Aromatic Organosilicon Compounds

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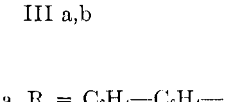
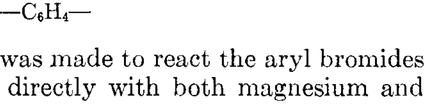
The use of silicone resins as high temperature insulating materials has led to the study of new types of polymerizable organosilane monomers. Four such compounds containing aromatic nuclei are reported herewith.

Compound I, bis(trimethylsilylmethyl) terephthalate and Compound II, *N,N'*-bis(trimethylsilylmethyl) terephthalamide were both prepared by interchange reactions starting with dimethyl terephthalate. According to the method of Speier,[1] chloromethyltrimethylsilane was converted *via* its acetate to hydroxymethyltrimethylsilane, and the reaction of this alcohol with dimethyl terephthalate using *p*-toluenesulfonic acid as a catalyst gave an 85% yield of Compound I. For the preparation of Compound II, an amide-ester interchange reaction was employed, starting with aminomethyltrimethylsilane[2] and dimethyl terephthalate. Removal of methanol from the reaction mixture yielded the diamide II.

Compound IVa, 4,4'-bis(chlorodimethylsilyl)biphenyl, and Compound IVb, 4,4'-bis(chlorodimethylsilyl)biphenyl ether, were both prepared by halogen-metal interconversion reactions. The appropriate aryl bromides IIIa and IIIb were treated with *n*-butyllithium according to the procedure of Gilman[3] to yield diaryllithium derivatives which were then coupled with excess dimethyldichlorosilane. Distillation of the reaction mixtures then gave good yields of the chlorosilanes IVa and IVb.



I



II

$$\underset{\text{III a,b}}{\text{Br—R—Br}} \xrightarrow{n\text{-BuLi}} \text{Li—R—Li} \xrightarrow{\text{Me}_2\text{SiCl}_2} \underset{\text{IV a,b}}{\text{Cl(Me}_2\text{)Si—R—Si(Me}_2\text{)Cl}}$$

a, R = C_6H_4—C_6H_4—
b, R = C_6H_4—O—C_6H_4—

An attempt was made to react the aryl bromides IIIa and IIIb directly with both magnesium and lithium. 4,4'-Dibromobiphenyl could not be made to react with either metal, and the reaction of 4,4'-dibromobiphenyl ether with lithium apparently yielded only a monolithio derivative which was carbonated to yield an acidic gum.

EXPERIMENTAL[4]

Bis(trimethylsilylmethyl) terephthalate (I). A mixture of 40.5 g. (0.39 mole) of hydroxymethyltrimethylsilane, 29.2 g. (0.15 mole) of dimethyl terephthalate (DMT), and 0.5 g. of *p*-toluenesulfonic acid was placed in a 500-cc. flask connected to a short stripping column. The flask was heated and with nitrogen sparging 10.2 ml. of methanol was collected (theory = 12.1 ml.) followed by 8 ml. of excess alcohol. Then one gram of unreacted DMT sublimed out of the reaction mixture. The flask containing the residue was connected to a small Claisen head and distilled. There was obtained 45 g. (89% crude yield) of the diester I, a pale yellow solid b.p. 155–160°/1. mm., m.p. 85–95°. The solid was recrystallized from a 4:1 methanol-benzene mixture to yield 40 g. of white flat shiny plates, m.p. 105–106°.

Anal. Calcd. for $C_{16}H_{26}O_4Si_2$: Si, 16.55; sapon. equiv. 169. Found: Si, 16.4; sapon. equiv. 166.

N,N'-bis(trimethylsilylmethyl) terephthalamide (II). In a 500-cc. round bottom flask was placed 38.8 g. (0.2 mole) of DMT and 62 g. 0.6 mole) of aminomethyltrimethylsilane. The flask was stoppered, shaken vigorously for nine days and then heated to 80° for 8 hr. The flask was then charged to a short stripping column and (with nitrogen sparging) 27 ml. of a mixture of methanol and excess amine was collected. The semisolid residue was placed in a small Claisen flask, distilled, and 20 g. of yellow solid was obtained, b.p. 130–5°/1. mm., m.p. 64–70°. This material is probably the monosubstituted silyl amide–ester and was not investigated further.

The residue from the Claisen distillation consisted of yellow-brown crystals, m.p. 190–210°, weight 22 g. (a 33% crude yield). One recrystallization from an ethanol-water solution yielded 16.3 g. of short colorless plates, m.p. 228–229°.

Anal. Calcd. for $C_{16}H_{28}N_2O_2Si_2$: Si, 16.65. Found: Si, 16.5.

4,4'-Bis(chlorodimethylsilyl)biphenyl (IVa). In a 1-l. three-necked flask fitted with a condenser, stirrer, and dropping funnel was placed 30.2 g. (0.1 mole) of 4,4'-dibromobiphenyl dissolved in a mixture of 150 cc. of toluene and 50 cc. of benzene. The flask was flushed with nitrogen and 200 cc. of a 1.6*N* solution of *n*-butyllithium[3] in diethyl ether was added with stirring. The mixture warmed slightly and a heavy white precipitate formed. Ether was distilled out through the condenser until the flask temperature had reached 78°. The mixture was then stirred and refluxed at this temperature for 0.5 hr. After cooling, the above mixture of 4,4-dilithiobiphenyl and excess *n*-butyllithium was added fairly rapidly with stirring to 64.5 g. (0.5 mole) of dimethyldichlorosilane. After two hours reflux, Color Test I[5] was negative.

The solution was cooled, filtered, and the precipitate was washed several times with hot benzene. The combined filtrates were stripped of mixed solvents and excess dimethyldichlorosilane. The residue was then Claisen distilled, and a fraction was collected having b.p. 195–205°/1.8 mm., solidifying in the receiver to a white crystalline solid m.p. 65–70°, weight 24 g. (71% yield). A redistilled sample of this material had b.p. 200–208°/1.8 mm., m.p. 68–70°.

Anal. Calcd. for $C_{16}H_{20}Cl_2Si_2$: Cl, 20.8; Si, 16.5. Found: Cl, 21.2; Si, 16.6.

4,4'-Bis(chlorodimethylsilyl)biphenyl ether (IVb). Following the general procedure given above, 320 cc. of a 1.5*N*

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(1) J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **70**, 1117 (1948).

(2) L. Sommer and J. Rockett, *J. Am. Chem. Soc.*, **73**, 5130 (1951).

(3) H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2337 (1940).

(4) The melting points were determined on a Fisher-Johns melting point block and are uncorrected.

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

n-butyllithium solution was added to 59 g. (0.15 mole) of 4,4′-dibromobiphenyl ether dissolved in 400 cc. of benzene. The solution was refluxed for 30 min., cooled, and added to 129 g. (one mole) of dimethyldichlorosilane. After refluxing for an additional 3 hr., the mixture was filtered, the excess chlorosilane and solvents were stripped from the filtrate, and Claisen distillation of the residue yielded a pale yellow oil, b.p. 200–205°/mm., weight 38 g. (71% yield). The oil crystallized on standing to a white waxy solid, m.p. 27–28°.

Anal. Calcd. for $C_{16}H_{20}Cl_2OSi_2$: Cl, 20.2; Si, 15.7. Found: Cl, 20.0; Si, 15.7.

Reaction of 4,4′-dibromobiphenyl ether with lithium. An organolithium reagent was prepared in the usual manner from 7 g. (one mole) of lithium wire, 75 g. (0.23 mole) of 4,4′-dibromobiphenyl ether, and 300 cc. of ether. An aliquot of this solution was taken for titration, and the solution was found to contain 0.25 mole of organolithium reagent. After cooling and filtering from excess lithium, the solution was poured rapidly onto a Dry Ice–ether slurry. The ether layer was washed and extracted with dilute potassium carbonate solution. Acidification of the aqueous solution gave a sticky yellow precipitate, weight 20 g. This material dried to a brittle resin, m.p. 150–170°.

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A New Synthesis of Menthofuran

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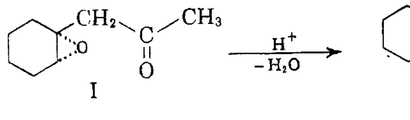
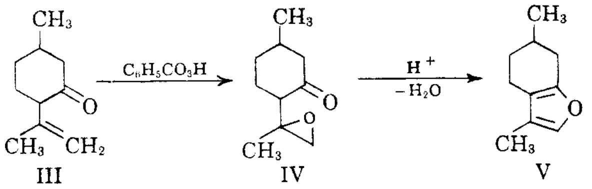
In a recent paper[1] it was shown that keto epoxides such as I could be cyclodehydrated readily to furans when heated with a catalytic amount of acid:



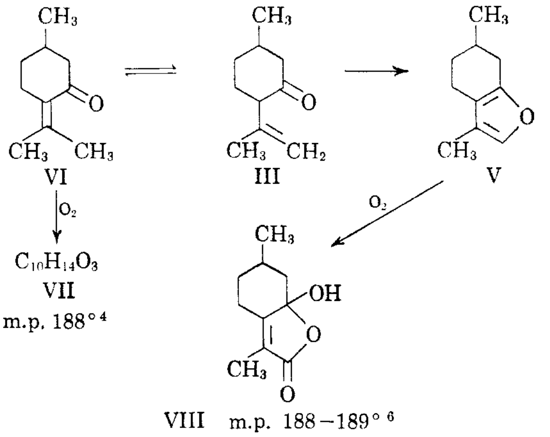
A similar synthesis has been performed on epoxyacetals resulting from a Darzens reaction on keto-acetals.[2]

This reaction has been extended now to the keto epoxide (IV), prepared by the action of perbenzoic acid on isopulegone (III). Menthofuran (V) was obtained in poor yield and shown to be identical with an authentic sample, prepared from pulegone according to the method of Treibs.[3] Cyclodehydration of IV occurs under very mild conditions, which are not essentially different from biological ones.



Autoxidation of pulegone[4] (VI) or pennyroyal oil[5] gives, among other compounds, a substance (VII), the melting point of which agrees with that of the lactone (VIII), isolated from the products of autoxidation of menthofuran[6]. The structure of VIII has been elucidated recently, but the identity of VII and VIII has not been verified completely.[6]

The results described in this note strengthen the hypothesis of biosynthesis of menthofuran *via* isopulegone:



EXPERIMENTAL

(*A*) To a solution of perbenzoic acid (0.04 mole) in chloroform, was added 4.32 g. of isopulegone.[7] The solution was kept at 0° and the course of the reaction was followed by titration of the unreacted peracid in aliquots. After completion of the reaction (14 hr.) the solution was washed with 10% sodium carbonate, saturated sodium chloride, dried and concentrated under reduced pressure. The residual oil was refluxed for 10 min. with a mixture of 20 ml. of water, 20 ml. of methanol, and 1 ml. of concentrated sulfuric acid, neutralized and steam distilled; the distillate was extracted with ether and worked up as usual. The yield of pure product was 0.55 g. (13%), b.p. 97–98°/22 mm., n_D^{22} 1.4805.[6,8,9]

The infrared spectrum was identical with that of authentic menthofuran. Menthofuran gives a wine-like characteristic color when treated with chloranil.

Maleic anhydride adduct: m.p. 134°, undepressed when mixed with an authentic sample.[8]

(*B*) When cyclodehydration of the keto epoxide was carried out at room temperature (14 hr.), the yield of menthofuran was lower (5%).

ECOLE POLYTECHNIQUE
PARIS, FRANCE

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(1) H. Fritel and P. Baranger, *Compt. rend.*, **241**, 674 (1955); H. Fritel, thesis (Paris 1956).

(2) D. M. Burness, *J. Org. Chem.*, **21**, 102 (1956).

(3) W. Treibs, *Ber.*, **70**, 85 (1937).

(4) E. Sernagiotto, *Gazz. chim. ital.*, **47** (I), 150 (1917).

(5) Y. R. Naves, *Perfumery Essent. Oil Record*, 121 (1945).

(6) R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.*, **72**, 399 (1950).

(7) C. Harries and G. Roeder, *Ber.*, **32**, 3368 (1899); our sample b.p. 98–101°/13 mm., n_D^{19} 1.4700, was purified through its semicarbazone m.p. 174–175°.

(8) P. Z. Bedoukian, *J. Am. Chem. Soc.*, **70**, 621 (1948).

(9) P. Carles, *Parfumerie mod.*, **22**, 615 (1929).