dione (IV, 0.75 g.), lithium chloride (202 mg.), and dimethylformamide (30 ml.) was heated under reflux for 50 min., concentrated *in vacuo* to a small volume, and treated with water. The solid so obtained was separated by filtration and recrystallized from acetone–petroleum ether (b.p. 60–70°) and from isopropyl alcohol; wt. 278 mg., m.p. 261–263° dec. The sample for analysis was obtained by recrystallization from methanol which lowered the m.p. to 250–251° dec., λ_{max} 239 mμ (ε 15,300); ν_{max} 3330, 1739, 1678, 1627, and 1610 cm.$^{-1}$; $[\alpha]_D^{25}$ +83° (dioxane).

Anal. Calcd. for $C_{21}H_{26}O_5ClF$ (412.90); C, 61.09; H, 6.35; Cl, 8.59; F, 4.60. Found: C, 60.93; H, 6.62; Cl, 8.81; F, 4.90.

In other runs it was found that the reflux time may be successfully shortened to 8 minutes or that the reaction mixture may be simply stirred at room temperature for 45 min.

21-Chloro-9α-fluoro-11β-hydroxy-16α,17α-isopropylidenedioxy-1,4-pregnadiene-3,20-dione (IX). To a suspension of 21-chloro-9α-fluoro-11β,16α,17α-trihydroxy-1,4-pregnadiene-3,20-dione (V, 0.16 g.) in acetone (8 ml.) at room temperature was added 70% perchloric acid (2 drops), and the mixture was stirred for 1 hr. when 0.5 ml. of 5% sodium bicarbonate solution was added. The mixture was diluted with 5 ml. of water and cooled. The solid was collected by filtration, washed with methanol, and air-dried to give 147 mg. of IX, m.p. 297° dec. Recrystallization from aqueous dimethylformamide afforded the sample for analysis, m.p. 297–299° dec., λ_{max} 238 mμ (ε 16,100); ν_{max} 3340, 1740, 1666, 1623, 1607, and 857 cm.$^{-1}$; $[\alpha]_D^{25}$ +139° (dimethylformamide).

Anal. Calcd. for $C_{24}H_{30}O_5ClF$ (452.96): C, 63.64; H, 6.68; Cl, 7.83; F, 4.19. Found: C, 63.32; H, 6.90; Cl, 7.58; F, 4.10.

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ORGANIC CHEMICAL AND EXPERIMENTAL THERAPEUTICS RESEARCH SECTIONS
AND PHARMACEUTICAL PRODUCT DEVELOPMENT SECTION
LEDERLE LABORATORIES
A DIVISION OF AMERICAN CYANAMID CO.
PEARL RIVER, N. Y.

Addition of Grignard Reagents to Hindered *N*-Sulfinylamines[1]

WALTER T. SMITH, JR., POO AN THIO, AND MICHAEL GRASLEY

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The addition of a Grignard reagent to several *N*-sulfinylamines has been found to give good yields of sulfinamides.[2–4] Klamann, Sass, and Zelenka[4] used both aliphatic and aromatic *N*-sulfinylamines, with both aliphatic and aromatic Grignard reagents. Their yields ranged from 40 to 88%. Since sulfinamides are easily hydrolyzed in either acidic or basic solutions, the conditions for the hydrolysis of the intermediate Grignard complex are very critical. These investigators surveyed the usual reagents for this hydrolysis and determined that a dilute ammonium chloride solution was the most favorable. The low yield listed above was for the reaction of *N*-sulfinyl-*n*-butylamine with phenylmagnesium bromide when the intermediate Grignard complex was hydrolyzed under unfavorable conditions. When dilute (10%) ammonium chloride was used for hydrolysis of the intermediate, the yield was 85% for the same reaction.

In none of the previous work was a hindered *N*-sulfinylamine used. To what extent the addition of a Grignard reagent to an *N*-sulfinylamine is subject to steric influences is of considerable interest for the information it might provide about the structure of the —NSO group and about the nature of the Grignard addition.

We have studied the reaction of phenylmagnesium bromide with two *N*-sulfinylamines, each of which may be considered to possess a certain amount of hindrance around the functional group. These sulfinylamines are *N*-sulfinylmesidine and *N*-sulfinyl-*t*-butylamine. The ultraviolet spectrum of 2,6-dimethyl-*N*-sulfinylaniline indicates that two *ortho* methyl groups force the —NSO group out of the plane of the benzene ring as a result of considerable interference of the *ortho* methyl groups with the —NSO group.[5]

It would be expected that the above situation also exists with *N*-sulfinylmesidine and that this compound provides a good example of a hindered *N*-sulfinylamine. However, we have found that a 71% yield of the expected sulfinamide can be obtained from phenylmagnesium bromide and *N*-sulfinylmesidine. This result indicates that there is essentially no inhibition of the Grignard addition and therefore none of the addition of the Grignard reagent takes place at the nitrogen-sulfur bond. This confirms the earlier work of Gilman and Morris.[3]

The reaction of phenylmagnesium bromide with *N*-sulfinyl-*t*-butylamine gave the sulfinamide in a yield of only 7% under reaction conditions which give high yields (72–92%) of sulfinamides from unhindered aliphatic *N*-sulfinylamines.[6] These reactions were carefully worked up using the optimum conditions worked out by Klamann, Sass, and Zelenka.[4] Hence, the low yield cannot be ascribed to decomposition during the isolation procedure.

EXPERIMENTAL

N-Mesitylbenzenesulfinamide. Phenylmagnesium bromide was prepared according to Fieser[7] from 4 g. (0.164 g.-atom)

(1) This research was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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of magnesium turnings and 18 ml. (27 g., 0.172 mole) of bromobenzene. *N*-Sulfinylmesidine[8] (9.64 g., 0.05 mole) in 50 ml. of dry ether was added slowly to the cold (ice bath) phenylmagnesium bromide solution with vigorous stirring. The immediate formation of a greenish precipitate was observed. The mixture was cooled and stirred for 3 hr., refluxed 30 min., cooled, and treated with ammonium chloride solution. The ether layer was separated, dried, and evaporated. The residue was recrystallized from a benzene–petroleum ether (b.p. 86–100°) to give 9.2 g. (71%) of product, m.p. 134–134.5°.

Anal. Calcd. for $C_{15}H_{14}NOS$: N, 5.47; S, 12.49. Found: N, 5.36; S, 12.25.

N-t-Butylbenzenesulfinamide. Phenylmagnesium bromide was prepared as above from 14.7 g. (0.093 mole) of bromobenzene and 2.27 g. (0.093 g.-atom) of magnesium. A solution of *N*-sulfinyl-*t*-butylamine (10 g., 0.093 mole) in 40 ml. of ether was added dropwise with stirring to the cold (ice bath) solution of phenylmagnesium bromide. The addition required 45 min. The mixture was stirred for 1 hr. after the addition was completed. It was then poured over 100 g. of ice and treated with 10% ammonium chloride solution (*ca.* 200 ml.). The layers were separated; the aqueous layer was extracted with 50 ml. of ether. The combined ether extracts were dried and distilled to give an oil which could be crystallized from petroleum ether to give 1.3 g. (7%) of product, m.p. 69–70°. An analytical sample melted at 70–70.5°.

Anal. Calcd. for $C_{10}H_{15}NOS$: C, 60.90; H, 7.67; N, 7.09. Found: C, 60.89; H, 7.70; N, 6.99.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KENTUCKY
LEXINGTON, KY.

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Separation and Identification of Methyl Phenyl Cyclic Siloxane Isomers by Gas Chromatography

C. B. MOORE[1] AND H. A. DEWHURST

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Methyl phenyl cyclic trimer (2,4,6-trimethyltriphenylcyclotrisiloxane) has been shown to exist in two forms, both solid at room temperature. Lewis[2] proposed that they were stereoisomeric forms, with *"cis"* and *"trans"* configurations. From symmetry considerations he proposed that the *cis* configuration be assigned to the higher melting isomer. He further proposed that this type of isomerization occurred with the methyl phenyl cyclic tetramer (2,4,6,8-tetramethyltetraphenylcyclotetrasiloxane). In this case, four stereoisomers are possible, but Lewis was not able to effect any separation. Young and co-workers[3] also prepared the methyl phenyl cyclic trimer and tetramers. They reported that the more volatile trimer melted at 100° (*cis* isomer), while the less volatile trimer melted at 45.5° (*trans* isomer). They observed a crystalline isomer of the cyclic tetramer which had not previously been found. The tetramer crystals obtained by Young had a melting point of 99°. They found that the infrared spectrum of the crystalline form was somewhat different from the liquid form.

We have found that the *cis* and *trans* forms of the cyclic trimer can be separated by gas chromatography. Similar but less well defined separations were found with the tetramer.

Figures 1(a) and 1(b) show the gas chromatograms of the *cis* and *trans* isomers of the methyl phenyl trimer. It is noteworthy that the isomers are separated according to their volatility; the more volatile *cis* isomer has a smaller retention time than the *trans* isomer. Only two isomers are possible in the cyclic trimer system; consequently an equilibrium mixture of isomers would be expected to contain 75% *trans* and 25% *cis* exclusive of any energy differences. The chromatograms in

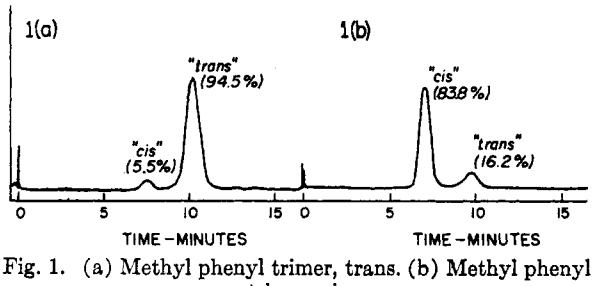

Fig. 1. (a) Methyl phenyl trimer, trans. (b) Methyl phenyl trimer, cis

2 ft. Apiezon L; temperature, 265°

Figure 1 were obtained with samples which were preferentially crystallized and, therefore, were not equilibrium samples. However, it is noteworthy that the ratio of trimer isomers shown by the chromatogram in Figure 3 correspond very closely to the expected statistical ratio. The conditions under which this chromatogram was obtained are likely equilibrium conditions.

The gas chromatograms of the methyl phenyl cyclic tetramer solid and liquid samples are shown in Figures 2(a) and 2(b), respectively. Both chromatograms show the presence of trimers to the extent of 0.16% in the solid sample and 4.4% in the liquid sample. The liquid sample clearly shows the presence of at least three components. Component C is only partially resolved from B and further attempts to effect a more complete separation have not as yet been successful. However, from the symmetry of the peaks it was possible to interpolate and separate components B and C as shown by the dotted lines in Figure 2(b). In the same way it was possible to estimate component C in the solid sample as shown in Figure 2(a). It is believed that the components marked A, B, and C, Figure 2, represent the stereoisomers possible in the tetramer system. It is reasonable that components A and C

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