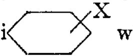
[Contribution from Dow Corning Corporation]

# Position Isomers of Substituted Aryltrimethylsilanes[1]

By H. A. Clark, A. F. Gordon, C. W. Young[2] and M. J. Hunter

This paper reports the preparation, physical properties, and infrared spectra of four series of substituted aryltrimethylsilanes of the formula $(CH_3)_3Si$  where X is $CH_3$, Cl, $C_6H_5$ and $(CH_3)_3Si$. The infrared spectra are shown to be an important physical property of these compounds and point to an easy method for identification of the various isomers.

In the development of new and more direct methods for preparing substituted arylsilanes, it was necessary to synthesize several series by classical methods so that individual isomers could be identified.

Although numerous position isomers of substituted arylsilanes are found in the literature, none appeared until very recently showing trimethylsilyl substitution.[3,4,5] Examination of the list of substituted arylsilanes, which were reported prior to the recent accelerated activity in the field, discloses that all the substituent groups were in the para position except one series of meta substituted compounds prepared by Kipping and Blackburn,[6] and tetra *m*-tolysilane prepared by Polis.[7] More recently, Gilman and Marshall,[4] and Roberts, McElhill and Armstrong[5] have described meta substituted compounds. Prior to the time this paper was first presented,[1] no silanes with any group ortho to the silicon atom had been reported. Shortly afterward, however, the preparation of a number of *o*-tolyl and mesitylsilanes by the organolithium technique was reported by Gilman and Smart.[8]

## Experimental

**Group I. Trimethyl-*o*-tolylsilane.**—To 1300 g. of dry ether and 68.6 g. of magnesium chips was added 450 g. of *o*-bromotoluene (Dow Chemical Company) (10% excess). A few crystals of iodine were necessary to start the reaction. To the approximately 2.0 molar Grignard which resulted, 302.1 g. of redistilled trimethylchlorosilane was added (10% excess). As little heat of reaction was noted, this addition was made rapidly. The coupling mix was placed on a stream-bath. There was no precipitation of MgBrCl after 3 hours reflux. 500–600 cc. of dry xylene were added and the three necked flask connected to a 3-ft. distillation column. Ether was fractionally distilled off until a pot temperature of 75° was reached. Under total reflux conditions at 75 to 80° sufficient salt accumulated during an overnight period to indicate fairly complete coupling. The coupling mix was poured with stirring into a large beaker containing 500 g. of cold water 1000 g. of cracked ice and 25 cc. of concd. hydrochloric acid. The organic layer was separated, washed once with water then shaken with 25 g. of $NaHCO_3$. After filtration, this product solution was fractionated. Slightly over 200 g. of material was distilled in the anticipated boiling range (less than 50% yield based on the bromide). Properties are listed in Table No. I.

**Trimethyl-*m*-tolylsilane.**—A mixture of 76.9 g. of *m*-bromotoluene (Eastman Kodak Co. Organic Chemicals Division) and 53.8 g. of $Me_3SiCl$ (10% excess) was slowly added with rapid stirring to a one-liter three-neck flask fitted with a stirrer and condenser containing 22.8 g. (10% excess) of molten sodium in 100 cc. of dry toluene and 150 cc. of dry xylene at reflux temperature. Reflux was maintained throughout the addition by the heat of reaction. Reflux and stirring were continued 1 hour after the end of the addition, then the coupling mix was filtered. Fractionation yielded approximately 65 g. of material at the estimated boiling point (85% yield). The properties are shown in Table I.

**Trimethyl-*p*-tolylsilane.**—The 2.0 molar Grignard was prepared from *p*-bromotoluene (Dow Chemical Company) in the same amount as for the ortho compound. Coupling with the $Me_3SiCl$ took place in 5–6 hours at the reflux temperature of the coupling mix. No higher boiling was necessary. After the reflux period the ether was allowed to distil off and the residue heated to 120°. The cake was broken up in toluene and poured into water, cracked ice and HCl as before. Fractionation yielded 250 g. of product (56% yield) (see Table I).

The molecular refractions (*MR*) are reported in milliliters per mole and were calculated from the bond refractions for organosilicon compounds published by Warrick.[9]

**Group II. The (Chlorophenyl)-trimethylsilanes.**—For the preparation of this series of compounds it was proposed to utilize the greater reactivity of bromine and iodine in the formation of Grignard reagents. This procedure was used by Grüttner and Krause[10] for one of the earliest preparations of *p*-chlorophenylsilanes.

**(*o*-Chlorophenyl)-trimethylsilane.**—1-Chloro-2-iodobenzene (Eastman Kodak Co., Organic Chemicals Division) was employed. All attempts to prepare the desired compound by Grignard coupling were unsuccessful. Chlorination of $C_6H_5SiCl_3$ seemed a possibility. Several gallons of $C_6H_5SiCl_3$ were chlorinated and the monochlorination product separated by fractionation. Redistillation of the monochlorinated product showed slightly increasing specific gravity and boiling point toward the end of the plateau. The last cut of 155 g. boiling at 226–227° at 743 mm. was methylated as follows: 2.0 molar MeMgBr was prepared by passing 765 g. of MeBr into 144 g. of magnesium chips in 2300 g. of dry ether with stirring and cooling.

The 155 g. of (chlorophenyl)-trichlorosilane was added with stirring to the Grignard without temperature control. The heat of reaction boiled off most of the ether. The coupling slurry was diluted with toluene and poured into cold water, cracked ice and HCl. Fractionation of the product yielded 26 g. (22% yield) of product at the anticipated boiling point. The material was concluded to be at least 80% ortho isomer as indicated by the infrared curves (Impurity is para isomer.) The approximate physical properties are shown in Table II.

**(*m*-Chlorophenyl)-trimethylsilane.**—An approximately one molar Grignard was prepared by adding 100 g. of 1-bromo-3-chlorobenzene (Eastman Kodak Co.) to 12.6 g. of magnesium chips in 450 cc. of dry ether with stirring and cooling. The preparation was satisfactory. 100 g. of $Me_3SiCl$ was diluted with 200 cc. of dry toluene, then added with stirring to the Grignard. Coupling was slow, and occurred only after enough ether had been fractionated from the mix to attain a 70° pot temperature. After several hours at that temperature the coupling mix was cooled and poured into water, cracked ice and HCl. Fractionation of the organic layer yielded 69 g. at the anticipated boiling point (72% yield based on the bromide) (see Table II).

**(*p*-Chlorophenyl)-trimethylsilane.**—This compound was recently reported by Burkhard.[3] His procedure as derived from Grüttner and Krause[10] was duplicated.

**Group III. Trimethyl-*o*-xenylsilane.**—A solution of 141.5 g. of 2-chlorobiphenyl (Dow Chemical Company) in 89.6 g.

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[1] Presented at the Spring Scientific Meeting of the Midland Section, American Chemical Society.

[2] The Dow Chemical Company.

[3] Burkhard, This Journal, **68**, 2103 (1946).

[4] Gilman and Marshall, *ibid.*, **71**, 2066 (1949).

[5] Roberts, McElhill and Armstrong, *ibid.*, **71**, 2923 (1949).

[6] Kipping and Blackburn, *J. Chem. Soc.*, 1085 (1935).

[7] Polis, *Ber.*, **19**, 1012 (1886).

[8] Gilman and Smart, *J. Org. Chem.*, **15**, 720 (1950).

[9] Warrick, This Journal, **68**, 2455 (1946).

[10] Grüttner and Krause, *Ber.*, **50**, 1559 (1917).

TABLE I

THE TRIMETHYLTOLYLSILANES

| Isomer | B.p., °C. | Mm. | $d^{25}_4$ | $n^{25}D$ | F.p., °C. | Molar ref. Calcd. | Molar ref. Obsd. | Si,[a] % Calcd. | Si,[a] % Found |
|---|---|---|---|---|---|---|---|---|---|
| Ortho | 196 | 748 | 0.882 | 1.5005 | $<-75$ | 54.74 | 54.82 | 17.08 | 16.60 |
| Meta | 188 | 748 | .865 | 1.4902 | $<-75$ | 54.74 | 54.91 | 17.08 | 16.80 |
| Para | 192 | 748 | .860 | 1.4892 | $-38$ | 54.74 | 55.14 | 17.08 | 17.02 |

[a] Silicon analysis by sodium peroxide fusion followed by oxine/ammonium molybdate precipitation. See McHard, Servais and Clark, *Anal. Chem.*, **20**, 325 (1948).

TABLE II

THE (CHLOROPHENYL)-TRIMETHYLSILANES

| Isomer | B.p., °C. | Mm. | $n^{25}D$ | $d^{25}_4$ | F.p., °C. | Molar refr. Calcd. | Molar refr. Obsd. | Cl,[a] % Calcd. | Cl,[a] % Found |
|---|---|---|---|---|---|---|---|---|---|
| Ortho | 207–208 | 740 | (1.512) | (1.0266) | $<-75$ | 55.43 | ... | 19.2 | 20.5[b] |
| Meta | 206–207 | 740 | 1.5095 | 1.013 | .... | 55.43 | 54.94 | 19.2 | 20.1 |
| Para | 206–207 | 740 | 1.5067 | 0.9959 | 0.5 | 55.43 | 55.17 | 19.2 | 19.5 |

[a] Parr bomb fusion followed by electrometric titration with $AgNO_3$. [b] This is thought to be high because of possible contamination with 1–2% of trichlorobenzene, b.p. 208.5°, formed in the chlorination of the phenyltrichlorosilane.

of $Me_3SiCl$ and 100 cc. of toluene was added slowly to 37.9 g. of molten sodium in refluxing toluene with stirring. The heat of reaction maintained reflux. After the addition, reflux was maintained for an additional hour with stirring. The coupling mix was filtered hot and stripped toluene free at atmospheric pressure. Distillation yielded 140 g. of product (77% yield) (see Table III).

**Trimethyl-*m*-xenylsilane.**—A meta halogenated biphenyl was not available from commercial sources. A liquid xenyltrichlorosilane obtained from the by-products from coupling $C_6H_5MgCl$ and $SiCl_4$ was available. A solution of 100 g. of this chloride diluted with 100 cc. of dry toluene was added to an excess of MeMgCl. The ether was evaporated in a steam-bath and the slurry worked up as usual. Distillation yielded 70 g. of material at the anticipated boiling point. Cleavage of this product with concentrated sulfuric acid was shown to yield biphenyl and hexamethyldisiloxane as did the other isomers. The infrared data

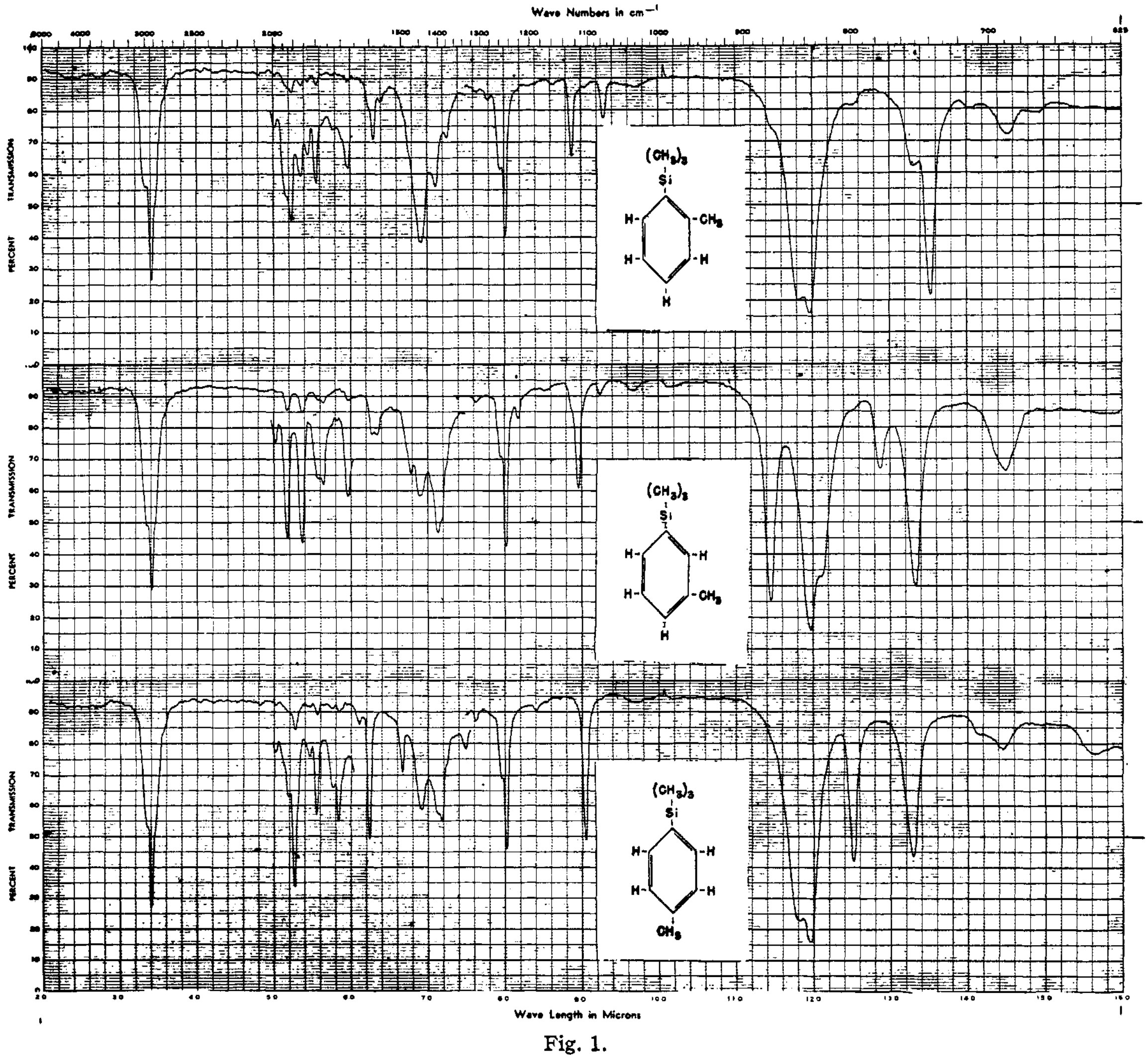

Fig. 1.

TABLE III

THE TRIMETHYLXENYLSILANES

| Isomer | B.p., °C. | B.p., Mm. | M.p., °C. | $d^{25}_4$ | $n^{25}D$ | Molar refr. Calcd. | Molar refr. Obsd. | Analyses, % Carbon[a] Calcd. | Analyses, % Carbon[a] Found | Analyses, % Silicon Calcd. | Analyses, % Silicon Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ortho | 148 | 13 | 21.7 | 0.9732 | 1.5612 | 75.97 | 75.23 | 79.62 | 79.75 | 12.30 | 12.53 |
| Meta | 138 | 4 | −51 | .9700 | 1.5652 | 75.97 | 76.02 | 79.62 | 76.29 | 12.30 | 12.35 |
| Para | 131 | 1 | 50–51 | | | | | 79.62 | 79.24 | 12.30 | 12.33 |

[a] Determined by an adaptation of the wet combustion method. See Niederl and Niederl, "Micro Methods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942, Chapt. 5.

herein presented are considered to be sufficient proof of structure. Since it is obvious that the compound is neither the ortho nor the para derivative, it must have the meta configuration (see Table III).

**Trimethyl-*p*-xenylsilane.**—The preparation of the ortho compound was duplicated as to quantities and procedure starting with 4-chlorobiphenyl (Dow Chemical Company). Fractionation yielded 155 g. of product (86% yield).

**Group IV. Bis-(trimethylsilyl)-benzenes.**—Several approaches for the preparation of these compounds seemed possible. Grignard compounds could be made from known dihalobenzenes and coupled with $Me_3SiCl$; sodium might be used as the coupling agent on the same materials; or (chlorophenyl)-trimethylsilanes might be coupled with $Me_3SiCl$ by either Grignard or Wurtz–Fittig reactions. All attempts to force the Wurtz–Fittig coupling of ortho and para dichlorobenzene with $Me_3SiCl$ were unsuccessful. Reaction in a sealed glass tube at 200° produced only $Me_3Si{\cdot}SiMe_3$.

***o*-Bis-(trimethylsilyl)-benzene.**—A mixture of 40 g. of the slightly impure (*o*-chlorophenyl)-trimethylsilane (above) and 25.8 g. of $Me_3SiCl$ was added with stirring to 11 g. of molten sodium in refluxing toluene. Some heat of reaction was noted. Reflux and stirring was continued 2 hours, then the coupling mix filtered hot. Distillation of the product yielded 35 g. of product (73% yield). This product was cooled, seeded with *p*-bis-(trimethylsilyl)-benzene and allowed to stand for 2 weeks at <0°. The liquid portion was decanted to yield essentially para isomer free product described in Table IV.

***m*-Bis-(trimethylsilyl)-benzene.**—A mixture of 85 g. of (*m*-chlorophenyl)-trimethylsilane and 55 g. of $Me_3SiCl$ was added with stirring to 23.5 g. of molten sodium in 500 cc. of refluxing toluene; procedure same as above. Distillation yielded 53 g. of product (52% yield), the properties of which are shown in Table IV.

***p*-Bis-(trimethylsilyl)-benzene.**—A mixture of 43.0 g. of crude (*p*-chlorophenyl)-trimethylsilane and 25.3 g. of

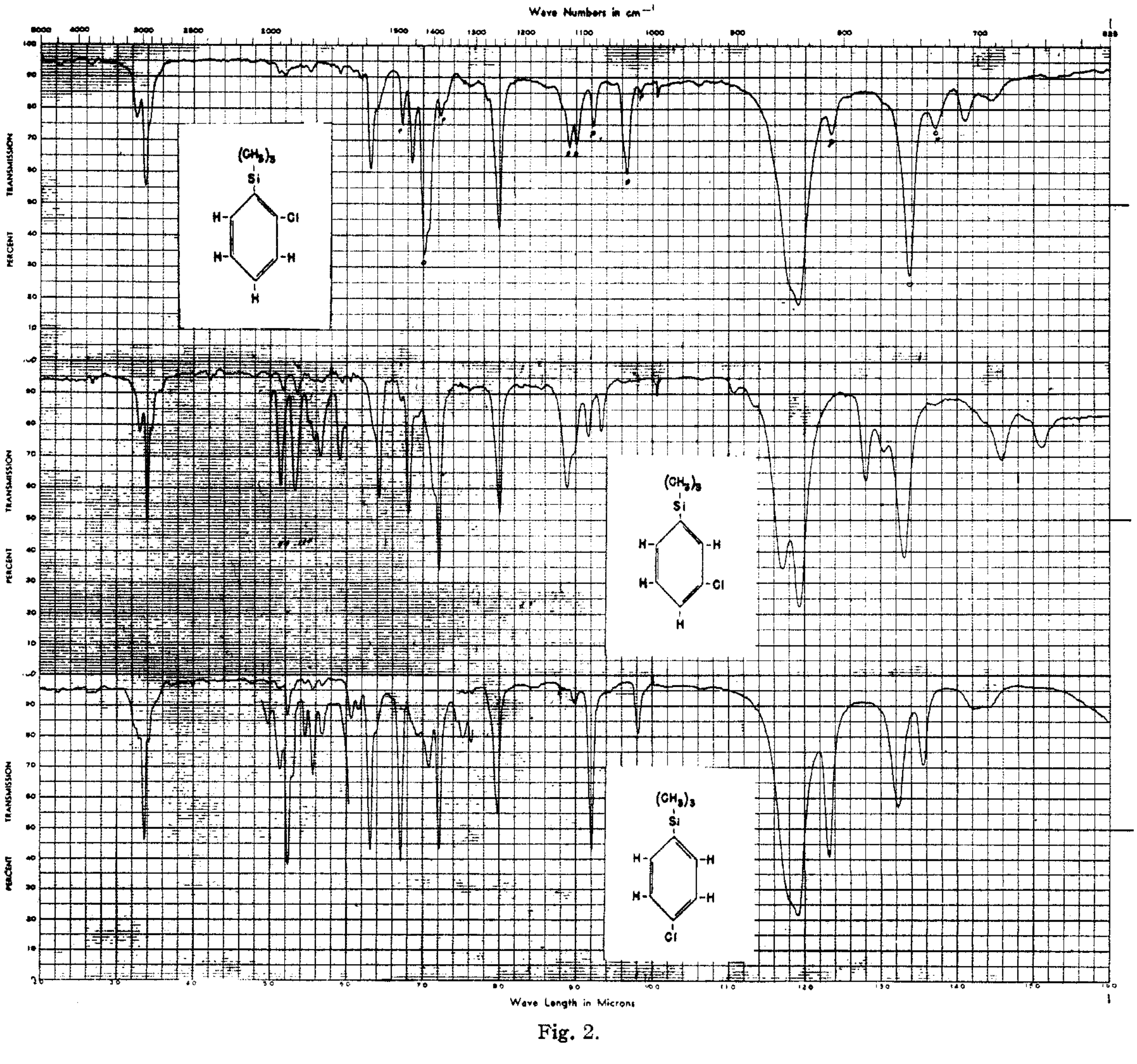

Fig. 2.

TABLE IV

THE BIS-(TRIMETHYLSILYL)-BENZENES

| Isomer | B.p., °C. | B.p., Mm. | M.p., °C. | $n^{25}_D$ | $d^{25}_4$ | Molar refr. Calcd. | Molar refr. Obsd. | Analyses, % Carbon[a] Calcd. | Analyses, % Carbon[a] Found | Analyses, % Silicon Calcd. | Analyses, % Silicon Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ortho | 135 | 20 | −72 | 1.5110 | 0.8985 | 73.68 | 74.17 | 64.90 | 65.46 | 25.22 | 24.14 |
| Meta | 112 | 22 | −26 | 1.4867 | 0.8685 | 73.68 | 73.62 | 64.90 | 64.05 | 25.22 | 24.23 |
| Para | 143 | 43 | 88 | | | | | 64.90 | 63.85 | 25.22 | 25.34 |

[a] These compounds are particularly resistant to oxidation which makes satisfactory analyses difficult. The molar refractions are perhaps a better indication of purity.

$Me_3SiCl$ was added with stirring to 11.8 g. of molten sodium in 500 cc. of refluxing toluene. Procedure same as above. Distillation yielded crystalline material which was recrystallized from absolute ethanol to yield 15 g. of long needles, m.p. 88° (30% yield).

**Discussion of Properties.**—The relative boiling points of these groups of isomers all assume the same pattern in that the meta and para isomers are virtually inseparable by distillation although the para is slightly the higher. It is noteworthy that the ortho isomer is always the highest boiling of the three isomers. This relationship is typical of the dihalobenzenes in the all-hydrocarbon system whether both halogens are the same or not. Chemically, however, a marked difference is apparent between these two classes of compounds. Dichlorobenzenes do not react to such a reagent as molten sodium, while the (chlorophenyl)-trimethylsilanes readily take part in Wurtz–Fittig type reactions.

In the non-silicon-containing hydrocarbon system, the para isomers usually have the highest melting points of the compounds in any given isomeric series. The information so far available indicates that this is also true of silicon-containing isomers.

**Preparation of Spectra.**—The infrared spectra shown here are photographic reproductions of records obtained on the Baird Associates double-beam spectrophotometer (sodium chloride prism) of The Dow Chemical Company. The samples

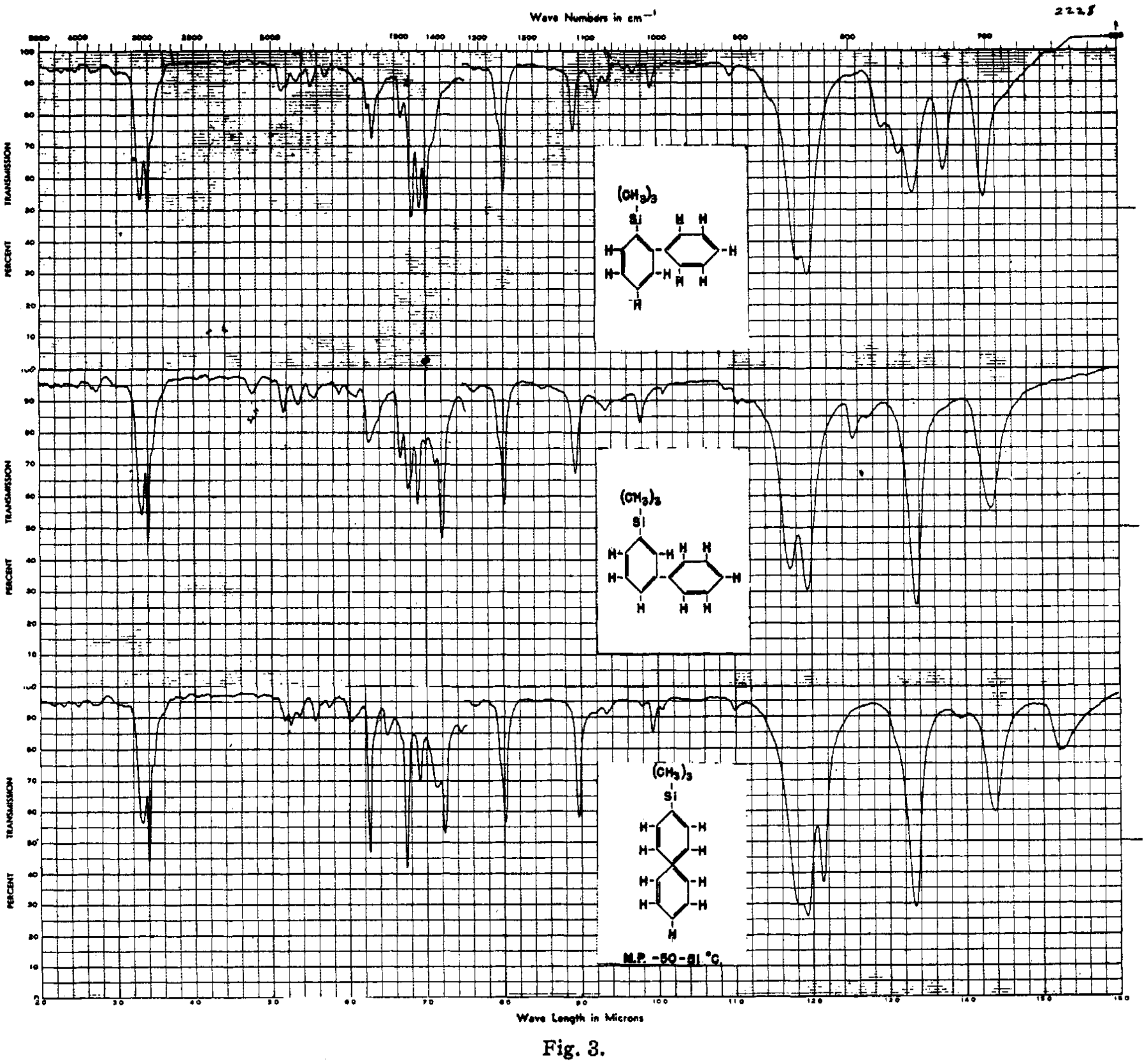

Fig. 3.

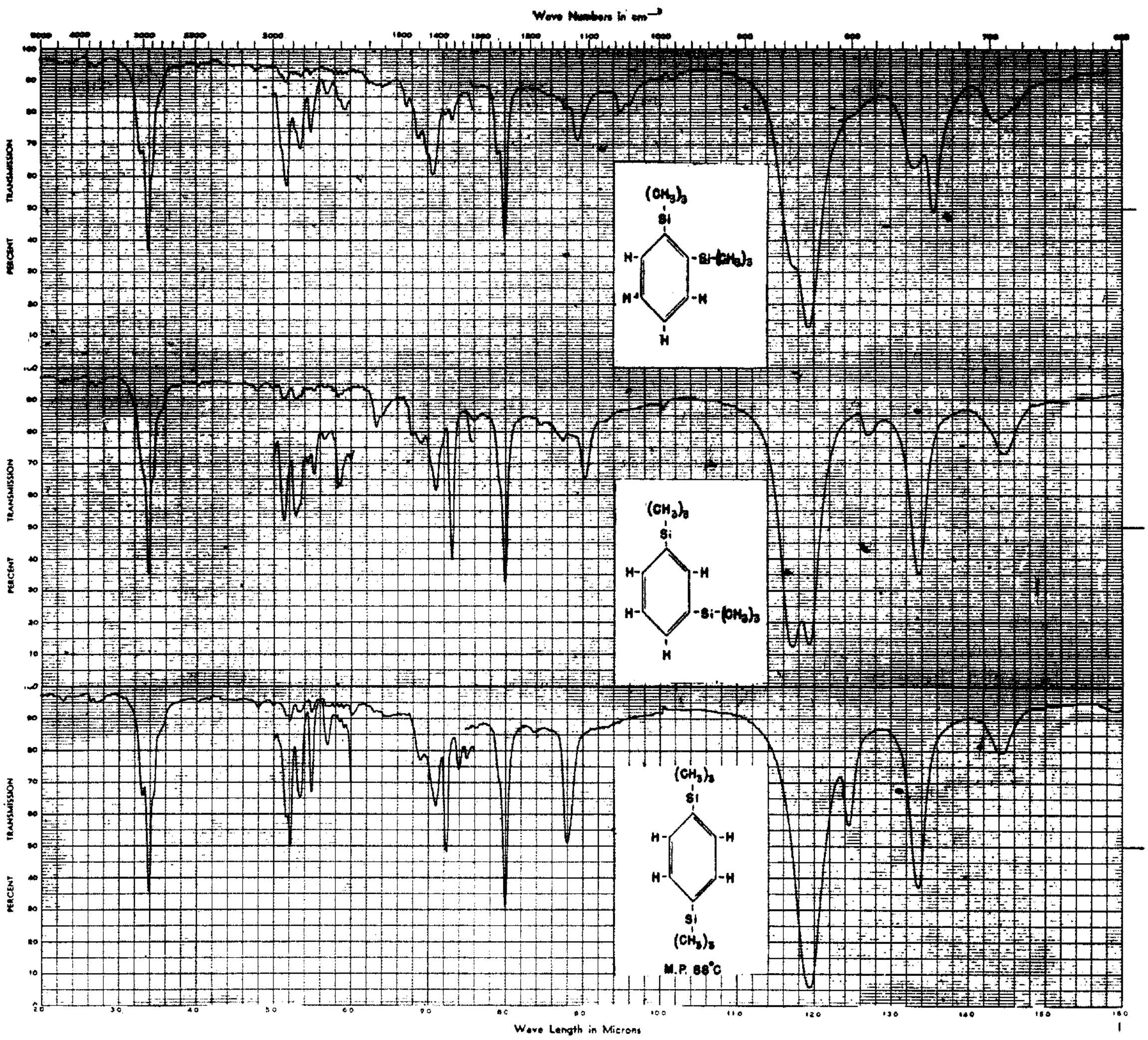

Fig. 4.

were observed in solution, 500 mg. made up to 5 ml. in $CCl_4$ from 2 to 7.5 $\mu$, 100 mg. made up to 5 ml. in $CS_2$ from 7.5 to 16 $\mu$. The sample cell was approximately 0.13 mm. thick; a compensating cell containing pure solvent of sufficient thickness to eliminate solvent bands was placed in the reference beam. For reasons to be taken up later, the region from 5 to 6 $\mu$ was studied at greater sample thickness for some compounds, either by obtaining the spectrum on the pure liquid in a 0.1 mm. cell or for solids, by using solutions in 1.1 mm. cells.

**Discussion of Spectra.**—Use of infrared spectra has been found very feasible for the analysis of difficultly separable position isomers. This avoids the involved and time consuming physical or chemical separations which would ordinarily be necessary. These infrared spectra are now available for analyzing preparations containing complex mixtures of these isomeric compounds.

We are not aware of any infrared spectra that have been published hitherto on disubstituted benzenes for which one or more substituents is a silyl group. It becomes of interest, therefore, to examine spectra of this type of compound in connection with methods for obtaining structural information.

Young, Duvall, and Wright[11] have shown how the 5 to 6 $\mu$ interval of the infrared spectra can be utilized for determining the positions of groups on substituted benzenes. The method is reported to have an extraordinarily wide range of applicability. It was gratifying to be able to apply the method to two of the sets of isomers reported here. Both the tolyl and chlorophenyl compounds can be characterized as ortho, meta and para by the spectral patterns in the 5 to 6 $\mu$ region as may be seen by reference to the Young, Duvall and Wright paper. It will be noted that inasmuch as the (*o*-chlorophenyl)-trimethylsilane was not pure, no attempt was made to study this spectral region.

The xenyl system, of couse, involves both the mono- and the disubstituted benzene rings so that the Young, Duvall and Wright method is not applicable.

The bis-(trimethylsilyl) system also gives patterns in the 5 to 6 $\mu$ region which cannot be utilized for isomer identification. Possible reasons why this may happen are discussed by Young, Duvall and Wright for other systems. Similar arguments may be applied to the bis-(trimethylsilyl) compounds.

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(11) Young, Duvall and Wright, *Anal. Chem.*, to appear shortly.

Ortho, meta and para compounds are ordinarily distinguished by utilizing certain longer wave length bands. Thus, it is well known that para compounds nearly always have a strong absorption band at 12–12.5 $\mu$, meta compounds at 12.5–13 $\mu$, and ortho compounds at 13–13.5 $\mu$. (See for example, Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).)

This appears to be true also for the compounds discussed here. However, the presence of the trimethylsilyl group introduces a very considerable complication. Other work[12] has established that the trimethylsilyl group usually is characterized by very strong absorption at about 12 $\mu$.

In general, organo-silicon compounds are best studied spectrally with optical paths equivalent to those employed for the spectra of this paper. Ordinarily, however, organic compounds are best studied for structural features at optical paths 5 to 10 times greater than these. Hence, the usual functional bands established for the infrared spectra of many organic compounds appear abnormally weak unless this factor of optical path is kept in mind. It is a nearly general feature of organosilicon compounds that many of the absorption bands in their infrared spectra are 5 to 10 times as intense as those of other organic compounds for equivalent optical paths. With this in mind, it is not too unreasonable to point out that in the ortho, meta and para systems studied here the characteristic longer wave length bands do appear as expected. The tolyl system, for example, has weaker bands at 12.5 $\mu$ for the para, 12.86 $\mu$ for the meta, and a strong band at 13.3 $\mu$ for the ortho. This latter band is probably misleading because the situation is further obscured by the fact that the spectra all show an intense band in the interval 13.3–13.5 $\mu$ which we have not attempted to interpret as characteristic of a particular mode of vibration. It may be supposed that the band characteristic of *o*-tolyl is completely merged in a much stronger band characteristic of the unexplained vibration. A similar ordering is readily discernible in the other isomer systems.

Of course, because of the complications introduced by the trimethylsilyl group, the longer wave length bands for ortho, etc., are really explained in a rather *ad hoc* fashion, reducing the usefulness and reliability of such bands for functional determinations.

It is of interest to note that the methyl group is well-marked by an absorption band near 8 $\mu$ as noted for other silicon compounds.[13,14] Detailed examination of the individual spectra, and intercomparison, shows that any considerable contamination of one isomer by others can be ruled out by utilizing particular infrared bands in the manner usual for quantitative infrared analysis. The spectra as presented in this paper do not, necessarily represent the optimum conditions for best quantitative analysis since they were chosen to bring out certain features associated with structural problems.

(12) Wright and Hunter, THIS JOURNAL, **69**, 803 (1947).

(13) Young, Koehler and McKinney, *ibid.*, **69**, 1410 (1947).

(14) Young, Servais, Currie and Hunter, *ibid.*, **70**, 3758 (1948).

MIDLAND, MICH.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE HERCULES POWDER COMPANY AND THE UNIVERSITY OF MARYLAND]

# Derivatives of Dehydroabietic Acid

BY YOLANDA T. PRATT[1]

Derivatives of dehydroabietic acid (I) with $\alpha$-hydroxyethyl, vinyl, succinoyl, chloromethyl, methylol and aminomethyl groups at the 6-position have been synthesized. An oxidation product of dehydroabietic acid has been identified as the 9-keto derivative (XIII) and 6-carboxydehydroabietic acid (III) and 6-chloromethyldehydroabietic acid (VIII) have been oxidized to 9-keto-6-carboxydehydroabietic acid (XIV).

Dehydroabietic acid (I), obtained by the dehydrogenation of resin acids[2,3] or dehydrogenation and hydrolysis of resin acid esters,[4] is a readily available acid containing a partially saturated phenanthrene nucleus. The aromatic ring serves as a reactive center for the introduction of functional groups leading to a wide variety of potentially useful products. Previous work in this field[3] has shown that the aromatic ring may be satisfactorily sulfonated, nitrated or acetylated at the 6-position. In the present study a number of derivatives have been obtained by way of the Friedel–Crafts and Blanc chloromethylation reactions. An oxidation product of dehydroabietic acid (I) has been identified as the 9-keto derivative (XIII) and both 6-carboxydehydroabietic acid (III) and 6-chloromethyldehydroabietic acid (VIII) have been oxidized to 9-keto-6-carboxydehydroabietic acid (XIV).

Methyl 6-carboxydehydroabietate had previously been obtained in low yield from methyl 6-acetyldehydroabietate (II) by means of the iodoform reaction.[3] The over-all yield for the conversion of II to the dicarboxylic acid (III) has been raised to 80% by application of King's[5] procedure which involves hydrolysis of the $\beta$-ketoalkylpyridinium iodide (VI). A good yield of methyl 6-$\alpha$-hydroxyethyldehydroabietate (IV) was obtained by the catalytic hydrogenation of the acetyl derivative (II). Upon dehydration the hydroxy compound (IV) yielded crude methyl 6-vinyldehydroabietate (V), which readily polymerized to a hard resin.

The keto dicarboxylic acid VII was obtained in about 50% yield when dehydroabietic acid (I) was

(1) Department of Chemistry, University of Maryland.

(2) E. E. Fleck and S. Palkin, THIS JOURNAL, **60**, 921 (1938).

(3) L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 2631 (1938); **61**, 2532 (1939).

(4) Unpublished results, Hercules Experiment Station.

(5) L. C. King, THIS JOURNAL, **66**, 894 (1944).