Q. **From 2-Heptanone (2) and Triphenylmethyllithium.**—To a solution containing triphenylmethyllithium (prepared from triphenylmethane and phenyllithium as previously described) in a mixture of 14 ml. of 1,2-dimethoxyethane and 6 ml. of ether was added 500.9 mg. of the ketone **2** which discharged the red color of the triphenylmethyl anion. Aliquots (5 ml.) were removed and quenched in deuterioacetic acid–deuterium oxide mixtures after time periods of *ca.* 30 sec. and 1 hr. In each case the recovered ketone samples contained 4% d_0, 95% d_1, and 1% d_2 species with a deuterium distribution in the monodeuterated ketone of 12% n-BuCHDCOCH$_3$ and 88% of n-BuCH$_2$COCH$_2$D. The 10 ml. of enolate solution remaining from the quenching experiments was added, dropwise and with stirring, to 18 g. (0.13 mole) of methyl iodide. The resulting mixture was stirred for 2 hr., allowed to stand overnight, diluted with water, extracted with pentane, and analyzed[27] (see Table VIII).

Although both the constancy of the composition of the enolate mixture and the formation of dialkylated products with excess methyl iodide indicated that these lithium enolates were equilibrating in the reaction medium, it seemed advisable to verify this point. Accordingly, a solution of triphenylmethyllithium in 7 ml. of 1,2-dimethoxyethane and 3 ml. of ether was treated with a mixture of 182.3 mg. (1.60 mmoles) of the ketone **2** and 76.6 mg. (0.64 mmole) of 2-hepanone-d_5 (composition 88% d_5, 10% d_4, 1% d_3) which served to discharge the red color of the triphenylmethyl anion. Aliquots (5 ml.) were removed and quenched in aqueous acetic acid after time periods of 30 min. and 60 min. The ketone sample recovered from the first quenching experiment (after 30 min.) contained 53% d_0, 11% d_1, 5% d_2, 13% d_3, 16% d_4, and 2% d_5 species. The ketone from the second quenching experiment (after 60 min.) contained 56% d_0, 18% d_1, 10% d_2, 8% d_3, 7% d_4, and 1% d_5. Thus, equilibration of the lithium enolates, although slower than equilibration of the potassium enolates, is clearly occurring in 1,2-dimethoxyethane solution at room temperature and appears to be nearly complete after 60 min.

Dialkoxyphthalocyaninosilicon Derivatives[1a]

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The preparations and reactions of a series of dialkoxyphthalocyaninosilicon complexes are described. The results obtained suggest that siliconium ions may be intermediates in some of the reactions discussed.

A variety of silicon phthalocyanines with groups oxygenbridged to the silicon have been described previously.[2–6] However the only representative of the dialkoxy series reported up to now has been the incompletely characterized but useful intermediate, bis(benzyloxy)phthalocyaninosilicon, PcSi(OCH$_2$C$_6$H$_5$)$_2$.[1b]

The series of dialkoxides described in this paper, together with the silicon phthalocyanines previously described, serve to illustrate the way in which the properties of ring unsubstituted trivalent and tetravalent metal phthalocyanines vary with the nature of the groups attached to the metal. Thus, for example, (PcSiO)$_x$ is thermally stable and insoluble in organic solvents,[2] PcSiF$_2$ is chemically inert,[7] PcSi(OH)$_2$ is chemically reactive,[2–5] and PcSi(OC$_{18}$H$_{37}$)$_2$ is benzene soluble. Ordinary melting point behavior is shown both by PcSi[OSi(C$_6$H$_5$)$_2$(CH$_3$)]$_2$, an interesting species recently reported by Weyenberg and Cekada,[6] and by PcSi(OC$_{18}$H$_{37}$)$_2$.

In all these cases the properties can be accounted for in terms of the nature of the side chain or group and the properties of the macrocyclic ring. Thus, to take the case of the dialkoxides in more detail, in the series PcSi(OC$_2$H$_5$)$_2$, PcSi(OC$_8$H$_{17}$)$_2$, and PcSi(OC$_{18}$H$_{37}$)$_2$ the increase in solubility is attributable to the decrease in molecular symmetry and the increase in molecular flexibility as the side chains are lengthened. Similarly accounted for is the fact that PcSi(OC$_2$H$_5$)$_2$ does not melt up to 360° in a vacuum, PcSi(OC$_8$H$_{17}$)$_2$ melts with decomposition at 260°, and PcSi(OC$_{18}$H$_{37}$)$_2$ melts at 152° without decomposition. In the same vein the changes of infrared spectra due to the presence of the side chains are as expected. For example, bands are shown which are characteristic of C–Cl in PcSi(OCH$_2$CCl$_3$)$_2$ at 842 cm.$^{-1}$, of monsubstituted benzene in PcSi(OCH$_2$C$_6$H$_5$)$_2$ at 696 cm.$^{-1}$, of aliphatic C–H in PcSi(OC$_5$H$_{11}$)$_2$ at 2946, 2898, 2860, 1473, and 1393 cm.$^{-1}$, in PcSi(OC$_8$H$_{17}$)$_2$ at 2926, 2854, 1466, and 1383 cm.$^{-1}$, and in PcSi(OC$_{18}$H$_{37}$)$_2$ at 2922, 2848, 1468, and 1385 cm.$^{-1}$.

Some properties of the dialkoxides, and in fact of the silicon phthalocyanines in general, which are properties of the macrocycle are little influenced by changes in the nature of the side groups. Thus the infrared absorptions attibutable to the macrocycle in the 1150–650-cm.$^{-1}$ range remain essentially unchanged[8] and the compounds all retain the characteristic blue to green color by transmitted light. The degree of constancy of the visible spectra of the dialkoxides is shown by the fact that the strongest band in benzene solutions is at 679 mμ in PcSi(OCH$_2$CCl$_3$)$_2$, 673 mμ in PcSi(OC$_5$H$_{11}$)$_2$, 674 mμ in PcSi(OC$_8$H$_{17}$)$_2$, and 674 mμ in PcSi(OC$_{18}$H$_{37}$)$_2$.[8] The slight blue shift for the band in PcSi(OCH$_2$CCl$_3$)$_2$ is probably due to the electron-withdrawing power of the side groups making the π–π^* transition in the ring more difficult.

It is evident that enough information is available about the characteristics imparted by various sorts of groups on the metal and the methods for attaching them to the metal so that ring unsubstituted phthalocyanines with specified physical and chemical properties can now be made on a rational basis.

In earlier work it was found that PcSi(OH)$_2$ condenses with itself,[2] and with PcAlOH·H$_2$O,[5] (C$_6$H$_5$)$_3$SiOH,[3] C$_6$H$_5$OH,[4] and C$_6$H$_5$CH$_2$OH.[3] Now it has been found that it condenses with simple aliphatic alcohols as well. These findings lead to the conclusion that the reaction

$$\mathrm{PcSi(OH)_2 + 2HOR \longrightarrow PcSi(OR)_2 + 2H_2O}$$

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[1] (a) This paper is based on the Ph.D. thesis of P. C. K., University Microfilms. The work was made possible by the National Science Foundation Grant NSF-G15833; (b) Pc = phthalocyanino ligand.

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[7] P. C. Krueger, Ph.D. thesis, University Microfilms, p. 13.

[8] Reproductions of the spectra are given in ref. 7, p. 105.

is quite generally applicable. Factors influencing the reaction are the acidity of the HOR reactant, the strength of the SiOR link formed, the insolubility of $PcSi(OH)_2$ in organic solvents, and the reaction temperature. Thus it was found that, while the relatively acidic trichloroethanol (b.p. 152°) reacted with $PcSi(OH)_2$ at reflux, a tetrahydronaphthalene solution of ethyl alcohol refluxing at 145–169° did not react. The importance of the strength of the SiOR link formed is implied by the reaction of $PcSi(OCH_2C_6H_5)_2$ in refluxing benzyl alcohol with triphenylsilanol to yield the siloxide.[3]

Several different kinds of phthalocyaninosilicon intermediates or transition states can be suggested for the reactions in which the *trans*-OH groups of $PcSi(OH)_2$ are exchanged for RO, PhO (fusion),[4] Ph_3SiO (fusion),[3] PcSiO,[2] and F (49% HF at 100°[7]). The plausible intermediates or transition states include free radicals, seven coordinate silicon species, siloxide anions (in the case of oxygen-bridged products), and siliconium ions. Free radicals seem unlikely for most of the reactions, although it is possible that they may occur in, for example, the condensation of $PcSi(OH)_2$ with itself in refluxing 1-chloronaphthalene. Seven coordinate silicon species also seem unlikely because of the difficulty in getting the silicon atom in a position which will allow it to associate with seven atoms [even though the tris(acetylacetonato)silicon(IV) cation, $Si(acac)_3^+$, has been reported to react by an S_N2 mechanism[9]]. Certainly the fact that the silicon is not removed from the ring by many chemical treatments including treatment with concentrated sulfuric acid shows that the four planar Si–N bonds are not easily deformed and such a deformation is surely required for the formation of seven coordinate intermediates. Siloxide anions, *i.e.*, $PcSi(OH)O^-$, are improbable because $PcSi(OH)_2$ apparently forms no stable sodium silanolate, and because $PcSi(OH)_2$ reacts with benzyl alcohol but not benzyl chloride in spite of the fact that OH^- is a poorer leaving group than Cl^-. The results of the neopentyl alcohol condensation show that neopentyl carbonium ions are not involved since, if they were, rearrangement would be expected. Accordingly on the basis of the available evidence it is concluded that siliconium ions are the most likely intermediates; *i.e.*, in the case of ROH

$$HO(Pc)SiOH \xrightarrow{ROH} HO(Pc)SiOH_2^+ \xrightarrow{-H_2O} HO(Pc)Si^+ \xrightarrow{RO^-} HO(Pc)SiOR$$

The fact that acidity of the ROH apparently is important and that the silicon probably can delocalize its positive charge into the ring by the use of its $3d_{xz}$- and $3d_{yz}$- orbitals[10] also fits with this hypothesis. Certainly positive silicon ions exist in the octahedral $Si(acac)_3^+$ series.

The easy hydrolysis of the dialkoxides by hot hydrochloric acid but not by refluxing 2 *M* sodium hydroxide suggests that in the acid hydrolyses protonation of the bridge oxygen is a preliminary step, and that the weakened bridge subsequently breaks easily.

The route by which $PcSi(OC_2H_5)_2$ is formed in the reaction of ethanol $PcSiCl_2$, and $NaBH_4$ has not been studied, but the possibility that $PcSiH_2$ is an intermediate does not seem unreasonable because neither $PcSiCl_2$ nor $PcSi(OH)_2$ react with refluxing absolute alcohol.

Experimental

Bis(ethoxy)phthalocyaninosilicon, $PcSi(OC_2H_5)_2$.—This compound was best prepared by the reaction of $PcSiCl_2$ with $NaBH_4$ and ethanol. A mixture of 0.51 g. of powdered $PcSiCl_2$, 1.6 g. of $NaBH_4$, and 50 ml. of absolute ethanol was refluxed for 1 hr., cooled, diluted with 40 ml. of water, and filtered. The product weighed 0.45 g. Recrystallization of 0.44 g. of it from 150 ml. of benzene and 150 ml. of absolute ethanol yielded 0.16 g. of an undissolved residue of $PcSi(OC_2H_5)_2$ and $PcSi(OH)_2$ and 0.096 g. of crystalline product.

Anal. Calcd. for $C_{36}H_{26}N_8SiO_2$: C, 68.55; H, 4.15; Si, 4.45. Found: C, 68.46; H, 4.38; Si, 4.69.

$PcSi(OC_2H_5)_2$ also was prepared from $PcSi(OCH_2C_6H_5)_2$, $NaBH_4$, and ethanol. A mixture of 0.50 g. of powdered $PcSi(OCH_2C_6H_5)_2$ (crystalline samples did not react), 1.25 g. of $NaBH_4$, and 50 ml. of absolute ethanol was refluxed for 1 hr. The 0.39 g. of product was identified by means of infrared spectra as $PcSi(OC_2H_5)_2$, containing some unchanged $PcSi(OCH_2C_6H_5)_2$.

The diethoxide also was prepared by a third route utilizing the direct condensation of $PcSi(OH)_2$ and ethanol. A suspension of 0.13 g. of $PcSi(OH)_2$ in 30 ml. of 1-chloronaphthalene and 1 ml. of ethanol was heated at reflux (179–188°) for 3.5 hr., filtered, cooled, refiltered, cooled to −20° for 3 hr., and allowed to stand 1 week. This yielded 0.036 g. of $PcSi(OC_2H_5)_2$.

Bis(2,2,2-trichloroethoxy)phthalocyaninosilicon, $PcSi(OCH_2CCl_3)_2$.—A 0.54-g. sample of $PcSi(OH)_2$ was suspended in 9.0 ml. of trichloroethanol and the mixture refluxed for 2 hr., cooled, diluted with 20 ml. of ether, and filtered. Recrystallization of the product (0.77 g.) from 15 ml. of 1-chloronaphthalene and 2 ml. of trichloroethanol yielded 0.19 g. of crystals.

Anal. Calcd. for $C_{36}H_{20}N_8SiO_2Cl_6$: C, 51.64; H, 2.41; Si, 3.35; Cl, 25.40. Found: C, 51.89; H, 2.53; Si, 3.39; Cl, 25.11.

Attempted recrystallization of this complex from 1-chloronaphthalene failed due to decomposition.

Bis(amyloxy)phthalocyaninosilicon, $PcSi(OC_5H_{11})_2$.—A mixture of 0.40 g. of $PcSi(OH)_2$, 2.5 g. of neopentyl alcohol, and 40 ml. of 1,2,3,4-tetrahydronaphthalene was refluxed (170–185°) for 2 hr. and cooled. Out of the 0.37 g. of product a 0.20-g. portion was recrystallized from 20 ml. of tetrahydronaphthalene containing 0.5 g. of neopentyl alcohol with a yield of 0.18 g.

Anal. Calcd. for $C_{42}H_{38}N_8SiO_2$: C, 70.56; H, 5.36; Si, 3.93. Found; C, 70.53; H, 5.64; Si, 4.11.

A comparison of the infrared spectra of $PcSi(OC_5H_{11})_2$, neopentyl alcohol, and *t*-amyl alcohol in both the 2900 and 1375-cm.$^{-1}$ regions was made. Although the study of the 1375-cm.$^{-1}$ region was hampered by the presence of a phthalocyanino band, the spectra indicated that the product was the neopentyl derivative.

Attempts were made to synthesize the *t*-amyl derivative by treating $PcSi(OH)_2$ with *t*-amyl alcohol in tetrahydronaphthalene and in 1-chloronaphthalene. The conditions of these experiments were similar to those used in the condensations of $PcSi(OH)_2$ with neopentyl alcohol but no dialkoxide was obtained.

Bis(benzyloxy)phthalocyaninosilicon, $PcSi(OCH_2C_6H_5)_2$.—A mixture of 0.80 g. of $PcSi(OH)_2$ and 80 ml. of freshly distilled benzyl alcohol was refluxed for 15 min., filtered through a heated funnel, cooled, and refiltered. A 0.32-g. portion of the crystalline product was recrystallized from 50 ml. of freshly distilled benzyl alcohol using a 15-min. reflux. This gave a yield of 0.23 g.

Anal. Calcd. for $C_{46}H_{30}N_8SiO_2$: C, 73.19; H, 4.01; Si, 3.72. Found: C, 73.37; H, 4.24; Si, 3.88.

Reaction of benzyl alcohol with $PcSi(OH)_2$ for 5 hr. at reflux gave a product with an infrared spectrum different from that of $PcSi(OCH_2C_6H_5)_2$. This result may have been caused by attack on phthalocyanino rings by the benzyl alcohol or by thermal decomposition of the dialkoxide.

Bis(1-octyloxy)phthalocyaninosilicon, $PcSi(OC_8H_{17})_2$.—A mixture of 10 ml. of 1-octanol and 0.50 g. of $PcSi(OH)_2$ was refluxed for 1 hr., filtered, and cooled. The product was crystalline and weighed 0.59 g. A 0.20-g. portion was recrystallized from 10 ml. of benzene yielding 0.04 g. of undissolved $PcSi(OC_8H_{17})_2$ and 0.13 g. of product.

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Anal. Calcd. for $C_{48}H_{50}N_8SiO_2$: C, 72.14; H, 6.31; Si, 3.52. Found: C, 72.38; H, 6.59; Si, 3.79.

Bis(1-octyloxy)phthalocyaninosilicon, $PcSi(OC_8H_{17})_2$, was put on a melting point block (Fisher-Johns) at 200° and then heated slowly. At 260° a green liquid phase appeared but upon continued heating the liquid turned violet and became solid. Infrared spectra indicated that this product contained $(PcSiO)_x$ and $PcSi(OC_{18}H_{37})_2$.

Bis(1-octadecyloxy)phthalocyaninosilicon, $PcSi(OC_{18}H_{37})_2$.—A mixture of 0.40 g. of $PcSi(OH)_2$, 5.6 g. of 1-octadecanol, and 40 ml. of tetrahydronaphthalene was refluxed for 1 hr., filtered, cooled to −20° for 1 hr., allowed to stand at room temperature for 0.5 hr., and diluted with 20 ml. of ether and 10 ml. of ethanol. This gave 0.57 g. of product. A 9.0-ml. portion of benzene was used to recrystallize 0.28 g. yielding almost no residue and 0.25 g.

Anal. Calcd. for $C_{68}H_{90}N_8SiO_2$: C, 75.65; H, 8.40; Si, 2.60. Found: C, 75.66; H, 8.84; Si, 2.80.

It melted at 152–153° in a sealed tube without decomposition.

Properties.—The dialkoxides were treated with hot hydrochloric acid to determine their acid stability. All but the trichlorethanol derivative were subjected to concentrated hydrochloric acid on a steam bath while it was refluxed with 6 *N* hydrochloric acid. In each case $PcSi(OH)_2$ was obtained as the product. The stability of the dialkoxides to the action of base was measured by refluxing them with 2 *M* sodium hydroxide. Only $PcSi(OC_2H_5)_2$ was hydrolyzed and it was hydrolyzed only to a small extent. $PcSi(OCH_2C_6H_5)_2$ and $PcSi(OCH_2CCl_3)_2$ also were not hydrolyzed by refluxing alcoholic sodium hydroxide. The fact that neither $PcSi(OC_2H_5)_2$ nor $PcSi(OCH_2C_6H_5)_2$ could be satisfactorily vacuum sublimed because of decomposition shows the relatively low thermal stability of these dialkoxides.

Spectra.—The maxima in the visible range obtained from benzene solutions containing 2 to 4×10^{-6} g./ml. were $PcSi(OCH_2CCl_3)_2$, 612, 650, 679; $PcSi(OC_5H_{11})_2$, 606, 643, 673; $PcSi(OC_8H_{17})_2$, 606, 645, 674; $PcSi(OC_{18}H_{37})_2$, 606, 644, 674 mμ. In all cases the 680-mμ band was strongest.[8]

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A Re-examination of the Reaction of Certain α-Acyloxy Ketones with Ammonium Acetate, Their Conversion to the Oxazoles, and Imidazoles, and the Identification of Intermediate Products

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The reaction of four α-acyloxy ketones with ammonium acetate has been reinvestigated, the resulting oxazoles and imidazoles characterized, and the identity of an intermediate product established in two cases.

The formation and reactions of substituted oxazoles from α-acyloxy ketones have been studied by several authors.[1–3] The mechanism of their formation, together with the corresponding imidazoles by the interaction of such esters with ammonium acetate, was formulated as follows by Davidson, Weiss, and Jelling,[1] the proportion of IV and V formed varying from case to case.

Although compounds of the type II have not been isolated in such reactions, Theilig[4] suggested that they might be intermediates in the formation of oxazoles from enediol esters by reaction with ammonium acetate. It also has been shown that amides of the type III are converted to the imidazole IV by the action of ammonium acetate,[5] and to the oxazole V by phosphorus pentachloride,[6] sulfuric acid,[7] thionyl chloride,[8] and polyphosphoric acid.

Aldous, *et al.*,[2] prepared ethyl 2,4-diphenylimidazole-5-carboxylate (IVa) from ethyl α-benzoyloxybenzoylacetate (Ia) and claimed to have converted it into 2,4-diphenyloxazole-5-carboxylic acid (Vb) by refluxing with potassium hydroxide. Whereas oxazoles may be converted into imidazoles, for example by the action of formamide,[4] the reverse conversion involved in the procedure referred to has not been reported. As the oxazole referred to was required for another investigation, the procedure mentioned was repeated. Although Aldous, *et al.*, reported the formation of only imidazole IVa by the action of ammonium acetate on Ia, we obtained in addition the oxazole ethyl 2,4-diphenyloxazole-5-carboxylate (Va). Hydrolysis of the compounds IVa and Va gave the corresponding carboxylic acids IVb and Vb, respectively. Hence the reaction with potassium hydroxide merely hydrolyzed the ester group without further change to the heterocyclic structure.

These authors also prepared a number of 4-phenyl-5-methyl-2-substituted oxazoles from the corresponding esters. In three cases they reported the formation in addition of a substituted amide in the preparation of these oxazoles in which the substituent in the 2-position was phenyl, 6-quinolyl, and 2,6-dipyridyl. To these by-products they assigned the structure VI in which R″ was one of the three radicals mentioned. This is, therefore, the first case of the isolation of an intermediate compound in the preparation of oxazoles from α-acyloxy ketones. Aldous, *et al.*, did not report the formation of an imidazole during the preparation of these oxazoles, whereas we have isolated these compounds in the examples studied.

As the amides VIa and VIb are different from, but isomeric with, the postulated intermediates IIIa and IIIb it was decided to re-examine the compounds VIa and VIb. Both VIa[9] and IIIa[10,11] are known compounds and were consequently synthesized when it was found that the intermediate isolated and described by

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