to Lawrence E. Brown for the carbon, hydrogen determinations, and to Frank C. Magne for assistance in the purification of the methyl palmitate.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

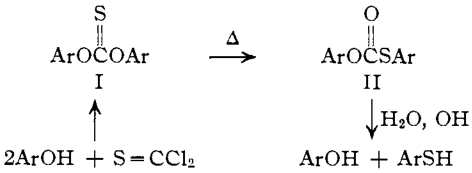
A Study of the Schönberg Rearrangement of Diaryl Thioncarbonates to Diaryl Thiolcarbonates[1]

BY H. R. AL-KAZIMI, D. S. TARBELL AND DEREK PLANT

RECEIVED SEPTEMBER 11, 1954

A study of twelve examples of the Schönberg rearrangement of diaryl thioncarbonates to diaryl thiolcarbonates has shown that the reaction is favored by electron-withdrawing groups in the *ortho* and *para* positions. It is suggested that the reaction involves a cyclic transition state, with a nucleophilic attack of the thion sulfur on the aromatic nucleus. The similarity of this rearrangement to the Smiles, Chapman and Stevens rearrangements, and to reactions involving a shift from oxygen to sulfur, is discussed.

The rearrangement of diaryl thioncarbonates I to diaryl thiolcarbonates II which was discovered by Schönberg[2] offers a way of converting phenols to thiophenols, and it appeared to be of synthetic value in obtaining some substituted thiophenols which were needed in studies on the cleavage of sulfides by acids.[3] In addition, the reaction offers some interesting problems from the mechanistic side. The present paper reports the preparation of a number of symmetrical and unsymmetrical diaryl thioncarbonates, and a study of their rearrangement to the thiolcarbonates. From the observations reported it is possible to establish some features of the mechanism of the reaction.



$$\begin{array}{ccc}\text{ArO}\overset{\overset{\displaystyle \text{S}}{\|}}{\text{C}}\text{OAr} & \xrightarrow{\Delta} & \text{ArO}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{SAr}\\ \text{I} & & \text{II}\\ \uparrow & & \downarrow{\scriptstyle H_2O,\ OH^-}\\ 2\text{ArOH} + \text{S}=\text{CCl}_2 & & \text{ArOH} + \text{ArSH}\end{array}$$

The symmetrical thioncarbonates were prepared by the action of thiophosgene on the phenols in two stages,[4] or, more conveniently, by treatment of a benzene solution of two moles of the phenol and one mole of thiophosgene with dry pyridine.[2] The compounds synthesized are listed in Table I, and the yields of pure material ranged from 20 to 28%.

TABLE I

DIARYL THIONCARBONATES, ArOC(=S)OAr

Ar, phenyl	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen % Calcd.	Hydrogen % Found
2,6-Dimethyl-	111–112	$C_{17}H_{18}O_2S$	71.65	71.37	6.34	6.18
2,4-Dimethyl-	76.5–77.5	$C_{17}H_{18}O_2S$	71.65	71.51	6.34	6.24
4-Chloro-	158–158.5	$C_{13}H_8Cl_2O_2S$	52.23	52.26	2.69	2.82
2-Chloro-	84–84.5	$C_{13}H_8Cl_2O_2S$	52.23	52.16	2.69	2.95
2,4-Dichloro-	94–94.5	$C_{13}H_6Cl_4O_2S$	42.16	42.43	1.72	1.97
4-Bromo-	174–175	$C_{13}H_8Br_2O_2S$	40.25	40.20	2.38	2.22
4-Methoxy-	161–162	$C_{15}H_{14}O_4S$	62.05	61.75	4.92	5.16
2-Methoxy-	68.5–69.5	$C_{15}H_{14}O_4S$	62.05	62.44	4.92	5.19
4-Nitro-	196–197	$C_{13}H_8N_2O_6S$	48.73	48.60	2.55	2.74

The rearrangement reactions were carried out for the most part by heating without solvent to temperatures in the 275–300° range. The product was isolated and characterized; its structure was checked by alkaline hydrolysis, which formed the phenol and the thiophenol. Oxidation of the hydrolysis mixture with hydrogen peroxide converted the thiophenol to the neutral diaryl disulfide, which was found in each case to have a m.p. agreeing with that previously reported.

The bis-(4-nitrophenyl) thioncarbonate decomposed violently when heated to 275–285°; it rearranged smoothly, however, at 252°, in a test-tube heated by refluxing diphenyl ether vapors. The bis-(4-methoxyphenyl) thioncarbonate was recovered virtually unchanged after heating to 300°: it was unchanged by refluxing in diphenyl ether solution for 6 hr., either alone, or in the presence of catalytic amounts of isoquinoline. The 2,4-dichlorothion compound was recovered unchanged after refluxing for 2 hr. in benzyl chloride solution.

From these and numerous other experiments relating time, temperature of heating and yield, it is possible to conclude that the effect of substituents in increasing the rate of the rearrangement is indicated by the series: 4-nitro > 2,4-dichloro > 2- and 4-chloro > 4-bromo > 2,4- and 2,6-dimethyl > 2- and 4-methoxy.

The effect of electron-withdrawing groups in promoting the rearrangement, which is indicated above, was confirmed by a study of the unsymmetrical thioncarbonates listed in Table III. The 2,6-dimethylphenyl 2′-nitrophenyl compound decomposed after standing some time at room temperature; the phenyl 4-chlorophenyl and phenyl 4-nitrophenyl compounds were decomposed by heating at 285°. Heating these two at 240°, however, gave the thiol compounds, in which the substituted phenyl groups had migrated to the sulfur in each case. The structure of the rearranged compounds was demonstrated by alkaline hydrolysis, oxidation and identification of the disulfide.

The rearrangement of the unsymmetrical thion compound, phenyl 2-naphthyl thioncarbonate (III), was examined in more detail. Heating this compound at 275° for 45 minutes yielded 44% of starting material, 12% of bis-(2-naphthyl) thioncarbonate (IV), no bis-(2-naphthyl) thiolcarbonate (V)

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[1] This research was supported in part by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command. Article not copyrighted.

[2] (a) A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930); (b) A. Schönberg, L. Vargha and W. Paul, *Ann.*, **483**, 107 (1930).

[3] *Cf.* D. P. Harnish and D. S. Tarbell, THIS JOURNAL, **70**, 4123 (1948); **74**, 1862 (1952); D. S. Tarbell and J. C. Petropoulos, *ibid.*, **74**, 244 (1952).

[4] H. Rivier, *Bull. soc. chim. France*, [3] **35**, 837 (1906).

TABLE II

REARRANGEMENT OF DIARYL THIONCARBONATES TO DIARYLTHIOLCARBONATES, ArOC(=O)SAr

Ar, phenyl	Rearrangement Temp., °C.	Rearrangement Time, min.	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,6-Dimethyl-	290	45	80	85–85.5	$C_{17}H_{18}O_2S$	71.65	71.66	6.34	6.38
2,4-Dimethyl-	290	45	56	43–44	$C_{17}H_{18}O_2S$	71.65	71.94	6.34	6.50
4-Chloro-	300	45	95	96–97	$C_{13}H_8Cl_2O_2S$	52.23	52.35	2.69	2.48
2-Chloro-	290	30	75	67–70	$C_{13}H_8Cl_2O_2S$	52.23	52.41	2.69	2.80
2,4-Dichloro-	260	50	84	84–85	$C_{13}H_6Cl_4O_2S$	42.16	42.23	1.72	1.62
4-Bromo-	300	45	80	120–120.5	$C_{13}H_8Br_2O_2S$	40.25	40.39	2.38	2.17
4-Nitro-	252	15	65	151–152.5	$C_{13}H_8N_2O_6S$	48.73	48.69	2.55	2.79

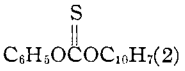
TABLE III

UNSYMMETRICAL DIARYL THIONCARBONATES, ArOC(=S)OAr′

Ar	Ar′	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,6-Dimethylphenyl	2-Nitrophenyl	80–81	$C_{15}H_{12}NO_4S$	59.50	59.78	4.32	4.54
Phenyl	4-Methylphenyl	135–136	$C_{13}H_{12}O_2S$	68.84	68.90	4.95	5.18
Phenyl	4-Chlorophenyl	125–126	$C_{13}H_9ClO_2S$	58.97	59.24	3.40	3.37
Phenyl	4-Nitrophenyl	181–182	$C_{19}H_9NO_4S$	56.8	56.93	3.32	3.54
Phenyl	4-Methoxyphenyl	103–104	$C_{14}H_{12}O_3S$	64.61	64.61	4.65	4.77
Phenyl	2-Naphthyl	143–144	$C_{17}H_{12}O_2S$	72.85	72.76	4.32	4.33

and 14% of bis-(phenyl) thioncarbonate. Heating the phenyl 2-naphthyl thioncarbonate (III) at 275° for 60 minutes or at 290° for 30 minutes yielded as the only isolatable product bis-(2-naphthyl) thiolcarbonate (V) in yields of 24 and 14%, respectively; the presence of the bis-(phenyl) thiolcarbonate in the product could not be established.

It appears that III first undergoes ester interchange on heating, to yield the two symmetrical thioncarbonates, which then rearrange to the symmetrical thiolcarbonates. Presumably the rearrangement of mixtures of thioncarbonates therefore would give no valid evidence about the intramolecular or intermolecular character of the rearrangement.

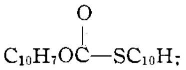


$C_6H_5O\overset{S}{\overset{\|}{C}}OC_{10}H_7(2)$

III

$(C_{10}H_7O)_2C{=}S$

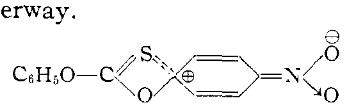
IV



$C_{10}H_7O\overset{O}{\overset{|}{C}}-SC_{10}H_7$

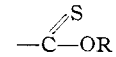
V

Discussion.—It is clear from the observations reported above that the presence of electron-withdrawing groups in the *o*- or *p*-positions to the oxygen atoms in the diaryl thioncarbonates facilitates the rearrangement. It therefore is to be regarded as a nucleophilic displacement of the oxygen on the aromatic ring by sulfur, which gets part of its driving force from the well-established fact that sulfur is a much stronger nucleophilic atom than oxygen in displacements on carbon.[5] Whether the transition state is that shown below can probably be determined by a more exact kinetic study, which is now underway.



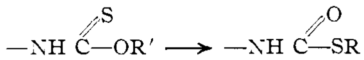
The rearrangement appears to be similar to the Smiles rearrangement of *o*-hydroxydiphenyl sulfones and related compounds,[6] and to the Chapman rearrangement[7] of arylimino ethers and amidines, in showing increased rate of rearrangement of the aryl group with electron-withdrawing substituents.[8]

A number of examples of rearrangement reactions are known, which are formally similar to the Schönberg rearrangement in involving the migration of a group from oxygen to sulfur[9] in the system



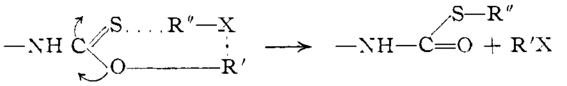
$-\overset{S}{\overset{/\!/}{C}}-OR$

These are best known in the thioncarbamate or xanthate system, and involve a change of the type[10]



$-NH\,\overset{S}{\overset{/\!/}{C}}-OR' \longrightarrow -NH\,\overset{O}{\overset{/\!/}{C}}-SR'$

The fact that this type of rearrangement is strongly catalyzed by alkyl halides or other esters,[10adf] and that treatment with a different halide R″X leads to —NHC(=O)—SR″, suggests that this reaction should be formulated as below, as a displacement reaction of a special kind and not as a true rearrangement. The driving force would be the high nucleophilic character of the sulfur and the electron-donating power of the R″ group.



The Schönberg rearrangement apparently does not go through this mechanism, because refluxing

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(5) (a) O. R. Quayle and E. E. Royals, THIS JOURNAL, **64**, 226 (1942); (b) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3331 (1952).

(6) For an excellent account of the Smiles rearrangement, see J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 362 (1951). The Smiles rearrangement usually involves a shift of aromatic carbon from sulfur to oxygen, however.

(7) A. W. Chapman, *J. Chem. Soc.*, 1743 (1927); 2462 (1930); K. B. Wiberg and B. I. Rowland, Abstracts of New York Meeting of American Chemical Society, September, 1954, p. 41-O.

(8) Similar effects are shown in the Stevens rearrangement of onium compounds, in which the migrating group is usually a benzyl or allyl group (T. T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 55 (1932); C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951)).

(9) The conversion of sulfinate esters into sulfones involves a shift from oxygen to sulfur in the -SO-OR system (J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1676 (1930); A. C. Cope, D. E. Morrison and L. Field, THIS JOURNAL, **72**, 59 (1950).

(10) For example, (a) H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **22**, 141 (1899); **24**, 60 (1900); H. L. Wheeler and G. K. Dustin, *ibid.*, **24**, 424 (1900); (b) A. Knorr, *Ber.*, **50**, 767 (1917); (c) E. Biilmann, *Ann.*, **364**, 314 (1908); (d) A. Bettschart and A. Bistrzycki, *Helv. Chim. Acta*, **2**, 118 (1919); (e) G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 677 (1945); (f) S. A. Karjala and S. M. McElvain, THIS JOURNAL, **55**, 2966 (1933).

in benzyl chloride did not affect the 2,4-dichlorophenyl thioncarbonate.

Experimental

Thiophosgene was prepared *via* perchloromethyl mercaptan.[11]

Preparation of Diaryl Thioncarbonates. A. By a Two-stage Procedure. Bis-(2,6-dimethylphenyl) Thioncarbonate.—A solution of 4 g. of 2,6-dimethylphenol in 5 ml. of 20% sodium hydroxide was added in portions to 3 g. of thiophosgene in 50 ml. of chloroform with vigorous shaking after each addition. The chloroform solution was washed thoroughly with water, dried over anhydrous sodium sulfate and the solvent was removed by evaporation to leave 4.5 g. of a reddish-brown oil. This oil, dissolved in 50 ml. of ethyl alcohol, was added to a solution of 4 g. of 2,6-dimethylphenol in 6 ml. of 20% potassium hydroxide, and the mixture was refluxed on the steam-bath for 10 min. The reaction mixture was concentrated on the steam-bath, finally under high vacuum, to produce a solid mass which was digested with *n*-hexane and filtered. The hexane solution was concentrated to about 25 ml. and chromatographed over neutral alumina. The hexane eluate afforded 2 g. (20% yield) of a white solid, m.p. 109–111°. Recrystallization from ethanol gave a white crystalline solid, m.p. 111–112°.

B. By a One-stage Procedure. Bis-(*p*-chlorophenyl) Thioncarbonate.—To a solution of 10 g. of *p*-chlorophenol and 4.4 g. of thiophosgene in 50 ml. of benzene was added 7.8 ml. of dry pyridine dropwise and with constant stirring. The reaction mixture was heated on the steam-bath and filtered while hot. The benzene solution was washed twice with 100-ml. portions of dilute sulfuric acid and then repeatedly with water, dried over anhydrous magnesium sulfate and concentrated to give a light brown solid. The product was recrystallized from 95% ethanol to yield a white crystalline material, m.p. 156–158°. Recrystallization from benzene–ethanol afforded 2.3 g. (27%) of a solid, m.p. 158–158.5°.

Rearrangement of Thion to Thiol Compounds: Bis-(2,6-dimethylphenyl) Thiolcarbonate.—The method described below illustrates the general procedure followed for the rearrangement of thioncarbonates to thiolcarbonates.

Bis-(2,6-dimethylphenyl) thioncarbonate in a dry test-tube was immersed in a molten Woods metal and the bath temperature was gradually raised to 270–300° over a period of 30 min. This temperature was maintained for various lengths of time. After cooling, the solidified product was crystallized from methanol to give a white crystalline material.

THE RESULTS OF THE DIFFERENT RUNS, BIS-(2,6-DIMETHYLPHENYL) THIOLCARBONATE

Run	Temp., °C.	Time, min.	Yield, %	M.p., °C.
1	270	30	0	.....
2	275	60	62	85–85.5
3	290	30	63	82–83
4	290	45	80	82–83
5	300	30	75	83–83.5

Hydrolysis of the Thiolcarbonate.—A solution of 80 mg. of the bis-(2,6-dimethylphenyl) thiolcarbonate in 20 ml. of ethanol was heated on the steam-bath with 1 ml. of 20% sodium hydroxide for 40 min. The reaction mixture was concentrated almost to dryness and the residue was dissolved in 15 ml. of 10% sodium hydroxide. An excess (15 ml.) of 30% hydrogen peroxide was added and the solution warmed on the steam-bath to start the reaction. Upon cooling, 25 mg. (65%) of a white crystalline solid separated, m.p. 99–102°, undepressed on admixture with authentic bis-(2,6-dimethylphenyl) disulfide.

Bis-(4-nitrophenyl) Thiolcarbonate.—The usual method for the rearrangement of thioncarbonates resulted in the decomposition of bis-(*p*-nitrophenyl) thioncarbonate. When heated at 285 or 275°, violent decomposition took place accompanied by the evolution of gases and leaving behind a tarry material. However, a modified procedure was found to be useful. Bis-(*p*-nitrophenyl) thioncarbonate (200 mg.) was placed in a test-tube fitted inside a larger test-tube containing diphenyl ether whose vapors served to heat the thioncarbonate in the inner tube to a temperature of 252°. The heating was continued for 15 min. during which the molten thioncarbonate acquired a dark brown coloration. On cooling, the oil solidified into a brown mass, m.p. 136–144°. Recrystallization from acetone–water afforded 130 mg. (65%) of a light brown crystalline substance, m.p. 151–152.5°.

Bis-(*p*-nitrophenyl) thiolcarbonate (60 mg.) in 10 ml. of ethanol was heated on the steam-bath for 30 min. with 10 ml. of 5% sodium hydroxide. The reaction mixture was concentrated *in vacuo* to dryness and the residue was dissolved in 5 ml. of 10% sodium hydroxide. On air oxidation, the alkaline solution afforded about 15 mg. of a solid, m.p. 179–181°.[12]

Phenyl Thioncarbonyl Chloride.[4]—A solution of 9.6 g. of sodium hydroxide (0.24 mole) in 200 ml. of water was added in portions and with vigorous shaking to a solution of 23.5 g. (0.25 mole) of phenol and 29 g. (0.253 mole) of thiophosgene in 150 ml. of chloroform. The chloroform solution was thoroughly washed with water, dried over anhydrous sodium sulfate and evaporated to yield 12.3 g. (28.4%) of a yellow oil. This oil was purified by distillation at 90° (0.5 mm.).

Preparation of an Unsymmetrical Thioncarbonate. Phenyl 2-Naphthyl Thioncarbonate.—A solution of 2-naphthol (7.0 g.) in dry benzene (100 cc.) was added to a solution of phenyl thioncarbonyl chloride (8.6 g.) in benzene (100 cc.). To this mixture, anhydrous pyridine (5.5 cc.) was added dropwise from a pipet over a period of about 8 min. A red oil separated at first, but at the end of the addition it had crystallized into colorless crystals. The mixture was heated for 10 min. on the steam-bath, cooled and was then washed three times with water. All of the solid dissolved in the water. The benzene solution was evaporated *in vacuo*, and the residue, after crystallization from alcohol, yielded 12.9 g. of product (91%), m.p. 136–138°. After recrystallization from alcohol, it melted at 141–143°.

Rearrangement of Phenyl 2-Naphthyl Thioncarbonate.—This compound (1.0 g.) was heated at 290° for 30 min. and the resulting black product was dissolved in ethanol and evaporated to a small volume. Cooling yielded a brown crystalline solid, which was recrystallized from alcohol (with charcoal) until it melted at 129–131°. Analysis and the m.p.[13] showed it to be bis-(2-naphthyl) thiolcarbonate. Hydrolysis by alcoholic alkali and oxidation with peroxide yielded di-2-naphthyl disulfide, m.p. 136–138°, reported[14] m.p. 136–137°.

Phenyl 2-naphthyl thioncarbonate (3.0 g.) was heated at 275° for 45 min. The pale brown crystalline mass which resulted on cooling was dissolved in ethanol and evaporated until crystallization commenced. The product obtained by filtration was 360 mg. of colorless plates, m.p. 204–205°, which melted, after crystallization from acetone-alcohol at 213–214°. Analysis and the m.p. showed that it was bis-(2-naphthyl) thioncarbonate.[15]

Evaporation of the filtrate yielded 730 mg. of crystals, m.p. 118–120°; crystallization from alcohol raised the m.p. to 142–143°. The product was shown by mixed m.p. to be the starting material, phenyl 2-naphthyl thioncarbonate.

The filtrate yielded a further 300 mg. of crystalline material, which, after three crystallizations from alcohol–water, melted at 105–106°, and was bis-(phenyl) thioncarbonate. The reported[2a] m.p. is 106°. The uncrystallizable residue may have contained bis-(phenyl) thiolcarbonate,[2a] m.p. 57°, but it could not be isolated.

Phenyl S-(*p*-Nitrophenyl) Thiolcarbonate.—On heating 200 mg. of phenyl *p*-nitrophenyl thioncarbonate at 240° for 35 min., 80 mg. of the starting material was recovered unchanged from a methanolic solution of the reaction products. After removal of the starting material by filtration, the methanolic solution was diluted with water to yield 60 mg.

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[11] O. B. Helferich and E. E. Reid, THIS JOURNAL, **43**, 591 (1921); P. Klason, *Ber.*, **20**, 2380 (1887); A. Sartori, "The War Gases," D. Van Nostrand Co., New York, 1939, p. 213. This simpler procedure is preferable to the one in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., p. 506.

(12) The reported m.p. for 4,4-dinitrodiphenyl disulfide, prepared by the oxidation of the thiophenol, is 181° (J. Elgersma, *Rec. trav. chim.*, **48**, 755 (1929)).

(13) Schönberg and Vargha (ref. 2a) report a m.p. of 136°.

(14) R. Leuckart, *J. prakt. Chem.*, [2] **41**, 221 (1890).

(15) The m.p. of this compound is reported to be 212° (H. Eckenroth and K. Kock, *Ber.*, **27**, 3411 (1894)).

(30%) of a yellow solid, m.p. 60–63°. Recrystallization from ethanol–water gave a crystalline solid of m.p. 65–67%.

Anal. Calcd. for $C_{13}H_9NO_4S$: C, 56.80; H, 3.32. Found: C, 56.82; H, 3.54.

A solution of the product, m.p. 65–67°, in ethanol was hydrolyzed with 10% sodium hydroxide and the resulting solution concentrated to dryness. The residue was dissolved in 10% sodium hydroxide and treated with excess 3% hydrogen peroxide to produce a dark brown solid, m.p. 153–160°. Recrystallization from ethanol–water gave a brown crystalline solid,[12] m.p. 174–177°. Since no diphenyl disulfide could be obtained, it was concluded that the rearrangement product, m.p. 65–67°, was the phenyl S-(*p*-nitrophenyl) thiolcarbonate and not the isomeric *p*-nitrophenyl S-phenyl thiolcarbonate.

Phenyl S-(*p*-Chlorophenyl) Thiolcarbonate.—Phenyl *p*-chlorophenyl thioncarbonate did not yield crystalline products when heated at 285° for 30 min. The rearrangement was, however, effected in the following way. The thioncarbonate (150 mg.) was heated at 240° for 30 min.; the ethanolic solution of the product deposited upon slow cooling, 95 mg. of the starting thioncarbonate, m.p. 122–124°, as shown by mixed m.p. Dilution of the ethanolic filtrate yielded 45 mg. (30%) of product, m.p. 90–96°, which, after recrystallization from 30% ethanol, yielded white phenyl S-(*p*-chlorophenyl) thiolcarbonate, m.p. 97–98°.

Anal. Calcd. for $C_{13}H_9ClO_2S$: C, 58.97; H, 3.40. Found: C, 58.84; H, 3.65.

Alkaline hydrolysis of this compound followed by peroxide oxidation yielded 4,4′-dichlorodiphenyl sulfide,[16] m.p. and mixed m.p. 72–74°. Isolation of this disulfide proves that the chlorophenyl group was the one which migrated in the rearrangement.

2,6-Dimethylthiophenol.—This was prepared from 40 g. of 2,6-dimethylaniline by diazotization and coupling with potassium ethyl xanthate[17]; the product (17 g.) had the following properties: b.p. 91° (50 mm.), $n^{20}D$ 1.5712.

Anal. Calcd. for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.26; H, 7.53.

2,6,2′,6′-Tetramethyldiphenyl disulfide, prepared by peroxide oxidation of the thiophenol, melted at 103–104°.[18]

Acknowledgment.—One of us (H. R. A.-K.) is indebted to the Royal Iraquian Government for a Fellowship, during tenure of which this work was performed.

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[16] R. Otto, *Ann.*, **143**, 111 (1867), reports the m.p. of the disulfide as 71°.

[17] The procedure of Tarbell and Fukushima, *Org. Syntheses*, **27**, 81 (1947), for *m*-thiocresol was followed.

[18] R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polymer Sci.*, in press (1955), report the m.p. as 105.5–106°. We are indebted to Dr. Weinstein for information about this paper.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Hybrid Paraffin-siloxanes Containing the 1,6-Disilahexane Grouping[1]

BY LEO H. SOMMER AND GERALD R. ANSUL

RECEIVED OCTOBER 9, 1954

Four organosiloxanes conforming to the general formula $Me_3SiO(SiMe_2CH_2CH_2CH_2CH_2SiMe_2O)_nSiMe_3$, with $n = 1, 2, 3$ and 4, have been synthesized. A study of the physical properties of these substances has shown that they are intermediate between the linear methylpolysiloxanes and the paraffin hydrocarbons.

Because of the important and unusual physical properties of the organosiloxanes,[2] the synthesis of a family of compounds intermediate in structure between the linear methylpolysiloxanes and the paraffin hydrocarbons was of interest. The present paper reports the synthesis and physical properties of four hybrid paraffin-siloxanes containing the 1,6-disilahexane group.

Monomers

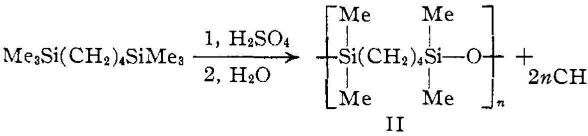
In the present study which deals with substances containing the 1,6-disilahexane system, 1,4-bis-(trimethylsilyl)-butane (I) may be termed a "mono-

$Me_3SiCH_2CH_2CH_2CH_2SiMe_3$ I

mer" from the fact that this compound can be converted to polysiloxanes by the sulfuric acid cleavage of one methyl group from each Me_3Si– grouping. Compound I was prepared in the present work by reaction of the di-Grignard reagent from 1,4-dibromobutane with trimethylchlorosilane, using tetrahydrofuran as a solvent. Use of tetrahydrofuran as the solvent in this preparation has several advan-

$$BrMg(CH_2)_4MgBr + 2Me_3SiCl \xrightarrow{T.H.F.} I$$

tages over the more conventional ethyl ether. In preliminary experiments performed with ether as the solvent, the di-Grignard reagent separated as an oily lower layer and the yield of desired product was only 32%. In contrast, the di-Grignard reagent is soluble in tetrahydrofuran and compound I was obtained in yields of 52–69%. Tetrahydrofuran has the additional advantage of providing a higher reaction temperature.[3]



$$Me_3Si(CH_2)_4SiMe_3 \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} \left[-\overset{Me}{\underset{Me}{Si}}(CH_2)_4\overset{Me}{\underset{Me}{Si}}-O- \right]_n + 2nCH_4$$

II

Treatment of a small sample of compound I with concentrated sulfuric acid gave 92% of the theoretical amount of methane (2 moles of methane per mole of I), thus indicating that silicon–carbon cleavage took place at both silicon atoms. On the basis of the above result it appeared that while Me–Si cleavage was the main reaction, about 8% of the reaction gave cleavage between silicon and methylene. In view of the latter fact, polymers II as obtained from the cleavage reaction would contain small amounts of products not having the 1,6-disila-

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[1] Paper 47 in a series on organosilicon chemistry. For paper 46 see THIS JOURNAL, **77**, 1677 (1955).

[2] For an excellent treatment of the rapidly expanding organosiloxane field see E. G. Rochow, "An Introduction to the Chemistry of the Silicones," second edition, John Wiley and Sons, Inc., New York, N. Y., 1951.

[3] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953), have reported the synthesis of compound I in 63% yield from reaction of the di-lithium reagent with trimethylchlorosilane in a pentane solvent.