potassium pellet was pressed out under hexane from freshly cut potassium metal in a calibrated metal die.[11] The reactor was pumped at 10^{-6} mm. for 60 min. Methyl vinyl sulfone, 3 ml., distilled and dried over calcium hydride, was distilled to a tube connected to the reactor and frozen at −190°. A potassium mirror was formed on the reactor wall and the bis-2-ethoxyethyl ether distilled onto the mirror using a Dry Ice–acetone bath as a condensing agent. A blue solution formed during distillation. After the bis-2-ethoxyethyl ether distillation was complete, the sealed-in magnetic stirrer was started, the monomer thawed and added to the blue solution by tipping the tube. Reaction temperature was maintained by a Dry Ice–acetone bath. The color changed to a yellow amber within less than 30 sec. The reaction was terminated by introducing helium into the reactor and the addition of 10 ml. of 1*N* methanolic hydrochloric acid. The color then changed to a pale yellow and the solvent was stripped off under vacuum. The residual oil was added to methanol and after filtering and drying, 99 mg. of a brownish solid was obtained, crude m.p. 185–198°. This represented a 93% yield based on an equimolar reaction with charged potassium. The solid was taken up in hot water, treated with decolorizing charcoal, and the solution allowed to slowly evaporate until crystallization occurred, 60 mg. (74%), m.p. 202–203.5°; a mixed melting point with authentic IV, 202–203.5°.

Preparation of 1,4-bis(methyl sulfonyl)butane (IV). 1,4-Butanedithiol, 50 g. (0.41 mole) was dissolved in a solution of 40 g. (1 mole) of sodium hydroxide in 200 ml. of water. Dimethyl sulfate, 78 ml. (0.82 mole) was added dropwise with stirring and slight cooling over a 60-min. period. The reaction was stirred overnight, the oil was taken up in chloroform and the combined extracts dried over anhydrous magnesium sulfate. The chloroform was removed under vacuum and the residue fractionated. 1,4-Bis(methylthio)butane, 48.3 g., 78%, was collected at 135–137°/48 mm., n_D^{27} 1.5103, d_4^{25} 0.8322.

Anal. Calcd. for $C_6H_{14}S_2$: C, 48.00; H, 9.35; S, 42.67. Found: C, 48.69; H, 9.56; S, 42.65.

Hydrogen peroxide, 30%, 79.1 g., (0.7 mole) was added dropwise with stirring during a 60-min. period to 23 g. (0.15 mole) of 1,4-bis(methylthio)butane containing 0.5 ml. of phosphoric acid. The temperature was allowed to rise slowly of its own during the addition. The reaction was refluxed for 2.5 hr. and the reaction mass solidified on cooling. The solid was recrystallized twice from water, 19.8 g. (60%), m.p. 202.5–203.5°.

Anal. Calcd. for $C_6H_{14}O_4S_2$: C, 33.64; H, 6.54; O, 29.91; S, 29.91. Found: C, 33.90; H, 6.86; O, 29.87; S, 30.21.

Methyl vinyl sulfone-lithium-hexane. Methyl vinyl sulfone, 0.7 g., and 20 ml. of hexane were charged to the reactor and thoroughly degassed on the vacuum line. Lithium dispersion, 75 mg. of a 30% dispersion, was added under argon. The reaction was stirred at room temperature for 16 hr. under argon. After termination, the mixture was evaporated to near dryness. A small amount of crystals were left behind—these were stirred with methanol, filtered and dried. After recrystallization from water, 10 mg. of 1,4-bis(methylsulfonyl)butane was obtained, m.p. 200–202°; a mixed melting point with authentic IV, melted at 201–203°.

Methyl vinyl sulfone-lithium-tetrahydrofuran. Methyl vinyl sulfone, 2.1 ml., and 50 ml. of tetrahydrofuran were charged and degassed throughly on the vacuum line. Lithium dispersion, 177 mg. of a 30% dispersion was added under argon and the reaction was stirred overnight under argon. After termination the reaction was treated as above. Only a few milligrams of product was obtained; a mixed melting point with authentic IV, melted at 198–201°.

Acknowledgment. The authors gratefully acknowledge the assistance of Norman Goldberg, a student from Jonathan Dayton Regional High School, Berkeley Heights, N. J., supported by a Summer Science Training Grant of the National Science Foundation, in the preparation of 1,4-bis(methylsulfonyl)butane.

This work was also supported by Materials Laboratory Contract No. AF 33(616)-6866.

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[CONTRIBUTION FROM THE LABORATORY OF PHARMACEUTICAL CHEMISTRY,
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Ethylene and Phenylacetyl Chloride in the Friedel-Crafts Reaction. Novel Syntheses of 2-Tetralones and Benzofuranones[1]

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Received May 15, 1961

Phenylacetyl chloride and *p*-methoxyphenylacetyl chloride were treated separately with ethylene and aluminum chloride to give, respectively, 2-tetralone and 6-methoxy-2-tetralone. Under the same conditions, 2,3-dimethoxyphenylacetyl chloride failed to react with ethylene but instead underwent monodemethylation and ring closure to the benzofuranone.

Together with other investigators,[4–6] we have been interested in employing appropriately substituted 2-tetralones as intermediates for the preparation of morphine and morphine-like compounds. While 1-tetralones are readily obtained through cyclization of substituted phenylbutyric acids, 2-tetralones are much more difficult to synthesize. Heretofore, preparation of 2-tetralones has been hampered either by poor yields or difficulty accessible raw materials or both. Numerous examples are

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(1) Abstracted from a portion of the Ph.D. thesis of J. R. Campbell, The University of Kansas, 1952.

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(4) G. Stork and H. Conroy, *J. Am. Chem. Soc.*, **73**, 4743 (1951).

(5) M. D. Soffer *et al.*, *J. Am. Chem. Soc.*, **72**, 3704 (1950); J. A. Barltrop, *J. Chem. Soc.*, 958 (1946) and 399 (1947).

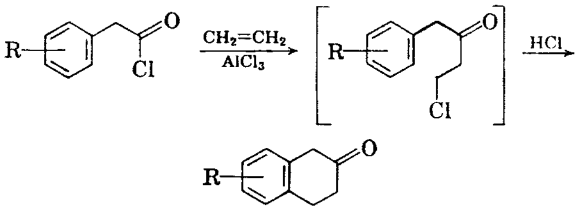
(6) R. Ghosh and R. Robinson, *J. Chem. Soc.*, 506 (1944).

found in the procedures for 2-tetralone itself. With a benzenedicarboxylic acid,[7] indanone,[8] substituted naphthalenes,[9] or various di- and tetrahydronaphthalenes,[10-12] ketone has been synthesized for the most part in low yield by fairly complex procedures.

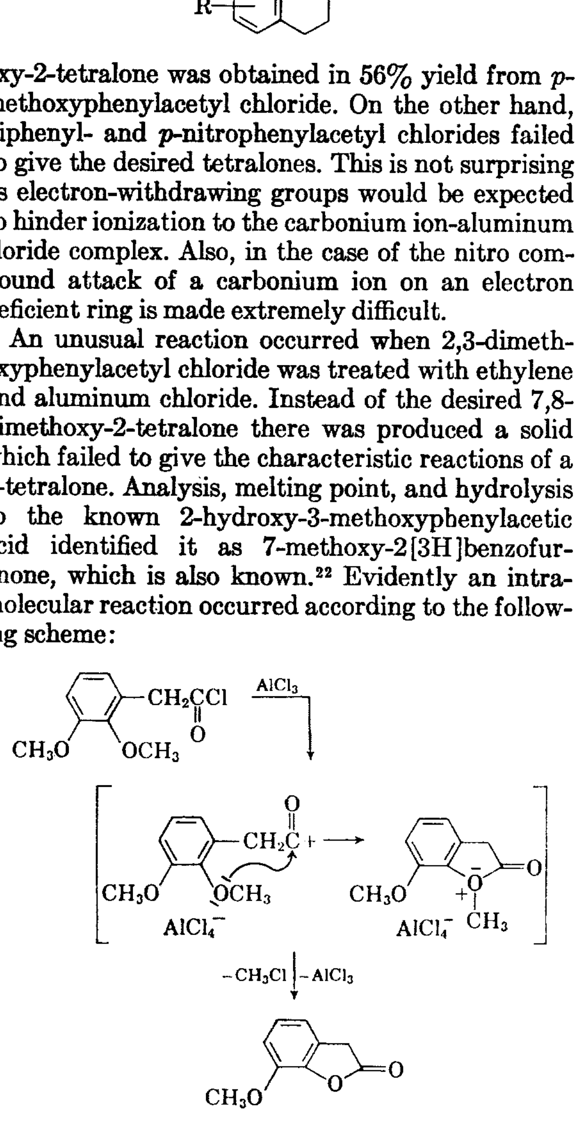
The most feasible preparation of 2-tetralone and its analogs has been by reduction of properly substituted naphthols and their alkyl ethers. Thus, 2-tetralone is formed from 2-naphthol or 2-methoxynaphthalene by catalytic reduction (40-50% yields)[13]; electrolytic reduction[14]; reduction with sodium in alcohol (56% yield)[11,15]; and sodium-liquid ammonia reduction (65% yield).[16] The last has been improved by Barltrop and Saxton[17] who increased the yield to 80%. Such reductive methods have been used to prepare a variety of substituted 2-tetralones,[5,15,18] but they suffer from one distinct disadvantage: easily reducible groups are attacked by the reagent employed.

Other valuable synthetic schemes for preparation of substituted 2-tetralones include mild oxidation of dihydronaphthalenes,[6] exhaustive halogenation of 2-naphthols,[19] and finally a double Friedel-Crafts reaction involving phenylacetyl chloride and 2-methyl-1-propene.[20] The last two mentioned reactants in the presence of stannic chloride yielded 2-methyl-5-phenyl-2-penten-4-one, which was then cyclized to 1,1-dimethyl-2-tetralone with aluminum chloride. Most of the studies reported in our paper had been completed prior to any knowledge of Colonge and Chambion's work.[1]

Our approach to the synthesis of 2-tetralone and substituted 2-tetralone also involved the Friedel-Crafts reaction. Phenylacetyl chlorides and ethylene in the presence of aluminum chloride might be expected to give 2-tetralones *via* the β-chloroethyl ketones[21] which need not be isolated. This proved to be the case when phenylacetyl chloride was converted to 2-tetralone in 75% yield. Also, 6-methoxy-2-tetralone was obtained in 56% yield from *p*-methoxyphenylacetyl chloride. On the other hand, diphenyl- and *p*-nitrophenylacetyl chlorides failed to give the desired tetralones. This is not surprising as electron-withdrawing groups would be expected to hinder ionization to the carbonium ion-aluminum cloride complex. Also, in the case of the nitro compound attack of a carbonium ion on an electron deficient ring is made extremely difficult.



An unusual reaction occurred when 2,3-dimethoxyphenylacetyl chloride was treated with ethylene and aluminum chloride. Instead of the desired 7,8-dimethoxy-2-tetralone there was produced a solid which failed to give the characteristic reactions of a 2-tetralone. Analysis, melting point, and hydrolysis to the known 2-hydroxy-3-methoxyphenylacetic acid identified it as 7-methoxy-2[3H]benzofuranone, which is also known.[22] Evidently an intramolecular reaction occurred according to the following scheme:



In the first complex the electron deficient carbonyl carbon reacts with an unshared pair of electrons and forms a new bond with the oxygen of the *o*-

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(7) A. Einhorn and J. S. Lumsden, *Ann.*, **286**, 275 (1895).

(8) B. Tchoubar, *Compt. rend.*, **215**, 224 (1942).

(9) E. Bamberger and R. Seligman, *Ber.*, **36**, 685 (1903); E. Bamberger and W. Lodter, *Ann.*, **288**, 74 (1895).

(10) J. von Braun, O. Braunsdorf, and G. Kirschbaum, *Ber.*, **55**, 3648 (1922); F. Straus and W. Ekhard, *Ann.*, **444**, 146 (1925); F. Straus and R. Rohrbadher, *Ber.*, **54**, 40 (1921); A. Kotz and W. Hoffmann, *J. prakt. Chem.*, (2) **110**, 101 (1925); B. Tchoubar, *Compt. rend.*, **214**, 117 (1942).

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(14) G. B. Diamond and M. D. Soffer, *J. Am. Chem. Soc.*, **74**, 4126 (1952).

(15) J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 689 (1942).

(16) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(17) J. A. Barltrop and J. E. Saxton, *J. Chem. Soc.*, 1038 (1952).

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(19) T. Zinke, *Ber.*, **21**, 3540 (1888).

(20) J. Colonge and J. Champion, *Compt. rend.*, **224**, 128 (1947).

(21) β-Chloroethyl ketones have been prepared in this way by others: E. M. McMahon *et al.*, *J. Am. Chem. Soc.*, **70**, 2971 (1948); K. Bowden *et al.*, *J. Chem. Soc.*, 45 (1946) and 1164 (1952).

(22) W. Mosimann and J. Tambor, *Ber.*, **49**, 1259 (1917).

methoxy group rather than with ethylene. The second complex loses methyl chloride to generate the benzofuranone. This reaction constitutes a useful alternative preparative method for benzofuranones.

Attempts were made to extend this 2-tetralone synthesis to the preparation of phenanthrones from naphthylacetyl chlorides. However, among the products isolated from treatment of 1-naphthylacetyl chloride with ethylene and aluminum chloride at 0° were ethylbenzene, acenaphthenone, and an unidentified white solid. Formation of these compounds was unexpected at the low temperatures employed. Also, an impure sample of 2-naphthylacetyl chloride, previously undescribed, failed to give a phenanthrone.

If optimum conditions for the ethylene reaction with arylacetyl halides can be developed, the method may have preparative value in the formation of cyclic ketones possessing two or more fused rings. Other solvents, catalysts and acyl halides should be investigated.

EXPERIMENTAL[23]

Phenylacetyl chloride. A mixture of 31 g. (0.2 mole) of phenylacetic acid and 24 g. (0.2 mole) of thionyl chloride was refluxed until gas evolution stopped. Distillation of the solution gave a small amount of unchanged thionyl chloride and 33 g. (94% yield) of reddish oil, b.p. 122°/70 mm. (lit.,[24] b.p., 110–111°/23 mm.).

2-Tetralone. After 16 g. (0.104 mole) of phenylacetyl chloride dissolved in 300 ml. of dry carbon disulfide was added to a well stirred suspension of 26.6 g. (0.2 mole) of anhydrous aluminum chloride in 400 ml. of dry carbon disulfide cooled in an ice bath, dry ethylene was passed into the stirred, cooled mixture for 4 hr. Good agitation was necessary, but sometimes was very difficult. The dark red mixture was poured onto ice and concentrated hydrochloric acid. Organic material was extracted with ether and the extract was washed with dilute sodium hydroxide and water. It was dried and evaporated to a dark residue which was distilled to give 11.4 g. (75% yield) of 2-tetralone, b.p. 140–143° (19 mm.) (lit.,[25] b.p., 142/15 mm.).

A saturated sodium bisulfite solution reacted with the product yielding white leaflets of water-soluble addition compound.

The *phenylhydrazone* crystallized from ethyl alcohol in yellow plates, m.p. 105°. After recrystallization from the same solvent, white plates were obtained m.p. 108° (lit.,[26] m.p., 107.5–108°).

The *semicarbazone* was recrystallized several times from ethyl alcohol, m.p. 188° (lit.,[25] m.p., 189–191°).

An intense purple-blue color was obtained on applying the "tetralone blue" test,[15] which consists in shaking a solution of the 2-tetralone in ethyl alcohol with dilute sodium hydroxide. Acidification of the alkaline solution separated an orange-red oil. This result conforms to the facts reported by Straus.[27]

2,3-Dimethoxyphenylacetic acid. A mixture of 100 ml. of 50% sodium hydroxide and 36 g. (0.2 mole) of 2,3-dimethoxyphenylacetonitrile[28] in 250 ml. of alcohol was heated at *reflux temperature overnight. Cooling and acidification of* the solution gave 38.7 g. (97% yield) of the crude acid, m.p. 79–81° (lit.,[29] m.p., 84°).

Attempted preparation of 7,8-dimethoxy-2-tetralone. 7-Methoxy-2[3H]benzofuranone. 2,3-Dimethoxyphenylacetyl chloride was prepared from 21 g. (0.1 mole) of 2,3-dimethoxyphenylacetic acid by heating the latter at reflux in benzene with an excess of thionyl chloride. Excess reagents were removed under reduced pressure at room temperature. Even a slight amount of heat caused decomposition of the acid chloride; therefore, it was utilized without purification.

A solution of 0.1 mole of crude 2,3-dimethoxyphenylacetyl chloride in 100 ml. of dry carbon disulfide was slowly added to a suspension of 26.6 g. (0.2 mole) of anhydrous aluminum chloride in 700 ml. of dry carbon disulfide kept cooled to 0°. The large quantity of solvent was necessary to prevent gumming and clumping. Following the addition, a steady stream of ethylene was passed into the stirred and cooled mixture for 6 hr. (Later results proved the addition of ethylene to be unnecessary.) The mixture was poured onto a mixture of concentrated hydrochloric acid and ice, the carbon disulfide layer was separated and the aqueous layer was washed with ether. The extracts were combined, washed with water, dried, and reduced to a residue. Distil*lation yielded 10.3 g. (62%) of yellow oily 7-methoxy-2[3H]-*benzofuranone, b.p. 120°/0.2 mm., which solidified immediately. Colorless plates were obtained upon recrystallization, of the solid from petroleum ether (b.p. 60–68°) m.p. 79° (lit.,[22] m.p., 80° in low yield).

Anal. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.88; H, 5.17.

A portion of the lactone was hydrolyzed with 10% sodium hydroxide giving 2-hydroxy-3-methoxyphenylacetic acid, m.p. 124°. It gives a green color with 5% ferric chloride in alcohol solution. These observations are identical with that of others.[19]

p-Methoxyphenylacetic acid. According to standard procedures, 138 g. (1 mole) of *p*-anisyl alcohol was converted to 141 g. (85% yield) of crude *p*-methoxyphenylacetic acid *via p*-anisyl chloride and nitrile. The acid was the only product isolated throughout and melted at 83–84°. The pure material melts at 86°.[30]

p-Methoxyphenylacetyl chloride. Treatment of 23.8 g. (0.14 mole) of *p*-methoxyphenylacetic acid with a slight excess of thionyl chloride as described before gave 22.4 g. (85% yield) of the corresponding acid chloride, b.p. 92° (1 mm.) and 144–145° (20 mm.) (lit.,[31] b.p., 139°/12.5 mm.; 90% yield).

6-Methoxy-2-tetralone. Used in the method devised previously for the synthesis of 2-tetralone, 30 g. (0.16 mole) of *p*-methoxyphenylacetyl chloride and 43 g. (0.32 mole) of anhydrous aluminum chloride gave 16 g. (56% yield) of 6-methoxy-2-tetralone, b.p. 183°/30 mm. and 111–116°/0.2 mm. (lit.,[12] b.p., 164°/11 mm.).

The product gave a positive "tetralone-blue test."[15] Its *semicarbazone* crystallized from alcohol, m.p. 158–159° (lit.,[32] m.p., 159°). The *2,4-dinitrophenylhydrazone* formed red-orange crystals, m.p. 136°, from ethyl alcohol (lit.,[12] m.p., 132°).

1-Naphthylacetyl chloride. By the same general procedure given previously, an excess of thionyl chloride and 26 g. (0.14 mole) of 1-naphthylacetic acid gave 24.5 g. (86% yield) of the acid chloride, b.p. 127–133°/0.5 mm. A higher boiling point, 148–155°/0.05 mm., has been reported.[33]

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(23) All melting points and boiling points are uncorrected.

(24) L. C. Raiford and H. P. Lankelma, *J. Am. Chem. Soc.*, **47**, 1111 (1925).

(25) E. Mosettig and A. Burger, *J. Am. Chem. Soc.*, **53**, 2295 (1931).

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(29) S. Chakravarti and M. Swaminathan, *J. Indian Chem. Soc.*, **11**, 107 (1934).

(30) O. Hromatka, *Ber.*, **75**, 123 (1942).

(31) A. Sosa, *Ann.*, **14**, 5 (1940).

(32) W. Salzer, *Z. Physiol. Chem.*, **274**, 46 (1942).

(33) D. R. Patent **562,391.**

Attempted preparation of 1,2,3,4-tetrahydro-3-phenanthrone. Used in the 2-tetralone method with benzene as a solvent, ethylene, aluminum chloride, and 1-naphthylacetyl chloride gave 20 g. of ethylbenzene, b.p. 134–135°, n_D^{25} 1.4931, and a small amount of di- and triethylbenzenes, b.p. 95–115° (25–30 mm.). Treatment of the residue with ethyl alcohol yielded 7 g. of acenaphthenone, m.p. 115–117°. Recrystallization from ethyl alcohol or petroleum ether (b.p. 60–68°) m.p. to 121°. A mixed melting point with a known sample showed no depression. Also isolated was 3 g. of a white, crystalline solid which could not be identified.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Participation of Carbon Disulfide in the Friedel-Crafts Reaction

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Received December 27, 1960

Carbon disulfide participated to a major extent when used as a solvent for the reaction of chloromethyltrimethylsilane with benzene in the presence of an equimolar amount of aluminum chloride. Bright red trimethylsilylmethyl dithiobenzoate, $C_6H_5CS_2CH_2Si(CH_3)_3$, was formed in about 50% yield. Under the same conditions *n*-amyl chloride behaved normally with formation of amyl-substituted benzenes and no sulfur-containing products. Extensive participation of carbon disulfide was also qualitatively observed in the reaction of chloromethyltrimethylsilane with chlorobenzene, octene-1, isooctane, and *n*-octane and also in the reaction of (chloromethyl)methyldichlorosilane with benzene, all in the presence of an equimolar amount of aluminum chloride.

Carbon disulfide is ordinarily regarded as an excellent solvent for Friedel-Crafts reactions because it is generally believed not to participate in such reactions.[1] However, we have found instances in which participation of carbon disulfide becomes the main reaction, apparently with formation of dithio esters as the major product.

Thus refluxing equimolar quantities of chloromethyltrimethylsilane, benzene and aluminum chloride in excess carbon disulfide resulted in gradual consumption of the aluminum chloride. There was no evolution of hydrogen chloride, but a bright red lower layer formed which reached a constant volume in four hours. Separating, hydrolyzing, washing, drying, and distilling this material gave a bright red liquid product.

This substance appeared to be trimethylsilylmethyl dithiobenzoate formed according to the following equation:

$$C_6H_6 + CS_2 + ClCH_2Si(CH_3)_3 \xrightarrow[AlCl_3]{} C_6H_5CS_2CH_2Si(CH_3)_3$$

Quantitative analysis for carbon, hydrogen, sulfur, silicon, chlorine, and molecular weight substantiated this supposition, although exact agreement with theoretical values was not achieved. The infrared spectrum of the product was consistent with the structure proposed[2] and also suggested that one of the contaminants was a thiol ester, $C_6H_5COSCH_2Si(CH_3)_3$, arising from hydrolysis or oxidation of the dithio ester or the intermediate reaction complex.

The identity of the product was further supported by experiments aimed at ascertaining its progenitor. Ethyldimethylchlorosilane, which might have arisen from chloromethyltrimethylsilane by rearrangement,[3] gave no red oil on being refluxed with benzene, carbon disulfide, and aluminum chloride. Neither did trimethylchlorosilane nor diethyldichlorosilane. When carbon disulfide was omitted from the reaction mixture—*i.e.* when chloromethyltrimethylsilane, benzene and aluminum chloride were refluxed—the major products were methylethylpolysiloxanes and toluene. The former apparently arose from rearrangement of the starting material.[3] The toluene probably arose from hydrogen chloride cleavage of benzyltrimethylsilane initially formed by coupling.

The preparation of trimethylsilylmethyl dithiobenzoate was carried out under various conditions. A yield of 43% was obtained upon refluxing equimolar amounts of chloromethyltrimethylsilane, benzene, and aluminum chloride in excess carbon disulfide for four hours; the bright red lower liquid layer was hydrolyzed on ice, washed, dried, and distilled. A product obtained from a similar run by steam distillation seemed to contain more thiol ester. In another run satisfactory results were obtained when the amount of carbon disulfide was reduced to theoretical and excess benzene was used as the solvent. When only a catalytic amount

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(1) Actually a few instances of such participation have been reported. The first such instance was with pyrazolones —E. Benary and A. Schmidt, *Ber.*, **57**, 517 (1924). Other instances were later demonstrated with phenol, phenol ethers and even benzene itself, but the yields were vanishingly small—H. Jorg, *Ber.*, **60B**, 1466 (1927).

(2) C. S. Marvel, P. de Radzitzky, and J. J. Brader, *J. Am. Chem. Soc.*, **77**, 5997 (1955), tentatively assigned the 8.5 μ infrared absorption band to the C=S group in dithio esters as a result of their studies of simple aliphatic dithio esters.

(3) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).