[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Some Chlorinated Aryl Silanes for the Examination of their Insecticidal Properties

BY HENRY GILMAN AND LEWIS S. MILLER

Several new silanes containing *p*-chlorophenyl and/or trichloromethyl groups have been prepared for examination of their insecticidal properties. In the course of the investigation it was found that two but not three chlorines can be substituted on a methyl group in dimethyl-bis-(*p*-chlorophenyl)-silane without cleavage of carbon–silicon bonds. The trichloromethyl group in trichloromethyl-tris-(*p*-chlorophenyl)-silane is cleaved by aqueous base, but not by water or aqueous acid, to yield hexakis-(*p*-chlorophenyl)-disiloxane.

During the course of some studies on the use of organolithium compounds in the preparation of substituted aryl silanes, a series of compounds containing active insecticidal groupings was prepared. Investigations[1] made during the development of DDT showed the insecticidal activity of compounds containing certain combinations of *p*-chlorophenyl groups and anesthetizing and liquid-solubilizing groups such as the trichloromethyl group. In the present work some of these groups have been incorporated in organosilicon compounds.

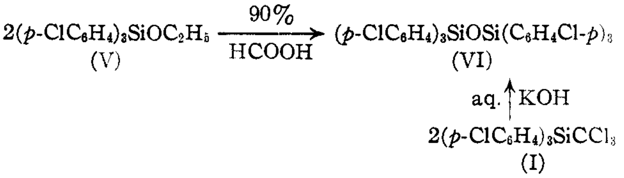
The series of silanes having the general formula $(C_6H_5)_nSi(C_6H_4Cl\text{-}p)_{4-n}$ where $n = 0$ to 3 was prepared by treating the corresponding phenylethoxy- or phenylchlorosilane with *p*-chlorophenyllithium prepared by the halogen–metal interconversion reaction.[2] Methyltris-(*p*-chlorophenyl)-silane and dimethylbis-(*p*-chlorophenyl)-silane were prepared similarly by treating methyltrichlorosilane and dimethyldiethoxy- or dimethyldichlorosilane, respectively, with *p*-chlorophenyllithium.

Direct chlorination of methyltris-(*p*-chlorophenyl)-silane gave a 22% yield of trichloromethyltris-(*p*-chlorophenyl)-silane (I)

$$CH_3SiCl_3 \xrightarrow{p\text{-}ClC_6H_4Li} CH_3Si(C_6H_4Cl\text{-}p)_3 \xrightarrow{Cl_2} Cl_3CSi(C_6H_4Cl\text{-}p)_3 \quad (I)$$

Under similar conditions, methyltriphenylsilane[3] gave a 38.6% yield of trichloromethyltriphenylsilane (II). Direct chlorination of dimethylbis-(*p*-chlorophenyl)-silane with and without carbon tetrachloride as a solvent gave none of the desired methyl-(trichloromethyl)-bis-(*p*-chlorophenyl)-silane (III). In the case of dimethyldichlorosilane,[4] substitution of up to three chlorine atoms has been shown to proceed on the methyl group first attacked. In the case of dimethylbis-(*p*-chlorophenyl)-silane, attempted substitution of more than two chlorine atoms on a methyl group resulted in cleavage of the molecule. Thus, in each experiment, *p*-dichlorobenzene was isolated and the only other product identified was methyl-(dichloromethyl)-bis-(*p*-chlorophenyl)-silane. Other attempts to prepare (III) by chlorination with sulfuryl chloride in the presence of benzoyl peroxide and by treatment of methyl-(trichloromethyl)-dichlorosilane[4] (IV) with *p*-chlorophenyllithium were not successful.

The treatment of ethyl orthosilicate with three equivalents of *p*-chlorophenyllithium followed by dilute acid hydrolysis gave tris-(*p*-chlorophenyl)-ethoxysilane (V). Treatment of (V) with a solution of potassium hydroxide in dioxane–ethanol (1:1) gave the expected tris-(*p*-chlorophenyl)-silanol. Heating (V) with 90% formic acid[5] gave hexakis-(*p*-chlorophenyl)-disiloxane (VI). (VI) was also formed by warming (I) with 50% aqueous sodium hydroxide.



$$\begin{tikzcd}[column sep=large] \underset{(V)}{2(p\text{-}ClC_6H_4)_3SiOC_2H_5} \arrow[r, "90\%", "HCOOH"'] & \underset{(VI)}{(p\text{-}ClC_6H_4)_3SiOSi(C_6H_4Cl\text{-}p)_3} \\ & \underset{(I)}{2(p\text{-}ClC_6H_4)_3SiCCl_3} \arrow[u, "aq.\ KOH"] \end{tikzcd}$$

Similarly, (II) was cleaved by 40% aqueous potassium hydroxide to yield hexa-phenyldisiloxane. Krieble and Elliott[4] found that (IV) was cleaved by water and acid as well as by aqueous base. In contrast, (I) was not cleaved by boiling water or 30% aqueous hydrochloric acid but only by base. These results are in accord with previous interpretations of nucleophilic displacements on silicon.[6] Since the *p*-chlorophenyl groups in (I) are less electron attracting than the corresponding chlorine atoms in (IV) (or hydroxyl groups resulting from their hydrolysis), the central silicon atom is less subject to attack by a nucleophilic agent.

The assay of some of these compounds for value as insecticides is being conducted by Dr. C. H. Richardson[7] and will be reported elsewhere.

Experimental

Tris-(*p*-chlorophenyl)-ethoxysilane.—A solution of *p*-chlorophenyllithium in 300 ml. of ether was prepared from 0.151 mole of *n*-butyllithium[8,9] and 0.166 mole of *p*-chlorobromobenzene (Gilman, Langham and Moore[2] reported a 90% yield of *p*-chlorobenzoic acid after carbonation). This solution was stirred for 30 minutes and then added to 10.4 g. (0.05 mole) of ethyl orthosilicate. After stirring 1 hour, Color Test I[10] was negative. The product was hydrolyzed with dilute acid and the ether layer was separated and dried over sodium sulfate. After removing the ether and other materials volatile below 150° at 20 mm., the residue solidified on standing. Two crystallizations from 95% ethanol gave 6.0 g. (29.5%) of white crystals melting at 128°. This material was shown to contain no active hy-

---

(1) Lauger, Martin and Muller, *Helv. Chim. Acta*, **27**, 892 (1944).

(2) Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

(3) Kipping, *J. Chem. Soc.*, **79**, 449 (1901); Kraus and Eatough, THIS JOURNAL, **55**, 5008 (1933).

(4) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

(5) Unpublished studies by H. W. Melvin.

(6) Krieble and Elliott, THIS JOURNAL, **68**, 2291 (1946).

(7) Department of Entomology, Iowa State College.

(8) Gilman, Beel, Brannen, Bullock, Dunn and Miller, THIS JOURNAL **71**, 1499 (1949).

(9) Gilman and Haubein, *ibid.*, **66**, 1515 (1944). This paper describes a procedure for the analysis of RLi compounds.

(10) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

drogen by treatment with a solution of methylmagnesium iodide.

Anal. Calcd. for $C_{20}H_{17}OCl_3Si$: Si, 6.88. Found[11]: Si, 6.84.

Hexakis-(*p*-chlorophenyl)-disiloxane.—A sample of tris-(*p*-chlorophenyl)-ethoxysilane was refluxed for 20 minutes with 90% formic acid.[5] After filtering, the solid was crystallized from methanol to give a product melting at 210°. This compound was also obtained as described under trichloromethyltris-(*p*-chlorophenyl)-silane.

Anal. Calcd. for $C_{36}H_{24}OCl_6Si_2$: Si, 7.58. Found: Si, 7.68.

Tris-(*p*-chlorophenyl)-silanol.—Three grams of tris-(*p*-chlorophenyl)-ethoxysilane was dissolved in 20 ml. of a 1:1 dioxane–ethanol solution containing 0.73 mole of potassium hydroxide and 2.63 moles of water per liter. After warming for 15 minutes, the mixture was acidified with dilute acid and extracted with ether. Evaporation of the ether layer and recrystallization of the residue from petroleum ether (b.p. 60–70°) gave 2.6 g. (93%) of crystals melting at 121°.

Anal. Calcd. for $C_{18}H_{13}OCl_3Si$: Si, 7.41. Found: Si, 7.54.

The silicon analysis of this compound was carried out according to the following micro procedure:

Procedure for the Microdetermination of Silicon.[12a]—A 5–15-mg. sample is weighed into a platinum boat, which, along with a platinum cylinder, has been previously tared. One drop of concd. sulfuric acid is carefully added to the sample and the boat is placed in the cylinder. The boat and cylinder are then inserted in the end of a Vicor tube heated electrically[12b] by a three-foot length of no. 30 nichrome wire wound around the tube for a distance of six centimeters. The other end of the tube is bent down slightly and heated with a burner to provide a current of air over the boat. The temperature of the cylinder and contents is raised slowly over a 10-minute period (or until all the acid has evaporated) by slowly increasing the voltage across the heating coil by means of a variable transformer. The voltage is then increased abruptly until the cylinder becomes a dull red and the ignition is continued for 5 minutes. The cylinder, boat and contents are then cooled and weighed together.

Tetrakis-(*p*-chlorophenyl)-silane.—An ethereal solution of *p*-chlorophenyllithium prepared from 0.27 mole of *n*-butyllithium and 51.7 g. (0.27 mole) of *p*-chlorobromobenzene was added to 10.4 g. (0.05 mole) of ethyl orthosilicate in 50 ml. of ether. After stirring 30 minutes, the product was recovered as described for tris-(*p*-chlorophenyl)-ethoxysilane. The residue was crystallized three times from ethanol–petroleum ether (b.p. 77–120°) to yield 15.5 g. (65%) of a white crystalline solid, m.p. 181°.

Anal. Calcd. for $C_{24}H_{16}Cl_4Si$: Cl, 29.8; Si, 5.93. Found: Cl, 29.6; Si, 6.03.

Phenyltris-(*p*-chlorophenyl)-silane.—To 15.0 g. (0.0625 mole) of phenyltriethoxysilane[13] was added a solution of *p*-chlorophenyllithium prepared by adding 0.36 mole of *n*-butyllithium in 360 ml. of ether to 68.5 g. (0.357 mole) of *p*-chlorobromobenzene in 100 ml. of ether. After stirring ten minutes, the product was recovered as described for tris-(*p*-chlorophenyl)-ethoxysilane. The solid material remaining was crystallized three times from ethanol to give 13 g. (47.5%) of white crystals melting at 134°.

Anal. Calcd. for $C_{24}H_{17}Cl_3Si$: Cl, 24.2; Si, 6.39. Found: Cl, 24.0; Si, 6.42.

Diphenylbis-(*p*-chlorophenyl)-silane.—Diphenyldiethoxysilane[14] was prepared by adding 0.543 mole of phenyllithium in 480 ml. of ether to 56.5 g. (0.271 mole) of ethyl orthosilicate in 100 ml. of ether over a one-hour period. After filtration of the ethereal solution, the ether was removed and the residue was fractionated yielding 29.5 g. of product boiling at 117–120° at 0.12 mm. To 25 g. (0.092 mole) of this product was added a solution of *p*-chlorophenyllithium prepared from 51.5 g. (0.27 mole) of *p*-chlorobromobenzene and 0.30 mole of *n*-butyllithium. After stirring one hour, the product was recovered as for tris-(*p*-chlorophenyl)-ethoxysilane. Crystallization of the residue from 95% ethanol gave 23 g. (61.5%) of white solid melting at 131°.

Anal. Calcd. for $C_{24}H_{18}Cl_2Si$: Cl, 17.58; Si, 6.94. Found: Cl, 17.5; Si, 6.98.

Triphenyl-(*p*-chlorophenyl)-silane.—Triphenylethoxysilane[15] was prepared by adding 0.3 mole of phenyllithium in 200 ml. of ether to 20.8 g. (0.1 mole) of ethyl orthosilicate. This solution was added to an excess of *p*-chlorophenyllithium and the product was recovered as for tris-(*p*-chlorophenyl)-ethoxysilane. Crystallization of the residue from ethanol gave 20 g. (54%) of white solid melting at 157°.

Anal. Calcd. for $C_{24}H_{19}ClSi$: Cl, 9.57; Si, 7.57. Found: Cl, 9.57; Si, 7.59.

Methyltris-(*p*-chlorophenyl)-silane.—To the *p*-chlorophenyllithium prepared from 0.30 mole of *n*-butyllithium and 59 g. (0.31 mole) *p*-chlorobromobenzene in 330 ml. of ether was added 15.0 g. (0.1 mole) of methyltrichlorosilane[16] in 50 ml. of ether. After stirring for 3 hours at room temperature the reaction mixture was poured into acidified water and the ether layer was separated and dried over sodium sulfate. The ether was removed and the residue distilled at 200–220° at 0.15 mm. After two crystallizations from methanol, 20 g. (53%) of white crystalline product was recovered, m.p. 86°.

Anal. Calcd. for $C_{19}H_{15}Cl_3Si$: Cl, 28.2; Si, 7.42. Found: Cl, 28.0; Si, 7.43.

Trichloromethyltris-(*p*-chlorophenyl)-silane.—Ten grams (0.0265 mole) of methyltris-(*p*-chlorophenyl)-silane was placed in a tube equipped with an alundum gas-dispersion inlet tube and a reflux condenser. The exit line led to a trap cooled with a Dry Ice–acetone mixture. The tube was heated to 170° and irradiated with light from an ultraviolet lamp while chlorine was passed through at a slow rate for 3 hours. At this time 2.6 g. (0.0732 g. atom) of chlorine had been absorbed. After flushing the system with nitrogen for 1 minute and cooling to room temperature, the reaction mixture was extracted four times with hot methanol. An insoluble residue was crystallized from petroleum ether (b.p. 79–119°) to yield 2.8 g. (22%) of white crystals, m.p. 161°. A sample of this product was boiled for 15 minutes in water and in 30% aqueous hydrochloric acid, respectively, without change. However, a small sample was converted to hexakis-(*p*-chlorophenyl)-disiloxane, m.p. 210° (mixed melting point), by warming for 10 minutes with 50% aqueous sodium hydroxide.

Anal. Calcd. for $C_{19}H_{12}Cl_6Si$: Cl, 44.3; Si, 5.84. Found: Cl, 44.2; Si, 5.68.

Dimethylbis-(*p*-chlorophenyl)-silane. A. From Dimethyldichlorosilane.—To a solution of *p*-chlorophenyllithium prepared from 0.32 mole of *n*-butyllithium and 63 g. (0.33 mole) of *p*-chlorobromobenzene in 520 ml. of ether was added 19.3 g. (0.15 mole) of dimethyldichlorosilane[9] in 50 ml. of ether. After stirring 2 hours at room temperature, the product was poured into acidified ice-water and the ether layer was separated and dried over sodium sulfate. Subsequent to removing the ether, the residue distilled at 135–175° at 0.2 mm. The distillate solidified on cooling and the solid melted at 47° after two crystallizations from methanol. The yield was 29.9 g. (71%). In another run, 0.27 mole of dimethyldichlorosilane gave 60 g. (0.216 mole) (80%) of product, b.p. 168° at 0.5 mm., m.p. 47°.

Anal. Calcd. for $C_{14}H_{14}Cl_2Si$: Cl, 25.2; Si, 10.0. Found: Cl, 25.0; Si, 10.0.

B. From Dimethyldiethoxysilane.—The dimethyldiethoxysilane[17] was prepared by the reaction of 0.165 mole of methylmagnesium bromide with 31.2 g. (0.15 mole) of ethyl orthosilicate in 352 ml. of ether. Filtration and fractionation of the product gave a 5.2-g. fraction, b.p. 113–117°. This 5.2 g. (0.035 mole) of dimethyldiethoxysilane in 50 ml. of ether was added to the *p*-chlorophenyllithium prepared from 0.087 mole of *n*-butyllithium and 15.3

---

(11) Gilman, Hofferth, Melvin and Dunn, THIS JOURNAL, **72**, 5767 (1950). The macro method used for the determination of silicon is described in this paper.

(12) (a) Niederl and Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1942, p. 62; (b) Rodden, *Mikrochemie*, **18**, 97 (1935).

(13) Corning Glass Works, U. S. Patent 2,386,452 (1945) [*C. A.*, **40**, 603 (1946)].

(14) Kipping, *J. Chem. Soc.*, **125**, 2728 (1927).

(15) Polis, *Ber.*, **19**, 1012 (1886).

(16) Anderson Laboratories, Inc., Adrian, Mich.

(17) Corning Glass Works, U. S. Patent 2,380,057 (1945) [*C. A.*, **40**, 88 (1946)].

g. (0.08 mole) of *p*-chlorobromobenzene in 310 ml. of ether. The product was recovered as above to yield 9.9 g. (71%) of product, m.p. 47°. A mixed melting point with the product from (A) showed no depression.

Direct Chlorination of Dimethylbis-(*p*-chlorophenyl)-silane.—Seven grams (0.0249 mole) of dimethylbis-(*p*-chlorophenyl)-silane was treated with chlorine under the same conditions as those used for methyltris-(*p*-chlorophenyl)-silane. During the chlorination, some crystals which sublimed onto the condenser were identified as *p*-dichlorobenzene by mixed melting point. After the reaction mixture plus the trap contents had gained 2.65 g. in weight (equivalent to 0.0736 g. atom of chlorine) the mixture was flushed with nitrogen. No crystals formed on cooling or on extraction with methanol. On distillation at 50 mm. a white solid sublimed on to the condenser. This solid melted at 53.4° and was identified as *p*-dichlorobenzene by a mixed melting point with an authentic specimen. The residue became dark on continued heating and no other product was isolated.

Another 5 g. (0.0178 mole) of dimethylbis-(*p*-chlorophenyl)-silane was dissolved in 20 ml. of carbon tetrachloride and treated with a rapid stream of chlorine for 2 hours at gentle reflux temperature with ultraviolet irradiation. The carbon tetrachloride was removed on a steam-cone leaving a viscous liquid which would not crystallize from methanol solution. An attempt to distil the liquid at 1 mm. resulted in some decomposition taking place above 200°. Two grams of clear distillate was obtained under high vacuum, b.p. 165–170° at 0.00001 mm.; n^{20}_D 1.6062, d^{20}_4 1.349; MR_D calcd.[18] for methyl-(dichloromethyl)-bis-(*p*-chlorophenyl)-silane, 89.14; obsd., 89.54.

Anal. Calcd. for $C_{14}H_{12}Cl_4Si$: Cl, 40.4. Found: Cl, 39.7. (The calculated chlorine analysis for methyl-(trichloromethyl)-bis-(*p*-chlorophenyl)-silane is 46.1%.)

A similar chlorination carried out at 50° without solvent, also yielded only the dichlorinated derivative.

Chlorination of Dimethylbis-(*p*-chlorophenyl)-silane with Sulfuryl Chloride.—To 10 g. (0.0356 mole) of dimethylbis-(*p*-chlorophenyl)-silane dissolved in 20 ml. of carbon tetrachloride was added 6.75 g. (0.05 mole) of sulfuryl chloride and 0.1 g. of benzoyl peroxide. The solution was refluxed for 5 hours in a dry atmosphere. The product was fractionated through a wire spiral column to yield 8 g. of light straw-colored liquid, b.p. 160–170° at 0.2 mm.; n^{20}_D 1.5978.

Anal. Calcd. for $C_{14}H_{13}Cl_3Si$: Cl, 33.5. Calcd. for $C_{14}H_{12}Cl_4Si$: Cl, 40.4. Found: Cl, 35.6.

The analysis indicates that this product is a mixture of methyl-(mono- and dichloromethyl)-bis-(*p*-chlorophenyl)-silane.

Another 10 g. (0.0356 mole) of dimethylbis-(*p*-chlorophenyl)-silane in 20 ml. of carbon tetrachloride was refluxed with 20.25 g. (0.15 mole) of sulfuryl chloride and 0.2 g. of benzoyl peroxide for 16 hours. Fractionation of the product gave 7.0 g. of liquid, b.p. 170° at 0.1 mm.; n^{20}_D 1.6068. This refractive index corresponds closely to that of the methyl-(dichloromethyl)-bis-(*p*-chlorophenyl)-silane previously identified.

An attempt was made to prepare methyl-(trichloromethyl)-bis-(*p*-chlorophenyl)-silane by another method. Methyl-(trichloromethyl)-dichlorosilane, was prepared in 58% yield by the method of Krieble and Elliott[4] using an excess of chlorine. Treatment of this latter material with *p*-chlorophenyllithium at room temperature gave none of the desired product. Again *p*-dichlorobenzene was formed on attempted distillation of the product.

(Trichloromethyl)-triphenylsilane.—Forty grams (0.1457 mole) of methyltriphenylsilane[3] was treated with chlorine at 150°, with ultraviolet irradiation, in the apparatus used for the chlorination of methyltris-(*p*-chlorophenyl)-silane. The chlorination was continued until the weight increase was 15.5 g., equivalent to 0.437 g. atom of chlorine. On cooling, the mixture solidified. This solid was extracted three times with hot methanol and then crystallized from a benzene–petroleum ether (b.p. 77–122°) mixture to yield 21.2 g. (38.6%) of a white solid, melting at 192–194°. Two further crystallizations from petroleum ether (b.p. 77–122°) gave white needles melting at 194°.

Anal. Calcd. for $C_{19}H_{15}Cl_3Si$: Si, 7.45. Found: Si, 7.66.

***n*-Dodecyltris-(*p*-chlorophenyl)-silane.**—To 15.2 g. (0.05 mole) of *n*-dodecyltrichlorosilane[19] in 50 ml. of ether was added an excess of *p*-chlorophenyllithium prepared from 0.3 mole of *n*-butyllithium and 57.3 g. (0.3 mole) of *p*-chlorobromobenzene. The product was refluxed 4 hours, then the ether was removed, chloroform was added, and the mixture was poured into a dilute HCl solution. The chloroform layer was separated, dried over calcium chloride, and the solvent was removed at reduced pressure on the steam-bath. The residue was distilled at 0.1 mm. to give a small forefraction boiling at 48°. The remaining residue did not distil up to 240° at 0.1 mm., but when the dark brown residue was heated in a Hickman molecular still for 8 hours, 17 g. (64.1%) of a viscous straw colored distillate was obtained; d^{22}_4 1.106, n^{22}_D 1.5679; MR_D obs., 157.0; calcd.,[18] 155.3.

Anal. Calcd. for $C_{30}H_{37}Cl_3Si$: Si, 5.28. Found: Si, 5.11.

AMES, IOWA RECEIVED JULY 19, 1950

---

[18] Warrick, THIS JOURNAL, **68**, 2455 (1946).

[19] Whitmore, *et al.*, *ibid.*, **68**, 475 (1946).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Alkylation of Grignard Reagents by Quaternary Ammonium Salts. A Novel Synthesis of 1,3-Dialkylindoles

BY H. R. SNYDER, E. L. ELIEL AND R. E. CARNAHAN[1]

1-Methylgramine methiodide reacts with methylmagnesium iodide and phenylmagnesium bromide to give, in fair yields, 1-methyl-3-ethylindole and 1-methyl-3-benzylindole, respectively. The reaction probably can be applied generally to the synthesis of 1,3-dialkylindoles. Gramine methiodide reacts in the same way to give 3-alkylindoles, but the yields are lower. Other quaternary ammonium salts which have been examined do not alkylate the Grignard reagent in the same way, and methylgramine methiodide apparently does not alkylate phenyllithium or *p*-tolylmercuric chloride. The free bases, 1-methylgramine and gramine, are not satisfactory for the alkylation of Grignard reagents.

In previous reports[2] 1-methylgramine (3-dimethylaminomethyl-1-methylindole) and its methiodide were observed to alkylate various esters containing active methylene or methinyl groups. Carbon alkylation by 1-methylgramine methiodide, and by gramine methiodide as well, now has been extended to include Grignard reagents. 1-Methylgramine methiodide has been found to react with phenylmagnesium bromide to produce 1-methyl-3-benzylindole (Equation 1, R = CH_3, R′ = C_6H_5) in 72.5% yield and with methylmagnesium iodide to produce 1-methyl-3-ethylindole in 43.5% yield. The structure of the last compound, which was previously unknown, was proved by comparison with a sample made by the Fischer synthesis.

---

[1] Minnesota Mining and Manufacturing Company Fellow, 1949–1950.

[2] (a) H. R. Snyder and E. L. Eliel, THIS JOURNAL, **70**, 3855 (1948); (b) *ibid.*, **71**, 663 (1949).