicon tetrachloride.[1] Attempted acylations of phenyltriethylsilane in the presence of aluminum chloride yielded benzene, hexaethyldisiloxane, and the corresponding ketones in which the triethylsilyl group had been displaced by the acyl group.[2] The best yields obtainable in the acetylation of 2-trimethylsilylthiophene and 2-trimethylsilylfuran with iodine as catalyst were 13 and 25%, respectively, of the desired ketones.[3]

In previous work from this Laboratory on the hydrogen chloride cleavage of *m*- and *p*-substituted phenyltrimethylsilanes[4] an empirical correlation was attempted between the ease of cleavage of *m*- and *p*-substituted phenyltrimethylsilanes and Hammett sigma constants.[5] This correlation suggested that side-chain reactions of substituted phenyltrimethylsilanes could be carried out involving acidic or electrophilic reagents with a minimum of cleavage of the trimethylsilyl group, if the substituent had a sigma value of *ca.* +0.4 or greater.

Accordingly it became of interest to attempt the preparation of the isomeric trimethylsilylbenzoyl chlorides, to treat them under Friedel-Crafts conditions, and to determine whether the principal reaction was that of scission of the silicon-carbon bond or that of acylation. The acid chloride group would presumably have a σ-value similar to a carboxyl and thus be in the neighborhood of +0.4 or greater.

In accord with these predictions the three isomeric trimethylsilylbenzoyl chlorides were prepared from the corresponding acids using thionyl chloride with little cleavage of the silicon-carbon bond. Likewise acylations with the *m*- and *p*-trimethylsilylbenzoyl chlorides were attended with practically no cleavage with either stannic chloride or aluminum chloride as catalysts. Attempted acylations with *o*-trimethylsilylbenzoyl chloride resulted in the formation of high-boiling polymeric material. It seems likely that the proximity of the trimethylsilyl group to the carbonium ion intermediate in the ortho case may have favored cleavage especially since the desired acylation is so disfavored by steric requirements. However, the ortho ketones (with anisole and toluene) were prepared easily enough through the appropriate organocadmium reagent and *o*-trimethylsilylbenzoyl chloride, although extensive purification was necessary. These ketones were quite sterically hindered as evidenced by their failure to form phenylhydrazones.

The structure of the ketones obtained from the

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(1) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931).

(2) B. N. Dolgov and O. K. Panina, *Zhur. Obschei Khim.* (*J. Gen. Chem.*), **18**, 1293 (1948); (*C. A.*, **43**, 2177 (1949).

(3) R. A. Benkeser and R. B. Currie, THIS JOURNAL, **70**, 1780 (1948).

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

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.