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

THE STEREOCHEMISTRY OF CARBODIIMIDES. XXII[1,2]

BY L. J. ROLL AND ROGER ADAMS

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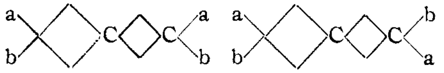
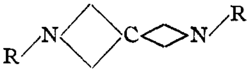
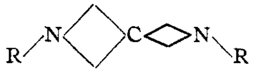
The preparation of stereoisomeric allenes of Type I (a and b) has been the subject of many investigations from the time van't Hoff first predicted that such compounds should be capable of existing in optically active forms. Somewhat analogous to the allenes is another class of asymmetric molecules, the carbodiimides II (a and b).



I (a and b)



IIa



IIb

On the assumption that the nitrogen atom has a fixed tetrahedral structure, it may be seen that the two substituting R groups are in planes different from those of the C=N linkages and, therefore, a pair of mirror images may exist even though the two R groups in the molecule are the same. If, on the other hand, the R groups may vibrate through the axis common to the N=C=N nucleus, isomerism will disappear whether the R groups are the same or different.

The results of many researches have indicated that trivalent nitrogen compounds of the type RR′R″N can be obtained optically active only with great difficulty or not at all. In fact, as yet no optically active trivalent nitrogen compounds have been isolated and as a consequence it has been assumed that the nitrogen atom in such molecules is probably very mobile and that the three valence bonds and the pair of unshared electrons may vibrate through such positions that optical isomerism will be prevented. On the other hand, *cis-trans* isomerism in the oximes is commonly explained on the assumption of a fixed tetrahedral nitrogen atom. It would follow, therefore, that the lack of mobility of the groups on the nitrogen atom in these molecules is due, presumably, to the presence of C=N. Since double bonds exist in carbodiimides, optical isomerism may be anticipated in this class of compounds.[3]

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[1] For previous paper see White and Adams, THIS JOURNAL, **54,** 2104 (1932).

[2] This communication is an abstract of a portion of a thesis submitted by L. J. Roll in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Faltis, Pirsch and Bermann, *Ber.*, **63,** 691 (1931), were unable to obtain stereoisomers of certain allene derivatives and have suggested a different conception of allene linkages which would involve no optical isomerism. Such an argument, though not too convincing, might also be applied to carbodiimides.

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 Herzog[5] 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.

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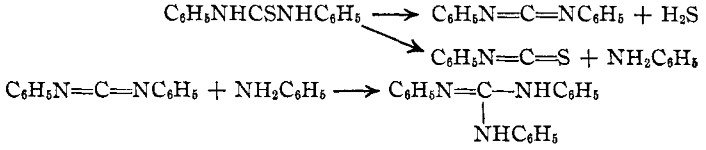
[4] Weith, *Ber.*, **7,** 10, 1305 (1874); Laubenheimer, *ibid.*, **13,** 2155 (1880); Schall and Paschkowetzky, *ibid.*, **25,** 2880 (1892); Schall, *ibid.*, **26,** 3064 (1893); **27,** 2260 (1894); McCoy, *ibid.*, **30,** 1090 (1897); Busch, Blum and Pings, *J. prakt. Chem.*, **79,** 11, 513 (1909); 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 (1869); Hoffmann, *Ann.*, **70,** 148 (1849); Ellis, "Synthetic Resins and Their Plastics," The Chemical Catalog Company, New York, 1923, p. 245.

In this investigation a careful study of the conversion of thiocarbanilide into carbodiimide has indicated that if the temperature during the reaction is much above 80°, not only is diphenylcarbodiimide produced, but simultaneously the thiocarbanilide is broken up into aniline and phenylisothiocyanate. Aniline then immediately reacts with the diphenylcarbodiimide with the formation of triphenylguanidine, which is the main product of the reaction.



$$C_6H_5NHCSNHC_6H_5 \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + H_2S$$

$$\searrow C_6H_5N{=}C{=}S + NH_2C_6H_5$$

$$C_6H_5N{=}C{=}NC_6H_5 + NH_2C_6H_5 \longrightarrow C_6H_5N{=}\underset{\displaystyle NHC_6H_5}{\underset{|}{C}}{-}NHC_6H_5$$

Herzog claims to have obtained polymeric diphenyl carbodiimide by heating thiocarbanilide with aniline in the presence of arsenious oxide. Upon repetition of his experiment, however, an excellent yield of triphenylguanidine was produced. Moreover, substitution of the arsenious oxide by cadmium carbonate or mercuric oxide gave consistently the same result. It was noticed, also, that if triphenylguanidine was heated somewhat above its melting point and allowed to cool, a brittle, transparent resin was produced which leaves a hard, transparent film on evaporation of a solution in the usual lacquer solvents. This resin was essentially monomeric in character as shown by molecular weight determinations.

At 80° the only satisfactory reagent for conversion of the thiocarbanilides was mercuric oxide. Under these conditions an excellent yield of monomeric diphenylcarbodiimide was produced which, however, gradually polymerized upon standing. A number of new substituted thiocarbanilides were made but it was found that the elimination of hydrogen sulfide takes place only with great difficulty when certain types of substituents are present. This fact has greatly limited the number of substituted diphenylcarbodiimides which could be prepared and studied.

Experimental

Elimination of Hydrogen Sulfide from Thiocarbanilide with Various Reagents. Triphenylguanidine.—A mixture of 22.8 g. (1 mole) of thiocarbanilide, 13.2 g. of arsenic trioxide (6 moles) and 11 g. (2 moles) of calcium oxide was placed in a 500-cc. flask fitted with a stirrer, thermometer and a reflux condenser. To this was added 75 cc. of dry xylene, then the stirrer was started and heat applied. The reaction mixture was held at 145° for fourteen hours and then filtered hot. From the filtrate a white solid separated. The triphenylguanidine was purified by recrystallization from benzene and then melted at 142–143°. The yield was 10 g. (70%).

By using cadmium carbonate in place of arsenic trioxide, a 48% yield of triphenylguanidine resulted, and with yellow mercuric oxide a 35% yield.

Elimination of Hydrogen Sulfide from Thiocarbanilide. Diphenylcarbodiimide.—By following exactly the procedure just described using yellow mercuric oxide except that benzene was substituted for xylene and the reaction was run at 80° instead of 145°, 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.

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[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.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

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

BY WILLIAM G. YOUNG[1]

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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 crotonaldehyde[3] was undertaken by several different methods. The first re-

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[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.