PREPARATION OF DISTILBENE (1,2,3,4-TETRAPHENYLCYCLOBUTANE)[1]

J. M. MORTON,[2] E. A. FLOOD, AND N. F. H. BRIGHT[3]

ABSTRACT

The reaction between benzyl chloride and potassium amide in liquid ammonia has been shown to yield, in addition to stilbene as the main product, considerable quantities of 1,2,3,4-tetraphenylcyclobutane. The isomer of this compound formed in this reaction is believed to be one that has not been reported previously.

The reaction between alkyl halides and metal amides leads to the formation of ethylenic compounds (5, 6). The reaction between benzyl chloride and potassium amide in liquid ammonia was first worked on by one of the present authors (2). In general it has been found previously that when a solution of potassium amide in liquid ammonia was added to a solution of benzyl chloride, also in liquid ammonia, a white solid precipitate formed. If excess potassium amide was present, a deep reddish purple color developed in the ammonia solution. This color was removed by the addition of excess benzyl chloride or any acid substance such as ammonium chloride. The white solid reaction product, after the liquid ammonia had been allowed to evaporate, was washed with water and dried. It has been reported by all who have worked on this reaction previously that this represents a yield of 95 to 100% stilbene (5, 7).

In the course of the present work it has been found that if the white solid product of the reaction is recrystallized from 95% alcohol, its melting point is higher than that of stilbene (124° C.). After five crystallizations, a material is obtained that is distinctly different from stilbene. This material, consisting of needle-shaped crystals rather than rhombic plates characteristic of stilbene, melts at 149° C. The experimental evidence is that this material is the dimer of stilbene, viz., 1,2,3,4-tetraphenylcyclobutane. The yield of the dimer varies considerably and we have not yet been able to find the most favorable conditions for its formation.

EXPERIMENTAL

1. Materials

The benzyl chloride used was a middle fraction from a vacuum distillation (75.5° to 76.0° C. at 14 mm.) of Eastman α-chlorotoluene. The metallic potassium was Baker and Adams Reagent Grade. The pieces were cut and the surface material removed under heavy mineral oil.

2. Reaction

The process was carried out by preparing a solution of benzyl chloride in liquid ammonia and a separate solution of potassium amide in liquid ammonia and adding one solution to the other with constant stirring over a period of 10–20 minutes. The solution of potassium amide was prepared by adding pieces of potassium metal to liquid ammonia and adding about 0.1 g. of ferric chloride. The deep blue color characteristic of alkali metals in liquid ammonia disappears after the solution had been allowed to stand and the fading out of the blue color was taken as an indication that all the potassium had

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[2]*Department of Chemistry, Carleton University, Ottawa.*
[3]*National Research Council Postdoctorate Fellow. Present address: Department of Mines and Technical Surveys, Ottawa.*

been converted to potassium amide. The solutions were then mixed by means of a good stirring and allowed to stand until the ammonia had evaporated. This usually took overnight since the reaction vessel was a vacuum-jacketted pyrex container. The reaction has been carried out in an open system with a slight positive pressure of ammonia and also in a system that could be evacuated and the reaction carried out under anhydrous conditions using ammonia from a cylinder containing sodium and therefore perfectly dry. The reaction appeared to give similar results by both methods. When the benzyl chloride is added to the solution of potassium amide a deep reddish purple color develops in the liquid and this will persist as long as there is excess of potassium amide. Most of the work was done using an excess of potassium amide of 25% and the purple color was marked at the end of the reaction.

3. Crystallization

The reaction products that had become almost free of ammonia by standing overnight were washed repeatedly with large quantities of water and transferred to a Buchner funnel and washed. The material was dried and dissolved in hot 95% alcohol and filtered while hot. This was set aside to crystallize and the crop of crystals separated, dissolved in fresh alcohol, and again crystallized. The fifth crystallization yielded a product that melted at 149.7° C. (corrected). Since the melting point of stilbene is 124° C. this is obviously a different substance. It is difficult to obtain exact figures for the percentage yield of the higher melting material because it is so hard to separate from stilbene. However, in two batches where careful separations by fractional crystallization were made, the percentages of the dimer obtained were 19.5% and 24.7%, based on the weight of benzyl chloride at the start. These are conservative figures since small losses are inevitable.

4. Characterization

Carbon Hydrogen Analysis

Calculated for $(C_7H_6)_x$	Found
C 93.36	C 93.03, 93.07
H 6.64	H 6.87, 6.68
	C 93.56, 93.49
	H 6.64, 6.72

Molecular Weight Determination

	Found		Calculated
Vapor pressure lowering of isopentane	346 377	av. 361±10%	360
Lowering freezing point of benzene	357 323	av. 340±10%	360

Under similar conditions a sample of pure stilbene gave a molecular weight in benzene of 178 (theoretical = 180). The conclusion is that our material is a dimer of stilbene. Since the compound shows no evidence of unsaturation it must involve a ring structure and it is concluded that it is 1,2,3,4-tetraphenylcyclobutane. An infrared spectrogram was done on a sample of the material using a solution in carbon disulphide. The characteristic absorption bands for monosubstituted benzene rings showed up in two places (a strong band at 695 cm.$^{-1}$ and four bands between 1700 and 2000 cm.$^{-1}$). There was

evidence of a band consistent with tertiary carbon atoms (2920–2940 cm.$^{-1}$) but this could have been due to secondary carbon atoms. There was no evidence of ethylenic linkages or of methyl groups. The literature does not, so far as we know, contain any information on the absorption bands due to four-membered rings, however everything in the infrared spectrogram was consistent with the material being the compound 1,2,3,4-tetraphenylcyclobutane.

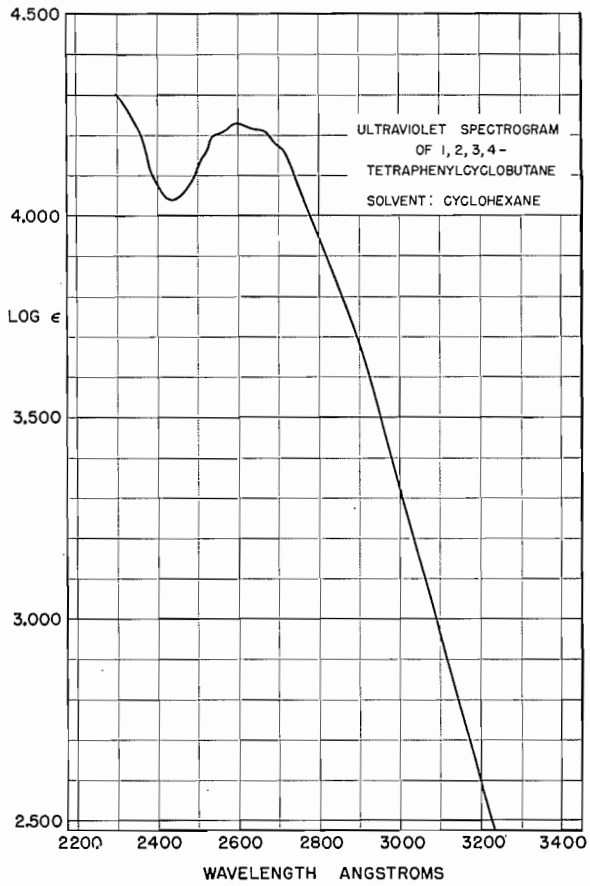
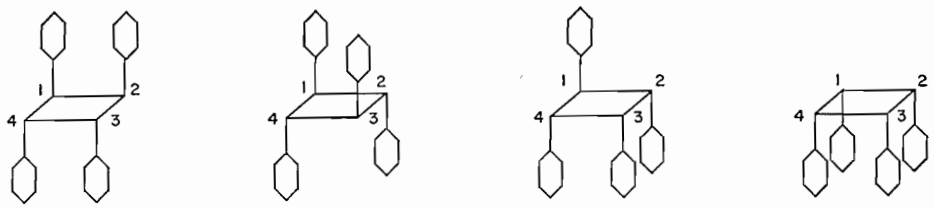


FIG. 1.

Stilbene dimers have been prepared by J. D. Fulton (3) by irradiating stilbamidine (4,4′-diamidinostilbene β-hydroxyethane sulphonate) and two have been found, one melting at 163° C. and another at 149° C. He also prepared the isomer of 1,2,3,4-tetraphenylcyclobutane melting at 163° C. by irradiation of stilbene in benzene solution. The melting point of the distilbene prepared by both methods was the same, 163°, and there was no change in melting point on mixture of the two. Dunitz (1) also showed that the two substances melting at 163° C. were identical by means of X-ray crystallographic analysis. Fulton further showed (3) that the two distilbenes prepared as above showed the same absorption spectra to ultraviolet radiation. His plot of the absorption spectrum for 1,2,3,4-tetraphenylcyclobutane in cyclohexane is very similar to what we have obtained for the material we have produced (see Fig. 1). He found an absorption

band at 2610 Å; our curve also shows an absorption band at 2603 Å. The extinction coefficient that we have found at this maximum of adsorption is 16,900 in cyclohexane. (This is a molar extinction coefficient with concentration in gram moles per liter.) The value seems high when compared with the results of Fulton (3) for his isomer of 1,2,3,4-tetraphenylcyclobutane melting at 163°. The isomer that we believe we have produced is different in melting point and in several other respects and the enhanced absorption at this frequency may be due to a different arrangement of the phenyl groups around the cyclobutane ring, but the significant thing is that the absorption band is in the same position. This leads to the conclusion that we have a compound with similar linkages and of similar structure but since it differs in melting point it is probably a different isomer of 1,2,3,4-tetraphenylcyclobutane. Not only is the melting point different but the X-ray analysis of our product has been found to be different from either of the two isomers previously studied by Fulton and Dunitz (4) and more comprehensively by Dunitz (1). The compound 1,2,3,4-tetraphenylcyclobutane can exist theoretically in four possible isomers (Fig. 2).



I	II	III	IV
Melting points: 163–164°	149°	?	?

FIG. 2.

The substance represented by formula I has been the subject of a comprehensive X-ray analysis by Dunitz (1). There seems to be no doubt that the isomer melting at 163° has the "chair" structure illustrated; the configuration about 1-2, 3-4 is *cis*-, while about 2-3, 1-4 it is *trans*-. Although no comprehensive study has been made by Dunitz of the isomer melting at 149°, preliminary X-ray examination indicates that it has the structure represented by II above, i.e., with alternate phenyl groups being above and below the cyclobutane ring as one goes round the ring.

Since our isomer was not the same as either I or II as shown by X-ray analysis, the possibilities remaining were III and IV. The structure represented by III seems more probable. This compound is one that has a unique hydrogen atom in the molecule and is therefore particularly suitable for characterization by the method of nuclear magnetic resonance.

Our compound melting at 149° and some material prepared by prolonged irradiation of stilbene in benzene solution to ultraviolet light, purified by recrystallization and melting at 163°, were both examined in 3% benzene solution by the nuclear magnetic resonance method. In the case of our compound melting at 149° there is one band at 3.25 parts per million on the high field side of benzene, with intensity one, and another at 4.0 parts per million at intensity three. The isomer melting at 163° shows a simpler spectrogram with a single band at 2.8 parts per million. These results indicate that our compound melting at 149° is the isomer with three phenyl groups down and one up (III in Fig. 2), since it is

the one isomer with a unique hydrogen atom. In any case, ours can not be the same as the compounds with two up and two down as prepared by Fulton (3).

CONCLUSION

From this study it is concluded that the reaction between benzyl chloride and potassium amide in liquid ammonia yields, in addition to stilbene, fairly substantial amounts of a dimer of stilbene. This dimer is believed to be the isomer of 1,2,3,4-tetraphenylcyclobutane having one phenyl group up and three down with respect to the plane of the cyclobutane ring. This method of preparing this compound is a simple one for producing a compound that is difficult to prepare by any other method.

When a better means of separating the stilbene from the distilbene or a method of analyzing the crude reaction product for distilbene has been found, it is hoped to investigate the optimum conditions for production of distilbene.

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