Anal. Calcd. for $C_{36}H_{26}$: C, 94.1; H, 5.9. Found: C, 93.9; H, 6.0.

Preparation of Pentaphenylphosphole Oxide.—The source of the hetero atom was phenyldichlorophosphine oxide. The same reaction scheme as described above led to a crystalline material having a melting point of 292–293° in 70% yield. This was identified as the phosphole oxide by comparison with an authentic sample prepared in our laboratories by another method.[11]

Anal. Calcd. for $C_{34}H_{25}OP$: C, 85.0; H, 5.25; P, 6.45. Found: C, 84.8; H, 5.1; P, 6.34.

Preparation of 1-Chloro-2,3,4,5-tetraphenylarsenole.—The standard procedure was repeated using arsenic trichloride. One mole of the dilithium compound was added per mole of trichloride and the resulting monochlorotetraphenylarsenole was obtained from an acetone–ligroin solvent system in the form of yellow needles, m.p. 182–184°. As opposed to the other recrystallization techniques, no methanol or other alcohols were used. The combination of the difficulties in purifying the sample and the problems inherent in an analysis of organometallic halides did not allow an unequivocal analysis for this product.

Anal. Calcd. for $C_{28}H_{20}AsCl$: C, 72.2; H, 4.3; Cl, 7.6. Found: C, 69.7; H, 4.5; Cl, 6.4.

Preparation of the monochlorotetraphenylarsenole was repeated without an isolation step. This was further treated with phenyllithium in anhydrous diethyl ether at room temperature for 30 minutes. A 35.4% yield (based on LTPBD) of pentaphenylarsenole was recovered. It was identified by melting point (214–215°), mixed m.p. (214–215°) and infrared as identical with an authentic sample. A similar preparation was carried out with an excess of phenylmagnesium bromide in anhydrous tetrahydrofuran. This reaction mixture was refluxed for 2 hours and a yield of 35.2% (based on LTPBD) of pentaphenylarsenole was recovered. Again, identification was based on melting point and infrared spectra.

Attempted Preparation of Mercuric Heterocycles.—A similar reaction was run with $HgCl_2$. An 8% yield of tetraphenyl-1,3-butadienylene-bis-mercury chloride, m.p. 245–248° with decomposition, was obtained. No other mercury-containing compounds were isolated.

Anal. Calcd. for $C_{28}H_{20}Cl_2Hg_2$: C, 40.6; H, 2.4; Hg, 48.5; Cl, 8.6. Found: C, 40.75; H, 2.55; Hg, 48.4; Cl, 8.25.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO, TORONTO 5, CANADA]

The Spectral and Chemical Properties of α-Silyl Ketones

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The ultraviolet and infrared absorption spectra of several α-silyl ketones and one α-germyl ketone are reported and reveal that the carbonyl groups of these ketones are abnormally polar. The reactions of some of these ketones with typical Grignard reagents have been investigated. The data are interpreted as evidence for the existence of partial bonding between the silicon and carbonyl-oxygen atoms in α-silyl ketones.

One of the outstanding features about benzoyltriphenylsilane,[1] the first α-silyl ketone prepared, is its yellow color, a property not possessed by its carbon analog β-benzpinacolone, nor by the only other α-silyl ketone reported, acetyltriphenylsilane.[2] The yellow color implies that silicon is acting as a chromophore, a phenomenon previously unknown. It therefore appeared to be of interest to prepare a variety of α-silyl ketones in order to study their ultraviolet and infrared spectra, as well as their chemical reactions.

The spectra of these compounds, as well as of benzoyltriphenylgermane, β-benzpinacolone and a few related aliphatic and aromatic ketones, are presented in Tables I and II.

It is immediately apparent that all the α-silyl phenyl ketones are colored, and in fact that their spectra are practically identical in the ultraviolet and in the carbonyl regions of the infrared, regardless of the nature of the groups attached to the silicon atom.

By analogy with the ultraviolet absorption spectra of acetophenone[3] where the band at 325 mμ has been assigned to carbonyl absorption, that at 280 mμ to phenyl absorption and that at 242 mμ to the benzoyl group,[4] we assign the low-intensity, long wave length band of the α-silyl ketones to absorption by the carbonyl group and the high-intensity, short wave length band to absorption by the benzoyl group present in these compounds. The compounds show no absorption in the 280–295 mμ region. By comparing suitable spectra (*e.g.*, acetone, acetophenone and benzoyltriphenylsilane) it is possible to assign additive bathochromic shifts of the carbonyl band caused by the introduction of groups adjacent to

TABLE I

ULTRAVIOLET SPECTRA OF α-SILYL AND OTHER KETONES[d]

Compound	Carbonyl mμ	Carbonyl ε	Phenyl mμ	Phenyl ε	Benzoyl mμ	Benzoyl ε
$Ph_3SiCOPh$	403(s)	264			258	15,500
	417	300				
$Ph_2MeSiCOPh$	403(s)	210			256	12,200
	417	235				
$PhMe_2SiCOPh$	403(s)	200			255	13,900
	415	216				
$Me_3SiCOPh$	402 (d)	117			252	11,700
	413 (d)	118				
$Ph_3SiCOMe$[a]	360 (d)	324	260	1510		
	372 (d)	366	265	1490		
	389(s)	239	272	1060		
$Ph_3GeCOPh$	403(s)	262			257	17,100
	415	306				
Ph_3CCOPh	329	299	293	782	253	11,600
PhCOMe[b]	325	50	280	1000	242	13,000
MeCOMe[c]	279	15				

[a] We are indebted to Dr. Henry Gilman, Iowa State College, for a sample of this compound. Subsequently, G. E. LeGrow in this Laboratory prepared additional material from triphenylsilyllithium and acetyl bromide in 4% yield following the published method (ref. 2). [b] See ref. 3. [c] See ref. 4. [d] (s) = shoulder, (d) = doublet.

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(1) A. G. Brook, THIS JOURNAL, 79, 4373 (1957).

(2) D. Wittenberg and H. Gilman, *ibid.*, 80, 4529 (1958).

(3) G. Scheibe, F. Backenholer and A. Rosenberg, *Ber.*, 59, 2617 (1926).

(4) E. A. Braude and F. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955.

TABLE II

INFRARED SPECTRA (CARBONYL REGION) OF α-SILYL AND OTHER KETONES

Compound	C=O, μ	PhCO, μ
$Ph_3SiCOPh$	6.18	6.28, 6.34
$Ph_2MeSiCOPh$	6.18	6.28, 6.33
$PhMe_2SiCOPh$	6.18	6.28, 6.32
$Me_3SiCOPh$	6.18	6.28, 6.33
$Ph_3SiCOMe$	6.08	....
$Ph_3GeCOPh$	6.14	6.28, 6.34
Ph_3CCOPh	5.91	6.28, 6.33
PhCOPh	6.01	6.27, 6.33
PhCOMe	5.91	6.28, 6.33
MeCOMe	5.81	....

the carbonyl. These amount to about 46 mμ for a phenyl group attached to carbonyl and about 92 and 78 mμ for an α-silyl group. These latter shifts, for example, added to the carbonyl band of acetone (279 mμ), predict the position of the two strongest carbonyl bands of acetyltriphenylsilane with considerable accuracy (371, 357 mμ compared with 372, 360 mμ observed).

Similarly in the infrared spectra, the position of the carbonyl absorption (6.18 μ for the silyl phenyl ketones, 6.08 μ for the silyl methyl ketone) is at an abnormally long wave length which is independent of the groups attached to the silicon atom. Normally aryl ketones absorbed in the region 5.88–5.95 μ and diaryl or α,β,α′,β′-unsaturated ketones absorb in the region 5.99–6.03 μ.[5] Again additive bathochromic shifts can be assigned for the introduction of groups adjacent to the carbonyl in the compounds studied: *viz.*, 0.1 μ for a phenyl group and 0.27 μ for a silyl group. On the other hand, the positions of the bands associated with benzoyl absorption at about 6.28 and 6.33 μ[6] appear unaffected by the introduction of silicon adjacent to the carbonyl group (*cf.* acetophenone, benzoyltriphenylsilane, etc.).

The abnormally long wave length absorption of the α-silyl phenyl ketones at 6.18 μ approaches the lower limits of the normal carbonyl absorption of the carboxylate ion, 6.2–6.45 μ,[5] or of an enolic β-diketone. Thus it is evident that the carbonyl groups of these molecules must have a very considerable degree of single bond character, and are exceedingly polar. Since the wave lengths absorbed, both in the infrared and ultraviolet regions, are independent of the nature of the groups attached to silicon, the effect cannot be associated with either inductive or conjugative effects acting through silicon on the carbonyl group, since quite different effects would be expected from the triphenylsilyl group as compared with the trimethylsilyl group.

The positions of the carbonyl absorptions of the α-silyl ketones are relatively insensitive to the polarity of the medium, as compared with related carbon compounds. Thus the carbonyl bands of benzoyltriphenylsilane and acetyltriphenylsilane are shifted toward longer wave lengths by only 0.02 and 0.01 μ, respectively, on changing the solvent from cyclohexane or carbon tetrachloride to acetonitrile or isopropyl alcohol, whereas the corresponding carbonyl bands of benzophenone or β-benzpinacolone are raised by 0.06 and 0.07 μ, respectively, with the same change in solvent.

This insensitivity to solvent of the α-silyl ketones may indicate merely that the carbonyl group is already so polarized that further polarization cannot be achieved simply by changing the dielectric constant of the medium or, alternatively, may indicate that, for example, the apparent electron excess on the oxygen atom is not free for association with solvent molecules.

The abnormal charge distribution in the carbonyl group could be stabilized by interaction of the electron excess on the oxygen atom with the much less electronegative silicon atom, through its vacant d-orbitals. This d_π–p_π bonding would distort and stretch the carbonyl group by transfer of electron density toward silicon, resulting in a lowered force-constant, and the consequent shift of the carbonyl absorption to longer wave lengths. A similar explanation has been suggested recently by several authors[7] to account for the acidities and basicities of the alkylsilanols as compared with the related carbinols, but the present situation is not exactly analogous since instead of the silicon and oxygen atoms being adjacent, as in the silanols, they are separated from one another by carbon.

The highly polar character of the carbonyl group of the α-silyl ketones probably is reflected in the recent finding that benzoyltriphenylsilane is converted by sodium ethoxide to benzhydryloxyethoxydiphenylsilane,[8] a rearrangement which involves the formation of a bond between the silicon atom and the oxygen of the carbonyl group. A similar bond formation between silicon and an oxygen atom once removed is encountered in the rearrangements of the α-silylcarbinols to their isomeric silyl ethers.[9,10] These rearrangements, which occur rapidly under mild conditions, might be expected to be facilitated by the existence of partial bonding between the silicon and carbonyl-oxygen atoms.

As a further means to assist in establishing the character of the carbonyl group of α-silyl ketones, the reactions of benzoyltriphenylsilane with typical Grignard reagents were investigated and the results compared with the behavior of the carbon analog of β-benzpinacolone. It already has been reported that benzoyltriphenylsilane is easily reduced by lithium aluminum hydride[10] to the carbinol and that it readily adds methylmagnesium halide.[10] As shown in Table III, benzoyltriphenylsilane also reacts normally with benzyl Grignard reagent, but with Grignard reagents having β-hydrogens, such as ethyl and β-phenylethylmagnesium halides, reduction occurred in high yield but no "normal" addition occurred. Isopropyl Grignard reagent mainly reduced the ketone (57%) although a slight amount (3%) of addition

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules" Methuen and Co., London, 1958.

(6) F. A. Miller in H. Gilman "Advanced Organic Chemistry," Vol. III, J. Wiley and Sons, Inc., New York, N. Y., 1953.

(7) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955); R. West and R. Baney, THIS JOURNAL, **81**, 6145 (1959).

(8) A. G. Brook, *J. Org. Chem.*, **25**, 1072 (1960).

(9) A. G. Brook, THIS JOURNAL, **80**, 1886 (1958).

(10) A. G. Brook, C. M. Warner and M. McGriskin, *ibid.*, **81**, 981 (1959).

Table III

Reactions of Carbonyl Compounds with Metallic Reagents

Ketone	Grignard reagent	Moles carbonyl compound /Moles metallic	Time, hr.	Product	M.p., °C.	Yield, %
$Ph_3SiCOPh$	MeMgI	1.0	0.5	$Ph_3SiCOHMePh$	116–118	55[a]
	EtMgBr	1.0	1	$Ph_3SiCHOHPh$	115.5–118	84[b]
	i-PrMgBr	1.0	1	$Ph_3SiCHOHPh$	116–118	57
				Ph_3SiCOH-*i*-PrPh	150–152	3[c]
	i-PrMgBr + $MgBr_2$[d]	0.5	2	$Ph_3SiCHOHPh$	116–118	36
				Ph_3SiCOH-*i*-PrPh	149–152	3
	$PhCH_2MgCl$	1.0	1	$Ph_3SiCOHPhCH_2Ph$	149–150.5	83[e]
	t-BuMgCl	1.0	1–48	$Ph_3SiCOPh$ (rec.)		71
	PhMgBr	1.0	1	Ph_2SiOH	150–152	39
	$PhCH_2CH_2MgBr$	1.0	1	$Ph_3SiCHOHPh$	117–119	53
Ph_3CCOPh[f]	MeMgI	1.0	0.5–18	Ph_3CCOPh (rec.)	178–180	92
	EtMgBr	1.0	1	$Ph_3CHOHPh$	147–149	86[g]
	$PhCH_2MgCl$	1.0	3	Ph_3CCOPh (rec.)		94
	$PhCH_2CH_2MgBr$	1.0	2	$Ph_3CHOHPh$	146–148	27
				Ph_3CCOPh (rec.)		48
	t-BuMgCl	1.0	48	Ph_3CCOPh (rec.)		80
$Me_3SiCOPh$	MeMgI	1.0	0.5	$Me_3SiCOHMePh$	.....	63[h]
	$LiAlH_4$	0.5	0.2	$Me_3SiCHOHPh$	.....	77[j]
	EtMgBr	1.0	1	$Me_3SiCHOHPh$		82[k]
$Ph_3GeCOPh$	$LiAlH_4$	1.0	0.2	$Ph_3GeCHOHPh$	106–107	63[l]
PhCHO	Ph_3GeLi	1.0	0.1	$Ph_3GeCHOHPh$	105–107	66[m]
Ph_2CO	Ph_3GeLi	1.0	0.1	$Ph_3GeCOHPh_2$	153–157	75[l]
	Ph_3GeK	1.0	0.1	$Ph_3GeCOHPh_2$	153–157	44

The recrystallization solvents are listed: [a] Benzene–petroleum ether (b.p. 90–100°). [b] Benzene–petroleum ether (b.p. 90–100°. [c] Benzene–petroleum ether. [d] See Experimental and ref. 17. [e] Benzene–petroleum ether (b.p. 90–100°). Calcd. for $C_{32}H_{28}OSi$: Si, 6.14. Found: Si, 6.28. [f] Tetrahydrofuran used as solvent for β-benzpinacolone. [g] Benzene–petroleum ether (b.p. 90–100°). [h] B.p. 183–186° (1 mm.), $n^{25}D$ 1.5093. Calcd. for $C_{11}H_{18}OSi$: C, 68.0; H, 9.28. Found: C, 67.2; H, 9.21. [j] B.p. 83–84° (1 mm.), $n^{25}D$ 1.5115. Calcd. for $C_{10}H_{16}OSi$: C, 66.6; H, 8.89. Found: C, 66.5; H, 8.79. [k] B.p. 83–84° (1 mm.), $n^{25}D$ 1.5113. [l] Petroleum ether (b.p. 90–100°). [m] Petroleum ether (b.p. 60–70°).

occurred. No reaction occurred with *t*-butyl Grignard reagent and only an abnormal reaction resulting in cleavage occurred with phenylmagnesium bromide under the conditions employed.

By contrast, all Grignard reagents employed failed to add normally to β-benzpinacolone, although reduction occurred with ethyl and to some extent with β-phenylethyl Grignard reagents. β-Benzpinacolone has been reported to undergo substitution (or addition) in the phenyl ring adjacent to the carbonyl group with phenyl,[11] benzyl[12] or *t*-butyl[12] Grignard reagents under forcing conditions.

It can be inferred from these results that the carbonyl group of β-benzpinacolone is considerably more sterically hindered than the same group in benzoyltriphenylsilane. However, it does seem surprising that when benzylmagnesium chloride could add normally to benzoyltriphenylsilane, the less bulky ethylmagnesium halide failed to give any normal addition product, but instead gave exclusively reduction, although it is not usually found to be a particularly effective reducing agent.[13]

Thus both *t*-butyl phenyl ketone and benzophenone which might be considered as sterically hindered ketones are reported to add both ethyl and benzyl Grignard reagents in excess of 75% yield.[14] Hence the exclusive reduction of benzoyltriphenylsilane by ethyl Grignard reagent probably is a further indication of the abnormally high degree of polar character of the carbonyl group, an effect which should facilitate attack by hydride ion.[15]

From the limited runs carried out with benzoyltrimethylsilane it appears to behave very similarly to its phenyl analog, adding non-reducing Grignard reagents but being reduced by those capable of acting as reducing agents. The compound reacts abnormally with phenylmagnesium bromide, a multiplicity of products having been isolated, but apart from the fact that neither addition nor reduction products are obtained, the products have not been completely identified as yet.

The spectra of α-silyl ketones clearly indicate that the carbonyl groups possess abnormal polar character and chemical evidence demonstrates both that bond formation between silicon and carbonyl-oxygen is possible under suitable conditions,[8] and that toward Grignard reagents at least the carbonyl groups show a marked predisposition toward reduction. These data can be interpreted by, and are consistent with, the existence of d_π–p_π bonding between the silicon and carbonyl–oxygen atoms in α-silyl ketones. This effect creates in

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(11) W. A. Mosher and M. L. Huber, This Journal, **75**, 4604 (1953).

(12) R. C. Fuson and P. E. Weigert, *ibid.*, **77**, 1138 (1955).

(13) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 153.

(14) See ref. 13, pp. 357, 358, 365, 366.

(15) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, p. 548.

essence a "super-chromophore" involving the silicon and carbonyl group whose ultraviolet and infrared absorptions are considerably shifted (toward longer wave lengths) relative to a normal carbonyl group, and where the shift is essentially independent of the groups attached to the silicon atom. Further study of this phenomenon is being carried out.

Benzoyltriphenylgermane was prepared to see whether the abnormal spectral properties of the silyl ketones occurred also with germanium. It is evident from Tables I and II that a great similarity exists between the compounds, and evidently d_π–p_π bonding occurs here also. The behavior of the compound toward Grignard reagents has not yet been investigated, but the ketone was readily reduced by lithium aluminum hydride to give triphenylgermylphenylcarbinol. This same compound was the major product of the reaction of triphenylgermyllithium with benzaldehyde, an outstanding contrast to the behavior of triphenylsilyllithium or -potassium with the same compound, where a diastereomeric mixture of 2-triphenylsiloxy-1,2-diphenylethanols is said to be obtained as well as benzyloxytriphenylsilane.[16] Similarly, triphenylgermyllithium, or -potassium, when treated with benzophenone gives the normal addition product triphenylgermyldiphenylcarbinol in good yield,[17] whereas triphenylsilyllithium or -potassium gives either benzhydryloxytriphenylsilane[18] or 2-triphenylsiloxytetraphenylethanol.[19] The significance of these differences in mode of addition will be discussed later.

Experimental[20]

Synthesis of Ketones.—Diphenylmethyl-, phenyldimethyl- and trimethylbenzylsilane were each prepared by treatment of the appropriate halide with benzylmagnesium chloride. Each of the benzylsilanes was dibrominated in carbon tetrachloride with N-bromosuccinimide and a trace of benzoyl peroxide. The dibromides then were hydrolyzed with silver acetate in an ethanol–acetone–water medium, according to published directions.[1] Benzoyltriphenylgermane was similarly prepared. The properties of the new compounds are listed in Table IV. In all cases the infrared spectra were consistent with the proposed structure.

Spectral Determinations.—The infrared spectra were determined using a Beckman IR-5 spectrophotometer with approximately 5% solutions in carbon tetrachloride in 0.5-mm. cells. The data are internally consistent and are correct probably to about 0.01 μ since they were calibrated with respect to a polystyrene spectrum. In determining the shift in wave length with change of solvent 25% solutions of the ketones in various solvents in 0.5-mm. cells were employed, except for isopropyl alcohol (0.1-mm. cells).

One useful fact discovered which may be well known but which we have failed to find mentioned specifically in the literature is that phenyl groups attached to silicon, which have a characteristic absorption band at about 7.0–7.05 μ, can be distinguished from phenyl groups attached to carbon, which absorb at about 6.9–7.0 μ. In all examples we have studied the C–phenyl band occurred about 0.1 μ lower than the Si–phenyl band. The relative intensities of these bands permit, after some experience, an accurate prediction of the number of C–phenyl to Si–phenyl groups present in a molecule.

TABLE IV

ORGANOSILICON AND -GERMANIUM COMPOUNDS

Compound	M.p., °C.	Yield, %
$Ph_2MeSiCH_2Ph$	66.5–67.5	84[a]
$Ph_2MeSiCBr_2Ph$	92–94	94[b]
$Ph_2MeCOPh$	. . .	51[c]
$PhMe_2SiCH_2Ph$	. . .	43[d]
$PhMe_2SiCBr_2Ph$	86.5–87	85[e]
$PhMe_2COPh$	54–55	70[f]
Me_3SiCH_2Ph	. . .	55[g]
Me_3SiCBr_2Ph	38–40	89[h]
$Me_3SiCOPh$	. . .	76[i]
Ph_3GeCH_2Ph	82.5–83.5	93[k]
Ph_3GeCBr_2Ph	105–106	88[l]
$Ph_3GeCOPh$	100–102	67[m]

The recrystallization solvents are listed: [a] Ethanol. [b] Carbon tetrachloride–petroleum ether (b.p. 60–70°). [c] B.p. 158° (0.08 mm.), $n^{20}D$ 1.6185. Calcd. for $C_{20}H_{18}OSi$: C, 79.5; H, 5.96. Found: C, 78.1; H, 6.06. [d] B.p. 92–93° (0.15 mm.), $n^{20}D$ 1.5584. [e] Carbon tetrachloride–petroleum ether (b.p. 60–70°). [f] Petroleum ether (b.p. 60–70°); b.p. 100–102° (0.04 mm.); calcd. for $C_{15}H_{16}OSi$: C, 75.0; H, 6.66. Found: C, 75.0; H, 6.72. [g] B.p. 185–190° (750 mm.), $n^{28}D$ 1.4862. [h] B.p. 114–120° (1 mm.). [i] B.p. 42–44° (0.02 mm.), $n^{25}D$ 1.5170. Calcd. for $C_{10}H_{14}OSi$: C, 67.4; H, 7.86. Found: C, 67.4; H, 7.80. [k] Ethanol–ethyl acetate, 7:1. [l] Petroleum ether (b.p. 90–100°). [m] Methanol. Calcd. for $C_{25}H_{20}OGe$: C, 73.4; H, 4.90. Found: C, 73.3; H, 4.86.

The ultraviolet spectra were determined in purified absolute ethanol using a Beckman DK spectrophotometer.

Reactions of α-Silyl Ketones with Grignard Reagents.—All reactions of Grignard reagents with ketones, as reported in Table III, were carried out in essentially the same way, of which the following will serve as an example. In most cases the Grignard reagent was added dropwise to an ether solution of the ketone since the fading of the yellow color served in some cases as a useful indicator. Reactions with β-benzpinacolone necessitated the use of tetrahydrofuran for this ether-insoluble ketone, but the Grignard reagents were ether solutions. The products in most cases were compared, by mixed melting point, and by infrared spectra, with authentic samples. For all compounds the infrared spectra were consistent with the proposed structures.

Benzoyltriphenylsilane and Isopropylmagnesium Bromide.—Standardized isopropylmagnesium bromide (0.0055 mole) in ether was added dropwise over 15 min. to a solution of 2.0 g. (0.0055 mole) of benzoyltriphenylsilane in 45 ml. of ether. The yellow color of the ketone faded during the addition. The mixture was hydrolyzed in dilute acid after 1 hr. when a negative Color Test I indicated that all the Grignard reagent had reacted.

After drying the ether layer over sodium sulfate, evaporation to dryness left a viscous yellow oil. Treatment with hot petroleum ether (b.p. 90–100°) gave on cooling 1.10 g. (54%) of triphenylsilylphenylcarbinol, m.p. 116–118° after recrystallization from benzene–petroleum ether (b.p. 60–70°). The mixed melting point of this material with an authentic sample,[10] m.p. 116–117°, was not depressed.

From the mother liquor slowly separated a total of 0.07 g. (3%) of triphenylsilylphenylisopropylcarbinol, m.p. 150–152° after recrystallization from benzene–petroleum ether (b.p. 90–100°). The infrared spectrum showed absorption bands at 2.88 (OH), 3.3 (C–H arom.), 3.4 and 3.5 (C–H aliph.), 6.95 (C–phenyl), 7.02 (Si–phenyl), 9.1 μ (Si–phenyl), consistent with the proposed structure.

Anal. Calcd. for $C_{28}H_{28}OSi$: C, 82.3; H, 6.86. Found: C, 82.2; H, 6.98.

Attempts to improve the extent of addition at the expense of reduction by stirring the ketone in ether–benzene with excess magnesium bromide prior to addition of the Grignard reagent, following the technique of Swain and Boyles,[21] were only partially successful. The yield of reduction product isolated was only 36% but only 3% of

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(16) D. Wittenberg, T. C. Wu and H. Gilman *J. Org. Chem.*, **24**, 1349 (1959).

(17) H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 5740 (1955).

(18) H. Gilman and T. C. Wu, *ibid.*, **75**, 2935 (1953); H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 607 (1958).

(19) A. G. Brook and N. V. Schwartz, *ibid.*, **82**, 2435 (1960).

(20) Experiments involving organometallic compounds were carried out in a dry, oxygen-free nitrogen atmosphere.

(21) C. G. Swain and B. Boyles, THIS JOURNAL, **73**, 880 (1951).

addition product could be isolated from the reaction mixture.

Triphenylgermyllithium with Benzaldehyde.—A solution of triphenylgermyllithium was prepared by stirring 10.0 g. (0.0165 mole) of hexaphenyldigermane with excess lithium wire in 60 ml. of dry tetrahydrofuran overnight. After removal of the excess lithium a solution of 3.5 g. (0.033 mole) of freshly distilled benzaldehyde in 20 ml. of dry tetrahydrofuran was added during 0.5 minute. Heat was evolved and Color Test I was negative at the end of the addition. After a further 5 min. stirring the reaction mixture was poured into dilute acetic acid. On workup as usual this gave, after recrystallization from petroleum ether (b.p. 60–70°), 9.0 g. (66%) of triphenylgermylphenylcarbinol, m.p. 103–105°. Recrystallization raised the melting point to 105–107°. A mixed melting point with the material obtained by reduction of benzoyltriphenylgermane with lithium aluminum hydride in 63% yield, m.p. 106–107°, was not depressed. The infrared spectra were identical.

Triphenylgermyllithium with Benzophenone.—To the triphenylgermyllithium prepared from 15.0 g. (0.025 mole) of hexaphenyldigermane in 30 ml. of dry tetrahydrofuran was added a solution of 9.0 g. (0.05 mole) of benzophenone in 50 ml. of tetrahydrofuran over 1 min. Heat was evolved and the reaction mixture changed from dark brown to dark green. Color Test I was negative and after 5 min. additional stirring the reaction mixture was drowned in dilute hydrochloric acid. Workup of the reaction gave, on crystallization from hexane, 18.2 g. (75%) of triphenylgermyldiphenylcarbinol, m.p. 145–155°. Recrystallization from hexane–benzene raised the melting point to 153–157°. Also obtained from the mother liquor was 0.65 g. (4%) of hexaphenyldigermoxane, m.p. 180–183°.

The triphenylgermyldiphenylcarbinol was identified by mixed melting point with an authentic sample obtained by the same route as was triphenylsilyldiphenylcarbinol.[1] Benzhydryltriphenylgermane, m.p. 156–159°, was obtained in 43% yield from benzhydryllithium and triphenylbromogermane. This was brominated with N-bromosuccinimide in 83% yield to give bromobenzhydryltriphenylgermane, m.p. 182–187°. Hydrolysis of this compound with silver acetate in acetone–benzene–water gave triphenylgermyldiphenylcarbinol in 76% yield, m.p. 153–156°. The infrared spectrum was consistent with the proposed structure, and was almost identical with that of triphenylsilyldiphenylcarbinol.

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Dichlorofluoromethanesulfenyl Chloride

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The compound resulting from reaction of mercuric difluoride with trichloromethanesulfenyl chloride has been shown to be dichlorofluoromethanesulfenyl chloride and not trichloromethanesulfenyl fluoride. The sulfenyl chloride structure has been demonstrated by characteristic sulfenyl chloride reactions, such as conversion to disulfides and addition to olefins, in conjunction with the n.m.r. F^{19} chemical shift.

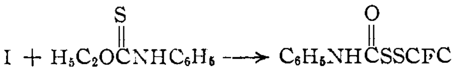
Trifluoromethanesulfenyl chloride was recently reported by Tullock[1] to be the main product resulting from fluorination of trichloromethanesulfenyl chloride with sodium fluoride in hot tetramethylenesulfone or acetonitrile. Difluorochloromethanesulfenyl chloride was also obtained as a low yield by-product but no products resulting from replacement of the chlorine on sulfur with fluorine were found.

$$CCl_3SCl + NaF \longrightarrow CF_3SCl + CF_2ClSCl + CF_3SSCF_3$$

More recently, however, Kober[2] reported that the fluorination of trichloromethanesulfenyl chloride with mercuric difluoride in methylene chloride led to the formation of compound I, with the empirical formula CCl_3FS, to which was assigned the sulfenyl fluoride structure, CCl_3SF (Ia). In view of the work of Tullock[1] and previous reports of unsuccessful attempts to convert sulfenyl chlorides to sulfenyl fluorides with fluorinating agents,[3–6] (including mercuric difluoride) we undertook an examination of compound I to see whether it was indeed the sulfenyl fluoride Ia or the expected isomeric sulfenyl chloride, $CFCl_2SCl$ (Ib).

A sample of compound I was prepared by the reaction of trichloromethanesulfenyl chloride with mercuric difluoride.[2] This compound was found to have a single sharp n.m.r. fluorine resonance with the F^{19} chemical shift corresponding to that normally observed for a CCl_2F group and not that reported for sulfur fluoride derivatives.[7] The following reactions, characteristic of sulfenyl chlorides, were carried out with this compound.

$$I + KI \longrightarrow FCl_2CSSCCl_2F \qquad (1)$$



$$I + H_5C_2O\overset{\overset{S}{\|}}{C}NHC_6H_5 \longrightarrow C_6H_5NH\overset{\overset{O}{\|}}{C}SSCFCl_2$$

(2)[8]

(3)

In each case, the products were shown by analysis to have the correct fluorine content for the proposed structures, and were further shown to have a F^{19} chemical shift similar to the starting compound I and corresponding to a $CFCl_2$ group. If compound I were the sulfenyl fluoride Ia, the fluorine would either have been lost during reaction (reactions 1 and 2) or else the F^{19} chemical shift would have changed significantly (reaction 3). It is thus concluded that the compound reported by Kober to be trichloromethanesulfenyl fluoride (Ia) is actually dichlorofluoromethanesulfenyl chloride (Ib).

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