was not made carefully, a violent and uncontrollable rearrangement reaction occurred.) The solution was then maintained at 0° for 70 minutes without stirring. The mixture was poured onto a slurry of ice and ammonium hydroxide. The white precipitate was removed by filtration, washed with water, and recrystallized from aqueous ethanol. After air-drying, 2,4,6-trimethylacetanilide was obtained as white needles: 0.85 g., m.p. 218–219°, mixed m.p. with authentic sample undepressed. An additional quantity of anilide was obtained from the mother liquors of the original recrystallization: 0.09 g., m.p. 217–218°. The total yield of 2,4,6-trimethylacetanilide was 0.94 g., 94%.

A second similar rearrangement, of 30-minute rather than 75-minute duration, using 0.50 g. of the oxime yielded 0.42 g. of the anilide contaminated with detectable amounts of unchanged oxime since the behavior on heating showed that softening commenced at 150° and melting occurred over the range 180–200°.

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DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE 5, TENN.

Reactions of Allylsilanes with Iodine

BY DANIEL GRAFSTEIN

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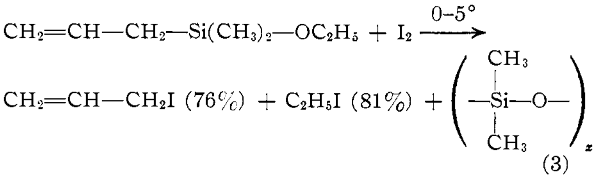
In 1948, Pray, Sommer, *et al.*,[1] reported the facile cleavage of trimethylphenylsilane with bromine at 100° and the difficult cleavage of trimethylphenylsilane with iodine at reflux. Eaborn[2] refers to this paper as the first reported preparation of an alkyliodosilane. Eaborn[2] described the preparation of alkyliodosilanes by the cleavage of tetraalkylsilanes with aluminum iodide and iodine. Deans and Eaborn[3] recently studied the kinetics of the reaction of trialkylsilanes with iodine.

Sommer, Tyler and Whitmore[4] described the addition of chlorine, hydrogen bromide and hydrogen iodide to the double bond of allyltrimethylsilane and the cleavage of the allyl–silicon bond in allyltrimethylsilane by bromine, hydrogen chloride and sulfuric acid. They postulated a carbonium ion (I) intermediate as common to both reactions. Electron-release from silicon to the electronically deficient β-carbon with simultaneous or subsequent union of the resulting "siliconium ion" with the negative part of the attacking reagent was proposed as the mechanism of the cleavage reaction.

$$(CH_3)_3SiCH_2CH{=}CH_2 \xrightarrow{A^+B^-} \underset{\text{I}}{(CH_3)_3SiCH_2\overset{+}{C}HCH_2A} \qquad (1)$$

$$(CH_3)_3Si\overset{\curvearrowright}{—CH_2—}\overset{+}{C}HCH_2A + B^- \longrightarrow (CH_3)_3SiB + CH_2{=}CHCH_2A \qquad (2)$$

This paper reports the vigorous exothermic reaction of iodine and allylsilanes at room temperature. More surprising, however, was the discovery that when the allylsilane has an ethoxy group attached to the silicon atom, ethyl iodide and a polymer are produced even at 0°, in addition to allyl iodide. No iodosilane was isolated. Thus with allylethoxydimethylsilane



$$CH_2{=}CH—CH_2—Si(CH_3)_2—OC_2H_5 + I_2 \xrightarrow{0-5^\circ} CH_2{=}CH—CH_2I\ (76\%) + C_2H_5I\ (81\%) + \left(\begin{matrix} CH_3 \\ | \\ —Si—O— \\ | \\ CH_3 \end{matrix}\right)_x \qquad (3)$$

In Table I are listed the compounds studied and the yields of iodosilane, allylic iodide and ethyl iodide observed. In addition to the compounds listed, qualitative test-tube experiments showed that iodine reacted violently with diallyldiethoxysilane but did not react with diethoxymethylphenylsilane, diethoxydimethylsilane, ethyl silicate and *m*-trifluoromethylbenzyltrimethylsilane.[5]

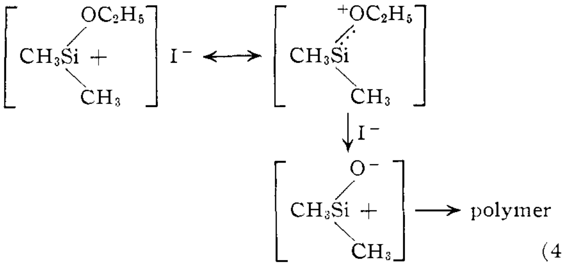
TABLE I

CLEAVAGE OF ALLYLSILANES BY IODINE

Silane	Yield, % Allyl iodide	Ethyl iodide	Iodosilane
Allylethoxydimethyl-	76	81	0
Allyldiethoxymethyl-	67	77[a]	0
Allyldiethoxyphenyl-	67	88[a]	0
	65	90[a]	0
"Methallyltriethoxy-[b]"	[c]	49[a]	. .
Allyltrimethyl-	Quant.[d]	. .	Quant.[d]

[a] Assuming only one ethoxy group/molecule available. [b] Prepared by C. E. Arntzen from the reaction of methallyl chloride, magnesium and ethyl silicate; n^{25}D 1.4109, d^{25} 0.8999, b.p. 102.5° (40 mm.); MR_D obsd. 60.27, MR_D calcd. 59.87. Infrared spectrum indicates crotyl structure. [c] Not isolated. [d] Isolated as the minimum boiling azeotrope of allyl iodide and hexamethyldisiloxane, b.p. 95° (740 mm.). Composition of azeotrope is approximately 48% hexamethyldisiloxane, 52% allyl iodide as determined from plot of specific volume *vs.* composition.

Since iodine does not normally cleave alkyl–oxygen bonds, it seems necessary to postulate an electronic interaction between the ether oxygen and the electron-deficient silicon atom in order to account for the cleavage as well as the failure to isolate an ethoxyiodosilane. Such an interaction would facilitate the nucleophilic displacement by iodide or iodine on carbon. Thus, expanding the Sommer–Whitmore mechanism leads to the attractive possibility of a silicon-oxygen "polar" or double bond as a transient intermediate:



(4)

An alternative mechanism is suggested by the work of Kumada,[6] who reported the cleavage of some ethoxysilanes by bromotrimethylsilane at elevated temperatures in the presence of pyridine

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(1) B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. Di Giorgio and F. C. Whitmore, THIS JOURNAL, **70**, 433 (1948).

(2) C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

(3) D. K. Deans and C. Eaborn, *ibid.*, 3169 (1954).

(4) L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948).

(5) Prepared by L. W. Frost, to be described later.

(6) M. Kumada and H. Hattori, *J. Inst. Polytech., Osaka City U.*, **3**, 77 (1952).

hydrobromide as a catalyst. Thus the "siliconium ion" or an intermediate ethoxyiodosilane might undergo rapid intermolecular elimination of ethyl iodide.

Experimental

All the reactions described were run under essentially the same experimental conditions and are illustrated by the following experiment with allyldiethoxyphenylsilane.

Allyldiethoxyphenylsilane (101.6 g./0.430 mole) was cooled in an ice-water-bath. A total of 116.5 g. of iodine (0.459 mole) was added in small portions over a 260-minute period with vigorous stirring. The cold mixture was stirred for an additional 1.5 hours and then quickly transferred to a claisen flask already equipped for vacuum distillation. The pressure was reduced rapidly and 58.1 g. (I) of product was collected over a one-hour period in a trap immersed in a Dry Ice–trichloroethylene-bath. The pressure in the system was 6 mm. and the temperature of the residue was $-6°$. The distillation was discontinued and the flask was allowed to warm to room temperature. Reapplying a vacuum of 5 mm. gave an additional 70.6 g. (II) of product, heat being applied to keep the temperature from falling. A dark viscous oil remained in the claisen flask; gross yield 128.7 g. (92.4%) of distillate.

Fraction I was distilled in a 2-ft. Podbielniak Minical column to yield 19.25 ml. of ethyl iodide, b.p. 71.1–72.2° (742 mm.), and 6.85 ml. of allyl iodide, b.p. 102.5–102.9° (742 mm.). Fraction II, combined with the column hold-up of fraction I was distilled in the same column and an additional 11.65 ml. of ethyl iodide and 19.4 ml. of allyl iodide was obtained; total yield ethyl iodide 88.3%, allyl iodide 66.9%. An intermediate fraction, 2.30 ml., was discarded. Ethyl iodide was characterized by its physical constants, n^{25}_{D} 1.5062–1.5089, lit. n^{25}_{D} 1.5076,[7] lit. b.p. 72.2–72.4°,[7] and as the anilide, m.p. 103.5–104°, lit. m.p. 104°.[8] Allyl iodide was characterized by its physical constants d^{25}_{4} 1.837, lit.[9] d^{22}_{4} 1.8454, b.p. 101–102°.

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[7] S. W. Prentiss, This Journal, **51**, 2830 (1929).

[8] H. W. Underwood and J. C. Gale, *ibid.*, **56**, 2119 (1934).

[9] R. L. Letsinger and J. G. Traynham, *ibid.*, **70**, 2818 (1948).

Westinghouse Research Laboratories
Pittsburgh 35, Pennsylvania

4-Hydroxyquinolines. Effect of a 7-Substituent on the Displaceability of the Hydroxyl Group[1]

By Gabriello Illuminati and Ludovico Santucci

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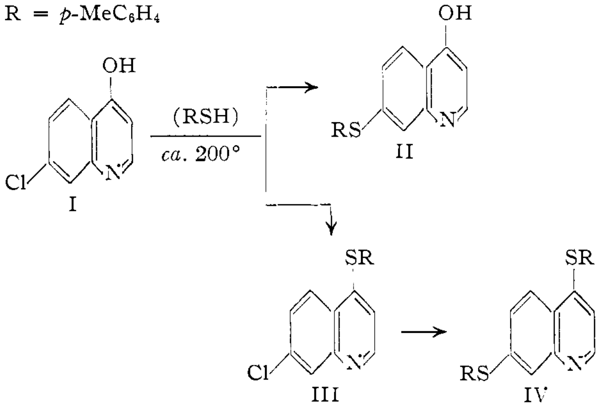
As shown in a previous paper,[2] the hydroxyl group can be displaced from 4-hydroxy-7-chloroquinoline (I) by the action of *p*-thiocresol in the fused state. The reaction yielded two substitution products, 4-hydroxy-7-*p*-tolylmercaptoquinoline (II) and 4,7-di-(*p*-tolylmercapto)-quinoline (IV). Since the displacement of a hydroxyl group with common nucleophilic reagents is rare in aromatic substitutions, it seemed of interest to investigate the course of this reaction in more detail.

We have found that compound II is not an intermediate in the reaction leading to compound IV; under identical experimental conditions it did not react with the thiol and could be recovered practically unchanged. The structure of compound II, which had been previously established,[2] was confirmed by additional evidence. By treatment with phosphorus oxychloride such a compound was converted to the expected 4-chloro-7-*p*-tolylmercaptoquinoline which, in turn, reacted with *p*-thiocresol to give compound IV. Compound IV is therefore formed from compound I by an independent process involving the primary displacement of the hydroxyl group and the consequent formation of 4-*p*-tolylmercapto-7-chloroquinoline (III) as the intermediate. This is shown by the fact that under the same experimental conditions compound III is converted to the dimercapto derivative IV.[3] Also, starting from compound I, in addition to products II and IV, we have detected small amounts of the intermediate compound III. The course of the total reaction is therefore as illustrated in the scheme



Based on the minimum yield (22%) of pure 4,7-di-(*p*-tolylmercapto)-quinoline, m.p. 100.5–101.5°, as deduced from several experiments, the extent of displacement of the hydroxyl group from compound I was found to be of the same order as that of the 7-chlorine atom from the same compound. Side-reaction products were isolated in the course of the product analysis as described in the Experimental part.

The main interest of our results is that they show the dependence of the ability of the hydroxyl group to be displaced on the nature of the far-removed substituent in the 7-position of the quinoline ring. Under the conditions of our experiments, the chlorine atom in this position allows the displacement of the hydroxyl group from the 4-position whereas the *p*-tolylmercapto group does not. Provided that compounds I and II react in the 4-hydroxyl form, their apparent relative reactivity is clearly consistent with the electronic effects of chlorine and of the *p*-tolylmercapto group in the 7-position. Basicity studies[4] show that chlorine in monochloroquinolines exerts an appreciably strong -I inductive effect[5] from the benzenoid ring to the nitrogen atom. The order of basicity constants as found by us[6] in a 4-chloroquinoline series is as follows: 7-*p*-tolylmercapto > 7-Cl, from which a reverse order of reactivity in nucleophilic substitutions would be expected. Kinetic studies in this Laboratory[6] on displacement of chlorine from the 4-position with eth-

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[1] Part IV in the series "Nucleophilic Displacements by Thiols." Part III: G. Illuminati and L. Santucci, *Gazz. chim. ital.*, **83**, 1106 (1953).

[2] G. Illuminati and H. Gilman, This Journal, **72**, 4288 (1950).

[3] See Part III, ref. 1.

[4] S. B. Knight, R. H. Wallick and C. Balch, This Journal, **77**, 2577 (1955).

[5] For the sign of the symbols used in this work see, for example, the appendix in J. W. Baker, "Hyperconjugation," Oxford at the Clarendon Press, 1952.

[6] Unpublished studies.