

In this preliminary investigation an attempt has been made to obtain optically active carbodiimides. The results thus far have been unsuccessful, due to certain inherent properties of these compounds which have introduced difficulties not as yet overcome. Carbodiimides are not only very reactive to reagents such as water, acids, etc., but they polymerize readily merely on standing at room temperature. The possibility of studying an amino or carboxy substituted diphenylcarbodiimide which might be resolved in the usual way was soon eliminated since the carboxy and amino derivatives of diphenyl carbodiimide could not be prepared by the ordinary methods. Even if such compounds could be synthesized, the probability of the formation of the salts and subsequent resolution without decomposition seemed remote. A much more feasible line of attack appeared to be the preparation of a mono- or dicarbo-*l*-menthoxythiocarbanilide which, upon elimination of hydrogen sulfide, should yield a mixture of separable diastereoisomeric carbodiimides. Unfortunately, the resulting reaction mixture after such treatment of monocarbo-*l*-menthoxy carbanilide was an oil which did not solidify but which polymerized gradually on standing. From this experiment it is obvious that the carbodiimide synthesized for the purpose proposed must be of such a character that the monomer is a solid which can be separated and kept in the solid form so as to prevent or greatly diminish the rate of polymerization.

The dicarboethoxy and the monocarboethoxy diphenylcarbodiimides were also oils and the dibromo derivative which has been reported previously in the literature would not solidify at room temperature.

A considerable portion of the time of this preliminary investigation was devoted to the general study of carbodiimides. Without attempting to review in detail the previous literature,⁴ it may be pointed out that diphenylcarbodiimide is an unstable liquid which polymerizes with ease. There appears to be an authentic crystalline tripolymer and a higher amorphous polymer. That two dimers exist also seems probable.

More recently Herzog⁵ has patented what he calls diphenylcarbodiimide resins. He reports a number of reagents for eliminating hydrogen sulfide from thiocarbanilides in order to obtain the carbodiimide from which the polymer may be produced. It is questionable, however, whether Herzog ever obtained resinous carbodiimides.

⁴ Weith, *Ber.*, **7**, 10, 1305 (1874); Laubenheimer, *ibid.*, **13**, 2155 (1880); Schall and Paschkowitzky, *ibid.*, **25**, 2880 (1892); Schall, *ibid.*, **26**, 3064 (1893); **27**, 2260 (1894); McCoy, *ibid.*, **30**, 1090 (1897); Busch, Blum and Pings, *J. prakt. Chem.*, **79**, 11, 513 (1909); Schall, *ibid.*, **81**, 11, 191 (1910); Miller and Plöchl, *Ber.*, **27**, 1283 (1894); **28**, 1004 (1895); Schall, *J. prakt. Chem.*, **53**, 11, 139 (1896); *Ber.*, **27**, 2696 (1894); Short and Smith, *J. Chem. Soc.*, **121**, 1803 (1922).

⁵ Herzog, *Z. angew. Chem.*, **33**, 140 (1920); see also Merz, Weith, *Chem. Zentr.*, **40**, 977, 993 (1899); Hoffmann, *Ann.*, **70**, 148 (1849); Ellis, "Synthetic Resins and Their Plastics," The Chemical Catalog Company, New York, 1923, p. 245.

diphenylcarbodiimide was produced which boiled at 142° at 5 mm. From 22.8 g. of thiocarbanilide, 8.5 g. of product was obtained. After five or six days the liquid carbodiimide had completely solidified to a product melting at 158–160°. Molecular weight determination indicated the liquid to be monomolecular.

No elimination of hydrogen sulfide took place at 80° when arsenic trioxide was used in place of the mercuric oxide.

Formation of a Resin-like Substance from Triphenylguanidine.—Two grams of triphenylguanidine was heated in a small crucible at 180° for two hours. Upon cooling, an amber-colored, brittle, glass-like solid which melted at 129–137° resulted. The molecular weight of this product by freezing point in benzene showed it to be 318 as compared with a theoretical of 287 for triphenylguanidine.

This resin, when dissolved in a mixture of benzene, butyl alcohol and ethyl acetate and poured on to a glass surface, yielded a transparent, hard film upon evaporation of the solvent.

***p*-Carbo-*l*-menthoxythiocarbanilide.**—A solution of 6.75 g. of phenyl isothiocyanate and 13.75 g. of menthyl *p*-aminobenzoate in 50 cc. of benzene was refluxed on a steam-bath for twenty hours. Two-thirds of the solvent was then distilled and the product allowed to crystallize. It was purified by crystallizing first from a mixture of benzene and 60–70° petroleum ether, and then from benzene and finally from alcohol. The yield was 15 g. of a product melting at 124–125°.

Anal. Calcd. for $C_{23}H_{30}O_2N_2S$: N, 6.83. Found: N, 7.43.

***p*-Carbo-*l*-menthoxydiphenylcarbodiimide.**—Sixteen grams of *p*-carbo-*l*-menthoxydiphenylthiourea, 16 g. of yellow mercuric oxide and 10 g. of powdered anhydrous calcium chloride were mixed with 100 cc. of dry benzene and refluxed with stirring for five hours. The cold mixture was filtered and the filtrate warmed on the steam-bath until the solvent was removed. A dark viscous oil was obtained which solidified upon standing overnight to an amorphous mass, insoluble in benzene.

***p,p'*-Dicarboethoxydiphenylcarbodiimide.**—From 22 g. of the *p,p'*-dicarboethoxydiphenylthiourea,⁶ following the same procedure for the preparation of *p*-carbo-*l*-menthoxydiphenylcarbodiimide, there was obtained 17 g. of an amber-colored viscous liquid which on standing at room temperature for about thirty days gradually solidified to a transparent, amber-like solid melting at 78–90°.

Anal. Calcd. for $C_{19}H_{18}O_4N_2$: N, 8.28. Found: N, 8.48.

Symmetrical Tri-(*p*-carboethoxy-phenyl)-guanidine.—A mixture of 11 g. of *p,p'*-dicarboethoxydiphenylthiourea, 13 g. of yellow mercuric oxide and 4 g. of powdered calcium oxide was placed in a 500-cc. flask fitted with a thermometer, mechanical stirrer and reflux condenser. Seventy-five cc. of dry xylene was added, heat applied and the reaction mixture stirred. After four hours at 135°, the solution was filtered while hot and the filtrate concentrated to 20 cc. The white precipitate which formed upon cooling was crystallized from a mixture of pyridine and petroleum ether. The product melted at 170–171°. The yield was 4 g.

Anal. Calcd. for $C_{25}H_{23}N_3O_6$: C, 65.73; H, 4.99. Found: C, 65.01; H, 5.18.

***p,p'*-Dibromodiphenylcarbodiimide.**⁷—The *p,p'*-dibromodiphenylthiourea was made according to the procedure of Fry and treated according to the previously described procedure with mercuric oxide and calcium chloride in dry benzene. A dark, viscous residue was obtained which distilled under diminished pressure at 208–212° at 4 mm. Upon standing, this viscous distillate gradually solidified to a resin-like solid.

⁶ Fry, *THIS JOURNAL*, 35, 1539 (1913).

⁷ Ingold, *J. Chem. Soc.*, 125, 101 (1924).

Summary

1. The structural relationship of allenes and diaryl carbodiimides has been pointed out and a method for proving the asymmetry of the carbodiimide proposed.

2. Experiments on the preparation of various carbodiimides have been described and the difficulties in the study of these substances pointed out.

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INVESTIGATIONS ON THE STEREOISOMERISM OF UNSATURATED COMPOUNDS. I. THE COMPOSITION OF CROTONALDEHYDE

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RECEIVED FEBRUARY 8, 1932

PUBLISHED JUNE 6, 1932

The program of research undertaken includes a study of the physical and chemical properties of a series of aliphatic hydrocarbons containing conjugated systems of double bonds. Since these compounds may occur in several stereoisomeric forms, it is necessary to isolate the individual isomers in order to obtain reliable physico-chemical measurements. Such procedure will enable one to determine the influence of the configuration of the individual double bonds on the physical and chemical properties of these hydrocarbons.

The keynote in this work is purity of materials. For this reason the separation of isomeric mixtures by fractional distillation was avoided because of the inherent difficulties.² Instead of this, the author is studying methods of synthesis which will lead to the production of pure isomers, the first of which is *trans,trans,trans*-dimethylhexatriene. To do this, one must know the configuration of the starting materials as well as the intermediate compounds.

One of the starting materials investigated is the so-called crotonaldehyde which is commonly obtained from aldol. This material might be a mixture of *cis*- and *trans*-crotonaldehydes and vinyl acetaldehyde. If this is the case the resulting hexatriene might be a mixture of as many as eight different isomeric hydrocarbons. Therefore a quantitative study of ordinary crotonaldehyde³ was undertaken by several different methods. The first re-

¹ The experimental part of this work was completed while the author was a National Research Fellow in Chemistry at Stanford University. This paper was presented at the Pasadena meeting of the American Association for the Advancement of Science, June 19, 1931. Original manuscript received June 29, 1931.

² Lucas, Dillon and Young, *THIS JOURNAL*, **52**, 1949 (1930).

³ Commercial crotonaldehyde was obtained from one manufacturer in order to ensure an unlimited supply of material of constant composition.