872. *Electronic Spectra of Organometallic Compounds. Part I. Phenyl Compounds of Group* IV *containing a Chromophoric Metal–Metal Linkage*

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The ultraviolet absorption spectra in solution of several organometallic compounds of Group IV elements of the general type R_6M_2 have been recorded. An intense absorption band centred at about 250 mμ is shown, by synthesis and examination of various compounds $RR'_2MM'R''_2R'''$, to be associated with the Ph–M–M system, provided that M has readily accessible *d*-orbitals.

MOST organometallic compounds containing phenyl groups have solution ultraviolet spectra which are " normal " in the sense that they exhibit partial chromophoric[1] behaviour. For example tetraphenylsilane has a spectrum in which both the primary and secondary bands[2] of benzene feature, and the latter has the same type of vibrational fine-structure[3,4] as that in benzene itself. Any interaction occurring between silicon and the phenyl ring is thus not extensive, and the benzene spectrum is only slightly perturbed.

Comparatively little has been published in this area of Group IV organometallic chemistry. La Paglia has recently discussed both the absorption and emission spectra of the tetraphenyls of carbon, silicon, germanium, tin, and lead;[3] the molar extinction coefficient of the secondary band is about 1000 in each case, which is about that expected from four independent phenyl groups. He assigns transitions to the various vibrational peaks in the $B_{2u} \longleftrightarrow A_{1g}$ (" secondary ") band and shows that, as the atomic number of the central atom increases, there is a gradual shift to lower wavelength. Since all these spectra occur at higher wavelengths than that of benzene, this gradation represents a decreasing perturbation of the benzene electron cloud. Bowden and Braude studied the electronic spectra of Group IV phenyl compounds[5] and concluded that the effects of the Group IV elements are relatively small. Our studies confirm this (Table 1). Eaborn[6] lists the compounds of silicon whose ultraviolet spectra have been measured up to the end

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[1] E. A. Braude, *Ann. Reports*, 1945, **42**, 105.
[2] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414.
[3] S. R. La Paglia, *J. Mol. Spectroscopy*, 1961, **7**, 427.
[4] G. Milazzo, *Gazzetta*, 1941, **71**, 73.
[5] K. Bowden and E. A. Braude, *J.*, 1952, 1068.
[6] C. Eaborn, " Organosilicon Compounds," Butterworths, London, 1960.

TABLE 1

Compounds with typical substituted-benzene spectra (in cyclohexane)

Compound	Maxima mμ (ε)
(Ph$_3$Si)$_2$O	253·0(1910); 264·5(2260); 271·5(1750)
(Ph$_3$Si)$_2$NH	253·5(1330); 260·0(1730); 265·0(1590); 271·0(1140)
PhCH$_2$Me$_3$Si	255·0 * (240*); 267·0(440); 274·0(400)
PhCH$_2$Me$_3$Ge	261·0(390); 268·0(450); 275·5(340)
(PhCH$_2$)$_2$Me$_2$Ge	253·0(640); 258·5(730); 261·5 * (700*); 264·5(590); 268·0(530)
Ph$_4$Si[4] (in CHCl$_3$)	254·0(1100); 260·0(1300); 265·0(1400); 272·0(1100)
Ph$_3$SiH (in hexane) †	254(830); 260(1140); 264(1200); 266*(1150*); 271(1050)

* Shoulder, ε, values estimated from spectrum given by H. Gilman and G. E. Dunn (*J. Amer. Chem. Soc.*, 1950, **72**, 2178).

of 1958, some two dozen compounds. Recently some ultraviolet data on phenyl compounds of Group IV elements have appeared.[7] Griffiths and Derwish have reported the spectra of a few phenyltin compounds [8,9] *e.g.*, those in the series Ph$_n$SnCl$_{4-n}$ (n = 1—4). The spectra are like those of typical substituted benzenes. The secondary-band vibrational structure has been analysed and it is found that gradual replacement of phenyl groups by chlorine is accompanied by progressive hypsochromic shifts.

It is convenient to discuss firstly and mainly the disilanes, and secondly the digermane, ditin, and dilead organometallic compounds collectively. Preliminary reports have already appeared.[10,11] Gilman *et al.* have published data on phenyl polysilanes [12] and Drenth *et al.* on organotin and organolead compounds.[13]

TABLE 2

Compounds with spectra exhibiting intense absorption bands (in cyclohexane) around 245 mμ

Compound	$\nu_{max.}$ (cm.$^{-1}$)	$\lambda_{max.}$ (mμ)	ε	Oscillator strength f	Band-width $f/\varepsilon(\times 10^5)$
Ph$_3$Si·SiPh$_3$	40,500	246·5	32,600	0·611	1·86
Ph$_3$Si·SiPh$_2$Cl	41,400	241·5	16,800	0·374	2·23
Me$_2$PhSi·SiPhMe$_2$	42,200	237·5	16,400	0·339	2·07
Ph$_3$Si·SiMe$_3$	42,700	236·0	18,400	0·377	2·05
Me$_2$PhSi·SiMe$_3$	43,480	230·0	4,900	0·0988	2·02
Ph$_3$Ge·GePh$_3$	41,770	239·0	30,400	0·599	1·96
Ph$_3$Sn·SnPh$_3$	40,400	247·5	33,900	0·670	2·01
Ph$_3$Sn·SnPh$_3$ *	40,570	246·5	32,600	0·703	2·16
p-Tol$_3$Sn·SnTol-*p*$_3$	40,400	247·5	43,000	0·901	2·10
(PhCH$_2$)$_3$Sn·Sn(CH$_2$Ph)$_3$	40,600	246·5	50,400	1·68	3·33
(PhCH$_2$)$_3$SnCl	40,350	247·5	22,400	0·601	2·68
Ph$_3$Pb·PbPh$_3$	34,130	293·0	35,000	0·645	1·88
	40,820 †	245·0 †	33,900 †	0·872 † (est.)	2·71 † (est.)

* In ethanol. † Shoulder.

Disilanes.—Hexaphenyldisilane, Ph$_3$Si·SiPh$_3$, has an electronic absorption spectrum in cyclohexane solution which is entirely different from those of most other phenylsilanes. An absorption band at about 245 mμ with molar extinction coefficient in excess of 30,000 is found in addition to a strong band with maximum below 220 mμ (Figure 1). By comparison, tetraphenylsilane (Figure 2) and all the other compounds listed in Table 1 have a strong band with maximum below 220 mμ (*i.e.*, in the far ultraviolet) and the weak " benzenoid " band at about 260 mμ. The fact that the long-wavelength tail of the strong

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[7] Yu. P. Egorov, E. A. Chernyshev, *Fiz. Sbornik, L'vovsk. Gos. Univ.*, 1957, no. 3, 390 (*Chem. Abs.*, 1961, **55**, 16,147); A. H. Konstam, Ph.D. Thesis, Pennsylvania, 1961 (*Diss. Abs.*, 1962, **23**, 72).

[8] V. S. Griffiths and G. A. W. Derwish, *J. Mol. Spectroscopy*, 1959, **3**, 165.

[9] V. S. Griffiths and G. A. W. Derwish, *J. Mol. Spectroscopy*, 1961, **7**, 233.

[10] D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 1962, 300; *Chem. and Ind.*, 1964, 1492.

[11] D. N. Hague and R. H. Prince, *Chem. and Ind.*, 1964, 1492.

[12] H. Gilman, W. H. Atwell, and G. L. Schwebke, *Chem. and Ind.*, 1964, 1063.

[13] W. Drenth, M. J. Janssen, G. J. M. van der Kerk, and J. A. Vliegenthart, *J. Organometallic Chem.*, 1964, **2**, 264.

245-mμ band of hexaphenyldisilane has vestigial fine structure suggests the partial submergence by this strong band of a shifted typical benzenoid band at about 270 mμ.

The origin of the effect. The intense 245-mμ band in hexaphenyldisilane may be due to (*a*) free radicals of the type $Ph_3Si\cdot$; (*b*) the unit $Ph_nSi\cdot SiPh_n$ ($n = 3$) in which one or more phenyl groups on one silicon atom interact with one or more phenyl groups on the other, by-passing the silicon atoms. The effect is then likely to be observed where the silicon atoms are replaced by other atoms, *M*, *i.e.*, $Ph_nM\cdot MPh_n$; (*c*) a unit of two or three phenyl groups on the same silicon atom interacting independently of the latter, *i.e.*, $Ph_nM\cdot M$ ($n = 2$ or 3); (*d*) two or three phenyl groups attached to two silicon atoms, *i.e.*, $Ph_nSi\cdot Si$ ($n = 2$ or 3); (*e*) one phenyl group β to one silicon atom, *i.e.*, Ph·X·Si where the nature of X is immaterial; (*f*) the unit Si–Si; (*g*) the unit $Ph_nSi\cdot SiPh_n$ ($n = 1$—3) involving the silicon atoms; (*h*) one phenyl group attached to two silicon atoms, *i.e.*, PhSi·Si.

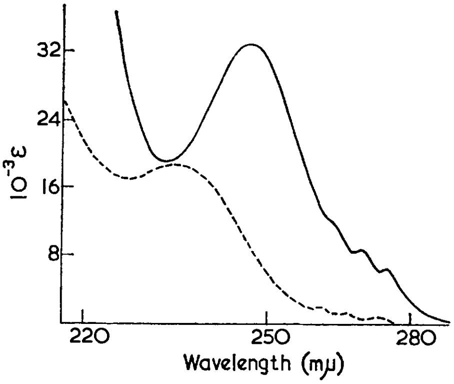

FIGURE 1. Electronic absorption spectra in cyclohexane solution of hexaphenyldisilane (——) and 1,1,1-trimethyl-2,2,2-triphenyldisilane (– – – –)

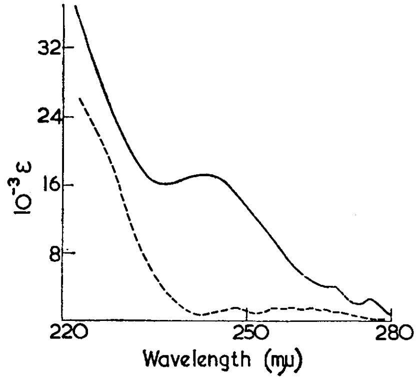

FIGURE 2. Electronic absorption spectra in cyclohexane solution of chloropentaphenyldisilane (——) and tetraphenylsilane (– – – –)

Certain structures have been synthesised in an attempt to find the structural feature responsible for the effect.

(*a*) It is possible that $Ph_3Si\cdot$ is the absorbing species, and that its spectrum swamps that of the undissociated Ph_6Si_2 molecule, which is presumably of the " normal " substituted-benzene type. This is unlikely because all the chemical properties of the disilane [14,15] are consistent with the comparative thermodynamic stability of the silicon–silicon bond. A significant feature of this spectrum is its high intensity; an oscillator strength of about 0·6 suggests that the electronic transition responsible for the absorption is quite strongly allowed. In contrast the absorption spectrum of the triphenylmethyl radical, $Ph_3C\cdot$, which does not seem to have been recorded below about 240 mμ, has a molar extinction coefficient that does not exceed 9000.[16] $Ph_3C\cdot$ absorbs in the visible region whereas the silane absorbs only in the ultraviolet. Finally the corresponding mixed carbon–silicon compound, $Ph_3C\cdot SiPh_3$, shows no corresponding strong absorption band * (cf. Figure 5).

(*b*) If the absorption band is associated with an interaction " through space " between two (or more) phenyl groups on the two silicon atoms then the band should be observed in $Ph_3C\cdot SiPh_3$. This compound has a spectrum quite unlike that of hexaphenyldisilane.

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* A band lying below the lower-wavelength limit of the environment absorption is said to be absent.

[14] N. V. Sidgwick, " The Chemical Elements and Their Compounds," Oxford University Press, Oxford, 1950.

[15] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, **60**, 459; J. G. A. Luijten and G. J. M. van der Kerk, " Investigations in the Field of Organotin Chemistry," Tin Research Institute, 1955.

[16] L. C. Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1673.

Since both $Ph_3Si{\cdot}SiMe_3$ and $PhMe_2Si{\cdot}SiMe_3$ possess intense bands this cannot be the active structural unit.

(*c*) Interaction through space between phenyl groups on the same silicon atom is also an unlikely origin since tetraphenylsilane, triphenylsilane, and hexaphenyldisiloxane, for example, all have no intense absorption band. It might be argued that the geometry of the disilane may be different from those of the other compounds containing the group Ph_3Si, and as a result the phenyl groups are very favourably aligned for such an interaction. Until the stereochemistry of Ph_6Si_2 is known this point has to remain unsettled. A satisfactory indication that this is not the cause of the band is the observation that two compounds in which only one phenyl group is bound to a silicon atom, $PhMe_2Si{\cdot}SiMe_3$ and $PhMe_2Si{\cdot}SiMe_2Ph$, possess absorption bands (Figure 3).

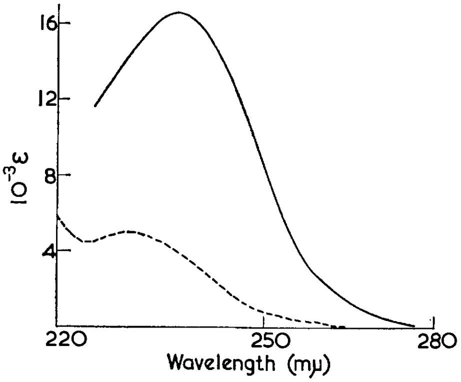

FIGURE 3. Electronic absorption spectra in cyclohexane solution of *sym.*-diphenyltetramethyldisilane (——) and phenylpentamethyldisilane (– – – –)

(*d*) The unit $Ph_nSi{\cdot}Si$ is also eliminated by the existence of bands in $PhMe_2Si{\cdot}SiMe_3$ and $PhMe_2Si{\cdot}SiMe_2Ph$.

(*e*) The interaction between a phenyl group and a silicon atom β to it is rather similar to (*b*) and (*c*) inasmuch as it is an interaction " through space." With this mechanism benzylsilanes as well as $Ph_3C{\cdot}SiPh_3$ would show intense bands in the near-ultraviolet. Benzyltrimethylsilane has been shown to possess a typical benzenoid absorption, as have several other benzyl-Group IV compounds (Table 1) (for the special case of the tin compound see below).

(*f*) The absorption band might be associated purely with the silicon–silicon bond and not be connected with the phenyl groups in any way, a view put forward by Drenth for the lead–lead system.[13] This is rejected because Me_6Si_2 (in cyclohexane) and Cl_6Si_2 (vapour phase) * show no significant absorption above 220 mμ (in this context " significant " is taken to mean an extinction coefficient of greater than 1000).

(*g*) The unit $Ph_nSi{\cdot}SiPh_n$, involving the silicon atoms [cf. (*b*)], is also rejected because the band is present in $Ph_3Si{\cdot}SiMe_3$ and $PhMe_2Si{\cdot}SiMe_3$.

(*h*) We conclude that the feature responsible for intense absorption in these compounds is the group Ph–Si–Si. A similar effect could occur with all Group IV elements, M, provided that both M atoms in Ph–M–M have vacant low-lying *d*-orbitals. An analogous suggestion has been made by Schott to account for the colour of chain- or ring-containing polysilanes in which a $\sigma \longrightarrow \pi$ (*d–d*) transition is proposed;[17] Gilman [12] also has shown that compounds of the type $PhSi_n$, ($n = 3$, 4, etc.) show intense ultraviolet absorption. Many organo poly-tin compounds containing several tin–tin bonds are deeply coloured.[15,18]

Cause of the absorption band in the Ph–Si–Si *system.* It is frequently assumed [19] that

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* Private communication from M. Tufail.

[17] G. Schott, *Z. Chem.*, 1963, **3**, 41.

[18] G. A. Razuvaev, O. A. Shchepetkova, and H. S. Vyazankin, *Zhur. obshchei Khim.*, 1961, **31**, 1401.

[19] H. H. Jaffé and M. Orchin, " Theory and Applications of U.V. Spectroscopy," Wiley, New York, 1962.

bands of substantially the same electronic origin in the spectra of a series of closely related compounds have the same shapes. The shape is determined largely by the band-width which is proportional to the ratio of the oscillator strength (f) and maximum extinction coefficient (ε). This ratio is shown in Table 2 for those compounds exhibiting intense absorption in the region of 245 mμ. Most of the band-widths lie in the range 1·85—2·25 ($\times 10^{-5}$, f/ε units) and so are probably caused by similar electronic transitions.*

It is rather difficult to specify the nature of the electronic transition, but it is possible that the electron is promoted from the π-cloud of the phenyl group to a π-bonding level in which the *d*-orbitals of the Si–Si group are involved. This may be compared with a concept proposed by Nagakura *et al.*[20] for explaining the spectra of nitro- and carbonyl-substituted benzenes. In this approach attention is focussed on the transfer of charge accompanying excitation, from the phenyl ring (electron donor) to the nitro or carbonyl group (electron acceptor). The highest occupied orbital of the donor interacts with the lowest unoccupied orbital of the acceptor to form two new orbitals extending over both groups. Excitation is believed to occur by promotion of an electron from the lower orbital of this pair to the higher one, and is accompanied by a considerable transfer of charge from the donor to the acceptor group. On the basis of this transfer of charge the spectra of nitrobenzene and the carbonyl-substituted benzenes are called " intramolecular charge-transfer spectra."

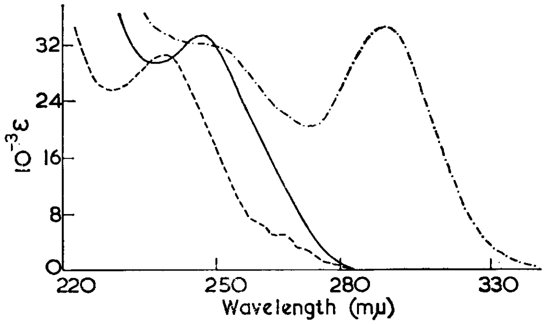

FIGURE 4. Electronic absorption spectra in cyclohexane solution of hexaphenyldigermane (– – – –), hexaphenylditin (——), and hexaphenyldilead (– · – · –)

This provides a picture which can be modified rather attractively for the present purposes. The intense band can originate in an electronic transition from the π-system of a phenyl group to the *d*–*d* π-system of the Si–Si bond; or alternatively the highest occupied π-orbital of the phenyl ring interacts with the lowest unoccupied orbital (π) of the Si–Si group to form two new orbitals extending over both groups. The excited electron passes from the lower to the higher of this pair.

Band intensities may be interpreted in terms of this picture. The band maxima usually occur on the long-wavelength " tails " of other, stronger, absorption bands and so only approximate correlations of maximum extinction coefficient with structure can be made. But in the methyl(phenyl)disilanes the intensity of absorption is roughly proportional to the number of phenyl groups in the molecule. The absorption involves the transition of an electron between a phenyl ring and the Si–Si group, *i.e.*, it involves only one phenyl ring per molecule. As the number of phenyl groups in the molecule increases, the intensity of absorption would also be expected to increase almost linearly with this number if each Ph–Si–Si system is acting in approximate isolation from the other phenyl groups, so a large number of phenyls means a greater probability of light absorption per molecule.

Digermanes. Ditins, and Dileads.—Several phenyl compounds of this type exhibit intense bands similar to those shown by disilanes and which may well have the same origin. Hexaphenyldilead has a spectrum which is similar to those of the other Ph_6M_2 compounds

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* A few related compounds have spectra with band-widths which are rather higher than this (see Table 2) but these will be discussed separately.

[20] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, 1954, **22**, 236; S. Nagakura, *ibid.*, 1955, **23**, 1441.

in showing an intense band, but is different in that (*a*) the band occurs at a considerably higher wavelength, and (*b*) a shoulder of high intensity is also observed, at about 245 mμ. Drenth *et al.* have observed an intense band at 254 mμ in hexacyclohexyldilead;[13] we have observed a similar absorption in hexacyclohexylditin, though at considerably shorter wavelength [$\lambda_{\text{max.}}$ <220 mμ (ε >34,500)].[21] It is interesting that hexabenzylditin shows this type of absorption and remarkable that tribenzyltin chloride shows it also, whereas benzylsilanes and germanes do not (Table 1, compounds 3—5).

We have established that the absorption is characteristic of the Ph–M–M system for M = Si, and this structural unit may be active in the corresponding germanium, tin, and lead compounds. However, it is clear that intense absorption is not caused solely by this unit when M = Sn or Pb.

EXPERIMENTAL

All the spectra were measured in solution with a Cary model 14 recording spectrophotometer. In all cases but one the solvent was spectroscopic-grade cyclohexane (H. & W.) which was used without further purification. The other solvent was 95% ethanol. All spectra were recorded three times. In a few cases separate solutions were made up and their spectra obtained independently: molar extinction coefficients agreed to within 1%.

The oscillator strengths, *f*, of strong absorption bands were evaluated from the area under the ε *vs.* ν (cm.$^{-1}$) curves. In most cases the curve was not isolated, *i.e.*, it was superimposed on the lower-wavelength tail of a larger absorption band. The total area enclosed by the band was thus not measurable. It was estimated by doubling the area under the high-wavelength side. The band-area associated with the shoulder in the spectrum of hexaphenyldilead was estimated by constructing the absorption curve in which the band at 293 mμ had been removed. This was done on the assumptions that (i) the band was symmetrical about its maximum, and (ii) from the maximum to higher wavelengths the band was isolated. The area under the new curve to the right of the shoulder was then doubled in the usual way.

Preparations. The compounds used were prepared by methods described in the literature, and purified to constant melting point (for solids) or by fractional distillation (for liquids). Boiling points and melting points agreed with those quoted in the literature, and the analyses agreed with the theoretical within experimental error.

Hexaphenyldisilane [22] and *sym*-diphenyltetramethlyldisilane [23] were made by coupling the corresponding chlorosilanes with sodium sand in boiling xylene; hexamethyldisilane [24] by treating dimethyltetrachlorodisilane with excess of methyl Grignard reagent. 1,1,1-Trimethyl-2,2,2-triphenyldisilane [25] and phenylpentamethyldisilane [26] were made from the corresponding lithium and chloro-compounds in scrupulously dry [26] tetrahydrofuran.[27,28] Hexaphenyldisiloxane [29] was made by coupling partially hydrolysed triphenylchlorosilane with sodium sand; and hexaphenyldisilazane [30] from triphenylsilane and sodium in liquid ammonia. Hexaphenyldigermane [31] was made from tetraphenylgermane *via* triphenylbromogermane.[32] Hexaphenylditin,[33] hexa-*p*-tolylditin,[34] hexabenzylditin,[35] and hexaphenyldilead [36] were made from the corresponding R_3M halide and sodium, either in boiling xylene or liquid ammonia.

Preparation and nature of triphenylmethyltriphenylsilane $Ph_3C{\cdot}SiPh_3$. The preparation from triphenylmethyl-lithium and triphenylchlorosilane in ether has been discussed by Gilman and

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[21] D. N. Hague, Ph.D Thesis, Cambridge, 1963.

[22] H. Gilman and T. C. Wu, *J. Org. Chem.*, 1953, **18**, 753.

[23] H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, 1953, **18**, 1743.

[24] M. Kumada, M. Yamaguchi, Y. Yamamoto, J.-I. Nakajima, and K. Shiina, *J. Org. Chem.*, 1956, **21**, 1264.

[25] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. and Ind.*, 1958, 1479.

[26] H. Gilman, and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 1958, **80**, 608.

[27] D. Wittenberg and H. Gilman, *Quart. Rev.*, 1959, **13**, 116.

[28] D. Wittenberg and G. D. Lichtenwalter, unpublished results, quoted in ref. 27.

[29] W. H. Daudt and J. F. Hyde, *J. Amer. Chem. Soc.*, 1952, **74**, 386.

[30] H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, *J. Amer. Chem. Soc.*, 1929, **51**, 3067.

[31] G. T. Morgan and H. D. K. Drew, *J.*, 1925, 1760.

[32] C. A. Kraus and L. S. Foster, *J. Amer. Chem. Soc.*, 1927, **49**, 457.

[33] H. Gilman and S. D. Rosenberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.

[34] M. P. Brown and G. W. A. Fowles, *J.*, 1958, 2811.

[35] K. K. Law, *J.*, 1926, 3243.

[36] H. Gilman and J. C. Bailie, *J. Amer. Chem. Soc.*, 1939, **61**, 731.

co-workers.[37] This method was used in the present investigation, but we noted several features which have not been reported previously. Firstly, there is no mention of the fact that triphenylmethyl-lithium is only sparingly soluble in ether and it is necessary to add it as a suspension to the ethereal solution of triphenylchlorosilane. Secondly, it is stated that triphenylmethyltriphenylsilane can be recrystallised from dioxan, benzene, toluene, or chloroform; but we have found that when it was crystallised from benzene a pale yellow solid resulted, whereas on crystallising from chloroform or cyclohexane a white "amorphous" solid was obtained. The pale yellow crystals from the benzene solution melted at a considerably different temperature (about 160—170°) from the white solid obtained from chloroform and from cyclohexane solutions (335—338°; lit.,[37] 334—336°). Gilman draws attention to a very characteristic colour change to deep red on melting; this was observed with the white solid, but the yellow crystals changed to orange on melting, and then to red at about 300°. The compounds had rather different ultraviolet absorption spectra (Figure 5). This phenomenon was completely reversible, *i.e.*, the white solid was deposited from benzene as pale yellow crystals whilst the latter could be converted into the white amorphous powder by crystallising from chloroform or cyclohexane.

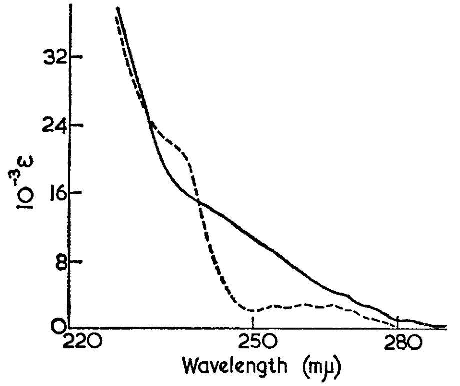

FIGURE 5. Electronic absorption spectra in cyclohexane solution of triphenylmethyltriphenyl silane (——) and its benzene complex, $Ph_3C\cdot SiPh_3\cdot[C_6H_6]_n$, (– – – –) (Extinction coefficients of the complex are evaluated assuming $n = 1$)

We suggest that the white solid is triphenylmethyltriphenylsilane and the yellow crystals are a complex between the silane and benzene, $Ph_6CSi\cdot[C_6H_6]_n$. If the compound is a monobenzene adduct the apparent molecular weight in methylene chloride (290) shows that complete dissociation occurs in this solvent (Calc. for monobenzene adduct, 581). Microanalysis of the white solid, after recrystallisation from chloroform only, gave results (both for carbon and hydrogen) which were consistently lower than those calculated for Ph_6CSi. The infrared spectrum indicated that no chloroform remained in the sample, however,. On further recrystallisation from cyclohexane, a better analysis was obtained (Found: C, 87·6; H, 6·1. Calc. for $C_{37}H_{30}Si$: C, 88·4; H, 6·1%). In view of Gilman's report that a significant amount of hexaphenyldisilane is produced with the monosilane, it is surprising that no band at about 245 mμ is observed in the ultraviolet spectrum.

We are very grateful to Dr. G. Tagliavini for the gift of a sample of chloropentaphenyldisilane; to Mr. J. A. Bedford for benzyltrimethylsilane, benzyltrimethylgermane, and dibenzyldimethylgermane; to Professor G. J. M. van der Kerk for tetraphenylgermane; to Imperial Chemical Industries Limited for dimethyltetrachlorodisilane; and to Dr. L. E. Orgel for discussion. One of us (D. N. H.) also acknowledges the award of a D.S.I.R. studentship.

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[37] A. G. Brook, H. Gilman, and L. S. Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 4759.