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.

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(7) L. F. Fieser, *Experiments in Organic Chemistry,* 3rd ed., D. C. Heath, Boston, 1957, p. 79.

(8) A. Michaelis and O. Storbeck, *Ann.,* **274,** 200 (1893).

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

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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[2] 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 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.

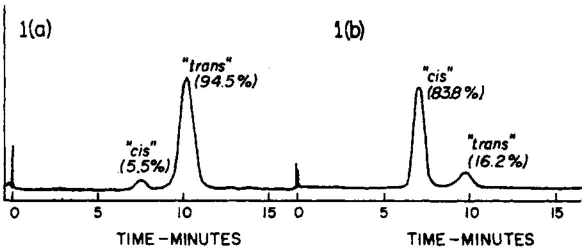

Fig. 1. (a) Methyl phenyl trimer, trans. (b) Methyl phenyl trimer, cis

2 ft. Apiezon L; temperature, 265°

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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(1) Present address, Department of Chemistry, University of California, Berkeley, Calif.

(2) R. N. Lewis, *J. Am. Chem. Soc.* **70,** 1115 (1948).

(3) C. W. Young, P. C. Servais, C. C. Curie, and M. J. Hunter, *J. Am. Chem. Soc.,* **70,** 3758 (1948).

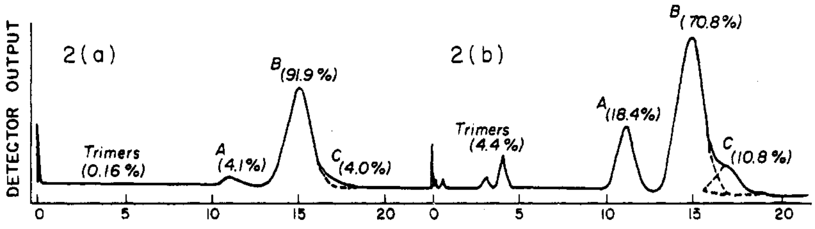
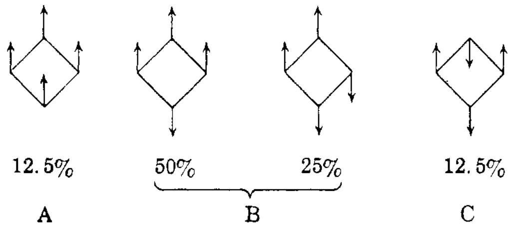


Fig. 2. (a) Methyl phenyl tetramer solid. (b) Methyl phenyl tetramer liquid

2 ft. Apiezon L; temperature, 290°

are single isomers while components B represents two isomers.

The following isomers are possible in the methyl phenyl cyclic tetramer system



Each silicon atom has one phenyl and one methyl substituent and in the above diagrams the arrows represent the phenyl substituent. The per cent composition for each isomer at equilibrium was calculated statistically discounting any energy differences. The assignments indicated above were made by analogy with the trimer system and on the basis of the observed peak areas.

The chromatogram in Figure 3 is included to show that rather extensive rearrangements have occurred in the highest boiling fraction. This fraction contains a large amount of trimer in addition to pentamer with smaller amounts of tetramer and other unidentified products. The rather large amount of trimer is of considerable interest and explains the observation of Young *et al.*[2] . . . "If the column was placed on total reflux at any time, the head temperature would drop to 155-160°." This temperature corresponds to the trimer fraction.

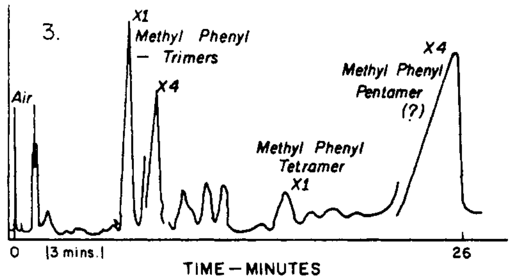


Fig. 3. Methyl phenyl cyclics

Distillation cut, 19-4305; 2 ft. silicone rubber; temperature program, 5.6° min.

It is conceivable that a complete separation of the cyclic tetramer isomers will be possible by gas chromatography. Although a number of stationary liquid phases were studied such as carbowax, silicone grease, and a mixed methyl phenyl silicone, the best separations were obtained with an Apiezon L column.

EXPERIMENTAL

Gas Chromatography. A Model 500 F and M linear programmed gas chromatograph was equipped with a two-foot column of either silicone rubber or Apiezon L grease on chromosorb. The hot-wire detector was maintained at a constant temperature of 305°, the injection port temperature was 300 ± 5° and the helium flow rate was 67 ml. per minute.

Preparation of siloxanes. The methyl phenyl cyclic tri- and tetrasiloxanes were prepared according to the method of Young *et al.*[2] Liquid samples (2 μl.) were injected directly into the chromatograph while the solid samples were used in a dilute benzene solution.

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Synthesis of 1,5-Diphenyl- and 1,1,5,5-Tetraphenyl-2,4-pentanedione

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In connection with another study, moderate quantities of 1,5-diphenyl-2,4-pentanedione (I) were required

$$C_6H_5CH_2COCH_2COCH_2C_6H_5 \quad \text{I}$$

This β-diketone has previously been prepared from phenylacetyl chloride and vinyl acetate by aluminum chloride,[2] and from the magnesium chloride derivative of sodium phenylacetate (Ivanov reagent) and malonyl chloride,[3] but the yields were only 1 and 5%, respectively. Two other

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(2) A. Sieglitz and O. Horn, *Chem. Ber.*, **84**, 607 (1951).

(3) D. Ivanov and N. Marekov, *Compt. rend. acad. bulgare sci.*, **4**, 41 (1953); *Chem. Abstr.* **49**, 978h (1955).