

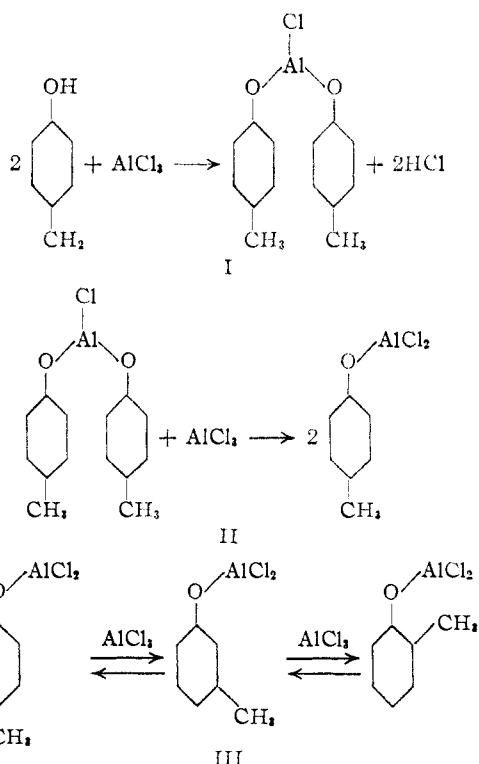
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## Isomerization of the Cresols by Aluminum Chloride<sup>1</sup>

BY H. P. MEISSNER AND F. E. FRENCH, JR.

The tolyloxyaluminum chlorides formed by the reaction of each of the three cresols with aluminum chloride undergo isomerization in the presence of excess aluminum chloride. Reaction rate data indicate the equilibrium composition of the tolyloxyaluminum chloride fraction at 134° to be 18.5 ± 2% ortho, 59.7 ± 3% meta and 21.8 ± 1% para. The same equilibrium proportions were obtained in a run on *p*-cresol at 164°, suggesting that the equilibrium constant is relatively independent of temperature.

A study has been made of the liquid phase, solvent-free isomerization of the cresols in the presence of aluminum chloride. When operating at atmospheric pressure, three stages of reaction were evident, depending upon the molar ratio of aluminum chloride to cresol. Melt viscosity was found to increase and hydrogen chloride to be evolved when up to 0.5 mole of aluminum chloride was added per mole of cresol. Further addition of aluminum chloride decreased melt viscosity with, however, no further hydrogen chloride evolution. Isomerization was observed only after more than one mole of aluminum chloride had been added per mole of cresol. These three stages presumably involved first the formation of ditolyloxyaluminum chloride, then the formation of tolyloxyaluminum chloride, and finally the isomerization of the latter under the influence of excess aluminum chloride as shown below in reactions I, II and III. The first two of these equations are written with the para-isomer, but it was found that equivalent reactions are common to all three cresols. Simultaneous with these reactions in all three states was the formation of by-products.



(1) Based in part on a thesis presented by F. E. French, Jr., in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology.

## Results

With each pure cresol isomer as starting material in turn, three runs were made at 134° with a molar ratio of aluminum chloride to cresols of 2:1. The weight percentages of the products formed at various times after the start of the operation are shown in Figs. 1, 2 and 3 on a by-product-free basis, while total products formed in these runs are shown in Figs. 4, 5 and 6. Inspection of Figs. 1, 2 and 3 shows that approximately the same final proportions are reached from each of the three isomers as starting material, namely, 60.5% meta, 21.5% para and 18% ortho from *o*-cresol in 52.3 hours; 61.2% meta, 22.1% para and 16.7% ortho from *p*-cresol in 71 hours; and 60.5% meta, 21.5% para and 18% ortho from *m*-cresol in 52.3 hours.

Conversion of cresols to by-products was apparently progressive and irreversible. By-products derived from each of the cresols showed similarities, as inspection of Figs. 4, 5 and 6 makes evident. Phenol and xylenol were formed in equimolar amounts, within experimental error, and these two by-products are therefore grouped together in all the graphs. At any time the amount of these by-products was slightly less than the amount of tar. Of the six possible xylenols, the symmetrical (1,3,5-) isomer was found to constitute more than half of the xylene fraction. Although the nature of the tar was not investigated, it is suspected that it consisted of biphenyl, diphenyl ether and diphenylmethane derivatives. Potowsky and Logowkin<sup>2</sup> report the formation of dimetatolyl ether and dimethylxanthene when aluminum chloride acts upon cresol.

It can be seen from the initial slopes of the curves that with ortho-cresol as the starting material the rate of isomerization is less and the rate of by-product formation is greater than when starting from meta and para. This difference is presumably caused by the steric hindrance to intramolecular migration of the methyl group when adjacent to the oxyaluminum chloride. As a consequence of these differences in rates, the final proportions of cresols attained on a by-product-free basis are not exactly equal to the true equilibrium values.

Experimental runs on each of the three isomers were carried out at catalyst ratios of 1.5:1. While reaction rates were substantially reduced, the data indicated that the same isomer ratios were ultimately obtained as with a catalyst ratio of 2:1.

To study effect of temperature, *p*-cresol was treated at 164° and a catalyst ratio of 1.13:1, with results shown in Fig. 7. The relatively low catalyst ratio used here was selected to keep reaction rates small enough for convenient sampling and analysis. No difference was found between the ultimate by-product-free ratios of the isomers at this temperature and at 134°, within experimental error.

When the reaction was carried out at 134° with equimolar quantities of aluminum chloride and *p*-cresol, it was found that no reaction occurred after a small initial isomerization, the latter presumably being due to temporary incomplete mixing encountered immediately after catalyst addition. Thus, more than equimolar quantities of aluminum chloride were required for the isomerization at 134°. As expected, no isomerization of *p*-cresol was detected when operating for 24 hours at 215 to 250° (the boiling range of the reaction mixture) with 0.25 mole of aluminum chloride per mole of cresol. In this run approximately 10% of the cresol was converted to tar.

By operating under substantial hydrogen chloride pressure, it should be possible to drive reaction I to the left. Thus "free" aluminum chloride for isomerization could be

(2) J. Potowsky and B. Logowkin, *J. prakt. Chem.*, [2] **122**, 141 (1929).

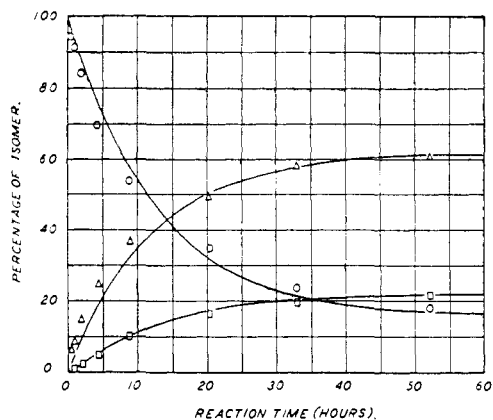


Fig. 1.—Reaction of *o*-cresol with 2 moles of aluminum chloride at 134° (by-product-free): solid line shows values calculated from equations presented in the text; the triangles represent *m*-cresol, the squares *p*-, and the circles *o*-.

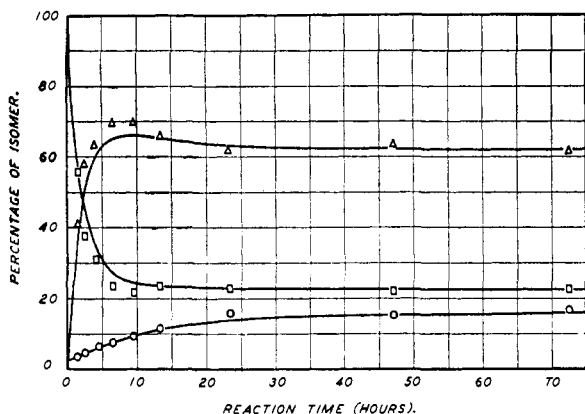


Fig. 2.—Reaction of *p*-cresol with 2 moles of aluminum chloride at 134° (by-product-free): solid line shows calculated value; the triangles represent *m*-cresol, the squares *p*-, and the circles *o*-.

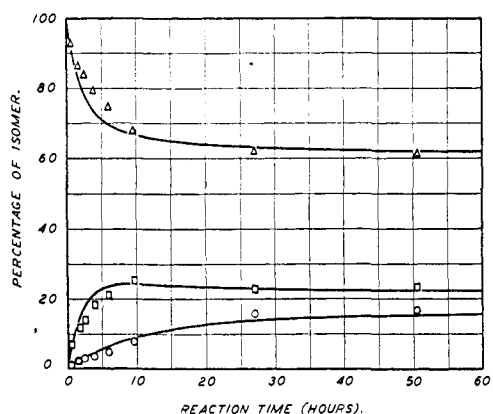


Fig. 3.—Reaction of *m*-cresol with 2 moles of aluminum chloride at 134° (by-product-free): solid line shows calculated value. The triangles represent *m*-cresol, the squares *p*-, and the circles *o*-.

provided even with molal ratios of aluminum chloride to cresol substantially below unity. This possibility was investigated by the Gesellschaft für Teerverwertung<sup>3</sup> and it was claimed that cresol could be isomerized at 400 to 500° in the presence of only small amounts of aluminum chloride

(3) German Patent 673,380, March 21, 1939.

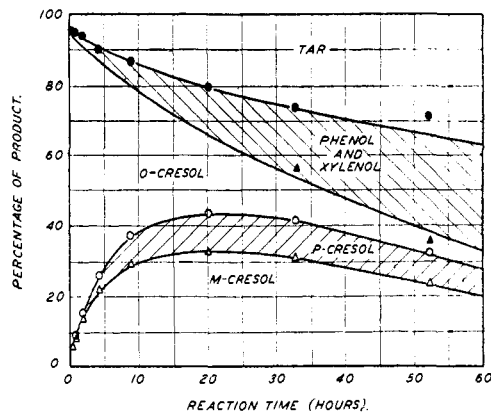


Fig. 4.—Reaction of *o*-cresol with 2 moles of aluminum chloride at 134°.

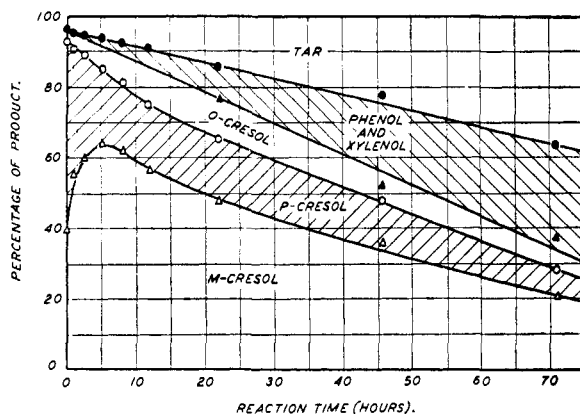


Fig. 5.—Reaction of *p*-cresol with 2 moles of aluminum chloride at 134°.

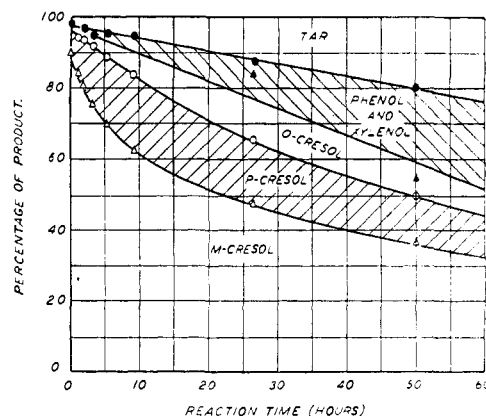


Fig. 6.—Reaction of *m*-cresol with 2 moles of aluminum chloride at 134°.

under hydrogen chloride pressure. Yields obtained were low, and by-product formation was excessive.

Operation at low aluminum chloride ratios has been further investigated at M.I.T.<sup>4</sup> and the low yields reported in the German patent have been confirmed. When one mole of *p*-cresol was heated in a rocker-type autoclave with 0.15 to 0.30 mole of aluminum chloride at temperatures of 165 to 200°, it was found that within a few hours hydrogen chloride pressure of 200 to 700 p.s.i.g. were produced. In all cases the autoclaved products contained more than 50% of tar and by-products and the useful yield of isomerized

(4) H. A. Dick and W. E. Katz, "Pressurized Catalytic Isomerization of Cresols," M.S. Thesis, Dept. of Chemical Engineering, Massachusetts Institute of Technology, 1949.

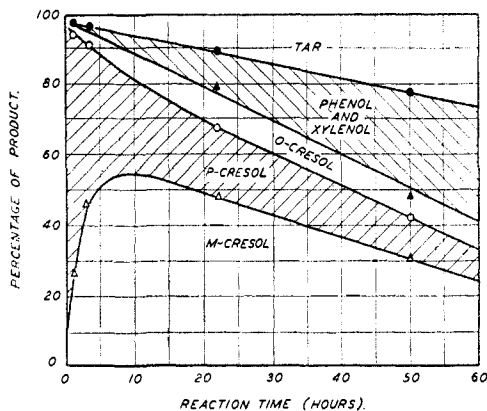


Fig. 7.—Reaction of *p*-cresol with  $1\frac{1}{8}$  moles of aluminum chloride at  $164^\circ$ .

cresols was of the order of 5 to 10% compared with the 20% of isomerized cresols claimed to be produced from *o*-cresol in the German process. Conditions have therefore not yet been found for obtaining substantial yields of isomerization products at low molar ratios of aluminum chloride to cresol.

### Discussion of Results

It was found possible to fit reaction rate equations to the data of the runs at  $134^\circ$  and a catalyst ratio of 2:1, after making the following assumptions: (1) That the six forward and reverse isomerization reactions are all of the first-order with respect to the corresponding cresol isomers. (2) That the formation of tar, phenol and xylenol can be grouped together under one constant for each isomer; that these reactions are irreversible; and that the reactions are also of the first-order with respect to cresol. (3) That the amount of free aluminum chloride remained constant throughout a run and that the reaction can be studied on an aluminum chloride-free basis.

The rate constants for the nine first-order reactions involved here were determined to be as follows (units in reciprocal hours)

Isomerization	$k_1 = \text{ortho to meta}$	$= 0.0530$
	$k_2 = \text{ortho to para}$	$= .0103$
	$k_3 = \text{meta to ortho}$	$= .0160$
	$k_4 = \text{meta to para}$	$= .0132$
	$k_5 = \text{para to ortho}$	$= .0090$
	$k_6 = \text{para to meta}$	$= .0362$
By-product formation	$k_7 = \text{ortho to by-products}$	$= .0260$
	$k_8 = \text{meta to by-products}$	$= .0090$
	$k_9 = \text{para to by-products}$	$= .0140$

These values were established by solving the following set of simultaneous equations by the method of successive approximations, using the experimental data at  $134^\circ$  and a catalyst ratio of 2:1. The letters *O*, *M*, *P* and *B* in these equations, respectively, represent the weight fractions of the ortho-, meta- and para-isomer, and of by-products present in the reaction mixture at any time,  $\theta$ .

$$\begin{aligned} -dO/d\theta &= (k_1 + k_2 + k_7)O - k_3M - k_6P \\ -dM/d\theta &= (k_3 + k_4 + k_8)M - k_1O - k_9P \\ -dP/d\theta &= (k_5 + k_6 + k_9)P - k_2O - k_4M \\ +dB/d\theta &= k_7O + k_8M + k_9P \end{aligned}$$

and  $O + M + P + B = 1$

The success with which these equations were made to fit the data can be judged from Figs. 1, 2 and 3 where the solid lines are in each case calcu-

lated from the above expressions. The close agreement with the experimental points lends some justification to the assumptions upon which these equations are based. Curves were also calculated (not presented) assuming zero- and second-order reactions, which showed much poorer agreement with the data.

Recognizing that at equilibrium (assuming no by-product formation)  $O(k_1 + k_2) = k_3M + k_6P$ , also that  $P(k_5 + k_6) = k_2O + k_4M$ , and that  $M + O + P = 1$ , the equilibrium concentrations at  $134^\circ$  calculate to  $18.5 \pm 2\%$  ortho,  $59.7 \pm 3\%$  meta and  $21.8 \pm 1\%$  para. The precision just indicated seems reasonable from consideration of the possible sources of error in analysis and in the mathematical treatment of the data. It should be emphasized that these proposed equilibrium concentrations actually apply to the isomeric tolyloxyaluminum chlorides, rather than the cresols. By way of contrast, the proportions of the cresols occurring in coal tar derived from normal high temperature coking operations are about 35% ortho, 40% meta and 25% para.

Of interest for possible commercial applications of this reaction is the conversion of *o*- and *p*-cresol to *m*-cresol. Maximum yield of meta from ortho at  $134^\circ$  with a catalyst ratio of 2:1 was 33% after 20 hours, as shown by Fig. 4. It is clear from Figs. 5 and 7 that the maximum yields of meta from para were 64% after 5 hours at  $134^\circ$  with a 2:1 catalyst ratio, and 55% after 8 hours at  $164^\circ$  with a 1.13:1 catalyst ratio. In these two para runs, it is interesting that the effect on rates of the increase in temperature was largely offset by the diminished catalyst quantity used. As a result, rates of isomerization and by-product formation were roughly the same for these two temperatures, judging by the initial slopes of the curves of Figs. 5 and 7. Since the final proportions between the cresol isomers reached after 60 hours were about the same for these two cases, it appears that the cresol proportions at equilibrium are little affected by temperature. This indicates that the enthalpy changes for the isomerization reactions are small.

The only quantitative investigation of cresol isomerization found in the literature was the work of Baddeley<sup>5</sup> who reported results with molar ratios of aluminum chloride to cresol from 1:1 to 2:1 and at various temperatures near  $150^\circ$ . These results definitely established the fact that *m*- and *p*-cresol do isomerize and gave an indication of the reaction rate. The equilibrium mixture was reported to contain 61% meta—a figure which agrees very well with the value of  $59.7 \pm 3.0\%$  reported in this paper. A final conclusion Baddeley presented was that the ortho-isomer neither isomerizes nor forms in the isomerization of the other two isomers. However, a bromination procedure was used for analysis whose adequacy is open to question because it does not distinguish between *o*- and *p*-cresols, and moreover is subject to further error if by-products are not completely removed.

### Experimental Details

Reactions were carried out in a 5-liter three-neck flask equipped with condenser, stirrer and thermostatically con-

(5) G. Baddeley, *J. Chem. Soc.*, 527 (1943).

trolled Glas-Col mantle. Commercial "98% plus" cresols were used and showed the following impurities by infrared analysis: *ortho*, 0.3% each of *para* and *meta*; *meta*, no *ortho* but 0.6% *para*; *para*, no *meta* but 2.3% *ortho*. The aluminum chloride used was commercial fine grind, 98% pure.

In all runs, 1440 g. of cresol was charged to the flask, and aluminum chloride added slowly after heating to 175°, which is the lowest temperature at which the reaction mass does not solidify when the molal ratio of aluminum chloride to cresol reaches 0.5. Aluminum chloride additions were stopped just short of a ratio of 1:1 at which point solidification temperature had dropped below 125°. The flask temperature was now adjusted so that addition of the remaining catalyst caused a drop to the desired operating temperature, which was then maintained to within  $\pm 3/4^\circ$ .

Substantially no tar formation (below 3%) or isomerization occurred until this final catalyst addition, which was taken as zero time. The reaction mixture was in all cases a homogeneous solution throughout the run, although it became more viscous and deeper black in color with time.

Samples of about 200 ml. were taken at intervals and poured directly onto about 2 kg. of cracked ice, to which enough hydrochloric acid had been added to keep the aluminum chloride in solution (about 400 ml. for a catalyst-cresol ratio of 2). The cresol layer was decanted, washed successively with two 100-ml. portions of water, and the washings added to the aqueous layer, which was then extracted with two 250-ml. portions of ethyl ether. The ether was next distilled off and the recovered cresol combined with the original cresol layer.

The water remaining in the cresol was separated in a simple distillation and the tar determined by continuing the distillation until the residue boiled over 230°. The principal part of the residual tar had a b.p. over 275° at normal pressure. Although the nature of this tar was not investigated, it appeared smooth and homogeneous and was almost completely soluble in acetone.

After drying over "Drierite" the cresol fraction was separated from phenol and xylenols by fractional distillation in a 90-cm. by 5-mm. i.d. Widmer spiral column using 50:1 reflux ratio.

**Infrared Analysis of Cresols.**—Since the cresols have strong, well-separated absorption bands in the infrared

region, infrared spectroscopy can be used for analysis if care is taken to remove phenol and the xylenols which have interfering bands.<sup>6</sup> Three grams of the cresol fraction were dissolved in 100 ml. of cyclohexane and part of this solution used to fill a sodium chloride cell with 0.1-mm. absorption path. The Beckman IR-2 spectroscope gave good results at this concentration when a slit width of 1.6 mm. was used. Since completion of this work two articles describing the infrared analytical procedure have appeared in the literature.<sup>7,8</sup>

To obtain standard samples the cresols were purified—*ortho* by careful fractional distillation, in the column previously described, to a b.p. of 190.8; and *m*- and *p*-cresols by fractional crystallization from a melt until their melting points were 11.6 and 35.2°, respectively. Using these samples a calibration chart of net optical density as a function of concentration was prepared at each of three absorption maxima: *ortho*, 750  $\text{cm}^{-1}$ ; *meta*, 774  $\text{cm}^{-1}$ ; and *para*, 815  $\text{cm}^{-1}$ . The optical densities obtained for the pure cresols at these frequencies and at 3 g. per 100 ml. were: *ortho*, 0.641; *meta*, 0.334; and *para*, 0.367. Using these calibration curves as standards the accuracy obtained on known samples of the cresols was about 0.5%. Samples from the experimental runs contained small amounts of homologous impurities which reduced the accuracy to 1%.

**Acknowledgment.**—We wish to express our appreciation to the Standard Oil Company of California and the California Research Corporation for the fellowship grant to the junior author under which this study was carried out. The infrared analyses were carried out in the M.I.T. Spectroscopy Laboratories through the courtesy of Professor Richard C. Lord.

(6) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

(7) R. A. Friedel, L. Pierce and J. J. McGovern, *Anal. Chem.*, **22**, 418 (1950).

(8) O. E. Knapp, H. S. Moe and R. B. Bernstein, *ibid.*, **22**, 1408 (1950).

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 6, 1951

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP ON TECHNICAL GLASSWARE MAINTAINED AT MELLON INSTITUTE BY THE CORNING GLASS WORKS, CORNING, N. Y., IN COÖPERATION WITH THE DOW CORNING CORPORATION]

## The Preparation and Properties of (Hydroxyorgano)-silanes and Related Compounds

By JOHN L. SPEIER

Certain halophenols were treated with chlorosilanes to form (halophenoxy)-silanes. Silylphenoxysilanes were prepared in good yields from (halophenoxy)-silanes, chlorosilanes and sodium or potassium metal. Hydrolysis of silylphenoxysilanes is described as leading to various silylphenols or, in some cases, complex cleavage products. Chlorohydrins were treated with chlorosilanes to form chloroalkoxysilanes, which reacted with sodium, lithium or magnesium and a chlorosilane to prepare silylalkoxysilanes. In the absence of a chlorosilane, silylalkanols were formed. These were also prepared by hydrolysis of the silylalkoxysilanes. An apparent rearrangement during the reaction of halophenoxy-silanes with a chlorosilane and sodium is described and a hypothesis explaining the rearrangement is described. An irreversible thermal rearrangement of silylphenols to form phenoxy-silanes is described. The catalytic hydrogenation of *p*-trimethylsilylphenoxy-trimethylsilane to form 4-trimethylsilylcyclohexyloxytrimethylsilane is described. The *cis*- and *trans*-isomers of 4-trimethylsilylcyclohexanol were prepared and separated. The oxidation of these with nitric acid to form 3-trimethylsilyladipic acid is described. The formation of 5-trimethylsilyloxy-pentylmagnesium chloride and its reaction with mercuric chloride is described.

The literature of organosilicon compounds contains no examples of a silane with a hydroxyphenyl substituent, and only a few with hydroxyalkyl substituents. Known methods of synthesis for organosilicon compounds do not readily lend themselves to the preparation of products containing reactive functional groups on organic substituents attached to silicon. Usually the formation of a silicon-carbon bond involves coupling an alkoxy or chlorosilane with organo-metallic reagents. The high temperature reaction of halogenated hydrocarbons with silicon is another well

known process of forming silicon-carbon bonds. A third process involves the addition of trichlorosilane to an olefin under the influence of a peroxide catalyst or under the influence of light or heat. No example could be found in which any of these methods were employed for the synthesis of functional products containing groups such as hydroxyl, carboxyl, carbonyl, etc., on an organic radical attached to silicon.

The few (hydroxyorgano)-substituted silicon compounds that are described in the literature were in general made from a (haloaryl)- or (haloalkyl)-