XIII.—*Benzyl Isocyanate and Isocyanurate.*

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THE first members of the group of compounds, now generally described as the isocyanates and isocyanurates, were discovered by Wurtz in the ethyl and methyl series. These bodies were called by him cyanic and cyanuric ether. They are, as is well known, obtained by the reaction of metallic cyanates on sulphovinates, and are decomposed by the elements of water into the corresponding amine and carbonic acid.

Later, Cloez discovered in the ethyl series an isomeric compound, which he designated by the name of cyanetholine; this is produced by the action of chloride of cyanogen on sodium alcoholate, and is decomposed by the elements of water into alcohol and cyanic acid (or rather the products of the latter's transformation), in consideration of which metamorphosis it must be viewed as the true cyanic ether (*Hofmann and Olshausen. Berichte der Deutschen Chemischen Gesellschaft*, 1870, p. 269). The recent researches of Hofmann and Olshausen make it probable that the body produced in the last mentioned transformation is the true cyanuric ether; in the methyl series at least this is certain.

In the aromatic series too there are many examples of this group of bodies; for instance, both the isocyanate and isocyanurate of phenyl are known, and side by side with them must be placed the singular compound known as phenyl isodicyanate, which is formed when phenylcyanate comes in contact with triethylphosphine. In the higher homologous series still more numerous examples may be expected. In the toluene group for instance, two different isomerides may be imagined, corresponding to each compound in the phenyl group, according as the benzene or methyl chains are influenced. Of the eight possible bodies thus producible only three have as yet been obtained, namely, isocyanate and isodicyanate of toluyl by Hofmann (*Berichte*, 1870, p. 656), and benzyl cyanurate by Cannizzaro (*Berichte*, 1870, p. 517).

The object of the following experiments was to supply some of the missing links in this chain of compounds:—

Benzyl Isocyanate.—If cyanate of silver be moistened with benzyl chloride and the mixture slightly warmed, pungent aromatic vapours are formed, causing the eyes to smart painfully, and having an odour which leave no doubt that the desired benzyl compound has been produced. For the preparation of a larger quantity of this body 100 grams of dry silver cyanate and 70 grams of benzyl chloride were submitted to distillation in a paraffin bath. Only 7—8 grams of a colourless, transparent liquid came over possessing the penetrating odour described. The operation was then proceeded with over the naked flame and the distillation commenced anew. The slightly yellow, oily liquid thus obtained solidified on cooling to a hard crystalline mass.

The colourless liquid is benzyl isocyanate, still, however, containing benzyl chloride. To free it from this impurity, distillation was resorted to, but owing to the slight difference between the boiling points of the two liquids it was found impossible to separate them by this means. The liquid boiled between 175° and 200° , and as the boiling point of benzyl chloride is 175° , it was hoped that at least the last portion of the distillate would be pure; but even this contained chlorine in perceptible quantity, and, besides, produced each time it was boiled a

small quantity of the solid crystalline body; it was thus found impossible to obtain it in a state fit for analysis.

That it was really the compound

was clearly proved by its reactions, the products of which could be easily purified and analysed.

Monobenzyl Urea.—If the impure cyanate be treated with alcoholic ammonia, the mixture becomes heated and solidifies on cooling to a crystalline mass. If these crystals are again dissolved by warming the solution, water added, and the mixture boiled for a short time to get rid of any chloride of benzyl, beautiful long, white needles are obtained on cooling, consisting of monobenzyl urea—

	Theory.	Experiment.
C..	64·0	64·2
H	6·6	6·8

This body is nearly insoluble in cold water, more soluble in hot water, and extremely so in alcohol. I have attempted, without success, to obtain a nitrate, but an insoluble platinum salt may be produced. The monobenzyl urea melts at 144°.

Dibenzyl Urea.—One of the most characteristic reactions of the cyanates generally is the transformation they undergo by treatment with water: carbonic acid is set free and a di-urea produced. The benzyl isocyanate likewise undergoes this metamorphosis; for if this compound be sealed up with water, in a tube, and heated for a couple of hours to 100°, a yellow oil, heavier than the water, is obtained, whilst on opening the tube carbonic acid escapes. When cold, the oily liquid solidifies into a crystalline mass. These crystals are the dibenzyl urea—

	Theory.	Experiment.
C.....	75·0	75·9
H.....	6·6	6·8

As will be seen on inspection, the numbers obtained agree only approximately with those required for the dibenzyl urea. I have not,

however, repeated the experiment, because dibenzyl urea has also been produced by Cannizzaro (*loc. cit.*) by heating monobenzyl urea :

I have repeated this experiment with the monobenzyl urea obtained from the cyanate, with exactly the same result, a body being produced having the appearance and properties of the dibenzyl urea obtained by treating the cyanate with water. I have, however, always remarked in this reaction the formation of more or less ammonia and cyanuric acid.

Regarding the properties of the dibenzyl urea I may further remark, that it is insoluble in water, but very soluble in alcohol, from which it crystallises in beautiful white needles. Like the monobenzyl urea, it forms a crystalline salt with platinum and hydrochloric acid, but no solid compounds with nitric or hydrochloric acid. It melts at 167°.

Phenyl-benzyl Urea.—Benzyl isocyanate mixed with aniline occasions an extrication of heat, and solidifies on cooling into a brown crystalline mass, which is purified by recrystallisation from alcohol. The body so prepared presents the form of white needles, insoluble in water and hydrochloric acid, which melt at 168°. They contain—

	Theory.	Experiment.
C.....	74·3	74·5
H.....	6·2	6·2

The mixed urea yields no crystallisable nitrate, but an insoluble platinum salt. On heating it, it shows the characteristic property of the ureas, evolving pungent fumes of benzyl isocyanate.

Benzyl Isocyanurate.—This compound is the principal product of the reaction of benzyl chloride on silver cyanate. The yellow, oily liquid before described as passing over at the latter stage of the distillation and solidifying on cooling, was treated with hot alcohol, in which it slowly dissolved. On cooling, beautiful silky needles were deposited from the solution, which, by a couple of recrystallisations from alcohol, are obtained pure. The analysis of these crystals showed that they possessed the composition of benzyl isocyanate. The boiling point lies so high that it could not be determined, and the other physical properties all characterize the isocyanurate—

	Theory.	Experiment.
C.....	72.2	72.4
H.	5.2	5.4

The extremely light needles of this body are insoluble in water, soluble with difficulty in ether, but more readily in alcohol, particularly if it be heated. They melt at 157° C. and boil above 320°.* Sublimed several times in a tube they are decomposed into the isocyanate, known at once by the smell.

When fused with caustic potash they yield carbonic acid and benzylamine, identified by the analysis of its platinum double salt—

This reaction is characteristic for the isocyanurate.

The body obtained by Cannizzaro by the action of benzyl chloride on potassium cyanide, which, considering the mode of its production, must be regarded as the true cyanurate, possesses the same properties, so far as they have been observed, as the isocyanurate examined by myself. The melting point agrees nearly with that observed by Cannizzaro, being 153°. Are the two bodies obtained in such different ways isomeric or identical? The investigation of the products formed by the decomposition of Cannizzaro's compound by potash, which must give benzyl alcohol and cyanuric acid, can alone decide this question. Should the two, as certainly appears to be the case, be demonstrated as identical, it must be admitted that the cyanurate formed in the first instance has undergone the same change as Hofmann and Olshausen have observed in methyl cyanurate, which, by distillation, is converted into isocyanurate.