dinitrofluorobenzene by means of stannous chloride and hydrochloric acid.[2]

The successful approach to 3,4-difluoroaniline involved the catalytic reduction of 3,4-difluoronitrobenzene, which was prepared by nitration of *o*-difluorobenzene.[3] The difluoro compound was obtained by means of the Schiemann reaction on *o*-fluoroaniline, which, in turn, was synthesized from *o*-fluorobenzoic acid by means of the Schmidt reaction or, less satisfactorily, from *o*-nitroaniline in a two-step process, (1) the Schiemann reaction, followed by (2) catalytic reduction. Conversion of 3,4-difluoroaniline to 3,4-difluorophenylarsonic acid was achieved by means of the Bart reaction.

Experimental

3,4-Difluoroaniline.—Exactly 142 g. (0.89 mole) of 3,4-difluoronitrobenzene, b.p. 85° (13 mm.), in 150 ml. of absolute ethanol was hydrogenated in a Parr apparatus at 60° and 3 atmospheres pressure in the presence of 2 g. of Raney nickel catalyst. Reduction proceeded slowly and fresh catalyst was twice added during the total 48-hour period. The catalyst was then removed by filtration, the solvent by distillation, and the residue distilled under reduced pressure to yield 107 g. (93%) of 3,4-difluoroaniline, b.p. 77° (7 mm.), n^{25}D 1.5110.

Anal. Calcd. for $C_6H_5NF_2$: C, 55.8; H, 3.9; N, 10.9. Found: C, 55.7; H, 3.9; N, 11.0.

3,4-Difluoroaniline hydrochloride was prepared by passing dry hydrogen chloride into a solution of the free base in absolute ether. The white crystalline product sublimed rapidly above 220°.

Anal. Calcd. for $C_6H_6NF_2Cl$: C, 43.5; H, 3.6; N, 8.5. Found: C, 43.9, 43.8; H, 3.6, 3.6; N, 8.6.

3,4-Difluorophenylarsonic Acid.—A mixture of 1 l. of ethanol, 52 g. (0.40) of 3,4-difluoroaniline, 40 g. of concentrated sulfuric acid and 112 g. (0.62 mole) of arsenic trichloride was cooled to 0°, and 28 g. (0.40 mole) of sodium nitrite in saturated aqueous solution was added with stirring while the temperature was maintained below 5°. When diazotization was complete, 4.0 g. of cuprous bromide was added, the solution was stirred for 30 minutes in the cold, and finally heated on a steam-bath until evolution of nitrogen ceased. The mixture was steam distilled and the residue evaporated to 200 ml. and then allowed to stand for 12 hours. The small amount of amorphous material which precipitated was removed by filtration and discarded. The filtrate was concentrated to a volume of 100 ml. and cooled; the colorless crystals which formed were washed, first with alcohol and then with ether, and dried to yield 30 g. (31%) of 3,4-difluorophenylarsonic acid, which did not melt below 300°. An analytical sample was prepared by recrystallization from water.

Anal. Calcd. for $C_6H_5O_3F_2As$: C, 30.3; H, 2.1. Found: C, 30.4; H, 2.3.

Acknowledgment.—These studies were aided by a contract between the Office of Naval Research, Department of Navy, and the University of Kansas.

(2) J. J. Blanksma, W. J. Van den Broek and D. Hoegen, *Rec. trav. chim.*, **65**, 329 (1946).

(3) J. G. McNally and J. R. Byers, U. S. Patent 2,391,179, Dec. 18, 1945.

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RECEIVED AUGUST 9, 1951

Anilinephthalein

BY MAX H. HUBACHER

In the course of a study of compounds with possible laxative properties,[1] it was decided to test anilinephthalein or 3,3-bis-(*p*-aminophenyl)-phthalide.

Baeyer[2] synthesized this compound from 3,3-bis-(phenyl)-phthalide and reported it to have a melting point of 180°. This synthesis was confirmed by v. Pechmann,[3] who, however, did not present any experimental evidence, and by Fischer and Römer,[4] who claimed to have obtained dimethylanilinephthalein from Baeyer's compound. On the other hand, Schwarzenbach and Brandenberger,[5] as well as we in our laboratory, failed to obtain the anilinephthalein which melted at 180° by following Baeyer's procedure.

More recently, Schwarzenbach and Brandenberger[5] described two new syntheses of anilinephthalein which they obtained as a compound melting at 204°. By their first method, starting from 3,3-bis-(*p*-tolyl)-phthalide, they obtained it in very low over-all yields. In their second and more efficient method, they condensed phthalyl chloride with *s*-diphenylurea and then hydrolyzed the intermediary amorphous condensation product with concd. hydrochloric acid at 140° in sealed glass tubes. This method was investigated further in our laboratory and an improved procedure was evolved, based on the observation that the condensation product can be hydrolyzed by a refluxing mixture of acetic and sulfuric acid.

Several new derivatives of anilinephthalein (I) were prepared, and further proof was obtained that I actually is the 3,3-bis-(*p*-aminophenyl)-phthalide. When reduced, anilinephthalin (II) is formed. On decarboxylation, this yields 4,4′-diaminotriphenylmethane (III).

In a similar manner, a toluidinephthalein (V) which melted at 197° was prepared from *s*-di-*o*-tolylurea. It was proved to be 3,3-bis-(*p*-amino-*m*-tolyl)-phthalide, as follows: By eliminating the two amino groups a ditolylphthalide (VI), which has different properties than those of the known *o*- and *p*-ditolylphthalides, was isolated. Compound VI must, therefore, be the 3,3-bis-(*m*-tolyl)-phthalide, which was further proved by synthesis.

Experimental[6]

Condensation Product from *s*-Diphenylurea and Phthalyl Chloride.—A 2-liter flask was charged with 500 ml. of nitrobenzene and 100 g. (0.75 mole) of aluminum chloride (anhydrous, technical or pure grade). After cooling to 25°, 40.6 g. (0.2 mole) of phthalyl chloride and finally 42.4 g. (0.2 mole) of *s*-diphenylurea (m.p. 239–243°) were added. The mixture was heated over a period of two hours from room temperature to 80° and kept at 80° for 30 minutes. The reddish-brown solution was then poured on an ice–hydrochloric acid mixture and the nitrobenzene removed by steam distillation. After the hard, brown residue had been pulverized and submitted to further steam distillation to remove traces of nitrobenzene, it weighed 60–68 g. It starts to melt at 260° and is not entirely melted at 300°. It is insoluble in common solvents and could not be obtained in crystalline form.

Anilinephthalein (I).—A mixture of 60–68 g. of the condensation product, 400 ml. of acetic acid, 5 ml. of water and

(1) (a) S. Loewe and M. Hubacher, *Arch. intern. pharmacodynamie*, **65**, 297 (1941); (b) M. H. Hubacher, THIS JOURNAL, **64**, 2538 (1942); **66**, 255 (1944); (c) M. H. Hubacher and S. Doernberg, *J. Am. Pharm. Assoc.*, **37**, 261 (1948).

(2) A. Baeyer, *Ann.*, **202**, 66 (1880).

(3) H. v. Pechmann, *Ber.*, **14**, 1866 (1881).

(4) O. Fischer and F. Römer, *ibid.*, **42**, 2934 (1909).

(5) G. Schwarzenbach and M. Brandenberger, *Helv. Chim. Acta*, **20**, 1253 (1937), and in more detail in "Untersuchungen in der Phtaleinreihe," Inauguraldissertation von Mark Brandenberger, Universität Zürich, 1936.

(6) All the melting points are corrected. Elementary analysis by Oakwold Laboratories, William Saschek and Francine Schwarzkopf.

40 ml. of concd. sulfuric acid was gently refluxed for four hours. Then 70 g. of Na_2CO_3 was added to the cooled solution, which exhibited a greenish fluorescence, and the bulk of the acetic acid was distilled off under reduced pressure. The gummy residue was dissolved in 600 ml. of boiling 1 *N* hydrochloric acid, then 600 ml. of water was added, cooled to 5° and black, tarry matter removed by filtration. On making the filtrate ammoniacal, a curdy precipitate was formed, which may agglomerate to a large lump, gradually becoming hard. The crude I (38.5–46.5 g., m.p. 176–186°) after one crystallization from methanol yielded 23.8–34.9 g. (38–55%) melting above 193°.

The pure anilinephthalein, crystallized from methanol, (1 g. in 50 ml.) melts at 202.5–203.2°. It is soluble in acetone, moderately soluble in ethyl acetate (absol.) or methanol, and insoluble in water, benzene or ether (absol.). On addition of I to a warm, concd. alcoholic solution of $ZnCl_2$, it slowly turns blue; I also produces the color reaction in acetic acid described by S. and B. The hydrochloride of I, cryst. from concd. HCl, sinters above 220°. On coupling diazotized I with an alkaline solution of β-naphthol, an alkali-insoluble tetrazo dye of strong reddish color is formed.

Anal. Calcd. for $C_{20}H_{16}O_2N_2$: C, 75.87; H, 5.09; N, 8.85; mol. wt., 316. Found: C, 76.22; H, 5.32; N, 8.77; mol. wt., 303.[7]

The formation of impure phenolphthalein from I, as described by S. and B., could be confirmed. On heating the crude phenolphthalein obtained from 0.04 mole of I in a nickel crucible with 100 g. of KOH at 230–235° for ten minutes, 5.33 g. of 4,4′-dihydroxybenzophenone, 3.95 g. of benzoic acid and 0.49 g. of *p*-hydroxybenzoic acid were formed.

Anilinephthalin (II).—A solution of 3.16 g. of I in 25 ml. of 5 *N* hydrochloric acid, to which 5.0 g. of tin (20 mesh) had been added, was refluxed for one day. After adding an additional 25 ml. of acid, refluxing was continued for another day. The decanted solution was made alkaline with 2 *N* sodium carbonate (160–172 ml.), the bulk of the solution decanted and the tin hydroxide separated by centrifugation. The last traces of tin were removed as tin sulfide. On addition of 3 *N* hydrochloric acid to the filtrate to a *p*H of 6.8 to 7.0, the anilinephthalin precipitated. It was dissolved in 180 to 200 ml. of methanol. Crystals will form after standing for several days at 5° (1.5 to 1.9 g., m.p. 235–237°; yield 49–59%).

Pure anilinephthalin (II) melts at 238.1–238.7°. It dissolves either in dil. hydrochloric acid or dil. sodium hydroxide; it is slightly soluble in acetone but insoluble in ether, petroleum ether, ethyl acetate, CCl_4, $CHCl_3$ or benzene. It can be sublimed at 180° and 5 microns pressure.[8] A solution in concd. sulfuric acid turns greenish on warming.

Anal. Calcd. for $C_{20}H_{18}O_2N_2$: C, 75.45; H, 5.70; N, 8.80; mol. wt., 318; –COOH, 14.1. Found: C, 75.42; H, 5.36; N, 8.71; mol. wt. 290 (Rast); –COOH, 13.2.[9]

Decarboxylation of II to 4,4′-Diaminotriphenylmethane (III).—The decarboxylation apparatus[9] was charged with 1.59 g. of II, 5 ml. of synthetic quinoline and 0.05 g. of basic cupric carbonate. On heating for thirty minutes at 250°, 0.2044 g. of CO_2 was evolved. After steaming out the quinoline, the dark residue was crystallized from 25 ml. of benzene and the resulting crystals dried at 120°; yield 1.06 g. (60%), m.p. 138.3–139.4°.[10]

The diacetyl derivative, crystallized from a large volume of benzene, melted at 240.0–243.3° and did not depress the m.p. of an authentic sample of 4,4′-diacetaminotriphenylmethane.[11]

4,4′-Diacetaminotriphenylmethane-2-carboxylic Acid (IV).—A mixture of 3.18 g. of II and 10 ml. of acetic anhydride was heated to 110° for 90 minutes. The resulting solution, showing a strong greenish fluorescence, was poured on ice contained in an erlenmeyer flask. The washed, sticky, yellow mass was refluxed for one hour with 40 ml. of 2 *N* sodium carbonate. The solution was acidified and the yellow precipitate recrystallized from 90 ml. of 41% ethanol; yield 2.9–3.4 g. (73–84%), m.p. 247–250°. The pure acid (IV), colorless crystals melting at 250.1–251.0°, forms a colorless solution in *N* sodium carbonate. Dissolved in concd. sulfuric acid, the colorless solution turns greenish on heating.

Anal. Calcd. for $C_{24}H_{22}O_4N_2$: C, 71.65; H, 5.51; N, 6.96; mol. wt., 402; –COOH, 11.2. Found: C, 71.11; H, 5.64; N, 7.18; mol. wt. (Rast), 410; –COOH, 10.7[9]; neut. equiv., 420 ± 8.

The sodium salt of IV, crystallized from a small quantity of water, was found to contain 5.1% Na (theory 5.4).

The acid was decarboxylated at 245°,[9] using 2.0 g. of IV, 5 ml. of synthetic quinoline and 0.05 g. of basic cupric carbonate. The product melted at 237–242°, after two crystallizations from much benzene.[11]

The Methyl Ester of IV.—An ethereal solution of diazomethane, prepared from 3.0 g. of nitrosomethylurea,[12] was added to a solution of 5.0 g. of IV in 800 ml. of acetone. After evaporation of the solvent the next day, the residue was crystallized from 2 liters of benzene; yield 4.0 g., m.p. 174–180°. The pure ester, crystallized from benzene (1 g. in 350 ml.), melts at 180.4–182.1°.

Anal. Calcd. for $C_{25}H_{24}O_4N_2$: C, 72.11; H, 5.81; N, 6.73; mol. wt., 416. Found: C, 71.82; H, 5.90; N, 7.30; mol. wt., 408.[7]

***o*-Toluidinephthalein or 3,3-Bis-(*p*-amino-*m*-tolyl)-phthalide (V).**—This compound was made by substituting 48.0 g. (0.2 mole) of *s*-di-*o*-tolylurea (m.p. 251–253°) for the *s*-diphenylurea in the procedure for the preparation of I. The 76–80 g. of amorphous condensation product yielded 40–50 g. of crude V, m.p. 180–187°. This, crystallized from methanol (1 g. in 50 ml.), gave 28.7–38.4 g. (42–55%) melting at 192–194°.

Pure V, colorless needles from methanol, melts at 196.8–197.3°. A 0.1 molar solution in acetic acid turns to purple on heating to 100°, becoming almost colorless on cooling.

Anal. Calcd. for $C_{22}H_{20}O_2N_2$: C, 76.72; H, 5.85; N, 8.13; mol. wt., 344. Found: C, 76.90; H, 6.12; N, 8.59; mol. wt., 349.[7]

The diacetyl derivative of V, crystallized from methanol (1 g. in 50 ml.) forms colorless crystals melting at 256.0–256.7°.

Anal. Calcd. for $C_{26}H_{24}O_4N_2$: C, 72.89; H, 5.64; N, 6.53. Found: C, 72.91; H, 5.80; N, 6.64.

3,3-Bis-(*m*-tolyl)-phthalide (VI). a. From *o*-Toluidinephthalein.—The two amino groups in V were eliminated by means of the Mai reaction.[13] A solution of 3.44 g. (0.01 mole) of V in 25 ml. of 2 *N* hydrochloric acid was diazotized at –4° with a solution of 1.4 g. (0.02 mole) of sodium nitrite in 6 ml. of water. The cold diazo solution was run slowly into 30 ml. of 50% hypophosphorous acid at 0°, contained in a 500-ml. beaker fitted with stirrer. Much foam developed during the reaction. After the temperature was raised overnight to 25°, the amorphous mass was filtered off and dissolved in 10 ml. of ethanol. Reddish crystals separated from the cooled solution. On sublimation at 100° and 20 microns pressure,[8] a snow-white sublimate was obtained. It was purified further, based on the observation that a by-product is more volatile on sublimation. The pure 3,3-bis-(*m*-tolyl)-phthalide (VI) forms colorless crystals from methanol and melts at 112.5–113.2° (1.50–1.72 g., yield 47–55%). It is very soluble in acetone, carbon tetrachloride or benzene. A 0.01 molar solution in concd. sulfuric acid is strong reddish in color.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77; mol. wt., 314. Found: C, 84.17; H, 5.83; mol. wt., 328.[7]

b. **From Phthalic Anhydride and *m*-Iodotoluene.**—The Grignard reagent was prepared from 43.6 g. of *m*-iodotoluene 4.86 g. of magnesium and 400 ml. of ether, the reaction being

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[7] Signer method, as described by E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941). Acetone was used as a solvent and azobenzene as a standard.

[8] M. H. Hubacher, *ibid.*, **15**, 448 (1943).

[9] M. H. Hubacher, *Anal. Chem.*, **21**, 945 (1949).

[10] C. Ullmann, *J. prakt. Chem.*, **36**, 246 (1887), reported 138.5–139.0°.

[11] A. Baeyer and V. Villiger, *Ber.*, **37**, 2860 (1904), reported 233–234°. The 4,4′-diacetaminotriphenylmethane, prepared according to their procedure and crystallized from a large volume of benzene, melted at 243.3–244.1°.

[12] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[13] J. Mai, *Ber.*, **35**, 162 (1902); a detailed discussion of this reaction by N. Kornblum can be found in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 277–282.

initiated by a few drops of methyl iodide.[14] After the magnesium had dissolved, 160 ml. of benzene was added. Since phthalic anhydride is but slightly soluble in either ether or benzene, 14.8 g. was charged into an extraction thimble, the latter mounted below the reflux condenser. The alkali-insoluble part was crystallized thrice from ethanol, then sublimed at 100° and 20 microns pressure,[8] yielding 5.6–7.6 g. melting at 112.0–113.1° (18–24%). A mixture of this compound with that obtained from V melted at 112–113°.

2-(*m*-Toluyl)-benzoic Acid.—The alkali-soluble portion obtained in the Grignard reaction was purified by sublimation at 145° and 15 microns pressure,[8] followed by a crystallization from benzene. The new acid, colorless needles, melts at 162.2–162.4° (yield 1.6 g.).

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.00; H, 5.04; mol. wt., 240. Found: C, 75.21; H, 4.92; mol. wt., 224[7]; neut. equiv., 241.5.

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[14] O. Grummitt and A. C. Buck, THIS JOURNAL, **65**, 295 (1943).

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RECEIVED MAY 4, 1951

The Hydrogen Chloride Cleavage of the C–Si Bond in Some Dibenzothienyl-silicon Compounds

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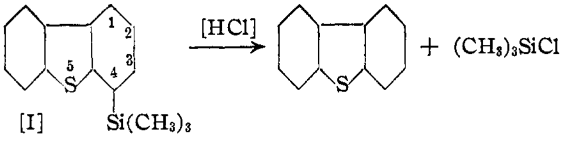
Recently[1] 4-trimethylsilyldibenzothiophene (I) and its corresponding 5-dioxide (IV) have been prepared. It has been observed that, by prolonged action of hydrogen chloride in glacial acetic acid, (I) undergoes an extensive cleavage in accordance with the reaction[1]



whereas (IV) remains practically unaffected.

The purpose of the present work was to prepare the 3- and 2-isomers of both (I) and (IV) and to determine the effect of position on ease of cleavage by hydrogen chloride. Both 3-trimethylsilyldibenzothiophene (II) and the 2-isomer (III) were prepared from the respective bromo-derivatives by halogen–metal interconversion with *n*-butyllithium and subsequent reaction with trimethylsilyl chloride. The preparation of 3-bromodibenzothiophene was made possible by a recent synthesis of 3-aminodibenzothiophene through a rearrangement reaction of 4-iododibenzothiophene with sodamide in liquid ammonia.[2] The conversion of the 3-bromo derivative into (II) was shown to be almost quantitative.

The corresponding 5-dioxides (V) and (VI) were obtained from (II) and (III), respectively, by hydrogen peroxide oxidation.

The cleavage by hydrogen chloride in glacial acetic acid of (II) and (III) gave results in agreement with that reported for compound (I). That is, the cleavage products identified were dibenzothiophene and trimethylsilyl chloride. Furthermore, the 5-dioxides (V) and (VI) were found to be extremely resistant to cleavage and most of the starting material was recovered after the hydrogen chloride treatment. It is evident that in this series, the 2- and 3-isomers react very much like the 4-isomer.[3]

Experimental

3-Bromodibenzothiophene.—On the basis of a study of several different conditions for the Sandmeyer reaction on 3-aminodibenzothiophene, the general procedure of Hodgson gave the best results.[4]

A 220-ml. solution of glacial acetic acid containing 19.9 g. (0.1 mole) of the amine[2] was diazotized by nitrosylsulfuric acid (10% excess) at 15°. The diazonium-salt was added to a warm solution of freshly prepared cuprous bromide (0.1 mole) in 400-ml. of 40% hydrobromic acid solution and the mixture refluxed for one hour. After pouring the cooled liquid into a large volume of water, the product which separated was thoroughly extracted with ether, taken up in hot ethanol, treated with charcoal and after filtration, allowed to separate by cooling. The yield of crude product (m.p. 93–96°) obtained after recrystallization from ethanol was 6 g. (23%). The sample used for analysis melted at 97.5–98.5°.

Anal. Calcd. for $C_{12}H_7BrS$: Br, 30.37; S, 12.18. Found: Br, 30.52; S, 12.30.

The structure was proved by preparing the corresponding 5-dioxide, m.p. 224–225°, which was identified by comparison with an authentic specimen.[5]

3-Trimethylsilyldibenzothiophene (II).—To 5.2 g. (0.020 mole) of 3-bromodibenzothiophene in 50 ml. of dry ether, under a dry nitrogen atmosphere and at 5°, a titrated solution[6] of *n*-butyllithium (0.022 mole) in ether was first added and then followed, after 2 minutes, by an ether solution of 2.6 g. (0.024 mole) of trimethylsilyl chloride. The mixture was stirred and refluxed for two hours longer, and decomposed by pouring into water. From the ether layer, a solid residue was obtained, which by crystallization from ethanol yielded 4.1 g. (80%) of white crystalline product melting at 102–104°. The sample used for analysis melted at 103.5–104.5°.

Anal. Calcd. for $C_{15}H_{16}SSi$: Si, 10.94. Found: Si, 10.74.

2-Trimethylsilyldibenzothiophene (III).—An ether suspension of 8.8 g. (0.035 mole) of 2-bromodibenzothiophene, prepared by direct bromination of dibenzothiophene,[7] was allowed to react with *n*-butyllithium in essential accordance with the directions described above, and then 4.5 g. (0.042 mole) of trimethylsilyl chloride was added. The crude product was distilled at 159–160° (1 mm.) as a colorless liquid which solidified on standing at 0°; yield 4.5 g. (50%). Further purification by crystallization from ethanol gave white crystals melting at 48.2–49.2°.

Anal. Calcd. for $C_{15}H_{16}SSi$: Si, 10.94. Found: Si, 10.92.

3-Trimethylsilyldibenzothiophene-5-dioxide (V).—A solution of 0.004 mole of (II) in 15 ml. of glacial acetic acid was treated with 30% hydrogen peroxide (10% excess) and heated between 95–100° for two hours. When cooled, the solution was poured into water and the resulting solid was removed by filtration to give 1.1 g. (98%) of (V), melting at 163–170°. Recrystallization from ethanol gave white crystals melting at 170.8–171.8°.

Anal. Calcd. for $C_{15}H_{16}O_2SSi$: Si, 9.73. Found: Si, 9.51.

2-Trimethylsilyldibenzothiophene-5-dioxide (VI).—This compound was obtained from (III), by using the same procedure and the same-sized run, described above for the 3-isomer. The yield of the crude product melting at 157–161°

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[1] H. Gilman and J. F. Nobis, THIS JOURNAL, **72**, 2629 (1950).

[2] H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945); see, also, R. K. Brown, R. G. Christiansen and R. B. Sandin, *ibid.*, **70**, 1748 (1948).

[3] This illustrates rather strikingly that the position of the so-called negative sulfonyl group with respect to the trimethylsilyl group, in this aromatic system, is without significant influence on the rate of cleavage of the C–Si linkage. See, F. C. Whitmore and co-workers, THIS JOURNAL, **69**, 1551 (1947); L. H. Sommer and co-workers, *ibid.*, **70**, 2869 (1948).

[4] H. Hodgson and J. Walker, *J. Chem. Soc.*, **1620** (1933).

[5] H. Gilman and S. Avakian, THIS JOURNAL, **68**, 1514 (1946).

[6] H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

[7] C. Courtot, L. Nicolas and T. H. Liang, *Compt. rend.*, **186**, 1624 (1928); C. Courtot and I. Kelner, *ibid.*, **198**, 2003 (1934).