[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Ultraviolet Absorption Spectra of Some Organosilicon Compounds

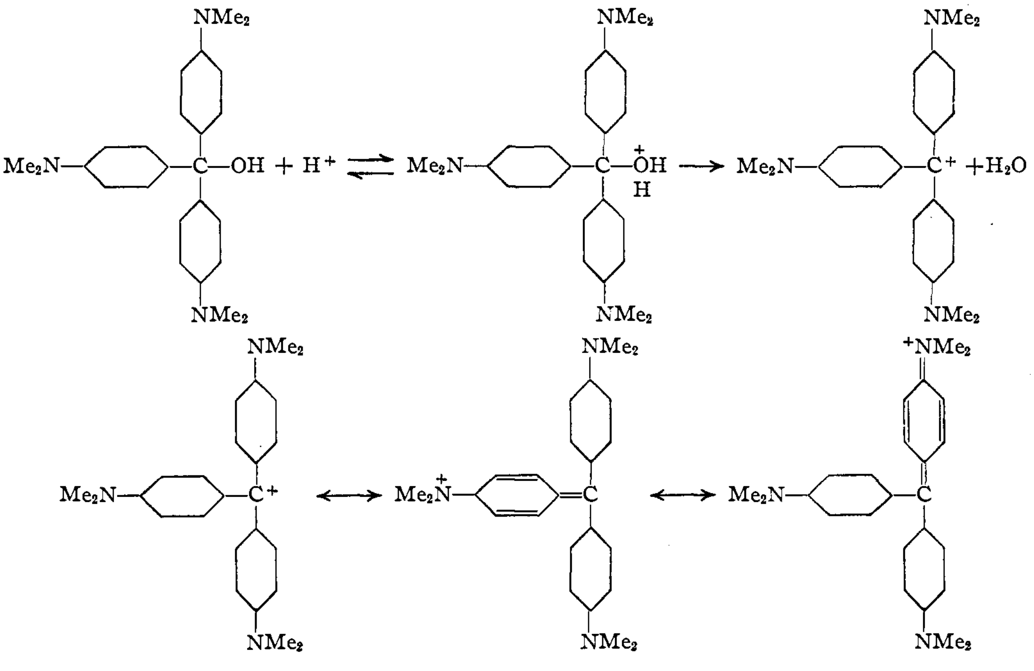
BY HENRY GILMAN AND G. E. DUNN

The strong bathochromic shift in the absorption maxima of the *p*-dimethylaminophenylcarbinols (Malachite Green, Crystal Violet) when changed from neutral to acid solution is a well known and striking phenomenon. Since comparable data have not been reported for the corresponding silicon compounds, we have examined the absorption spectra of some *p*-dimethylaminophenylsilanols in order to determine whether or not acid produces a similar shift in the maxima of these compounds.

Ultraviolet absorption curves for several colorless triarylsilicon compounds and their carbon analogs in neutral alcoholic solution are shown in Fig. 1. Wave lengths for the maxima of these compounds are listed in Table I. It is seen that the substitution of silicon for carbon as the central element makes only small changes in the absorption spectra of these types. Large changes are not to be expected when it is considered that structures involving resonance through the central element must make very small contributions in these neutral molecules, so that the aryl groups behave more or less as isolated units.[1]

When diphenyl-*p*-dimethylaminophenylcarbinol in absolute alcohol is treated with three equivalents of anhydrous hydrogen chloride the colorless solution becomes orange-red. Tris-(*p*-dimethylaminophenyl)-carbinol, of course, becomes deep violet (Crystal Violet). Diphenyl-*p*-dimethylaminophenylsilanol and tris-(*p*-dimethylaminophenyl)-silanol, however, show no color change under similar conditions. Figure 2 compares the ultraviolet absorption spectra of some of these compounds in acid solution and Table II lists their maxima. The absorption maxima of the carbinols exhibit a strong bathochromic shift into the visible in acid solution, whereas the corresponding silanols show no shift whatever. The only effect of the acid on the silanols is to inhibit the strong maximum due to the dimethylaminophenyl group, just as acid inhibits the strong maximum of dimethylaniline by converting it to its conjugate acid.[2]

The bathochromic shift in the dimethylaminophenylcarbinols on the addition of acid is attributed to the formation of triaryl-carbon cations (carbonium ions) which are stabilized by resonance involving structures such as are shown below.



The energy difference between ground state and excited states of the cations formed by the action of acids on the carbinols is less than that for the carbinols, and the wave length at which light is absorbed is consequently increased.[3] The fact that the silanol maxima exhibit no shift shows that any new species formed in acid solution has about the same energy difference between ground and ex-

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(1) Jones, THIS JOURNAL, **67**, 2021 (1945).

(2) Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(3) For a review of the theory of ultraviolet absorption and references to the original literature, see Ferguson, *Chem. Rev.*, **43**, 385 (1948).

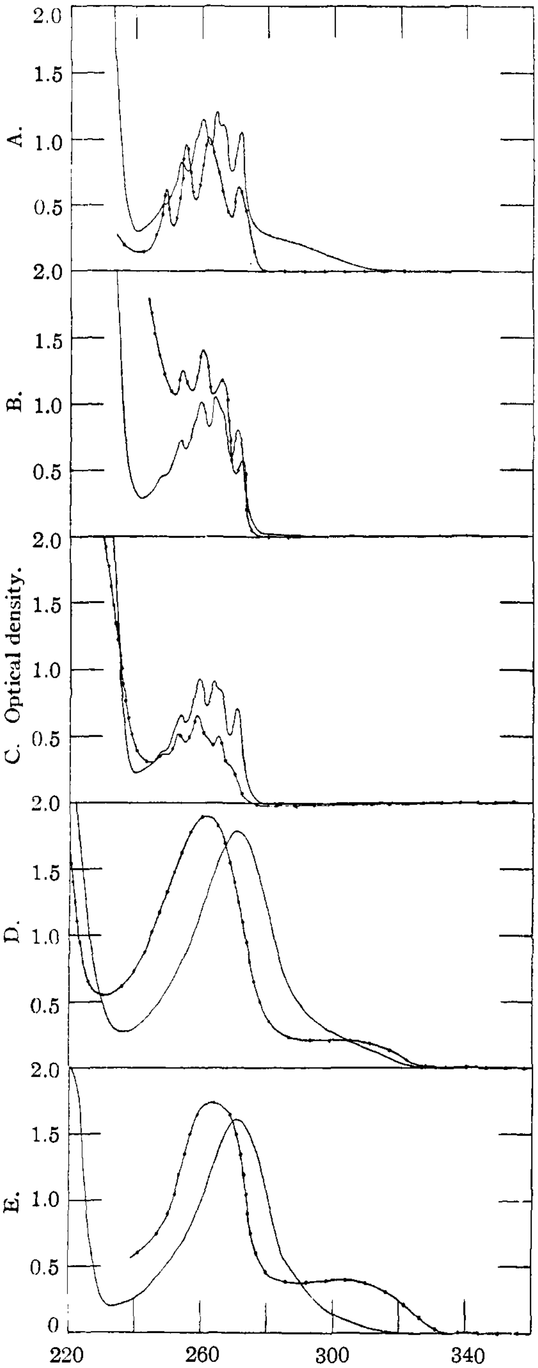

Fig. 1.—Absorption spectra in neutral absolute ethanol: A, — triphenylsilane 1 × 10^{-3} *M;* —·—·— triphenylmethane, adapted from the data of Anderson, THIS JOURNAL, 50, 208 (1928). B, — triphenylethoxysilane 1 × 10^{-3} *M;* —·—·— triphenylethoxymethane, adapted from the data of Anderson, *loc. cit.* C, — triphenylsilanol 1 × 10^{-3} *M;* —·—·— triphenylcarbinol, 1 × 10^{-3} *M.* D, — diphenyl-*p*-dimethylaminophenylsilanol 1 × 10^{-4} *M;* —·—·— diphenyl-*p*-dimethylaminophenylcarbinol 1 × 10^{-4} *M.* E, — tris-(*p*-dimethylaminophenyl)-silanol 1 × 10^{-5} *M;* —·—·— tris-(*p*-dimethylaminophenyl)-carbinol, adapted from the data of Heertjes, Kerkhof and de Vries, *Rec. trav. chim.*, 62, 745 (1943), determined in ether.

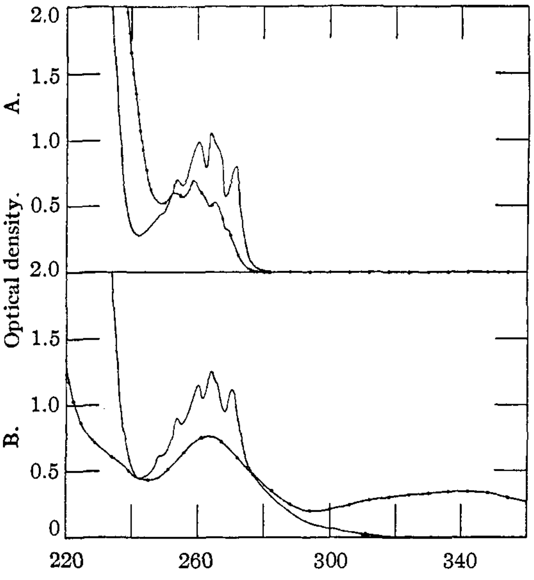

Fig. 2.—Absorption spectra in 3 × 10^{-3} *M* hydrogen chloride in absolute ethanol, all solutes 1 × 10^{-3} *M:* A, — triphenylsilanol; —·—·— triphenylcarbinol; B, — diphenyl-*p*-dimethylaminophenylsilanol; —·—·— diphenyl-*p*-dimethylaminophenylcarbinol.

cited states as has the silanol. It is possible that the energy difference between ground and excited states is the same in the silanols as in the corresponding triaryl-silicon cations (siliconium ions). However, the very close agreement of the curves for the *p*-dimethylaminophenylsilanols in acid solution with that for triphenylsilanol in neutral solution suggests very strongly that the silanol is the species concerned in both cases. An obvious conclusion, then, is that the formation of triaryl-silicon cations is much more difficult than the formation of the corresponding carbon cations.

In view of the fact that silicon is a more electropositive element than carbon (silicon 1.8, carbon 2.5 on Pauling's scale of electronegativities), this is an interesting result. Due to this more positive character of silicon and by analogy with reactions in the corresponding carbon compounds, there has been some tendency to formulate the mechanism of certain displacement reactions on silicon as follows.[4]

$$R_3SiX \rightleftarrows R_3Si^+ + X^-$$

$$R_3Si^+ + Y^- \longrightarrow R_3SiY$$

However, recent work suggests that such mechanisms should be accepted with reservations, and that reactions involving pentacovalent silicon

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[4] Whitmore, *Chem. Eng. News*, 26, 672 (1948); Whitmore, Sommer, Gold, and Van Strien, THIS JOURNAL, 69, 1551 (1947).

intermediates are more probable.[5]

$$R_3SiX + Y^- \rightleftarrows \left[R_3Si\begin{matrix} X \\ Y \end{matrix}\right]^-$$

$$\left[R_3Si\begin{matrix} X \\ Y \end{matrix}\right]^- \longrightarrow R_3SiY + X^-$$

Explanations of the preference of silicon compounds for the latter mechanism have emphasized the ease with which the silicon atom can expand its valence shell of electrons, as compared with carbon. Our results indicate that this difference in ability to assume a pentacovalent state is not the only factor favoring the latter mechanism. In addition, the difficulty of formation of silicon cations as compared with carbon cations must be considered.

Among the factors contributing to the difficulty of formation of triaryl-silicon cations, two possibilities suggest themselves at once. The first is a steric consideration. In silanols the aryl groups are at greater distances from the oxygen atom and from each other than in the carbinols. Thus electrostatic repulsions and strains may be much diminished in the silanols as compared with the carbinols. The second possibility concerns resonance stabilization of the cations. Resonance structures which tend to stabilize the triaryl-carbon cations have been illustrated above. Similar structures for triaryl-silicon cations must involve silicon to carbon double bonds. Since such bonds have never been identified in any compound, it is reasonable to suppose that there will be less resonance stabilization of silicon cations than of the corresponding carbon cations.[6]

TABLE I

ABSORPTION MAXIMA FOR SILANOLS AND CARBINOLS IN NEUTRAL ABSOLUTE ETHANOL

Compound	$\lambda_{max.}$, mμ					
Triphenylsilane	248	254	260	264	266	271
Triphenylmethane[a]	249	255	262			271
Triphenylethoxysilane	248	254	260	264	266	271
Triphenylethoxy-methane[a]		254	260		266	272
Triphenylsilanol	248	253	259	264	266	270
Triphenylcarbinol	249	253	259	265		269
Diphenyl-*p*-dimethyl-aminophenylsilanol						270
Diphenyl-*p*-dimethyl-aminophenylcarbinol			261			304
Tris-(*p*-dimethylaminophenyl)-silanol						272
Tris-(*p*-dimethylaminophenyl)-carbinol[b]				264		300

[a] Anderson, THIS JOURNAL, **50**, 208 (1928). [b] Heertjes, Kerkhof and de Vries, *Rec. trav. chim.*, **62**, 745 (1943), determined in ether.

TABLE II

ABSORPTION MAXIMA FOR SILANOLS AND CARBINOLS IN ALCOHOLIC HYDROGEN CHLORIDE

Compound	$\lambda_{max.}$, mμ						
Triphenylsilanol[a]	249	254	260	264	266	271	
Triphenylcarbinol[a]	249	253	259	265		269	
Diphenyl-*p*-dimethylamino-phenylsilanol[a]	248	254	260	264	266	271	
Diphenyl-*p*-dimethylamino-phenylcarbinol[a]				263		345	460
Tris-(*p*-dimethylaminophenyl)-silanol[b]	249	256	261	265	267	272	
Tris-(*p*-dimethylaminophenyl)-carbinol[c]				262		319	441

[a] Three moles of hydrogen chloride per mole of silanol or carbinol. [b] Thirty-three moles of hydrogen chloride per mole of silanol. [c] In concd. hydrochloric acid, Heertjes, Kerkhof and de Vries, *Rec. trav. chim.*, 62, 745 (1943).

Experimental

All measurements were made on a Cary Recording Spectrophotometer Model 12, using 1-cm. quartz cells and commercial absolute ethanol as the solvent. Materials used for spectrophotometric measurements were purified by crystallization to constant melting point from at least two solvents. The preparation of diphenyl-*p*-dimethylaminophenylsilanol and tris-(*p*-dimethylaminophenyl)-silanol as well as several other *p*-dimethylaminophenylsilicon compounds will be reported in a subsequent paper.

Diphenyl-*p*-dimethylaminophenylcarbinol.—To 0.045 mole of *p*-dimethylaminophenyllithium in 100 ml. of ether under nitrogen was added 7.4 g. (0.026 mole) of benzophenone in 50 ml. of ether at such a rate as to maintain mild reflux. When spontaneous reflux had stopped the solution was heated to refluxing temperature for another half-hour. The mixture was then hydrolyzed with water, and the ether layer separated and dried. On removal of the ether a brown liquid remained which was taken up in hot petroleum ether (b. p. 90–120°). On cooling to about 60° a brown oil separated. The mother liquor was decanted and on cooling to room temperature deposited a sticky brown solid. This process was repeated three times until the solid had become colorless and crystalline, melting at 86–86.5° and weighing 0.8 g. (10% yield). This was identified as diphenyl-*p*-dimethylaminophenylcarbinol by mixed melting point determination with an authentic specimen.[7]

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Summary

1. Ultraviolet absorption spectra have been determined for several organosilicon compounds.

2. No shift has been found in the absorption maxima of the *p*-dimethylaminophenylsilanols on passing from neutral to acid solution.

3. It is suggested that the lack of a shift in the absorption maxima of the silanols is due to a greater difficulty in the formation of triaryl-silicon cations as compared with triaryl-carbon cations.

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(5) Swain, Esteve and Jones, THIS JOURNAL, **71**, 965 (1949); Price, *ibid.*, **69**, 2600 (1947).

(6) See also Roberts, McElhill and Armstrong, *ibid.*, **71**, 2923 (1949).

(7) This sample was very kindly supplied by Prof. P. M. Heertjes of Delft, Holland.