Relative Solubilities of Lithio and Sodio Salts of β-Hydroxy Esters in Ether.—A solution of 14.8 g. (0.0625 mole) of *t*-butyl β-hydroxy-β-phenylbutyrate in 25 ml. of ether was added during 3 minutes to a stirred suspension of 0.0625 mole of lithium amide in 100 ml. of liquid ammonia, and the ammonia driven off rapidly by means of a hot water-bath as 40 ml. of ether was being added. As soon as the liquid ammonia had evaporated (about 5 minutes), 3 g. of filter aid (Hyflo Supercel) was added and the mixture filtered rapidly with suction. The solid remaining on the funnel, less the tared weight of the filter aid, weighed 0.4 g., corresponding to only 2% of insoluble lithio salt. Distillation of the solvent from the clear filtrate yielded a glassy, viscous residue which, after sucking dry under vacuum, weighed 14.6 g., corresponding to 97% of ether soluble lithio salt.

When ethyl β-hydroxy-β-phenylbutyrate was similarly converted to its sodio salt by sodium amide and the mixture filtered under the above conditions, the material on the funnel corresponded to 9% of insoluble sodio salt and that obtained on evaporation of the filtrate, to 88% of soluble sodio salt.

Ethyl α-Bromoacetate with Acetophenone and Zinc.—Treatment of 83.5 g. (0.5 mole) of ethyl α-bromoacetate, 73.2 g. (0.61 mole) of acetophenone, 40 g. (0.62 mole) of purified zinc dust and 100 ml. of anhydrous benzene under the conventional Reformatsky conditions,[9] (refluxed 1.25 hours), gave 62.3 g. (60%) of ethyl β-hydroxy-β-phenylbutyrate, b.p. 143.5–145.5° (15 mm.).

When the same quantities of reactants (using purified 20–30 mesh granulated zinc) were refluxed for a total of 29 hours in benzene and toluene (50 ml. of each), and the reaction mixture allowed to stand another 23 hours (the majority of the zinc dissolving within the first hour), there was isolated only 1.2 g. (1%) of ethyl β-hydroxy-β-phenylbutyrate, b.p. 133–136° (10 mm.). In addition there was obtained 2.2 g. (6%) of benzoylacetone, b.p. 129–132° (10 mm.), 33.0 g. (49%) of dypnone, b.p. 156–158° (1 mm.), and 10.2 g. of dark viscous residue. The β-diketone was identified by its positive enol test and copper salt, m.p. 194–195° (reported m.p. 195–196°).[18] The dypnone was identified by its phenylhydrazone, m.p. 181.5–182.5° (see above).

DURHAM, N. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Analogs of Hexaphenylethane. II.* Triphenylmethyltriphenylsilane

BY A. G. BROOK, HENRY GILMAN AND L. S. MILLER

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Triphenylmethyltriphenylsilane, a very stable solid showing no tendency to dissociate into free radicals, has been isolated in 40–70% yield from the reaction of triphenylmethylsodium or -lithium with triphenylhalosilanes. Its synthesis is accompanied by the formation of from 8–15% of the isomeric *p*-triphenylsilylphenyldiphenylmethane. When attempts were made to prepare triphenylmethyltriphenylsilane from triphenylsilylpotassium and triphenylchloromethane, the only products obtained were hexaphenyldisilane and hexaphenylethane, isolated as the peroxide. These products were shown conclusively to have arisen as the result of a halogen–metal interconversion, a phenomenon not previously observed with silicon compounds.

The well known and much studied dissociation of the hexaarylethanes into triarylmethyl radicals has given rise to considerable speculation as to whether analogous compounds containing other group IVB elements dissociate similarly. Numerous studies have been made on some of the members of this series, namely, the symmetrical disilanes, digermanes, distannanes and diplumbanes, but little attention has been paid to the unsymmetrical members containing two different group IVB elements, particularly in the case where only one carbon atom has been replaced.

Evidence is lacking for the dissociation of the hexaaryldisilanes[1] or digermanes,[2] but certain evidence, particularly cryoscopic and ebullioscopic molecular weight determinations, has been presented which suggests that the hexaaryl- and hexaalkyldistannanes[3] and -diplumbanes[4] dissociate to some extent, although this dissociation is not detected by magnetic susceptibility measurements.

Of the possible unsymmetrical hexaaryl compounds, only triphenylsilyltriphenyltin,[5] triphenylmethyltriphenyltin[6] and triphenylmethyltriphenyllead[6] have been prepared. Of these, the dissociation of the first has not been studied, while on the basis of cryoscopic molecular weight determinations in benzene, the second appears not to dissociate, while the latter appears to be about 50% dissociated at low concentrations.

No reports have been made of attempts to prepare triphenylmethyltriphenylsilane, the carbon–silicon analog of hexaphenylethane. The present investigation concerns the synthesis of this compound and a study of its properties, in particular its tendency to dissociate. A similar study of triphenylmethyltriphenylgermane is now in progress in this Laboratory.

Two alternative syntheses of triphenylmethyltriphenylsilane appeared to be possible, as outlined in equations 1 and 2.

$$(C_6H_5)_3C\text{-}M + (C_6H_5)_3Si\text{-}X \longrightarrow (C_6H_5)_3C\text{-}Si(C_6H_5)_3 + MX \qquad (1)$$

$$(C_6H_5)_3Si\text{-}K + (C_6H_5)_3C\text{-}Cl \longrightarrow (C_6H_5)_3C\text{-}Si(C_6H_5)_3 + KCl \qquad (2)$$

When triphenylchloro- or -bromosilane is treated with one mole equivalent of triphenylmethylsodium or -lithium, two isomeric products (I and IV) are obtained in ratios varying from about 3:1 to 9:1, depending on the conditions, each of which has the correct analysis for the desired triphenylmethyltriphenylsilane. The higher melting compound, which melts at about 330–335°, was identi-

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* For paper I, of this series see H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 3762 (1953).

[1] (a) W. Schlenk, J. Renning and G. Racky, *Ber.*, **44**, 1178 (1911); W. C. Schumb and C. M. Saffer, THIS JOURNAL, **61**, 363 (1939); (b) H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951); H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[2] P. W. Selwood, THIS JOURNAL, **61**, 3168 (1939); G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

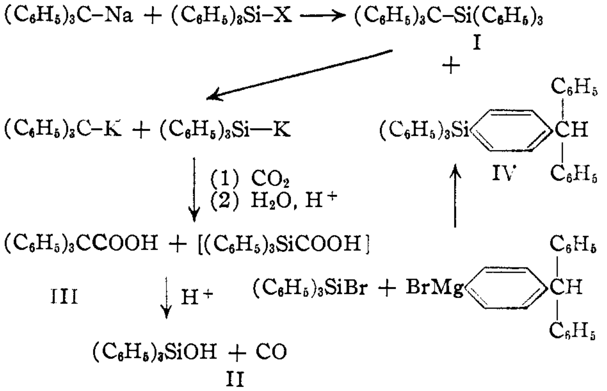
[3] H. Morris, W. Byerly and P. W. Selwood, THIS JOURNAL, **64**, 1727 (1942); C. A. Kraus and W. V. Sessions, *ibid.*, **47**, 2361 (1925).

[4] R. Preckel and P. W. Selwood, *ibid.*, **62**, 2765 (1940); T. Midgley, C. A. Hochwalt and G. Calingaert, *ibid.*, **45**, 1821 (1923); E. Krause, *Ber.*, **54**, 2560 (1921).

[5] H. Gilman and S. D. Rosenberg, THIS JOURNAL, **74**, 531 (1952).

[6] J. C. Bailie, *Iowa State Coll. J. Sci.*, **14**, 8 (1939) [*C.A.*, **34**, 6241 (1940)]; see also J. C. Bailie, Doctoral Dissertation, Iowa State College, 1938.

fied as the desired triphenylmethyltriphenylsilane (I), since, when treated with sodium–potassium alloy, followed by carbonation, triphenylsilanol (II) and triphenylacetic acid (III) were isolated in reasonable yield.



The second product isolated from the reaction, which melted at 214–216°, was identified as *p*-triphenylsilylphenyldiphenylmethane (IV) by an unambiguous synthesis from triphenylbromosilane and the Grignard reagent of *p*-bromophenyldiphenylmethane (V).

Unfortunately, accompanying the formation and isolation of triphenylmethyltriphenylsilane, a small and variable amount of hexaphenyldisilane is obtained, which cannot be easily removed, since its properties are very similar to those of triphenylmethyltriphenylsilane. A mixed melting point of these two compounds is, in fact, not depressed, suggesting that the two compounds are isostructural in the crystalline state and may even form solid solutions. Fractional crystallization of a mixture of hexaphenyldisilane and triphenylmethyltriphenylsilane from chloroform or dioxane does indeed yield fractions with slightly different melting points and silicon analyses, but after five such crystallizations, neither the low melting (331–333°) triphenylmethyltriphenylsilane fraction was pure (based on silicon analysis) nor was the higher melting (347–349°) fraction pure hexaphenyldisilane.

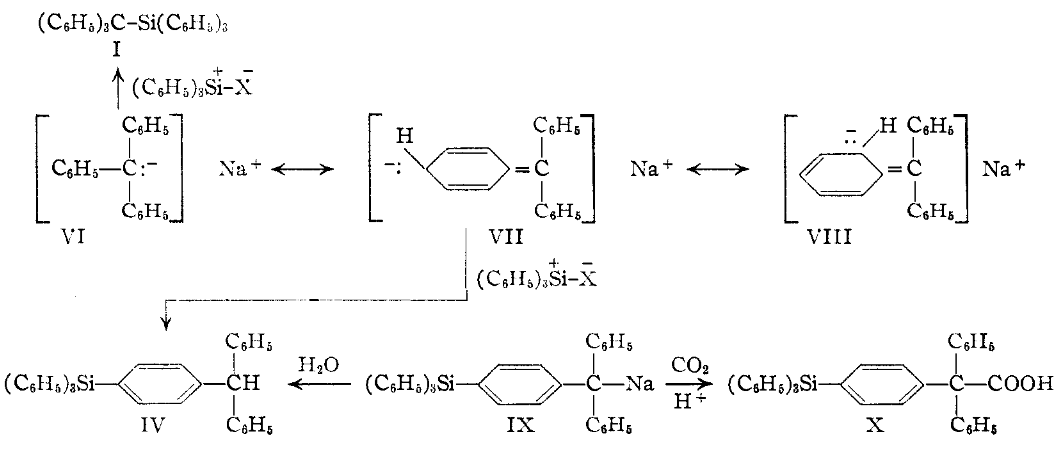
The presence of hexaphenyldisilane was confirmed from X-ray powder diffraction patterns,[7] the pattern characteristic of this compound being present in reduced intensity in the triphenylmethyltriphenylsilane pattern. That this hexaphenyldisilane was a true reaction product, and that it did not arise subsequently during recrystallization from cleavage of I followed by recombination as hexaphenyldisilane and hexaphenylethane, was demonstrated by identifying the pattern of hexaphenyldisilane in the diffraction pattern taken of the crude reaction product as filtered from the reaction mixture before recrystallization.

In the light of evidence presented later in this paper, the formation of hexaphenyldisilane can be attributed to a small amount of halogen–metal interconversion[8] between triphenylbromosilane and triphenylmethylsodium, the triphenylsilylsodium formed then reacting with the triphenylbromosilane to yield hexaphenyldisilane. The triphenylmethyltriphenylsilane appears to be purer and the formation of hexaphenyldisilane appears to be minimized by the use of the chlorosilane and the lithium salt, although this reaction is much slower (six days in refluxing benzene) than from use of the bromosilane and the sodium salt (48 hours in refluxing ether). The silyl chloride and sodium salt require an intermediate period of time for essential completion of the reaction (4–5 days in refluxing ether).

$$(C_6H_5)_3C\text{-}Na + (C_6H_5)_3Si\text{-}Br \rightleftarrows (C_6H_5)_3C\text{-}Br + (C_6H_5)_3Si\text{-}Na$$

$$(C_6H_5)_3Si\text{-}Na + (C_6H_5)_3Si\text{-}Br \longrightarrow (C_6H_5)_3Si\text{-}Si(C_6H_5)_3 + NaBr$$

The isolation of both triphenylmethyltriphenylsilane and *p*-triphenylsilylphenyldiphenylmethane from the reaction of triphenylmethylmetallics with triphenylhalosilanes is remindful of the isolation of the isomer of hexaphenylethane, *p*-triphenylmethylphenyldiphenylmethane, by Gomberg[9] and other workers, prepared amongst other ways, by treatment of hexaphenylethane with hydrogen chloride or sodium. It appears reasonable to suggest that in the present case these compounds arise from reaction of the silyl halide with the mesomeric anion of triphenylmethylsodium, which can exist in at least three forms.



Nucleophilic displacement on triphenylsilyl halide by anion VI with separation of a halide ion will give

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[7] We are indebted to Dr. R. E. Rundle and Mr. F. Hollenbeck for the X-ray powder diffraction determinations.

[8] For a general reference to halogen–metal interconversion see R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

[9] M. Gomberg, *Ber.*, **35**, 3918 (1902).

rise to triphenylmethyltriphenylsilane (I). A similar attack by the triphenylmethyl anion VII, with displacement of a proton from the ring, on the triphenylhalosilane molecule will give rise to *p*-triphenylsilylphenyldiphenylmethane (IV) after addition of a proton to the methyl carbon. Evidence that the reaction product was IV and not the sodium salt IX which on hydrolysis would yield IV, was demonstrated by carbonation of a completed reaction, prior to hydrolysis. Were IX present, *p*-triphenylsilylphenyldiphenylacetic acid (X) would be obtained, but careful scrutiny of the reaction products failed to detect any acid whatsoever. That no product corresponding to reaction of triphenylhalosilane with anion VIII was isolated must be attributed to steric hindrance, and examination of molecular models indicates that this position is highly hindered to the approach of a triphenylsilyl group. Unfortunately for a good case, this is also true to some extent for anion VI.

When attempts were made to prepare triphenylmethyltriphenylsilane by treatment of triphenylsilylpotassium with triphenylchloromethane (equation 2) none of the desired compound or its isomer, was obtained. Instead, high yields of hexaphenyldisilane and hexaphenylethane, isolated as the peroxide, were obtained.

$$2(C_6H_5)_3SiK + 2(C_6H_5)_3CCl \longrightarrow$$

$$(C_6H_5)_3Si\text{-}Si(C_6H_5)_3 + (C_6H_5)_3C\text{-}C(C_6H_5)_3 \xrightarrow{O_2} (C_6H_5)_3C\text{-}O\text{-}O\text{-}C(C_6H_5)_3 \quad (3)$$

When the chloromethane was added to the triphenylsilylpotassium, a deep red color, indicative of the triphenylmethyl anion was observed, which persisted for from several seconds up to a few minutes, depending on the rate of addition. That this species was truly present was demonstrated by the rapid addition of one equivalent of triphenylchloromethane to triphenylsilylpotassium in 15 seconds, followed 60 seconds later by rapid carbonation of the reaction mixture by addition of a slurry of Dry Ice in ether, which immediately discharged the red color. When the reaction was worked up, an appreciable amount of triphenylacetic acid (14%) was isolated which must have been derived from triphenylmethylpotassium. This species, together with the hexaphenyldisilane and hexaphenylethane that were found as the other reaction products, must have arisen from a halogen–metal interconversion between triphenylsilylpotassium and triphenylchloromethane according to the following scheme. Such halogen–metal interconversions have not previously been observed to occur with silicon compounds.

$$(C_6H_5)_3SiK + (C_6H_5)_3CCl \longrightarrow$$

$$(C_6H_5)_3SiCl + (C_6H_5)_3CK \xrightarrow{CO_2} (C_6H_5)_3CCOOH \quad (4a)$$

$$(C_6H_5)_3CK + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3C\text{-}C(C_6H_5)_3 + KCl \quad (4b)$$

$$(C_6H_5)_3SiK + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3Si\text{-}Si(C_6H_5)_3 + KCl \quad (4c)$$

Of these various reactions 4b appears to be very rapid[10] and 4a is in all probability rapid. On the other hand, 4c, the reaction of triphenylsilylpotassium with triphenylchlorosilane, is probably much slower than 4a or 4b since unpublished work by T. C. Wu in this Laboratory has shown that several days are required for this reaction to proceed to completion. In agreement with this, the reaction carbonated after one minute gave a reasonably high yield of bis-triphenylmethyl peroxide (63%) but a much lower yield of hexaphenyldisilane (28%), the unreacted triphenylsilylpotassium appearing as triphenylsilylcarboxylic acid[11] which, being unstable, is most easily isolated as triphenylsilanol.

When the order of addition of the reagents is reversed so that the silylpotassium is added to triphenylchloromethane, the red color of the triphenylmethyl anion is barely noticeable, forming as each drop hits the stirred solution but disappearing almost immediately, evidence that reactions 4a and 4b are rapid.

In order to justify the halogen–metal interconversion postulated above, it is necessary to eliminate the possibility that the triphenylmethylpotassium did not arise from reaction of triphenylchloromethane with metallic potassium introduced with the triphenylsilylpotassium. Triphenylsilylpotassium is normally prepared by the cleavage of hexaphenyldisilane with sodium–potassium alloy. The excess alloy can be removed quite thoroughly by stirring the ethereal suspension of triphenylsilylpotassium and sodium–potassium alloy with mercury which forms an amalgam with the alloy.[12] This was done in the present case very carefully and the triphenylsilylpotassium was twice decanted from the liquid amalgam to ensure its complete removal. The run which was carbonated gave a 14% yield of triphenylacetic acid, and this amount of material far exceeds that which might reasonably have been expected to be formed from any triphenylmethylpotassium arising from reaction of triphenylchloromethane with minute quantities of sodium–potassium alloy introduced with the triphenylsilylpotassium.

Studies of the dissociation and reactions of triphenylmethyltriphenylsilane indicate that this compound does not dissociate into free radicals to any detectable extent and that the compound is relatively unreactive. When small amounts of the material were refluxed for 15 hours in xylene containing iodine and a trace of quinoline, or in chloroform containing a trace of iodine, they were recovered unchanged in excess of 95% yield. Similarly, when a small amount of the compound was refluxed in xylene for 48 hours while dry air was bubbled through the solution, although the solution became somewhat yellow, the starting material was recovered in 95% yield. This stability indicates, as with the silicon–silicon bond,[1b] that there is little or no tendency for the carbon–silicon bond in this compound to break yielding free radicals, which then react under these conditions to form either iodides or peroxides as has been found to occur with hexaphenylethane.

Triphenylmethyltriphenylsilane, as we have iso-

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[10] C. A. **Kraus** and T. **Kawamura**, THIS JOURNAL, **45**, 2759 1923); M. **Gomberg** and W. E. **Bachmann**, *ibid.*, **52**, 2455 (1930).

[11] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

[12] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952).

lated it, is a white semi-crystalline solid melting at about 335° with a 2–5° melting range. On melting it forms a red liquid. It is moderately soluble in pyridine and dioxane, and slightly soluble in benzene and chloroform, but in alcohols, ether and the various grades of petroleum ether it is highly insoluble. It is not cleaved cleanly by chlorine or bromine in refluxing carbon tetrachloride, but some nuclear substitution evidently occurs, and a considerable amount of starting material is recovered. It is not appreciably cleaved by refluxing for 12 hours in a concentrated potassium hydroxide–dioxane–ethanol solution,[13] and is unaffected by refluxing for 28 hours with excess phenyllithium or by stirring for a short time in a mixture of sulfuric and acetic acids. However, it is extensively cleaved by stirring at room temperature with sodium–potassium alloy in ether.

p-Triphenylsilylphenyldiphenylmethane is a white crystalline solid melting at 214–216°, soluble in chloroform, benzene and ether, but not appreciably soluble in petroleum ethers or alcohols. The compound is not cleaved by heating in a concentrated alkaline solution but is cleaved by sodium–potassium alloy to yield, after carbonation, a mixture of acids.

Experimental[14]

Triphenylmethyltriphenylsilane. A. From Triphenylmethyllithium and Triphenylchlorosilane.—Triphenylmethyllithium was prepared in 75% yield, as estimated by the double titration procedure,[15] by metalation in ether of triphenylmethane with a 50% excess of *n*-propyllithium[16] stirred for 48 hours under reflux. To 20 g. (0.07 mole) of recrystallized triphenylchlorosilane in 150 ml. of ether was added over 10 minutes 0.07 mole of triphenylmethyllithium. The bright red color of the triphenylmethyllithium did not disappear, so that 200 ml. of dry benzene was added while the ether was simultaneoulsy distilled off until the boiling point was 67°. The material was then refluxed for 70 hours, during which time the red color slowly disappeared and a white precipitate formed. At the end of this time the very pale-red suspension was hydrolyzed with dilute ammonium chloride solution.

Filtration of the suspension yielded a residue weighing 12.1 g. (34%) after recrystallization from dioxane, melting at 330–335° and forming a red liquid. Recrystallization of this triphenylmethyltriphenylsilane from pyridine raised the melting point to 334–336°. A mixed melting point with hexaphenyldisilane (m.p. 360–362°) was not depressed, but melted at 338–346°. The material could also be crystallized from benzene, toluene or chloroform in which it is slightly soluble, but it was found to be insoluble in methanol, ethanol or petroleum ether (b.p. 60–70° or 77–115°).

Anal. Calcd. for $C_{37}H_{30}Si$: C, 88.2; H, 5.98; Si, 5.59; mol. wt., 502. Found: C, 86.9; H, 5.86; Si, 5.61, 5.69, 6.20; mol. wt. (cryoscopic in benzene), 496, 420.

The ether and water layers filtered from the above solid were separated, and the ether layer dried over sodium sulfate. Removal of the ether left a yellow oil, to which was added 50 ml. of petroleum ether (b.p. 60–70°), and from this solution a white solid separated out which was filtered from the mother liquor (A). This solid, after recrystallization from 1:1 benzene–petroleum ether (b.p. 60–70°), yielded 3.0 g. (8%) of white crystals melting at 213–216°. A mixed melting point of this material with a sample of *p*-triphenylsilylphenyldiphenylmethane, prepared as described below, was not depressed, and the infrared spectra[17] of the two compounds were identical.

Anal. Calcd. for $C_{37}H_{30}Si$: C, 88.2; H, 5.98; Si, 5.59. Found: C, 88.4; H, 5.94; Si, 5.54, 5.63.

From the mother liquor (A) above was isolated, by fractional crystallization and passage of a petroleum ether (b.p. 60–70°) solution of the material through a 3 × 20 cm. column of alumina, followed by elution with petroleum ether (b.p. 60–70°) and then benzene, 4.5 g. (25%) of triphenylsilanol, m.p. 149–151°, identified by mixed melting point, and 4.5 g. (26%) of triphenylmethane, m.p. 91–94°, also identified by mixed melting point with an authentic sample.

B. From Triphenylmethylsodium and Triphenylbromosilane.—Triphenylsilane was prepared by reduction of 148 g. (0.5 mole) of triphenylchlorosilane in 400 ml. of ether with 13.0 g. (0.34 mole) of lithium aluminum hydride. The reaction was stirred for 22 hours and then carefully hydrolyzed under nitrogen with 100 ml. of water followed by 100 ml. of 1:1 hydrochloric acid with only occasional stirring to prevent hydrolysis of the triphenylsilane. The ether layer was removed, dried, and then distilled at 145° (0.45 mm.) to yield 112 g. (86%) of triphenylsilane, m.p. 42–45°. Bromination of 50 g. (0.192 mole) of triphenylsilane in 100 ml. of carbon tetrachloride with 32 g. (0.2 mole) of bromine with from 3–12 hours refluxing, gave after removal of the solvent and recrystallization from petroleum ether (b.p. 77–115°), 57 g. (88%) of triphenylbromosilane, m.p. 123–125°.[18]

To 0.055 mole of triphenylmethylsodium in 226 ml. of ether, prepared from triphenylchloromethane and 3% sodium amalgam[19] in 76% yield,[15] was added 20.0 g. (0.059 mole) of triphenylbromosilane in 200 ml. of ether. The reaction was refluxed under nitrogen for 48 hours during which time the red color faded and a white solid precipitated out. Hydrolysis of the suspension, and working up of the reaction essentially as described for the run above, led to the isolation of 17.1 g. (62%) of triphenylmethyltriphenylsilane, m.p. 330–335°, and 2.3 g. (8.3%) of *p*-triphenylsilylphenyldiphenylmethane, m.p. 211–214°, identical with the products described above, since the mixed melting points of the compounds were not depressed. Also isolated from the mother liquors were 1.3 g. (8%) of triphenylsilanol, 1.5 g. (10%) of hexaphenyldisiloxane and 2.8 g. (21%) of triphenylmethane. These products represent a recovery of 91% of the triphenylmethyl group based on triphenylmethylsodium and an 88% recovery of the triphenylsilyl group based on triphenylbromosilane.

When a similar reaction was carried out with 0.0675 mole of triphenylmethylsodium in 240 ml. of ether and 23.8 g. (0.07 mole) of triphenylbromosilane in 250 ml. of dry benzene under reflux, the red color of the solution disappeared in 30 hours, although the solid which settled out was pale pink. The reaction mixture was carbonated with Dry Ice prior to hydrolysis, and then worked up as described above. While the higher reaction temperature afforded by the presence of benzene was found to accelerate the reaction, its presence complicated the separation of the *p*-triphenylsilylphenyldiphenylmethane as described above, since triphenylmethyltriphenylsilane is somewhat soluble in this solvent. Thus the material isolated melted over the range 180–240°, and several recrystallizations were required to separate the two components in pure form. After recrystallization, triphenylmethyltriphenylsilane was isolated in 38% yield and *p*-triphenylsilylphenyldiphenylmethane in 12% yield, together with considerable impure material. The aqueous alkaline layer, separated after the hydrolysis, was filtered and then acidified carefully, but no acidic material could be found.

When a 1:5 benzene–ether mixture was used as solvent for the reaction, triphenylmethyltriphenylsilane was isolated in 52% yield and *p*-triphenylsilylphenyldiphenylmethane was obtained in 17% yield.

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(13) H. Gilman, A. G. Brook and L. S. Miller, This Journal, **75**, 4531 (1953).

(14) All melting points are uncorrected. All reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

(15) H. Gilman and A. H. Haubein, This Journal, **66**, 1515 (1944).

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

(17) We are grateful to Dr. V. A. Fassel and Mr. M. Margoshes for infrared spectra of this and other compounds. These workers will report their studies on the infrared absorption of silicon compounds elsewhere.

(18) This preparation of triphenylbromosilane is unpublished work of T. C. Wu of this Laboratory.

(19) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

C. From Triphenylmethylsodium and Triphenylchlorosilane.—To 12.7 g. (0.043 mole) of triphenylchlorosilane in 50 ml. of ether was added 0.043 mole (260 ml.) of an ethereal solution of triphenylmethylsodium. The reaction was refluxed for 5 days, at which time it was still pale red, although a considerable amount of white solid had precipitated. Hydrolysis with water and isolation of the products as described above yielded 13.0 g. (60%) of triphenylmethyltriphenylsilane, m.p. 334–336°, and 3.0 g. (14%) of *p*-triphenylsilylphenyldiphenylmethane, m.p. 212–214°. No attempt was made to isolate the other reaction products.

Cleavage of Triphenylmethyltriphenylsilane with Sodium-Potassium Alloy.—To 3.5 g. (0.007 mole) of triphenylmethyltriphenylsilane in 10 ml. of ether was added 1 ml. of 1:5 sodium-potassium alloy. After stirring rapidly for 15 minutes, the suspension turned red. After an additional 50 ml. of ether had been added, the reaction was stirred for 19 hours and was then carbonated with a Dry Ice-ether slurry, followed by hydrolysis with water. The layers were filtered leaving a residue weighing 0.5 g. of a white solid which melted over the range 164–169° with evolution of a gas. This material was probably triphenylsilylcarboxylic acid.[11] The aqueous layer, after separation from the ether layer, was acidified precipitating 0.5 g. (25%) of a white solid, melting over the range 200–250°, which after two recrystallizations from ethyl acetate still melted crudely at 225–263°, although a mixed melting point with authentic triphenylacetic acid was not depressed. The acid was converted into the methyl ester using excess diazomethane, and after recrystallization melted at 178–181°, the mixed melting point with authentic methyl triphenylacetate melting at 179–182°. Comparison of the infrared spectra of the suspected and authentic samples of methyl triphenylacetate established their identity. The over-all yield of methyltriphenylacetate was 2.4%.

The ether layer from hydrolysis of the cleavage reaction mixture was dried, the ether removed, and without attempting to isolate the triphenylsilylcarboxylic acid, which is reported to be unstable,[11] the residue was refluxed for 15 minutes in acetone containing a few drops of concentrated hydrochloric acid, and was then poured into water. The gummy product was crystallized from petroleum ether (b.p. 60–70°) to yield 0.47 g. (26%) of triphenylsilanol, m.p. 149–150°, which did not depress the mixed melting point with an authentic specimen.

Repetition of this cleavage with longer reaction times led to improved recoveries of the acid and triphenylsilanol. When the reaction was allowed to proceed for 50 hours, triphenylacetic acid, m.p. 266–267°, was obtained in 15% yield (40% crude) and triphenylsilanol in 37% yield (70% crude), together with a 15% recovery of starting material.

Reactions of Triphenylmethyltriphenylsilane. A. With the Halogens.—A suspension of 0.3 g. of triphenylmethyltriphenylsilane, m.p. 332–335°, in 50 ml. of chloroform containing 3 drops of an approximately 0.001 *M* solution of iodine in chloroform was refluxed for 15 hours, during which time the material dissolved. The pale iodine color did not fade during the reaction period and removal of the solvent left 0.295 g. of material, m.p. 331–335°, which did not depress the mixed melting point with the starting material. When the same amount of material was refluxed for 15 hours in 50 ml. of xylene containing 0.1 g. of iodine and 3 drops of quinoline, no consumption of iodine was observed, and after removal of the iodine with aqueous sodium sulfite and of the xylene under reduced pressure, a 95% recovery of material melting 325–330° was obtained which did not depress a mixed melting point with the starting material. Recrystallization raised the melting point to 331–334°.

When 2.0 g. (0.004 mole) of triphenylmethyltriphenylsilane was refluxed in 25 ml. of carbon tetrachloride containing 0.22 ml. (0.004 mole) of bromine for 3 hours, the compound slowly dissolved, but the bromine color did not diminish appreciably, and hydrogen bromide was slowly evolved. The solvent and excess bromine was removed under reduced pressure, to yield a gummy solid, which was treated with petroleum ether (b.p. 60–70°), and the insoluble material was shown by mixed melting point to be starting material, recovered in 67% yield. Removal of the petroleum ether left a gummy solid which fumed in the air, and which could not be obtained crystalline.

Treatment of 4.0 g. (0.008 mole) of triphenylmethyltriphenylsilane in 100 ml. of refluxing carbon tetrachloride with dry chlorine gas led to solution of the compound over a ten-hour period. During this time hydrogen chloride appeared to be slowly and continuously evolved, since ammonium hydroxide placed near the top of the condenser fumed. The solvent was removed under reduced pressure to give a frothy gum which dissolved in petroleum ether (b.p. 60–70°) but which would not crystallize. The solid evolved hydrogen chloride in the air. The solid was taken up in ether, which was shaken vigorously for 0.5 hour with excess 5% aqueous potassium hydroxide. After drying the ether layer, the ether was removed to again yield a sticky gum which dissolved in petroleum ether (b.p. 60–70°) but refused to crystallize, and which still evolved hydrogen chloride in the air.

B. With Oxygen.—A solution of 0.3 g. of triphenylmethyltriphenylsilane in 50 ml. of xylene was refluxed for 48 hours while a stream of dry air was bubbled through the solution. The xylene slowly developed a yellow color. Removal of the solvent under reduced pressure, followed by a washing of the residue with two 3-ml. portions of petroleum ether (b.p. 60–70°) left 0.29 g. (96%) of starting material, m.p. 327–330°, which did not depress a mixed melting point with the original material. Recrystallization from chloroform raised the melting point to 330–334°.

C. With Phenyllithium.—A suspension of 2.0 g. (0.004 mole) of triphenylmethyltriphenylsilane in 50 ml. of ether was treated with 0.016 mole of phenyllithium in 15 ml. of ether. The reaction mixture was refluxed for 28 hours, and was then carbonated and hydrolyzed. Filtration of the suspension yielded 1.7 g. (85%) of starting material, m.p. 332–334°, which did not depress a mixed melting point. Acidification of the aqueous layer yielded a white solid which after recrystallization from hot water weighed 1.27 g. (65%) and melted 119–121°. A mixed melting point with benzoic acid was not depressed. The ether layer yielded only a trace of material after removal of the ether.

D. With Potassium Hydroxide.—A suspension of 2.0 g. (0.004 mole) of triphenylmethyltriphenylsilane in an alkaline solution made from 20 ml. of dioxane, 20 ml. of ethanol, 1 ml. of water and 2.0 g. of potassium hydroxide was refluxed overnight.[13] After cooling the yellow suspension, two liquid layers and a solid separated out. The solid was filtered off, washed with water, and then suspended in water to which 10% hydrochloric acid was added until the suspension was acidic. The insoluble white triphenylmethyltriphenylsilane was filtered and after drying weighed 1.25 g. (62%) and melted at 332–335°. A mixed melting point with the starting material was not depressed.

The original alkaline filtrate was acidified and then was evaporated to near dryness, diluted with water and ether extracted. A small amount (0.1 g.) of both ether- and water-insoluble starting material was filtered off. The ether was removed from the ether extracts after drying, and the residue remaining was dissolved in hot ethanol. A white solid (0.11 g. or 11%) slowly separated from the solution and melted at 83–88°. Recrystallization from ethanol raised the melting point to 92–93° and a mixed melting point with triphenylmethane was not depressed. Concentration of the mother liquors yielded an additional 0.1 g. (9%) of a white solid melting at 133–143°, which after recrystallization from petroleum ether (b.p. 60–70°) melted at 149–151° and which did not depress a mixed melting point with triphenylsilanol.

E. With Concentrated Acids.—To 1.05 g. (0.0021 mole) of triphenylmethyltriphenylsilane was added 6 ml. of concentrated sulfuric acid, followed by 10 ml. of glacial acetic acid, to assist in wetting the solid. The suspension became warm and turned pale yellow. The solid was ground intimately with the acid for 10 minutes and appeared to partially dissolve. At the end of this time the suspension was poured into 500 ml. of water. The yellow color immediately disappeared. The white solid was filtered off, washed and dried to yield 1.02 g. (97%) of starting material (mixed melting point) which melted from 329–335°.

Identification of Hexaphenyldisilane as a Contaminant in the Formation of Triphenylmethyltriphenylsilane.—It was found that the percentage of silicon and the melting point of the product varied slightly in the different preparations of triphenylmethyltriphenylsilane. When this material was prepared from triphenylmethyllithium and triphenylchlorosilane, the recrystallized product melted variously from 331–334° to 336–340° and silicon values ranged from 5.61–5.70 (calcd. for $C_{37}H_{30}Si$: Si, 5.59) although any one sample gave reproducible results. When prepared from the sodium and bromo compounds the melting points were found to range from 328–333° to 333–339° and the silicon values varied from 6.4–6.8. The material prepared from the sodium and chloro compounds melted from 331–335° and the silicon analysis[20] was 6.2%. When a large amount of material originally melting over the range 331–334° and analyzing as 6.4% silicon was fractionally recrystallized five times successively from chloroform, the higher melting fraction melted at 347–349° with softening at 342° and contained 6.9% silicon, while the lower melting, and more soluble, fraction melted at 331–333° with softening at 329° and analyzed as 5.8% silicon. This anomaly was resolved by comparing the X-ray powder diffraction patterns of crude triphenylmethyltriphenylsilane as filtered from the reaction flask, the purified material after recrystallization from dioxane or pyridine, and authentic hexaphenyldisilane. The pattern characteristic of hexaphenyldisilane was found to be present, but with reduced intensity, in the patterns of all the triphenylmethyltriphenylsilane samples. The presence of varying amounts of this material accounts for the variable analyses obtained and for the slightly low carbon and hydrogen values, and also would appear to account for the 3 to 5 degree range over which even the most carefully purified samples melted. It was observed, as mentioned previously, that mixed melting points of hexaphenyldisilane and triphenylmethyltriphenylsilane were not depressed. The infrared absorption spectrum of triphenylmethyltriphenylsilane showed essentially the same features as the spectrum of hexaphenyldisilane, but in addition showed a band characteristic of phenyl–carbon absorption.

***p*-Triphenylsilylphenyldiphenylmethane.**—*p*-Bromophenyldiphenylcarbinol was prepared by treatment of methyl *p*-bromobenzoate with excess phenylmagnesium bromide. The crude carbinol, isolated as an oil, was not purified, but instead 93 g. (approx. 0.27 mole) was refluxed overnight with 160 ml. of 98% formic acid, by which time the bright red heterogeneous system had changed to yellow-orange. The lower yellow layer was separated and diluted with 200 ml. of water, forming two layers. Ether was added and the initial ether layer and two additional ether extracts were combined, washed twice with water, and then with 5% potassium hydroxide until the aqueous layer was basic. After one additional washing with water, the ether layer was dried over sodium sulfate, and then the ether was removed under reduced pressure. The resulting oil was treated with petroleum ether (b.p. 60–70°) causing solidification of the oil and the crystallization of a total of 58 g. of crude *p*-bromophenyldiphenylmethane. Crystallization of the material from petroleum ether (b.p. 60–70°) yielded 46.3 g. (53%) of product melting 80–82° (reported 82.5°).[21]

The Grignard reagent of *p*-bromophenyldiphenylmethane was prepared from 5.0 g. (0.0155 mole) of the halide in 50 ml. of ether and 0.4 g. (0.017 g. atom) of magnesium. The reaction between the magnesium and a small portion of the solution of the halide did not start, even when magnesium, activated by heating with iodine, was added. The reaction was finally started by introducing about 0.05 ml. of methyl iodide. The magnesium was consumed only very slowly by the halide, and slowly turned black, so that an additional 0.4 g. of magnesium was introduced, and the reaction was refluxed for 28 hours, during which time it slowly turned deep red. At the end of this time a strong positive Color Test I[22] was obtained, and a 5-ml. aliquot of the solution was carbonated with Dry Ice. This mixture was worked up in the normal way and the 0.3 g. (67%) of *p*-benzhydrylbenzoic acid obtained after recrystallization from 1:1 acetic acid, melted at 160–162° (reported 162 and 164°).[23]

To the remaining Grignard reagent was added 5.45 g. (0.016 mole) of triphenylbromosilane in 70 ml. of ether. After stirring for 5 days under reflux, Color Test I was still positive so that the ether was replaced with 50 ml. of dry xylene, and the solution refluxed at 100° for 24 hours, by which time Color Test I was negative. The reaction was hydrolyzed with water, acidified, and the xylene layer and two ether extracts were combined and dried. Removal of the ether and xylene under reduced pressure left a yellow gum, to which was added 20 ml. of petroleum ether (b.p. 60–70°), which precipitated 2.7 g. of white solid melting at 201–205°. This *p* - triphenylsilylphenyldiphenylmethane was recrystallized from 20 ml. of 1:1 benzene–petroleum ether (b.p. 60–70°) to yield 2.0 g. (26%) of material melting 214–216°. A mixed melting point with the lower melting compound isolated from the reaction of triphenylmethylsodium with triphenylbromosilane was not depressed and their infrared spectra were identical. Additional material isolated from the mother liquors raised the total yield to 40%.

When 0.251 g. (0.0005 mole) of this material was treated with 5 ml. of a potassium hydroxide solution, prepared from 200 ml. of dioxane, 200 ml. of ethanol, 10 ml. of water and 20 g. of potassium hydroxide, for 12 hours at 94°, and was then acidified and filtered, 0.225 g. (90%) of starting material (mixed melting point) was recovered.[13]

Reaction of Triphenylsilylpotassium with Triphenylchloromethane. A. Addition of Triphenylchloromethane to Triphenylsilylpotassium.—Triphenylsilylpotassium was prepared from 10 g. (0.0193 mole) of hexaphenyldisilane and sodium–potassium alloy, and was then carefully treated with mercury to remove the excess alloy.[12] The triphenylsilylpotassium suspension was twice decanted from the amalgam to ensure its absence in the next stage of the reaction. To this material in a flask equipped with stirrer funnel and nitrogen inlet, and cooled in a Dry Ice–acetone-bath, was added over a period of 15 seconds a solution of 10.6 g. (0.038 mole) of triphenylchloromethane in 100 ml. of ether. The suspension rapidly turned dark red in color, and 60 seconds after the addition of the halide was complete, a slurry of Dry Ice in ether was added rapidly, discharging the red color. The reaction mixture was then hydrolyzed and worked up.

Filtration of the liquid layers from the insoluble white solid yielded 4.5 g. (45%) of crude hexaphenyldisilane (mixed melting point) which after refluxing with 75 ml. of benzene and filtration, weighed 2.8 g. (28%) and melted at 359–361°. The yellow ether layer was separated from the alkaline, aqueous layer and dried over sodium sulfate, air being excluded as much as possible during these operations. The yellow ethereal solution was separated from the sodium sulfate, and a stream of dried air was passed into it until no more white solid separated out. This bis-triphenylmethyl peroxide weighed 6.2 g. (63% based on triphenylchloromethane) and melted at 184–186°. A mixed melting point with an authentic sample was not depressed. The ether filtrate after removal of the peroxide was concentrated under reduced pressure, and after the resulting gum had been treated with petroleum ether (b.p. 60–70°) a total of 1.5 g. (14% based on triphenylsilylpotassium) of hexaphenyldisiloxane, m.p. 220–223°, and 3.6 g. (34% based on triphenylsilylpotassium) of triphenylsilanol, m.p. 149–151°, was recovered (identified by mixed melting points).

The alkaline, aqueous layer, separated above, was acidified, precipitating a white solid which melted over the range 213–237° with the evolution of gas. Purification was effected by re-solution in dilute alkali, which was ether extracted, followed by reacidification, and recrystallization from ethanol. This procedure yielded 1.5 g. (14%) of triphenylacetic acid, m.p. 267–269°, which did not depress the melting point when mixed with an authentic sample.

A similar reaction to the above was allowed to proceed to completion, as indicated by the absence of a positive Color Test I. This required 3 hours during which time the initially formed red color slowly disappeared. The reaction was hydrolyzed directly, and gave on working up as above a 41% yield of hexaphenyldisilane, 20% of hexaphenyldisiloxane, a small amount of triphenylsilanol (5%) and, after recrystallization from toluene during which considerable decomposition occurred, a 45% yield of purified bis-triphenylmethyl peroxide, together with some intractable tar.

B. Addition of Triphenylsilylpotassium to Triphenylchloromethane.—Amalgamated[12] triphenylsilylpotassium, in

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(20) Silicon analyses were made following the procedure of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, This Journal, **72**, 5767 (1950). Duplicate results invariably checked within 1% of each other, but it was found essential that the initial heating of the sample be done very slowly in order to avoid the formation of a black residue which could only be converted to the white silicon dioxide with great difficulty.

(21) A. E. Tschitschibabin, *Ber.*, **44**, 455 (1911).

(22) H. Gilman and F. Schulze, This Journal, **47**, 2002 (1925).

(23) A. Bistrzycki and J. Gyr, *Ber.*, **37**, 662 (1904); H. Wieland and H. Kloss, *Ann.*, **470**, 222 (1929).

100 ml. of ether prepared from 4.0 g. (0.0077 mole) of hexaphenyldisilane, was added over 25 minutes to a stirred solution of 5.24 g. (0.0184 mole) of recrystallized triphenylchloromethane in 50 ml. of ether. Each drop of the suspension as it was added caused a localized red color in the flask which rapidly disappeared, and at the end of the 25 minutes the flask contained a pale yellow suspension, due to the precipitation of a white solid. The reaction was stirred for an additional 2 hours, and a sample of the suspension failed to give a positive Color Test I. The reaction was hydrolyzed with water, and the solid filtered from the ether and water layers. The residue (0.45 g. or 11%) was recrystallized from pyridine and melted at 360–363°, and did not depress the mixed melting point with hexaphenyldisilane. During the filtration of this residue, a white flaky solid precipitated from the deep-yellow ether layers. The flask was allowed to stand in the air until precipitation ceased (overnight) and then the 5.5 g. of material melting 167–215° was filtered off. This solid was refluxed with 100 ml. of 1:1 ethanol–ethyl acetate and the hot suspension was filtered. The residue weighed 4.2 g. (88%), melted at 184–186°, and did not depress a mixed melting point with authentic bis-triphenylmethyl peroxide. The ether layer, from which this material precipitated, and the ethanol–ethyl acetate extract were worked up and from them a total of 4.9 g. (50%) of hexaphenyldisiloxane, m.p. 220–222° was recovered (mixed melting point), together with some gummy material which resisted purification.

A similar run in which the reaction flask was immersed in a Dry Ice–acetone-bath at about −30° behaved as above except that the red color formed on addition of the triphenylsilylpotassium persisted for some time. The products isolated were hexaphenyldisilane (16%), hexaphenyldisiloxane (53%), bis-triphenylmethyl peroxide (63%) and some gum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XI. Some New Cyclobutane, Cyclobutene and Cyclobutanone Derivatives Derived from the Adduct of Phenylacetylene with 1,1-Difluoro-2,2-dichloroethylene

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The adduct (I) of phenylacetylene and 1,1-difluoro-2,2-dichloroethylene (obtained in 76% yield in 2 hours at 130°) has been shown to be 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene. Hydrogenation of I yielded 1,1-difluoro-3-phenylcyclobutane (II), while hydrolysis with concentrated sulfuric acid at 100° gave crystalline 2,2-dichloro-3-phenylcyclobutenone (III). The structure of III was firmly established by base-induced cleavage to 4,4-dichloro-3-phenyl-2-butenoic acid (IV) and by reduction to 3-phenylcyclobutanone. I was found to rearrange to 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (VIII) on heating with triethylamine. VIII on hydrolysis with concentrated sulfuric acid yielded 2,4-dichloro-3-phenylcyclobutenone (IX), the structure of which was established by reactions similar to those used for III and reduction to phenylcyclobutane. IX displayed no tendency to yield 1-acetoxy-2,4-dichloro-3-phenylcyclobutadiene with isopropenyl acetate and *p*-toluenesulfonic acid under conditions where other ketones are converted to enol acetates.

The principal obstacle to the elucidation of the chemistry of cyclobutane and its derivatives is the difficulty encountered in large-scale laboratory synthesis of four-membered carbocyclic rings. Perkin's classical malonic ester syntheses and their modifications[2] have been of considerable utility but are customarily limited by rather low yields and restriction to acyl- or carboxyl-substituted derivatives. Ideal syntheses of cyclobutane and cyclobutene would be afforded by addition of ethylene to ethylene or acetylene, respectively, but these reactions do not appear to have so far been achieved. Substituted ethylenes and ketenes have been converted to cyclobutane derivatives in thermal or photochemical reactions.[3] However, with few exceptions,[3,4] the yields are low or the products are not well-suited for further transformations. The fairly recent discovery that fluorinated ethylenes will often thermally dimerize[5] or add to other unsaturated compounds[6] to give high yields of cyclobutane derivatives provides an excellent synthetic route to a wide variety of fluorinated cyclobutanes, which unfortunately usually display the customary chemical inertness of the fluorine functions.[5b,7] In the present research we have utilized the activating influence of fluorine in the cycloaddition reaction and attempted to find useful processes by which the fluorine could be subsequently removed. The most interesting results so far obtained relate to the adduct from 1,1-difluoro-2,2-dichloroethylene and phenylacetylene and will be described in this paper.

1,1-Difluoro-2,2-dichloroethylene reacts smoothly with phenylacetylene at 130°, and, after 2 hours, a 76% yield of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (I) may be obtained.[8] The structure

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(1) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, California.

(2) *Cf.* (a) R. C. Fuson in H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., Vol. I, 2nd Ed., Chap. 2; (b) E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, THIS JOURNAL, **64**, 2696, 2703 (1942); (c) H. M. Walborsky, *ibid.*, **71**, 2941 (1949); (d) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(3) (a) W. E. Hanford and J. C. Sauer in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. III, 1946, Chap. 3; (b) H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920), and earlier papers; (c) L. I. Smith, C. L. Agre, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 7 (1939); (d) E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949); (e) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

(4) (a) B. T. Brooks and G. Wilbert, THIS JOURNAL, **63**, 870 (1941); (b) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

(5) (a) J. Harmon, U. S. Patent 2,404,374 (1946); (b) A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947); (c) P. L. Barrick, U. S. Patent 2,427,116 (1947); (d) P. L. Barrick and R. D. Cramer, U. S. Patent 2,441,128 (1948); (e) M. Prober and W. T. Miller, Jr., THIS JOURNAL, **71**, 598 (1949).

(6) (a) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949); (b) A. L. Barney and T. L. Cairns, *ibid.*, **72**, 3193 (1950).

(7) Some very interesting reactions of hexafluorocyclobutene have been described lately by K. E. Rapp, *ibid.*, **73**, 5901 (1951), and R. L. Pruett, C. T. Bahner and H. A. Smith, *ibid.*, **74**, 1633, 1638, 1642 (1952).

(8) The reaction also has been carried out independently by E. T. McBee, H. M. Hill and G. B. Bachman, *Ind. Eng. Chem.*, **41**, 70 (1949), but other than the physical properties and analysis no evidence for the structure of the product was adduced.