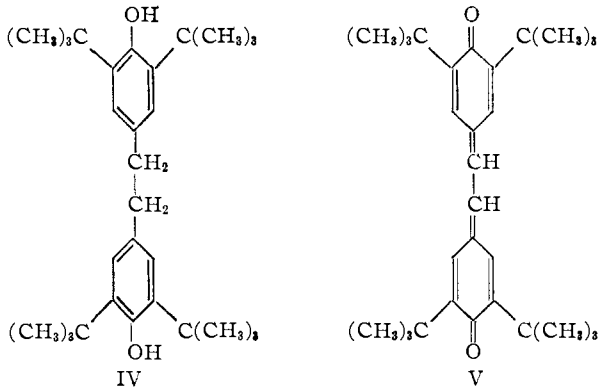
spectral evidence for the existence of a peroxy derivative of a dicyclohexadienone, but the compound has not been isolated.



IV V

The isolation of these compounds is consistent with the reaction of II with Co^{++}–Co^{+++} to form RO· and RO_2·. It has been demonstrated that RO· is capable of converting I to IV.[7] In these reactions RO· is converted to ROH (III) with the apparent formation of a benzyl radical from I which then dimerizes IV. Compound IV is oxidized to V by RO·.[7]

The fate of RO_2· is not clear. Bickel and Kooyman[3] report that whereas a number of different peroxy radicals react with I to form peroxides of structures corresponding to II, triphenylmethylperoxy radical converts I in part to IV and V. It thus seems possible that a steric effect exists which depends upon the size of the R group in RO_2·, which determines whether RO_2· adds to the phenol or abstracts hydrogen from the phenol which results in the formation of a benzyl radical.

Experimental

4-Methyl-4-hydroperoxy-2,6-di-*t*-butyl-2,5-cyclohexadienone (II).—A solution of 0.1 mole of 2,6-di-*t*-butyl-*p*-cresol, 10 mg. of an appropriate metal salt and 1 mole of hydrogen peroxide (50w.%) in 250 ml. of *t*-butyl alcohol was allowed to stand at room temperature for 6 hr.; the metal salts used were cobalt naphthenate, cuprous chloride, cupric acetate, ferrous chloride and ferric chloride. The reaction is mildly exothermic. The copper salts occasionally produced a highly exothermic reaction. The decomposition is always accompanied by evolution of oxygen.

At the end of 6 hr. the solution is extracted with an equal volume of isoöctane and washed with water to remove the *t*-butyl alcohol. The isoöctane was removed at reduced pressure and the crystalline material was recrystallized from isooctane, m.p. 115°.

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.5; H, 9.5. Found: C, 71.8; H, 9.4.

The yield of II varied from experiment to experiment. Calculations from the infrared spectra of the isoöctane extracts indicate the average yield of I was 25–30% of the parent phenol. The doublet at 6 μ was used for these estimations.

4-Methyl-4-hydroxy-2,6-di-*t*-butyl-3,5-cyclohexadienone (III).—Compound II was reduced in isoöctane solution with platinum-on-charcoal as catalyst, m.p. 112–113°. A mixed melting point with a sample of III obtained from air oxidation of 2,6-di-*t*-butyl-*p*-cresol in the presence of alkali was 112–113°.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.4; H, 9.7. Found: C, 76.7; H, 9.6.

3,5-Di-*t*-butyl-4-hydroxybenzyl Acetate.—A solution of 1 g. of III and 10 mg. of *p*-toluenesulfonic acid in 10 cc. of acetic acid was allowed to stand at room temperature for 24 hr. At the end of this time the acetate had partially crystallized. Additional acetate was obtained on dilution with water; total yield 1 g., m.p. 105–106°, mixed m.p. with a sample prepared by the method of Coppinger and Campbell,[6] 102–104°. The infrared spectra of the two samples were identical. Coppinger and Campbell report 98° as the m.p. for the acetate. Compound II does not undergo this rearrangement in acetic acid.

Reaction of I, II and Co^{++}.—A solution of 2 g. of II, 1 g. of I and 10 mg. of cobalt naphthenate in 25 cc. of *t*-butyl alcohol was allowed to stand at room temperature for 24 hr. The reaction mixture was extracted with 50 cc. of ether and washed free of *t*-butyl alcohol with water. The ether was removed and the residue was fractionally crystallized from methanol. The stilbene quinone V was isolated first, m.p. 293–295°, mixed m.p. 293–296°. Compound IV was obtained as the second fraction, m.p. 173–175°, mixed m.p. 173–175°. The third fraction obtained by removal of the methanol was recrystallized from isoöctane to obtain III, m.p. 110–112°, mixed m.p. 111–113°.

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(7) RO· as $C_6H_5C(=O)$—O, S. C. Cosgrove and W. A. Waters, THIS JOURNAL, 388 (1951); RO· as $(CH_3)_3C$—O, G. M. Coppinger, unpublished.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Substituent Effects on Naphthalene. Association Constants of Substituted Naphthalene–Picric Acid Complexes

BY PETE D. GARDNER AND WARREN E. STUMP

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Association constants of the complexes formed by twenty-five systematically substituted naphthalenes with picric acid have been determined. The partition method was chosen for the study, wherein the donor compound and the acceptor (picric acid) are equilibrated between chloroform and water and the extent to which the donor is capable of retaining the acceptor in the chloroform phase is determined. It was found that complex stability is dictated by steric factors, inductive effects and resonance effects in the various series.

Molecular complexes formed by aromatic substances appear to be of two distinct types,[1,2] the type being determined largely by the nature of the acceptor. Those of the σ-type, exemplified by the aromatic–$HAlCl_4$[2] and aromatic–HBF_4[3] complexes, exhibit a very great stability dependence upon substituents, electron-donating substituents in the donor imparting increased strength to the complex. Complexation of the π-type,[2,4] on the other

(1) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954). This review describes current theories concerning complexation of this type and defines terms used here.

(2) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(3) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(4) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

hand, is not as easily defined, as it appears that the effect of substituents varies somewhat unpredictably with the nature of the acceptor.[2,5] It has been shown, for example, that stability in the benzene–silver ion complex is determined by substituents in the donor molecule so as to permit a correlation with Hammett's σ-values.[5] Such a correlation is not possible with complexes formed by substituted benzenes with picryl chloride and picric acid. The stability of the latter type of π-complex appears to reflect, among other things, the steric requirement[6] and the electron-withdrawing properties of the substituent.[7,8]

This paper is the first of several concerned with general substituent effects in naphthalene[9] and with those factors influencing π-complex formation by this compound. The method chosen for the present work is the partition method. Association constants determined in this way are invariably higher than those measured by the spectrophotometric method. There can be little doubt that complexation as measured by the partition method is more extensive than simple π-complex formation. The spectrophotometric method, on the other hand, appears to measure only π-complexation[10] involving the ring, and thus the two data correspond to two different processes. Whatever the differences are, they should not vary appreciably within a given class of substituents, and the series-correlations described below should be a reasonable measure of substituent effects. Apparent anomalies peculiar to the method include donors containing the nitro group and, as will be seen later, probably acetyl and alkoxy donors as well. For this reason caution must be exercised in the interpretation of data in these series. They are not without value, however, since one of the objectives of the study, which will include a later examination of the spectrophotometric method,[11] is an evaluation of those additional forces (dispersion, etc.) superimposed upon charge-transfer complexation and contributing to the higher association constants observed here.

Experimental

Partition Procedure.—The method used was a modification of that used by Moore, Shepherd and Goodall[12] and improved by Anderson and Hammick[6] in which the donor compound and the acceptor (picric acid) are equilibrated between chloroform and water, and the extent to which the donor is capable of retaining the acceptor in the chloroform phase is determined. Modifications incorporated are apparent from the description given below. This procedure proved to be less cumbersome than those previously used, and the precision and accuracy did not seem to be impaired.

Picric acid in the amount of 0.85–1.05 g. was weighed into each of four equilibration vessels by means of a weighing stick. Fifty milliliters of water was delivered into each vessel from a calibrated pipet, followed by the similar addition of 50.00 ml. of a chloroform solution of the compound (0.083–0.174 M) under investigation. The latter solution was prepared on a weight–weight basis and its concentration determined using the density of chloroform at 27°.[13] The stoppered vessels were tumbled at approximately 26° for 10–30 min. and then placed in a bath maintained at 27 ± 0.1° for at least 12 hr. with occasional agitation. Twenty milliliters of the clear, aqueous phase from each vessel was diluted with 50 ml. of equilibrium water and titrated with approximately 0.016 N sodium hydroxide solution (carbonate-free)[14] using methyl purple indicator[15] to the disappearance of brown. From data thus obtained, the quantity of picric acid in the aqueous phase and in the chloroform phase was determined.

A reference distribution curve was determined as a straight line plotted from ten points by the method of least squares. The resulting equation is

$$\log C_{CHCl_3} = 1.11564 \log C_{H_2O} + 1.27563$$

The average deviation of the ten points was 0.00270 in log C_{CHCl_3} which is an average deviation of 0.00066 in the "average" point. The probable deviation was 0.00021.

The change in picric acid content of the chloroform phase due to the presence of a donor compound was used to calculate the association constant for the interaction by eq. 1[6]

$$K_1 = \frac{Y - P}{Pz} \qquad (1)$$

where K_1 is the apparent stability constant, Y is the experimentally determined concentration of picric acid, P is the concentration of picric acid in the absence of donor compound and z is the concentration of donor compound. The "salting-out" effect of the donor substance on the solubility of picric acid in the chloroform phase was taken into account.[16,17] The association constant K_s is the sum of K_1 and the solubility-depression constant k.[6] It was found that, due to the considerably larger values of K_1 obtained in this work, one of the simplifying assumptions made in the original derivation of eq. 1[6] was not valid. Calculation of K_s values was therefore made using eq. 2.

$$K_s = \frac{1 - \sqrt{1 - 4P(K_1 + k)}}{2P} \qquad (2)$$

Confidence limits of the mean of K_s values were based on the "t" test of significance using the 90% confidence level. Rejection of individual determinations was decided upon after K_1 values were calculated, discarding any single value of the four which differed greatly from the remaining three, or upon comparing K_s values, again using the "t" test at the 90% confidence level. Eight determinations were used with many of the compounds.

Materials.—Chloroform was stored over calcium chloride and fractionally distilled before use. All reagents used were purchased or prepared by routine procedures except where noted. Solids were recrystallized to constant m.p. and liquids were fractionally distilled or, in many cases, purified by crystallization of the picric acid complex followed by decomposition of the complex and fractional distillation of the donor. No significant discrepancies with literature values of physical constants were found; consequently, references to these are not included. The preparation of compounds followed procedures abstracted in Beilstein's "Handbuch" or *Chemical Abstracts*.

Experimental Results and Discussion

Association constants for all naphthalene derivatives studied are given in Table I along with mean K_1 and k values. Some of these data are represented graphically in Fig. 1.

A few of the complexes described below have been studied in other laboratories. Unfortunately, the various temperatures used render impossible

(5) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **72**, 3113 (1950).

(6) H. D. Anderson and D. L. Hammick, *J. Chem. Soc.*, 1089 (1950).

(7) C. B. Coleman, Abstracts of Papers presented at the Meeting of the Am. Chem. Soc., Sept., 1955, p. 4-O.

(8) C. E. Castrow and L. J. Andrews, THIS JOURNAL, **77**, 5189 (1955).

(9) A study of the problem of substituent effects on naphthalene was initiated by C. C. Price and R. H. Michel, *ibid.*, **74**, 3652 (1952).

(10) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *ibid.*, **76**, 69 (1954).

(11) See for, example, R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

(12) T. S. Moore, G. Shepherd and E. Goodall, *J. Chem. Soc.*, 1447 (1931).

(13) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., pp. 27–28.

(14) Standardized against picric acid using methyl purple indicator

(15) Fleisher Chemical Co., Washington, D. C.

(16) R. Behrend, *Z. physik. Chem.*, **9**, 405 (1892).

(17) R. Behrend, *ibid.*, **10**, 265 (1892).

TABLE I

ASSOCIATION CONSTANTS FOR INTERACTIONS OF SUBSTITUTED NAPHTHALENES WITH PICRIC ACID IN SOLUTION AT 27°

Donor	Source[c]	K_1 (mean)	k	K_s, l. mole^{-1}
Naphthalene	P	1.60	0.47	2.31 ± 0.03
1-Methyl-	P	2.24	.53	3.16 ± .04
1-Ethyl-	L	1.72	.59	2.61 ± .04
1-Isopropyl-	L	1.06	.65	1.87 ± .02
2-Methyl-	P	2.49	.54	3.50 ± .05
2-Ethyl-	L	1.87	.60	2.77 ± .02
2-Isopropyl-	L	1.57	.66	2.51 ± .09
1-Fluoro-	P	0.90	.49	1.49 ± .02
1-Chloro-	P	1.19	.52	1.87 ± .03
1-Bromo-	P	1.31[b]	.53	2.06 ± .05
1-Iodo-	P	1.38	.55	2.13 ± .02
2-Fluoro-	P	0.71	.49	1.28 ± .05
2-Chloro-	[a]	.87	.52	1.50 ± .03
2-Bromo-	P	.92	.53	1.57 ± .03
2-Iodo-	L	.93	.55	1.62 ± .02
1-Methoxy-	P	3.45	.56	4.89 ± .05
1-Ethoxy-	P	3.90	.62	5.78 ± .09
1-Isopropoxy-	L	3.22	.68	4.81 ± .16
2-Methoxy-	P	2.33	.56	3.30 ± .08
2-Ethoxy-	P	1.99	.62	3.01 ± .09
2-Isopropoxy-	L	1.98	.68	3.09 ± .09
1-Acetyl-	P	1.84	.59	2.76 ± .01
2-Acetyl-	P	1.60	.60	2.47 ± .03
1-Nitro-	P	0.80		
Acenaphthene	P	2.55	0.58	3.59 ± 0.16

[a] Kindly supplied in a good state of purity by Dr. R. R. Twelves, Department of Chemistry, University of Minnesota. [b] The significant discrepancy between this value and that previously reported[12] (0.17) cannot be explained. [c] P, purchased. L, prepared as described in the literature.

any correlations within series. The temperature-dependence of complexation is illustrated in thermodynamic functions calculated from association constants determined in this study of the naphthalene complex at 27° (K_s = 2.31) and 8° (K_s = 3.31). An Arrhenius plot of log K_s *vs.* T^{-1} gives ΔH −3.1 kcal. mole^{-1} and from this and the ΔF values, $\Delta F_{27°}$ = −670 and $\Delta F_{8°}$ = −500 cal. mole^{-1}, there is obtained ΔS = −8.7 cal. deg.$^{-1}$. These values differ significantly from those reported for this complex as determined by the spectrophotometric method.[18] This general phenomenon is discussed above and by Ross, *et al.*[10]

Alkylnaphthalenes.–It is apparent that complex stability in both series of alkylnaphthalenes is determined by the steric requirement of the substituent. The order is also that expected of hyperconjugative participation of substituents. In view of the nature of the π-complex,[1] of which these are examples, there is little reason to suspect that hyperconjugation can contribute significantly to the π-electron density on the ring even under the demand of complexation.[19] The relative decrease in complex stability with increasing size of substituent in the 2-alkyl series parallels rather closely that observed in the alkylbenzene series, CH_3 > C_2H_5 > iso-C_3H_7.[6] The relative decrease is even greater in the 1-series, a trend reported previously in the pair CH_3 > C_2H_5.[12] Extension of the series to the isopropyl substituent supports the suggestion that steric interaction between a bulky substituent in the 1-position and the 8-position of the ring decreases complex stability,[20] the order being CH_3 > C_2H_5 >> iso-C_3H_7.[21] The importance of the inductive effect is manifest in a comparison of these values with that for the complex of naphthalene itself; all except the 1-isopropylnaphthalene complex exhibit greater stability than the complex of naphthalene. Nonetheless, this is superimposed upon the steric requirement of substituents and the latter effect determines the order.

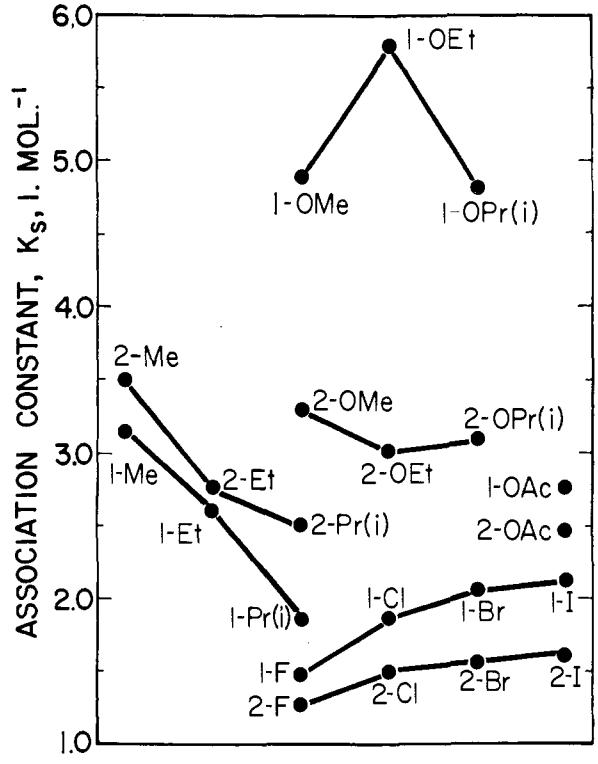

Fig. 1.

Halogenonaphthalenes.–As might be anticipated, association constants in these two series are much lower than those in the alkylnaphthalenes. The trend in both series is that dictated by the inductive effect of the substituent, constants in these series being in the order I > Br > Cl > F. It will be noted that this order is the reverse of that expected on the basis of steric requirement as well as that expected on the basis of the capacity for double bond formation by the substituent.[23] Values in these series parallel the order of substituent electronegativity.[24] Certainly it can be said that all of

(18) S. D. Ross and I. Kuntz, THIS JOURNAL, **76**, 74 (1954).

(19) See, for example, G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 152.

(20) M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951).

(21) The value for 2-*t*-butylnaphthalene is not included as this hydrocarbon preparation was found to be impure. The value does, however, fall in line with those of other 2-alkylnaphthalenes reported here. A sufficient quantity of the 1-*t*-butyl isomer could not be obtained by the only method[22] reported to give an unequivocally pure substance.

(22) E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).

(23) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 103.

(24) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed. Cornell University Press, Ithaca, N. Y., 1948, p. 64.

the above-mentioned modes by which π-electron density on the ring can be altered are operative but that the inductive effect determines the order. The effect must, in fact, be very strong to overshadow the steric factor so important in the alkyl series. These values do not at all approach a reasonable Hammett σ-plot.[25]

It is interesting that values in the 1-series are greater than those in the 2-series. This order of difference, which is the reverse of that expected on the basis of steric considerations, is best interpreted on the basis of a greater facility for electron transmission through the 1-position than the 2-position. This is a capacity for double bond formation or a resonance phenomenon. An examination of the various contributing resonance structures for each series leads one to the same conclusion. The difference between these two series parallels that observed in molecular polarization as reflected in molar Kerr constants; values for the 1-series are one-third to one-half of those for the 2-series.[26]

A comparison of the acidities of α- ($K_a = 2.0 \times 10^{-4}$) and β-naphthoic acid ($K_a = 6.9 \times 10^{-5}$) does not support this, but the carboxyl group of the α-isomer is somewhat hindered by the 8-position, and the difference in acidities is perhaps better explained in terms of an "*ortho* effect."[27]

Alkoxynaphthalenes.–The 1-alkoxynaphthalene complexes are significantly more stable than those of the 2-series. Here again it is apparent that the difference between the two series is best explained in terms of a greater facility for double bond formation at the 1-position; resonance effects here, as in the halogenonaphthalenes, dictate the relative series difference. Values within each series, however, do not follow any reasonable order and as yet are unexplained.

Acetonaphthones.–The association constant for the 1-acetonaphthone complex is seen to be greater than that of the 2-isomer, but both values are significantly higher than might be anticipated. The presence of the acetyl group in either position should effectively diminish the π-electron density on the ring and thereby weaken the complex binding. The fact that these values are comparable with those of the ethylnaphthalenes, which have a similar steric requirement in the substituent, suggests that other factors are involved in the acetonaphthones. It is possible, for example, that the carbonyl group behaves as a "localized" donor as appears to be the case with aryl amines,[1] and possibly with the alkoxynaphthalenes considered above and the association constants reflect both types of complexation. This explanation is supported by the higher value for the 1-isomer; resonance effects, transmitted through the 1-position more readily than the 2-position, should permit greater polarization of the carbonyl group in the 1-isomer. In this regard, it should be noted that even 1-nitronaphthalene has an appreciable tendency to complex with picric acid.

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(25) This is perhaps apparent from a cursory inspection of the σ-values (*meta* or *para*) in the halogen series. The order of electron-withdrawing power is the reverse of that observed here.

(26) C. H. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 1641 (1955).

(27) J. F. J. ippy, *Chem. Revs.*, **25**, 151 (1939).

[CONTRIBUTION NO. 752 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Formation of the Silicon–Hydrogen Bond by the Reducing Action of Certain Sterically Hindered Grignard Reagents on Phenyltrichlorosilane

BY MACK C. HARVEY, WILLIAM H. NEBERGALL AND JOHN S. PEAKE

RECEIVED DECEMBER 10, 1956

Certain sterically hindered Grignard reagents have been found to react with phenyltrichlorosilane, $C_6H_5SiCl_3$, to form dialkylphenylsilanes, $R_2C_6H_5SiH$, and unsaturated hydrocarbons. By such reactions dicyclohexylphenylsilane and cyclohexene, dicyclopentylphenylsilane and cyclopentene, diisopropylphenylsilane and propene and di-*t*-butylphenylsilane and isobutylene have been obtained. Attempts to prepare di-*o*-tolylphenylsilane by this method were unsuccessful.

In 1933, Cusa and Kipping[1] reported that when no precautions were taken to exclude atmospheric oxygen, cyclohexoxydicyclohexylphenylsilane, $(C_6H_{11})_2C_6H_5SiOC_6H_{11}$, was formed when the product of the reaction of phenyltrichlorosilane with an excess of cyclohexylmagnesium bromide was hydrolyzed. When the reaction was carried out under nitrogen, however, the principal reaction product was found to be dicyclohexylphenylsilane, $(C_6H_{11})_2C_6H_5SiH$. These investigators suggested that $(C_6H_{11})_2C_6H_5SiMgBr$ was formed as an intermediate, which upon hydrolysis gave $(C_6H_{11})_2C_6H_5SiH$.

$$C_6H_5SiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiCl + 2MgBrCl$$

$$(C_6H_{11})_2C_6H_5SiCl + C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiMgBr + C_6H_{11}Cl$$

$$(C_6H_{11})_2C_6H_5SiMgBr + H_2O \longrightarrow (C_6H_{11})_2C_6H_5SiH + Mg(OH)Br$$

It should be noted that tricyclohexylphenylsilane is not formed here due to the steric effects of the cyclohexyl group.[1,2]

Because various workers[3,4] have been unsuccessful in attempts to prepare stable Grignard type silicon–magnesium compounds, it was decided to repeat the work of Cusa and Kipping in an effort to determine the mechanism of the formation of

(1) N. W. Cusa and F. C. Kipping, *J. Chem. Soc.*, 1040 (1933).

(2) W. H. Nebergall and O. H. Johnson, THIS JOURNAL, **71**, 4022 (1949).

(3) E. R. Van Artsdalen and J. Gavis, *ibid.*, **74**, 3196 (1952).

(4) R. A Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).