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).

RESEARCH LABORATORY OF
EX-LAX, INC.
BROOKLYN 17, N. Y.
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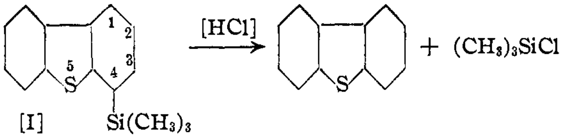
The Hydrogen Chloride Cleavage of the C–Si Bond in Some Dibenzothienyl-silicon Compounds

BY GABRIELLO ILLUMINATI, JOHN F. NOBIS AND HENRY GILMAN

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).

was 98%. The pure crystals were obtained from ethanol, m.p. 164–165°.

Anal. Calcd. for $C_{15}H_{16}O_2SSi$: Si, 9.73. Found: Si, 9.60.

Cleavage by Hydrogen Chloride.[1,8]—Hydrogen chloride was allowed to pass for 15 hours through a refluxing solution of 0.01 to 0.02 mole of organosilicon compound in glacial acetic acid (50 to 100 ml.) and successively through a small ground glass trap immersed in a Dry Ice–acetone-bath. After cooling, the solution was poured into water and the solid which separated removed by filtration. When cleavage took place, the liquid in the trap was purified by two distillations and was shown to be trimethylsilyl chloride. The reagent used for characterizing the trimethylsilyl chloride was 9-fluorenyllithium. The product[9] formed in this manner was shown to be 9-trimethylsilylfluorene (m.p. and mixed m.p. 97–99°). The yields of dibenzothiophene from the cleavage of (II) and (III) were 99 and 97%, respectively. The percentage recoveries of dioxide from the attempted cleavages of (V) and (VI) were 94 and 97%, respectively.

Acknowledgment.—One of us (G. I.) wishes to express his appreciation to the Institute of International Education and to the Research Council of Iowa State College for fellowship aid.

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[8] See H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949), for earlier cleavage studies by this procedure.

[9] Unpublished studies by R. A. Benkeser.

CONTRIBUTION FROM THE CHEMICAL
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The Mechanism of Cellulose Nitration[1]

BY RALPH KLEIN AND MORRIS MENTSER

The mechanism of nitration of aromatic molecules by mixed acid has been established by rate studies[2,3,4] which show that nitration is effected by the NO_2^+ ion. Physical and chemical evidence has established the presence of this ion in the concentrated mixed acid used in nitration reactions.[5] Since cellulose is nitrated most effectively in the acid concentration region in which the NO_2^+ ion is found to exist, by analogy it might be expected that nitration of cellulose occurs *via* an electrophilic attack on the hydroxyl oxygen by the NO_2^+ ion with proton elimination. Indeed, such a mechanism has been postulated for nitration of starches.[6] It is evident that, if this mechanism is operative, cellulose nitrate prepared from ordinary cellulose and O^{18}-enriched mixed acid should have nitrate groups in which only two of the three nitrate oxygens are O^{18}-enriched. This is confirmed by the present experiments. It may be concluded that the oxygen of the alcohol groups of the cellulose is not eliminated in the nitration reaction and thus remains unenriched. An analogous result has been obtained from studies of the esterification of methyl alcohol with benzoic acid.[7]

Experimental

Samples of O^{18}-enriched cellulose nitrate were prepared by nitration of cotton linters with an O^{18}-enriched sulfuric acid–nitric acid–water mixture. Since both nitric acid and sulfuric acid exchange oxygen with water,[8,9] the admixture of heavy water to ordinary acids provides a convenient method for preparing the enriched acids. The O^{18}-enrichment factor was determined by mass spectrometer analysis of the NO resulting from a nitrometer reaction with the mixed nitrating acid.

The cellulose nitrate was analyzed for O^{18} by the method of von Grosse, *et al.*[10] The samples were heated at 750° for 1.5 hours in a quartz bulb. Under such conditions, oxygen randomization occurs among the decomposition products, and the enrichment factor could be determined by an O^{18} analysis of the CO_2 formed. The results are shown in Table I. Experiment 1(b) shows that, at the temperatures and times involved in these experiments, oxygen exchange with the quartz is negligible.

TABLE I

ENRICHMENT FACTORS FOR EQUILIBRATED DECOMPOSITION PRODUCTS OF O^{18}-ENRICHED CELLULOSE NITRATE

Expt.	Heating time, hours	Nitrogen content, %	O^{18}-Enrichment factor of nitrating acid	O^{18}-Enrichment factors of equilibrated decomposition products Calcd.		
				3 Enriched O-atoms in NO_3 group	2 Enriched O-atoms in NO_3 group	Exptl.
1(a)	1.5	11.1	4.9	3.6	2.7	2.2
1(b)[a]	3.0	..	...	...	...	2.2
2	1.5	11.1	4.9	3.6	2.7	2.6
3	1.5	11.1	4.9	3.6	2.7	2.7
4	1.5	8.7	5.7	3.5	2.7	2.6

[a] Same gas sample as (a) but heated 1.5 hours longer.

The number of nitrate groups per glucose unit was determined from nitrogen analysis. It was thus possible to calculate the enrichment factor resulting from oxygen randomization of the total oxygen of the cellulose nitrate molecule, assuming that either three or two of the three nitrate oxygens were enriched. These values are given in columns 4 and 5 of Table I. Except for the slightly low result of experiment 1, which may be attributed to incomplete preliminary outgassing of the quartz bulb, the experimental results of column 6 agree with column 5. This shows that the oxygen of the hydroxyl groups is not eliminated in the nitration reaction.

The authors express their appreciation to Dr. R. A. Friedel for the mass spectrometer isotope analyses.

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[1] Publication approved by the Office of Public Information, U. S. Department of Defense. Not copyrighted.

[2] F. H. Westheimer and M. S. Kharasch, THIS JOURNAL, **68**, 1871 (1946).

[3] A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950).

[4] R. J. Gillespie, E. D. Hughes, C. K. Ingold, D. J. Millen and R. I. Reed, *Nature*, **163**, 599 (1949).

[5] G. M. Bennett, J. C. D. Brand and G. Williams, *J. Chem. Soc.*, 869 (1946).

[6] S. Israelashvili, *Nature*, **165**, 686 (1950).

[7] I. Roberts and H. C. Urey, THIS JOURNAL, **60**, 2391 (1938).

[8] R. Klein and R. A. Friedel, *ibid.*, **72**, 3810 (1950).

[9] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940).

[10] A. V. Grosse, S. G. Hindin and A. D. Kirshenbaum, *Anal. Chem.*, **21**, 386 (1949).

EXPLOSIVES AND PHYSICAL SCIENCES DIVISION
BUREAU OF MINES
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PITTSBURGH, PENNA.
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A New Preparation of 2,4-Dinitrophenylhydrazones

BY G. DANA JOHNSON

A phosphoric acid–ethanol solution of 2,4-dinitrophenylhydrazine has been found to be indefinitely stable and avoids the use of the more reactive sulfuric acid.

Reagent.—To make one liter of approximately 0.25 *M* reagent, 50 g. of 2,4-dinitrophenylhydrazine was dissolved in 600 ml. of 85% phosphoric acid in a one-liter beaker on a steam-bath. The solution was diluted with 395 ml. of 95% alcohol and clarified by suction filtration through a thin layer of Filter-Cel.

Use.—To a solution of the carbonyl compound in alcohol was added the calculated volume of reagent. Amino car-