permanganate were negative. Although the structures of these products have not been proven we suggest structures based on addition of the triphenylsilyl radical to the terminal carbon atoms.

$$(C_6H_5)_3SiCH_2CH{=}CH_2 + (C_6H_5)_3SiH \xrightarrow{\text{peroxide}} (C_6H_5)_3SiCH_2CH_2Si(C_6H_5)_3$$

This reaction was attempted with triallylphenylsilane and with tetraallylsilane but as yet crystalline products have not been isolated.

It is noteworthy that a much cleaner reaction was obtained with triphenylgermane which added to allyltriphenylsilane in 76% yield.[2]

The compounds diallyldiphenylsilane and triallylphenylsilane were prepared by treatment of the appropriate chlorosilane with allylmagnesium bromide.[3] These reactions proceeded rapidly in refluxing ether solution which is in marked contrast to the sluggish reactions exhibited by most Grignard reagents in comparable reactions.[4]

EXPERIMENTAL[5]

Diallyldiphenylsilane. A solution of 0.448 mole of allylmagnesium bromide[6] in 350 ml. of ethyl ether was added to a solution of 47.2 g. (0.186 mole) of diphenyldichlorosilane in ethyl ether at such a rate that gentle refluxing occurred. A heavy precipitate formed during the addition. When 1.72 equivalents of the Grignard reagent had been added Color Test I[7] was negative, indicating a rapid reaction. The mixture was stirred under reflux for 12 hr. and then hydrolyzed with cold dilute hydrochloric acid. The ether layer was washed with water, dried over sodium sulfate and distilled, finally, at 1.2 mm., giving a main fraction of 25.1 g. (51%), b.p. 128–130°, n_D^{20} 1.5753, d_D^{20} 0.995.

Anal.[8,9] Calcd. for $C_{26}H_{20}Si$: Si, 10.6; M_D, 87.6. Found: Si, 10.8, 10.8; M_D 87.9.

Triallylphenylsilane. The preceding procedure was used with 0.696 mole of allylmagnesium bromide and 40.9 g. (0.194 mole) of phenyltrichlorosilane giving a main fraction of 33.6 g. (76%), b.p. 90–92° (0.8 mm.) n_D^{20}, 1.5339, d_4^{20} 0.924.

Anal. Calcd. for $C_{15}H_{10}Si$: Si, 12.3; M_D 76.6. Found: Si, 12.4, 12.4; M_D, 76.9.

1,3-bis(Triphenylsilyl)propane. A mixture of 4.81 g. (0.016 mole) of allyltriphenylsilane,[10] 26.0 g. (0.10 mole) of triphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, and 25 ml. of hexane was stirred in a 75° bath for 24 hr. Distillation gave a volatile fraction b.p. 110–135° (0.05 mm.) consisting of unchanged triphenylsilane and 0.50 g. (10%) of unchanged allyltriphenylsilane. The residue from the distillation was a viscous liquid. Dilution with a few milliliters of benzene and 50 ml. of absolute ethanol gave 1.1 g. of a solid melting at 123–132°, after several days at 0°. Repeated recrystallizations from benzene–absolute ethanol, *n*-propyl alcohol, and acetone gave 0.09 g. (1%) of crystals melting at 150–152°.

Anal.[11] Calcd. for $C_{39}H_{36}Si_2$: Si, 10.0. Found: Si, 10.2, 10.3.

When this procedure was repeated in a quartz flask at 45° with ultraviolet irradiation in place of the peroxide none of the product could be isolated.

Diphenyl-bis(3-triphenylsilylpropyl)silane. When 2.20 g. (0.0083 mole) of diallyldiphenylsilane was treated with 26.0 g. of triphenylsilane using peroxide catalyst as in the preceding experiment, there was obtained 0.61 g. (9%) of a solid melting at 108–111° after crystallization from *n*-propyl alcohol. Recrystallization from petroleum ether (b.p. 100–120°) gave 0.30 g. (5%) of crystals m.p. 115–117°.

Anal. Calcd. for $C_{54}H_{52}Si_3$: Si, 10.7. Found: Si, 10.7, 10.7.

1-Triphenylsilyl-3-triphenylgermanylpropane. A mixture of 2.40 g. (0.008 mole) of allyltriphenylsilane, 15.3 g. (0.05 mole) of triphenylgermane, 0.16 g. (0.00066 mole) of benzoyl peroxide, and 25 ml. of hexane was stirred at 75° for 24 hr. After distillation of unchanged triphenylgermane at 125–135° (0.05 mm.) there was obtained 5.3 g. of a viscous residue. Dilution with 12 ml. of petroleum ether (b.p. 60–70°) gave 4.52 g. (93%) of crystals that melted at 128–131°. Three recrystallizations from absolute ethanol–benzene gave 3.66 g. (76%) of crystals, m.p. 134–135°.

Anal. Calcd. for $C_{39}H_{36}GeSi$: $GeO_2 + SiO_2$, 27.2. Found: $GeO_2 + SiO_2$, 27.4, 27.4.

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(2) Dr. R. Fuchs has already demonstrated in this laboratory that triphenylgermane adds to octene-1 to give triphenyl-*n*-octylgermane.

(3) A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 635 (1952) [*Chem. Abstr.*, **47**, 10471 (1953)] have described the preparation of triallylphenylsilane by the simultaneous addition of phenyltrichlorosilane and allyl bromide to magnesium.

(4) See H. Gilman, J. Eisch, and T. Soddy, *J. Am. Chem. Soc.*, **79**, 1245 (1957) for the high reactivity of allylmagnesium types to the azomethine linkage.

(5) All melting and boiling points are uncorrected. All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen.

(6) H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France* [4], **43**, 1322 (1928).

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

(8) Molar refractions were calculated from the values of A. D. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

(9) Silicon analyses were performed by the procedure of H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(10) Prepared from triphenylchlorosilane and allylmagnesium bromide in accordance with directions provided by L. F. Cason and H. G. Brooks, in unpublished studies.

(11) Microdetermination of silicon, H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 968 (1951).

Preparation of Alkylnaphthalenes

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Incidental to the preparation of some organosilicon compounds, 1-*n*-butylnaphthalene was isolated in 40 to 60% yields when 1-naphthyllithium was prepared by halogen-metal interconversion between 1-bromonaphthalene and *n*-butyllithium. This result was not surprising since this type of coupling reaction has been observed frequently.

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A survey of the literature revealed considerable discrepancy in regard to the physical constants of the *n*-butylnaphthalenes.[3] Also, a search of the literature disclosed that there are very few synthetic methods for obtaining alkylnaphthalenes and related hydrocarbons in good yield. Some of the methods, particularly the Friedel-Crafts synthesis, leave much to be desired concerning the structure of the isolated product. The Wurtz-Fittig reaction apparently leaves the alkyl residue intact during the reaction but the yields are low.[3]

Methyl iodide is reported to react immediately with 1-naphthyllithium to give an 80% yield of 1-methylnaphthalene.[4] Experiments indicated the reaction of alkyllithium compounds with naphthyl halides to be a method of choice for the synthesis of authentic specimens of hydrocarbons. 1-*n*-Butylnaphthalene and 1-*n*-hexylnaphthalene were prepared in good yields by this procedure.

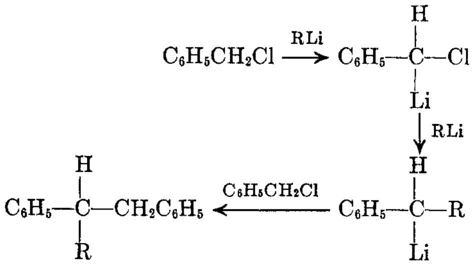
The following two facts leave little doubt that the formation of these alkylnaphthalenes proceeds as indicated in reaction sequence A. 1-Naphthoic acid is obtained in 90% yield by carbonating a mixture of 1-bromonaphthalene and *n*-butyllithium after the reagents have been stirred for 20 min.[5] Color Test II[6] becomes negative after the reaction mixture is stirred for 2 hr., while Color Test I[7] remains positive for 36 hr.

$$1\text{-}C_{10}H_7Br + RLi \longrightarrow 1\text{-}C_{10}H_7Li + RBr \longrightarrow 1\text{-}C_{10}H_7R + LiBr \quad (A)$$

$R = n\text{-alkyl}$

The reaction of benzyl chloride with 1-naphthyllithium failed to yield the expected 1-benzylnaphthalene. A colorless product, melting at 82–83°, was isolated; 1-benzylnaphthalene has a melting point of 58°.[8] The ultraviolet spectral curve of this compound showed four maxima, all of which are within 1 mμ of the maxima shown by 1-benzylnaphthalene. This evidence strongly suggests that the product is of the benzylnaphthalene type and not a phenylnaphthalene derivative. The latter type of compound shows a definite bathochromic shift due to the interaction of the two aromatic nuclei.

The reaction between phenyllithium and benzyl chloride is reported[9] to yield 1,1,2-triphenylethane and the proposed mechanism is summarized in reaction sequence B:



$$C_6H_5CH_2Cl \xrightarrow{RLi} C_6H_5\text{—}\overset{H}{\underset{Li}{C}}\text{—}Cl \xrightarrow{RLi} C_6H_5\text{—}\overset{H}{\underset{Li}{C}}\text{—}R \xrightarrow{C_6H_5CH_2Cl} C_6H_5\text{—}\overset{H}{\underset{R}{C}}\text{—}CH_2C_6H_5 \quad (B)$$

Wittig and Witt considered it more likely that diphenylmethane was formed as an intermediate but found that diphenylmethane was not metalated to any appreciable extent by phenyllithium. Assuming that a similar reaction occurred between 1-naphthyllithium and benzyl chloride, the end product, where R = 1-naphthyl, would be 1-naphthylphenylbenzylmethane.

Efforts to prepare 1-naphthylphenylbenzylmethane by other methods were unsuccessful. 2,3-Diphenylheptanoic acid is obtained by carbonating the mixture resulting from the addition of *n*-butyllithium to stilbene;[10] an attempt to prepare 2,3-diphenyl-3-(1-naphthyl)propionic acid, which could be decarboxylated to yield the desired compound, was not successful. Attempts were made to dehydrate 1-naphthylphenylbenzylcarbinol; the resulting ethylenic compound could then have been subjected to catalytic hydrogenation. Dehydration experiments with sulfuric acid and by Chugaev's method were futile. An attempt to prepare 1-naphthylphenylbenzylmethyl chloride, which subsequently could be reduced with lithium aluminum hydride, failed to yield the desired product.

EXPERIMENTAL[11]

1-n-Butylnaphthalene. To 101.5 g. (0.49 mole) of 1-bromonaphthalene was added an ethereal solution of 0.49 mole of *n*-butyllithium;[12] this mixture was allowed to reflux gently. After the exothermic reaction had subsided, the solution was heated to maintain reflux conditions until Color Test I[7] became negative (36 hr.). The mixture was hydrolyzed with water and the ether layer was washed with dilute hydrochloric acid. The solvent was removed from the dried organic layer and the residual oil was vacuum distilled; the main fraction (78.0 g., n_D^{20} 1.5805) boiled at 136–143° (3.5 mm.). Careful fractionation of this material through a column of 11 theoretical plates gave 71.0 g. (79%) of a colorless oil, b.p. 287–288° (745 mm.), n_D^{20} 1.5812, d_{20}^{20} 0.978. These physical constants are in good agreement with the published values.[3]

The *sym*-trinitrobenzene complex was prepared[3] by mixing and fusing equivalent quantities of the two reactants to obtain a yellow solid melting at 72–74°. A mixture melting point with the corresponding complex of 2-*n*-butylnaphthalene[13] (m.p. 75°) showed a large depression.

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(3) The literature is reviewed by A. S. Bailey, G. B. Pickering, and H. C. Smith, *J. Inst. Petroleum*, **35**, 103 (1949).

(4) H. Gilman and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 1843 (1940).

(5) H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **73**, 4640 (1951).

(6) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

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

(8) G. Egloff, *Physical Constants of Hydrocarbons*, Reinhold Publishing Corp., New York, N. Y., 1947, Vol. IV, p. 227.

(9) G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

(10) K. Ziegler, F. Crössman, H. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929).

(11) All melting points and boiling points are uncorrected.

(12) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(13) Kindly supplied by A. S. Bailey, The Dyson Perrins Laboratory, Oxford University, England.

This experiment was repeated in essentially the same manner except that a 20% excess of *n*-butyl bromide was added to the refluxing solution immediately after the *n*-butyllithium and 1-bromonaphthalene were mixed. It was necessary to reflux the reaction for only 24 hr. before Color Test I was negative. The product was worked up and purified as before to obtain an 87% yield of the pure 1-*n*-butylnaphthalene.

In another run, the ether was replaced by benzene immediately after the *n*-butyllithium had been added. Color Test I was negative after refluxing the mixture for 15 hr., but the yield of pure product was only 38%.

1-n-Hexylnaphthalene. An ethereal solution of 0.41 mole of *n*-hexyllithium was prepared by the usual method[12] in 70% yield and was added to 85.0 (0.41 mole) of 1-bromonaphthalene. A 20% excess of 1-bromohexane was then added; even after refluxing the mixture for 5 days, Color Test I remained positive. The mixture was poured onto a dry ice–ether slurry and the acid was isolated in the customary manner by basic extraction. A 4.2% yield of 1-naphthoic acid (mixture melting point) melting at 155–156° was obtained. The neutral ether solution was worked up by fractional distillation in essentially the same manner as that described above for 1-*n*-butylnaphthalene to obtain a 61% yield of 1-*n*-hexylnaphthalene, n_D^{20} 1.5652, d_{20}^{20} 0.957. These physical constants are in good agreement with the reported values:[3] n_D^{20} 1.5652, d_4^{20} 0.958.

Reaction of 1-naphthyllithium with benzyl chloride. To 207.1 g. (1.0 mole) of 1-bromonaphthalene was added, at −5°, an ethereal solution containing 1.0 mole of *n*-butyllithium; the mixture was stirred for 30 min. and then 190 g. (1.5 moles) of freshly distilled benzyl chloride was slowly added. Color Test I was negative immediately after all of the benzyl chloride had been added. After pouring into water and separating the layers, the organic material was distilled at reduced pressure. The fraction boiling from 250–270° (3.5 mm.) was digested with petroleum ether (b.p. 30–60°) and the solution was allowed to crystallize undisturbed. After 2 days, 33 g. of white solid melting at 81–83° was removed. Recrystallization from ethanol raised the melting point to 82–83°.

The expected product, 1-benzylnaphthalene, melts at 58°.[8] A sodium fusion test showed halogen to be absent. The compound was insoluble in concentrated sulfuric acid, and a picrate could not be made. The ultraviolet absorption spectrum of the compound showed maxima at 273, 283.5, 292.5 and 276 mμ. On the basis of these data and the report by other investigators of a similar reaction,[9] the compound is believed to be 1-naphthylphenylbenzylmethane.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.86, 93.96; H, 5.99, 6.21.

Attempted addition of 1-naphthyllithium to stilbene. An ethereal solution of 5.0 g. (0.028 mole) of stilbene and 0.056 mole of 1-naphthyllithium (prepared in 86% yield) was refluxed for 16 hr. Following hydrolysis and separation of the layers, the organic material was distilled at 3.0 mm. The fraction boiling from 240–305°, a red oil, was digested with 4 ml. of petroleum ether (b.p. 30–60°) and cooled to give 2.3 g. of stilbene (mixture melting point) melting at 118–120°. The remaining oil was dissolved in petroleum ether (b.p. 30–60°) and the petroleum ether solutions were combined and chromatographed on alumina. Six distinct bands developed on the column. After extruding and separating the 6 bands, the organic material was eluted with methanol. Evaporation of all fractions gave only colored oils which could not be crystallized.

1,2-Diphenyl-1-(1-naphthyl)ethylene (attempted). A number of substituted stilbenes have been prepared by distilling the corresponding carbinol at reduced pressure in the presence of a trace of sulfuric acid.[14] 1-Naphthylphenylbenzylcarbinol, m.p. 148–149°, was prepared by the method of Bauer.[15] Seven grams (0.021 mole) of 1-naphthylphenylbenzylcarbinol was distilled at 0.1 mm., after adding 3 drops of 50% sulfuric acid to the dry solid. The fraction boiling at 215–220°, 6 g. of a yellow viscous oil, was collected and dissolved in petroleum ether (b.p. 60–80°). Only oils were obtained from methanol, ethanol, petroleum ether, and various combinations of these solvents.

Attempted dehydration of 1-naphthylphenylbenzylcarbinol by Chugaev's method. Although this reaction was carried out in essential accordance with the procedure of Alexander and Mudrak[16] for use with a similar carbinol, a 92% recovery of starting alcohol was obtained. Since it was believed that the sodium salt of the carbinol was not formed initially in the 3-step reaction, the lithium salt was made by adding an equivalent amount of *n*-butyllithium to the alcohol. The above procedure was then followed but an 84% recovery of the carbinol was obtained.

1-Naphthylphenylbenzylmethyl chloride (attempted). A mixture of 2.0 g. (0.006 mole) of 1-naphthylphenylbenzylcarbinol and thionyl chloride (freshly distilled from quinoline) in benzene was refluxed for 2 hr. The solvent and excess thionyl chloride were removed by distillation at reduced pressure to give a yellow oil. This material could not be crystallized from petroleum ether (b.p. 60–80°), ethanol, or benzene.

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[14] W. Tadros, K. Farahat, and J. M. Robson, *J. Chem. Soc.*, 439 (1949).

[15] H. Bauer, *Ber.*, **42**, 2588 (1909).

[16] E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

An Improved Metalation Procedure for Dibenzofuran

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Dibenzofuran has been metalated successfully in the past with various organolithium compounds.[1] A comparative metalation study of dibenzofuran with *n*-butyllithium has been carried out in diethyl ether, di-*n*-butyl ether and petroleum ether (b.p. 28–38°) to give yields of 56%, 76%, and 1%, respectively, of 4-dibenzofurancarboxylic acid after carbonation of the metalated product. In all of these cases the reaction mixtures were refluxed for 4–24 hr. with the yields of 4-dibenzofuryllithium increasing slightly with increased refluxing periods.[2] The use of organolithium compounds other than *n*-butyllithium generally results in smaller yields of 4-dibenzofuryllithium.[2,3] It might be mentioned that 4-dibenzofuryllithium has been derived in rather good yields with *O*-methylhydroxylamine and with oxygen to give the amine and hy-

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[1] For a general discussion of metalation reactions see H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **VIII**, Chap. 6 (1954).

[2] H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

[3] H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **67**, 877 (1945).