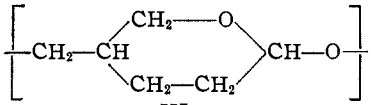
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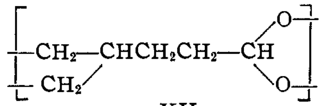
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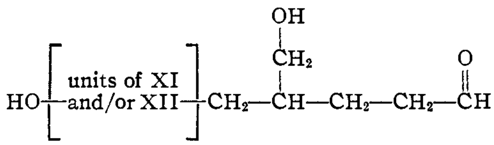
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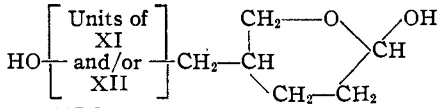
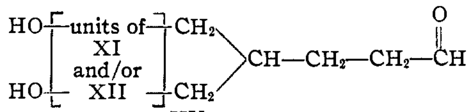

XIV


XV

Distillation of the residue gave 58 g. (50%) of α-(3,3-diethoxypropyl)-succinic acid diethyl ester (VIII), b.p. 157–158° (3.8 mm.), $n^{20}D$ 1.4370–1.4378, d^{31}_4 1.022.

6-Hydroxy-4-hydroxymethylhexanal Diethyl Acetal (II).—Fifty-eight grams (0.19 mole) of compound VIII was reduced with 10 g. (0.0264 mole) of lithium aluminum hydride, according to the procedure of Marvel and Hill,[3] to give 31.5 g. (75%) of 6-hydroxy-4-hydroxymethylhexanal diethyl acetal, b.p. 152–153° (1 mm.). A small sample was distilled from sodium carbonate and analyzed, b.p. 131° (0.06 mm.), $n^{20}D$ 1.4610. Infrared analysis in chloroform showed a hydroxyl band at 3336 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{24}O_4$: C, 59.97; H, 10.98. Found: C, 60.20; H, 10.70.

2-Ethoxy-5-hydroxymethyltetrahydropyran (III).—When 5-hydroxy-4-hydroxymethylpentanal diethyl acetal was polymerized (see below) at temperatures above 100° (1.5 mm.), a clear white liquid, 2-ethoxy-5-hydroxymethyltetrahydropyran, distilled from the reaction mixture, b.p. 95–97° (1.5 mm.), $n^{20}D$ 1.4563. Infrared analysis showed a hydroxyl group (3418 cm.$^{-1}$) and the absence of an aldehyde group.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.98; H, 10.60. Found: C, 60.25; H, 10.36.

2-Ethoxy-5-(β-hydroxyethyl)-tetrahydropyran (IV).—A small sample of 6-hydroxy-4-hydroxymethylhexanal diethyl acetal was heated at reduced pressure for a short time and then fractionated to give a polymeric residue and a colorless liquid, 2-ethoxy-5-(β-hydroxyethyl)-tetrahydropyran (IV), b.p. 97° (1.6 mm.), $n^{21.5}D$ 1.4602. Infrared analysis on the pure liquid showed a hydroxyl band at 3418 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.03; H, 10.41. Found: C, 62.06; H, 10.52.

Polymerization of Compound I.—One gram of 5-hydroxy-4-hydroxymethylpentanal diethyl acetal (I), $n^{20}D$ 1.4530–32, was placed in a small tube connected with a distillation system, a small crystal of *p*-toluenesulfonic acid monohydrate was added, the pressure in the distillation system was reduced to 0.02 mm., and heat was applied by means of an oil-bath. The bath temperature was kept slightly below the reflux temperature of the cyclic acetal III until the reaction mixture became quite viscous. The bath temperature was then raised to 120° and heating was continued for a total of 15 minutes. The reaction mixture was cooled, neutralized with concentrated ammonia, and extracted with chloroform. The chloroform extract was decolorized with Darco and evaporated to dryness under reduced pressure. The average molecular weight of the polymer as determined in bornyl bromide was 1190 ± 100; inherent viscosity in chloroform was 0.14. Infrared analysis of a film of the polymer showed a hydroxyl absorption at 3440 cm.$^{-1}$ and a carbonyl absorption at 1736 cm.$^{-1}$. The polymer softened at 49° to give a transparent glass.

Anal. Calcd. for $(C_6H_{10}O_2)_{7x}(C_6H_{12}O_3)_{3x}$: C, 60.29; H, 8.93. Found: C, 60.28; H, 8.67.

The above data are consistent with a branched structure whose internal $C_6H_{10}O_2$ units may have structure XI and/or XII and whose end $C_6H_{12}O_3$ units may have structure XIII, XIV and/or XV, and in which the average ratio of internal to external units is 7/3.

Polymerization of compound I in the above manner with a reaction time of 2 hours produced a polymer which was approximately 80% insoluble in chloroform; inherent viscosity in chloroform of the soluble portion, 0.17.

Polymerization of II.—Five grams of the dihydroxy acetal (II) was placed in a 25-ml. pear-shaped flask and the flask attached to a small distillation system. The system was evacuated to 1 mm. and the flask immersed in an oil-bath maintained at 210–220°. After 27 hours, heat was applied to the distillation column and a small amount of the cyclic acetal IV removed. A sample of material removed from the reaction flask at this time had an inherent viscosity in chloroform of 0.04.

The reaction flask was heated for 24 hours more at 210–220° (39 mm.) to give a firm, light red, translucent solid, inherent viscosity in chloroform 0.10. Continued heating in the above manner failed to raise the observed viscosity but did produce increasing amounts of gel. This polymer was assumed to contain a branched structure and structural units similar to the polymeric acetal I.

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Synthesis of 3,5-Dibromophenylsilanes

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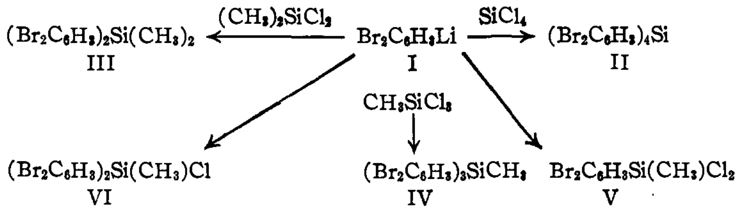
RECEIVED APRIL 10, 1953

In the course of an investigation of organosilanes of high density it became of interest to attempt the conversion of 1,3,5-tribromobenzene to 3,5-dibromophenylsilane derivatives. Following a brief unsuccessful effort to prepare a Grignard reagent from the tribromobenzene, we decided to employ 3,5-dibromophenyllithium (I) for reaction with the chlorosilanes. Gilman had reported[1] a 56% yield of 3,5-dibromobenzoic acid upon carbonation of the dibromophenyllithium compound, but no study was made of the optimum conditions for the halogen–metal interchange between *n*-butyllithium and 1,3,5-tribromobenzene. We have examined the effect of reaction time, as measured by the yield of 3,5-dibromobenzoic acid and find that in ether, with reaction times of 0.5, 1.0, 2.0 and 5.0 minutes, measured from the end of the addition of reagents, yields of 77, 78, 54 and 38%, respectively, were obtained. In petroleum ether, a one-minute reaction time gave only 18%. From the neutral portion of the reaction mixtures a product melting at 208.5–209° was isolated. This does not appear to correspond to the expected 3,5,3′,5′-tetrabromobiphenyl (m.p. 186°), but may be the tetrabromodiphenyl ketone.

Reactions of I were conducted with silicon tetrachloride, dimethyldichlorosilane and methyltrichlorosilane. The accompanying equations illustrate the methods used to prepare the various dibromophenylsilanes employing a one-minute reaction time for preparation of the lithium reagent. Yields of the tetrasubstituted silanes generally were good, but difficulties were encountered in con-

(1) H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).



trolling reaction conditions for monosubstitution of methyltrichlorosilane. In the initial attempts to prepare V none of the monosubstituted product was isolated, and only VI was obtained in 18% yield. Small yields of both V and VI were realized only by mixing, successively, small equivalent amounts of tribromobenzene and *n*-butyllithium solutions, followed by immediate addition to a large excess of the trichlorosilane. After separation of VI the distillation residue yielded a product melting at 247.5–248°, believed to be a pentabromoterphenyl.

Experimental[2]

***n*-Butyllithium.**—The procedure of Gilman[3] was used for preparation of *n*-butyllithium. In experiments where storage of the reagent was necessary, petroleum ether (Skellysolve A) was used as the solvent instead of diethyl ether.

Reaction Time Studies on Formation of 3,5-Dibromophenyllithium.—The apparatus used to study the optimum reaction time for the formation of 2,4-dibromophenyllithium (yield based on conversion to its acid) was a simple 250-ml. wide mouth erlenmeyer flask equipped with a 2-hole rubber stopper for helium inlet and outlet.

To 3.15 g. (0.01 mole) of 1,3,5-tribromobenzene in 100 ml. of diethyl ether or petroleum ether was added 20 ml. of 0.5 *N* *n*-butyllithium in diethyl ether solution. This mixture was allowed to stand for the prescribed reaction time under an atmosphere of dry helium at 25–28°. The reaction mixture was then poured onto a slurry of Dry Ice and diethyl ether. 3,5-Dibromobenzoic acid, m.p. 215–216°, was obtained from the aqueous extract of the ether solution.

One gram of a neutral product melting at 203–204° was isolated from the ether layer. The material was recrystallized from dioxane–water solution and then chromatographed in benzene solution on an alumina column, yielding a colorless product, m.p. 208.5–209°.

Anal. Calcd. for $C_{13}H_6Br_4O$: C, 31.36; H, 1.22; Br, 64.21. Found: C, 31.75, 31.30; H, 1.53, 1.58; Br, 64.17, 63.16.

Tetra-(3,5-dibromophenyl)-silane (II).—Using the simple reaction flask described in the preceding section, 1.57 g. (0.005 mole) of 1,3,5-tribromobenzene in 50 ml. of ether was treated with 10 ml. of 0.5 *N* *n*-butyllithium in petroleum ether solution. After one minute reaction time at 25°, 0.21 g. (0.00125 mole) of silicon tetrachloride in 5 ml. of ether was added with swirling. The mixture was allowed to stand for 15 minutes. The solvent was then distilled and the residue treated with petroleum ether producing a gummy precipitate which was crystallized from acetone. Recrystallization from benzene gave crystals melting at 298–302°. The yield was 0.52 g., 43%, based on tribromobenzene.

Anal. Calcd. for $C_{24}H_{12}Br_8Si$: C, 29.79; H, 1.25; Br, 66.07. Found: C, 29.74; H, 1.34; Br, 65.72.

Dimethyldi-(3,5-dibromophenyl)-silane (III).—The process above was repeated using 0.25 g. (0.0025 mole) of dimethyldichlorosilane in place of silicon tetrachloride. The reaction mixture was stripped of ether, extracted with benzene and the benzene solution concentrated to give 0.98 g. of product, 75% yield based on tribromobenzene. After two recrystallizations from ethanol, the melting point was 113–114°.

Anal. Calcd. for $C_{14}H_{12}Br_4Si$: C, 31.84; H, 2.29; Br, 60.55. Found: C, 31.99; H, 2.35; Br, 60.14.

(2) All melting points are uncorrected.

(3) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

Methyltri-(3,5-dibromophenyl)-silane (IV).—The above preparation was repeated using 0.15 g. (0.0015 mole) of methyltrichlorosilane. A total of 0.86 g. of product was obtained (76%, based on tribromobenzene), melting at 214–215° after two recrystallizations from benzene.

Anal. Calcd. for $C_{19}H_{12}Br_6Si$: C, 30.51; H, 1.62; Br, 64.12. Found: C, 30.87; H, 1.98; Br, 63.84.

Methyldi-(3,5-dibromophenyl)-chlorosilane (VI) and Pentabromoterphenyl (?).—1,3,5-Tribromobenzene, 7.5 g. (0.0237 mole) in 125 ml. of ether, was placed in a 250-ml. addition funnel. The funnel was so arranged to have outlet through one neck of a 2-liter three-necked flask equipped with a rapidly run trubore stirrer and a condenser, and fitted with inlet and outlet for a vigorous stream of dry nitrogen.

In the flask was placed a solution of 28 g. (0.174 mole) of methyltrichlorosilane in 250 ml. of diethyl ether. After cooling the flask in an ice-bath, 50 ml. of 0.475 *N* *n*-butyllithium in petroleum ether was added as quickly as possible from a pipet with rapid stirring by means of the emptying pipet. One minute after the end of this addition, at which time the solution passed through a bright yellow to slightly dark color the dropping funnel was emptied quickly into the rapidly stirred chlorosilane solution. The funnel was swept out with dry nitrogen, the stopcock was closed, and the interchange was repeated on a second portion of 1,3,5-tribromobenzene. This solution was run into the flask and the final reaction mixture was allowed to stir for one-half hour as it warmed up to room temperature.

The ether was removed and the yellow liquid residue containing precipitated lithium chloride was treated with 125 ml. of hot benzene and filtered in a nitrogen atmosphere. The benzene was stripped under vacuum, using a small column and take-off, the whole apparatus being under dry nitrogen introduced at the ebulliator. The product was then fractionated under vacuum, using a small integral pot still of 25-ml. capacity with attached condenser. After a small forerun, a white crystalline solid came over which, from its subliming properties, appeared to be tribromobenzene. (This was later shown to be correct since its melting point was 119–120°, and the material gave no depression in a mixed melting point with authentic 1,3,5-tribromobenzene.) The difficulty in removing the tribromobenzene necessitated interruption of the distillation to clean the fraction cutter.

A third fraction, 2.34 g., was then obtained at 185° and 0.1 mm. This product (VI) solidified in the receiver, and represented a yield of 18%. The di-substituted silane was recrystallized from petroleum ether three times. After drying in vacuum, the white prisms melted at 109–110°.

Anal. Calcd. for $C_{13}H_9SiClBr_4$: C, 28.47; H, 1.65; Cl, 6.47. Found: C, 28.96; H, 1.71; Cl, 6.38.

After collecting the third fraction, the distillation was stopped and the residue was dissolved in hot benzene. Upon concentration and cooling, a precipitate was obtained which was crystallized from benzene solution (m.p. 246–247°). Recrystallization from dioxane–water solution yielded 1 g. of product, m.p. 247.5–248°.

Anal. Calcd. for $C_{18}H_9Br_5$: C, 34.61; H, 1.44; Br, 64.00. Found: C, 34.79; H, 1.79; Br, 63.73.

Methyl-(3,5-dibromophenyl)-dichlorosilane (V).—Using the apparatus described by Gilman,[1] there was placed 75 ml. of an ether solution of 0.64 *N* *n*-butyllithium in funnel A and 15 g. (0.047 mole) of 1,3,5-tribromobenzene in 250 ml. of diethyl ether in funnel B. In flask II, immersed in an ice–salt-bath, was placed 55.9 g. (0.38 mole) of methyltrichlorosilane in 250 ml. of diethyl ether. A nitrogen atmosphere was maintained in both reaction flasks. From funnel A, 5 ml. of solution was added to flask I, immediately followed by addition of 18 ml. of the tribromobenzene solution. The mixture then was added instantly to flask II with vigorous stirring.

This sequence of additions was carried out fifteen times until all reactants were consumed. The ice-bath was then removed and the mixture was stirred until it reached room temperature (30 minutes). Ether was stripped at atmospheric pressure over a steam-bath, and the residue was treated with hot, dry benzene and filtered under a nitrogen atmosphere.

The benzene solution was then distilled, first at atmospheric pressure to remove all solvent, followed by vacuum distillation at 0.1–0.05 mm. In the first fraction there was collected 0.1 g. of a low boiling liquid, b.p. 35–55°, which was not identified. A second fraction, 0.50 g., was collected at 65–75° and this solidified in the receiver. Some tribromobenzene was also obtained, but because of its tendency to condense as a solid on the walls of the fraction cutter its partial separation from this product was effected. The third fraction was collected at 185°, and consisted of 2.5 g. of (VI).

The last two fractions were redistilled, and the more volatile fraction was collected at 65° and 0.1 mm. Distillation was not continued beyond this point. The product solidified in the receiver and was found to melt at 44–45°.

Anal. Calcd. for $C_7H_6SiBr_2Cl_2$: C, 24.06; H, 1.73; Si, 8.04. Found: C, 24.27; H, 1.78; Si, 7.80.

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Pentaphenylethanol

BY WILLIAM A. MOSHER AND MELVIN L. HUBER[1]

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In connection with other work it was desirable to prepare substantial quantities of pentaphenylethanol, a compound reported by Schmidlin and Wohl[2] from the reaction of phenylmagnesium iodide and β-benzopinacolone under forcing conditions. This same reaction had been attempted previously but with negative results[3] and other reactions which were expected to yield pentaphenylethanol gave other products.[4] Only two other references to the compound have been found,[5] and in these small amounts of a compound corresponding to the Schmidlin and Wohl substance were reported. No proof of structure has yet been presented.

Schmidlin and Wohl[2] found that their substance ($C_{32}H_{26}O$) was converted to $C_{32}H_{24}O$ by treatment with hydrochloric acid, acetyl chloride, or phosphorus pentachloride and the new substance was called "dehydropentaphenylethanol." We have recently established the structure of "dehydropentaphenylethanol" as *o*-biphenylyl triphenylmethyl ketone,[6] and this information now permits attack on the structure of the original substance.

When the compound from the reaction of phenylmagnesium iodide and β-benzopinacolone is catalytically dehydrogenated at its melting point with palladium on charcoal, *o*-biphenylyl triphenylmethyl ketone, identical with "dehydropentaphenylethanol," is formed. The original substance shows a strong infrared absorption for carbonyl but hydroxyl absorption is absent. These facts are consistent with a 1,4-addition of the Grignard reagent to the conjugated system of the carbonyl and the aromatic ring, in the matter described by Kohler and Nygaard[7] with diphenylbenzalacetophenone, followed by rearrangement of hydrogen. Figure 1 indicates the complete series of reactions. The only uncertainty is the location of the double bonds in the rather unstable, partially hydrogenated ring. Our formulation is based on the simplest tautomeric shifts.

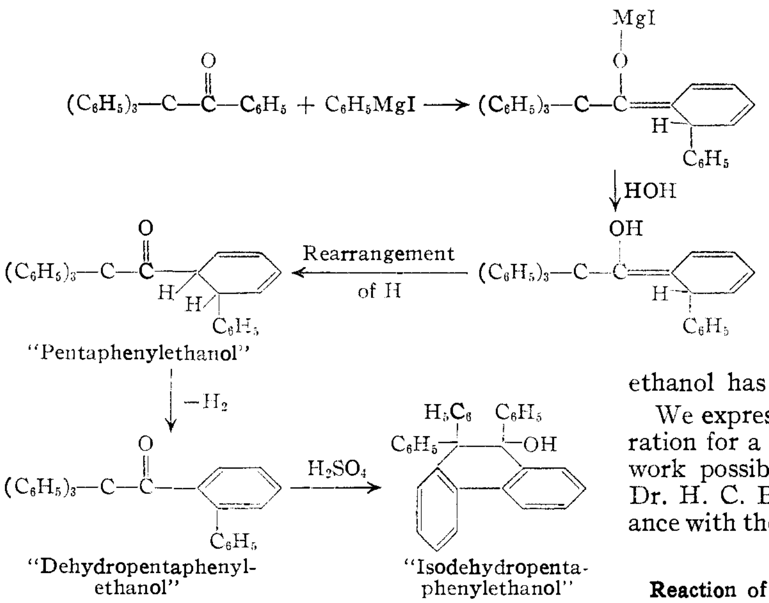

Fig. 1.

We have some evidence that the original enol may be present; before recrystallization the infrared absorption is strong at the hydroxyl band and the material decolorizes permanganate. A simple recrystallization removed the hydroxyl absorption completely both from the solid and from the mother liquor.

It seems safe to say that "pentaphenylethanol" as previously reported is actually a dihydroketone, probably 1-triphenylacetyl-2-phenyl-1,2-dihydrobenzene. Pentaphenylethanol has not yet been prepared.

We express our appreciation to Research Corporation for a F. G. Cottrell Grant which made this work possible and to Mrs. Margaret Kraus and Dr. H. C. Beachell of this Department for assistance with the infrared data.

Experimental

Reaction of Phenylmagnesium Iodide and β-Benzopinacolone.—The method was essentially that of Schmidlin and Wohl[2]; 100 g. of benzene, 13 g. (0.54 mole) of magnesium turnings, 102 g. of phenyl iodide (0.5 mole) and 400 ml. of dry ether were used to prepare the Grignard reagent, which was filtered, added to a flask containing 20 g. (0.057 mole) of β-benzopinacolone (m.p. 179–80°) and refluxed for 20 hours. The reaction mixture was cooled in an ice-bath and carefully decomposed with a mixture of ice and water containing 46 ml. of concd. hydrochloric acid. After shaking in a separatory funnel, the solid which separated in the ether layer was filtered off and washed. Recrystallization of this product from acetic acid and then from benzene or a mixture of benzene and petroleum ether (b.p. 65–110°) gave a white solid melting at 175–176°. *Anal.* Calcd. for

(1) F. G. Cottrell Research Fellow. From the Ph.D. Dissertation of M. L. Huber, Univ. of Delaware School of Graduate Studies, 1950. Presented before Division of Organic Chemistry, American Chemical Society, Chicago, September 7, 1950.

(2) J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

(3) M. Gomberg and L. H. Cone, *ibid.*, **38**, 2454 (1905); **39**, 1461, 1469 (1906).

(4) J. Schmidlin, *ibid.*, **39**, 4200 (1906); **43**, 1137 (1910); W. Schlenk and R. Ochs, *ibid.*, **49**, 608 (1916); W. E. Bachmann, THIS JOURNAL, **53**, 2759 (1931).

(5) W. Schlenk and H. Mark, *Ber.*, **55**, 2298 (1922); H. Gilman and R. E. Fothergill, THIS JOURNAL, **51**, 3149 (1929).

(6) W. A. Mosher and M. L. Huber, *ibid.*, **73**, 795 (1951).

(7) E. P. Kohler and B. M. Nygaard, *ibid.*, **52**, 4128 (1930).