

stated that when R = H the absorption band appears at 7.8 μ , when R = CH₃ it appears at 8.1–8.2 μ , while in dimethyldi-*n*-propylsilane the same band appears at 8.3 μ and in butylsilanes at 8.4–8.6 μ . The fact that the band is absent in the spectrum of vinylsilane was given as further evidence that absorption in the 7.8–8.6 μ region can be assigned to the silicon–methylene frequency.

In the present study, bands of medium intensity were found in the range 7.8–8.6 μ for methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and *n*-hexylphenylsilane, all of which contain the Si–CH₂R group. However, bands of medium intensity also were found in this range for cyclohexyl- and isopropylsilane, neither of which contain the silicon–methylene group. Moreover, the spectra of phenylsilane and phenylbromosilane contain weak bands at 8.66 and 8.64 μ , respectively, and this same band is much stronger in the spectrum of diphenylsilane. It would appear, then, that absorption in the region 7.8–8.6 μ is not restricted to the Si–CH₂R frequency.

Vibrations Involving the Si–H Bond.—West and Rochow⁵ have assigned bands appearing in the 4.77–4.80 μ region to the Si–H bond of dialkylsilanes, and those in the 4.72–4.77 μ region to the Si–H bond of diarylsilanes. The absorption band characteristic of the Si–H bond in all the compounds reported in this paper was found to appear at 4.70 μ , except in phenylbromosilane, where it appeared at 4.61 μ . This shift to a shorter wave length for the absorption by the Si–H bond is due to the inductive effect caused by the substitution of the bromine atom for the alkyl groups of the alkylphenylsilanes.

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Potassium Hydroxide as a Metalating Agent. Fluorene¹

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Fluorene is metalated easily by potassium hydroxide in ether solution at room temperature in spite of the fact that the acidity (*pK* value) of fluorene is lower by 11 than water. Metallic sodium can be used to good advantage as a dehydrating agent.

This study originated from the observation that benzene–azodiphenylamine gave the color indicative of an acid in contact with solid potassium hydroxide and other reagents.² One explanation might be that the hydroxide had metalated the amine with formation of a colored anion. Accordingly tests have been made of the metalating activity of potassium hydroxide upon fluorene which has an acidity 11 lower in *pK* value³ than water. Normally little or no metalation would be expected unless the reaction is carried out at elevated temperature so that water is removed and indeed such is the condition employed when fluorene⁴ is treated with this reagent in recovery and purification processes. However, despite the difference in acidity a yield of 28% and even as high as 48% (no. 7 and 11 in Table I) has been obtained at moderate temperature and every test but one (no. 1), in ether as a medium, showed some formation of fluorenylpotassium.

An explanation for the great ease of metalation in the face of this large difference in acidity lies in the fact that potassium hydroxide removes wa-

TABLE I
METALATION OF FLUORENE BY POTASSIUM HYDROXIDE IN THE HIGH-SPEED STIRRING APPARATUS

No.	Fluorene, moles $\times 10^2$	KOH, moles	Solv.	Time, hr.	Without Na	Yield, %	With Na
1	2.5	3	E	3	0, 2		
2	5.0	0					0
3	5.0	0.5	E	3	11		
4	5.0	1.0	E	1	12		
5	5.0	1.0	E	3	26		
6	5.0	2.0	E	1	27		
7	5.0	2.0	E	3	27, 28		45, 51
8	5.0	2.0	E	6	23		
9	5.0	2.0	B	3	0		
10	5.0	2.0	P	3	6		
11	5.0	3.0	E	3	48		27, 32, 47 ^a
12	5.0	3.0	P	3	15		
13	10.0	2.0	E	3			56 ^b
14	15.0	2.0	E	3			62
15	20.0	0.5	E	3			41
16	20.0	1.0	E	3			34
17	20.0	2.0	E	3	12, 13		62, 66
18	20.0	2.0	E	3			63 ^c
19	25.0	2.0	E	3			63

^a This mixture was extremely thick and the reproducibility was difficult. ^b In two experiments, where a little water was added to the reaction mixture, this yield rose to 59 and 65%. ^c Twice the usual amount of sodium metal was used in this experiment.

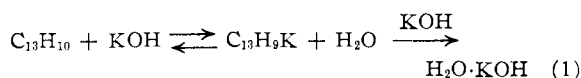
ter from the equilibrium mixture in the equation below by formation of a hydrate. The existence of

(1) This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) A. A. Morton and F. H. Bolton, *THIS JOURNAL*, **75**, 1146 (1953).

(3) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(4) R. Weissberger, *Ber.*, **34**, 1659 (1901); M. Weger and K. Doring, *ibid.*, **36**, 878 (1903); S. M. Grigorev, L. D. Gluzman, V. A. Ivanushkina and D. T. Braslavskaya, *Chemie et industrie*, **44**, 43 (1940).



this hydrate has been known⁵ for some time. Also the vapor pressure of water over potassium hydroxide is very low,⁶ at most 0.007 mm. at 50°. The corresponding value over sodium hydroxide is 1.15 mm.

The reaction was affected readily by a number of factors. An increase in the quantity of hydroxide usually raised the yield (no. 11 > 7 or 5 > 3), but the thickness of the mixture when large quantities were used made some later results erratic. Interestingly enough, a huge excess of hydroxide, as in no. 1, caused little or no metalation when the concentration of fluorene was very low, but with one-third, or even one-sixth, the hydroxide (no. 4 or 5 and 3, respectively) and twice the concentration of fluorene, the yield was 11 to 26% and with two-thirds of the hydroxide and with this higher concentration of fluorene, the percentage yield was 27% (no. 7). At four times as high a concentration of fluorene (no. 17) the percentage yield fell, as might be expected because the grams of product was doubled and a larger proportion of hydroxide was required to remove water from the equilibrium mixture.

Metallic sodium as a dehydrating agent was extremely effective. Under some conditions (no. 14, 17, 19) the yield rose to above 60%. The alkali metal caused no direct metalation of fluorene, as shown by no. 2. Its erratic effect in no. 11 was caused by the aforementioned thickness of the reaction mixture. Calcium sulfate was relatively ineffective as a drying agent and gave a yield of 30% in comparison with no. 7 which was 27%. Barium oxide actually caused the yield to fall to 11% under these same conditions.

Several miscellaneous features connected with this reaction deserve mention. Sodium hydroxide caused only a 1% yield in comparison with the 11% yield by potassium hydroxide in no. 3. Sodium isopropoxide under the same conditions failed to metalate fluorene. As a medium for the reaction, ethyl ether was much superior to pentane which in turn was better than benzene (no. 12 > 11 and also no. 5 > 10 > 9). Triethylamine, in an experiment otherwise like no. 7, reduced the yield from 27 to 8%, and sodium chloride likewise cut back the yields of 45 and 51% in no. 7 to 31 and 34%. A few attempts to use fluorenylpotassium as a stepping stone to metalation of benzene or toluene produced decided colors but yielded no carboxylic acid other than that from fluorene. Further studies of these reactions will be made.

The action of this hydroxide provides another illustration of the unusual effects which can be attained by proper use of solid alkali metal reagents.

(5) S. U. Pickering, *J. Chem. Soc.*, **63**, 890 (1893).

(6) G. P. Baxter and H. W. Starkweather, *THIS JOURNAL*, **38**, 2038 (1916).

In company with the reactive organosodium compounds, they are regarded as electrophilic in character and unable to show nucleophilic activity except as the electron attracting influence of the cation is removed by solvation or otherwise. Unlike the more active analogs in the carbon series,⁷ the hydroxide has not yet shown any special effect which requires the assumption that it functions in a reaction by a radical mechanism.

Experiments

Reagents.—Commercial solid potassium hydroxide was used in all experiments. After the first five or six experiments in the high-speed stirrer, the hydroxide was dried in a vacuum oven at 80–85° overnight before use. Eastman Kodak Co. practical grade of fluorene melted at 114–115° (uncor.) and was used without further purification. Commercial anhydrous ether was further dried by standing over sodium wire. The pentane and benzene were likewise dried over sodium wire. Sodium sand was made in decane in the usual way. The decane was removed by decantation, the sand was washed twice with anhydrous ether and then stored in a wide mouth bottle under ether. It was removed by measured spoonfuls, usually two for each reaction when used. By reaction with water and titration this amount of sand equalled 9.8 g.

Reactions in a Bottle (By H. P. K.).—The procedure used in the initial experiments can be illustrated by one example in which 4 g. (24 meq.) of fluorene was shaken in a 12-oz. soft drink bottle with 1000 meq. of solid potassium hydroxide in about 300 ml. of ether. The mixture turned yellow almost immediately. At the end of 5, 11 or 15 days, most of the time with shaking, the bottle was opened and the contents poured on solid carbon dioxide. The yields of fluorene-carboxylic acid were 20, 21 and 23%, respectively.

A similar experiment in toluene but with 8.3 g. (50 meq.) of fluorene gave an orange-brown color. After four days, carbonation yielded 2% of fluorene-carboxylic acid. A similar experiment, but with only 1.7 g. of fluorene, produced a violet color in toluene, a brownish-red color in benzene. No carboxylic acid was isolated from either experiment, in spite of these distinct colors.

Reaction in the High-speed Stirrer.—This series of experiments was carried out by Mr. James Howard, to whom the authors are greatly indebted. A 1-l. creased flask with 500 ml. of solvent dried over sodium wire was used in each case. The potassium hydroxide was stirred at 5000 r.p.m. for one-half hour in the solvent in order to break up the solid. The other reactants were then added in the quantities listed in the table.

The temperature of the reaction rose to between 25–30° within the first 15 minutes and was maintained at that level by a Cellosolve-carbon dioxide cooling bath for the duration of the experiment.

At the end of that time the contents of the flask were forced onto solid carbon dioxide. The next day ice and water were added to decompose traces of sodium that might be present, although apparently none remained by that time. The organic layer was removed and the basic salt solution was carefully acidified with hydrochloric acid at ice-bath temperature. The 9-fluorene-carboxylic acid was extracted with ether, recovered by evaporation, and dried in vacuum overnight. The crude acid usually melted at 204–208° before purification and at 216–219° after one crystallization from glacial acetic acid (reported 221–223°),⁸ and had a neutralization equivalent of 212–220 (calculated 210.2).

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(7) A. A. Morton and E. F. Cluff, *ibid.*, **74**, 4056 (1952); A. A. Morton and A. E. Brachman, *ibid.*, **76**, 2973 (1954); A. A. Morton, C. E. Clafr, Jr., and F. W. Collins, unpublished.

(8) A. Kliegl, *Ber.*, **64**, 2420 (1931).