

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Halogen-acetylureas

BY IRWIN A. PEARL AND WILLIAM M. DEHN

There are nine possible halogenated derivatives of monoacetylurea; only five have hitherto been reported, namely, monochloro-,^{1,2} monobromo-,³ monoiodo,⁴ trichloro-,⁵ and tribromo-^{3,6} derivatives. The data concerning some of these are meager and conflicting. This study was under-

alcohol that it melts at 188–189°. It is also a strong sternutator. Dibromoacetylurea was prepared in the same manner. The diiodo- and triiodo-acetylureas were prepared from the corresponding chloro- compounds by treatment with sodium iodide.

COMPLETE TABLE OF HALOGEN-ACETYLUREAS

Compound	M. p., °C. ^a	Formula	Analyses, % N	
			Calcd.	Found
Monochloroacetylurea ^b	190–191	C ₂ H ₅ N ₂ Cl	26.8	26.9
Monobromoacetylurea ^b	188–189	C ₂ H ₅ N ₂ Br		
Monoiodoacetylurea ^c	182–184	C ₂ H ₅ N ₂ I		
Dichloroacetylurea ^b	149–150	C ₂ H ₄ N ₂ Cl ₂	Cl, 51.08	51.32
Dibromoacetylurea	180–181	C ₂ H ₄ N ₂ Br ₂	12.3	12.5
Diiodoacetylurea	192–193	C ₂ H ₄ N ₂ I ₂	8.70	8.75
Trichloroacetylurea	150	C ₂ H ₃ N ₂ Cl ₃		
Tribromoacetylurea	158	C ₂ H ₃ N ₂ Br ₃		
Triiodoacetylurea ^d	74–75	C ₂ H ₃ N ₂ I ₃	6.26	6.84

^a All melting points were taken on compounds recrystallized from alcohol. ^b These compounds are sneeze producers.

^c This compound is a strong lachrymator. ^d This compound decomposes on exposure to air.

taken to prepare the other four members of the series and to clarify the data of the monochloro- and monobromo-acetylureas.

Tommassi¹ treated chloroacetyl chloride with urea and obtained chloroacetylurea which "decomposed at 160°." By the same method Aberhalden and Riesz,² obtained chloroacetylurea melting at 180°. In the same process we obtained monochloroacetylurea, but our compound, after repeated crystallization from alcohol, melted sharply at 190–191°. Besides its analytical data, proof of its constitution is given by its conversion into monoiodoacetylurea through treatment with sodium iodide in dry acetone. In addition to the pain and burning sensation produced by monochloroacetylurea when placed in the mouth,¹ this compound, even in the solid state, is a violent sneeze producer. Dichloroacetylurea was prepared and, like the monochloro-derivative, it has strong sternutatory properties.

Baeyer³ prepared monobromoacetylurea by treating urea with monobromoacetyl chloride. However, he neglected to report its melting point. We found after repeated recrystallization from

Experimental

Preparation of Monochloroacetylurea.—Twenty-three grams of chloroacetyl chloride (b. p. 104–105°) was mixed with 12 g. of urea. After the initial vigorous reaction subsided, the mixture was warmed on the steam-bath for fifteen minutes, and then diluted with an excess of cold water. Almost the theoretical yield of monochloroacetylurea separated. Two recrystallizations from alcohol gave white needles melting sharply at 190–191°.

Upon treatment of monochloroacetylurea with sodium iodide in dry acetone according to Jacobs and Heidelberger's process,⁴ monoiodoacetylurea melting at 182–184° was obtained.

Preparation of the Dihalogenoacetylureas.—Dichloroacetylurea was prepared in approximately theoretical yield by treating one mole of dichloroacetyl chloride with urea. Recrystallization from alcohol gave white needles melting at 149–150°. Dibromoacetylurea was prepared from urea and dibromoacetyl bromide. Recrystallization from alcohol gave crystals melting at 180–181°. Diiodoacetylurea was prepared from dichloroacetylurea in the same manner as the monoiodo compound. Upon recrystallization from alcohol it melted at 192–193°.

Preparation of Triiodoacetylurea.—Fifteen grams of sodium iodide, 6 g. of trichloroacetylurea,⁵ and 75 cc. of absolute alcohol were shaken together in a flask for fifteen minutes. The mixture was allowed to stand one week, when a clear solution resulted. Evaporation of the alcohol gave long transparent yellow crystals. These were dried quickly on porous plate and transferred to a stoppered bottle because they decompose on continued exposure to the atmosphere. Recrystallization from alcohol gave needles melting at 74–75°.

- (1) Tommassi, *Bull. soc. chim.*, [2] **19**, 243 (1873).
- (2) Aberhalden and Riesz, *Fermentforschung*, **12**, 180 (1930).
- (3) Baeyer, *Ann.*, **130**, 156 (1864).
- (4) Jacobs and Heidelberger, *THIS JOURNAL*, **41**, 2100 (1919).
- (5) Meldola and Tommassi, *J. Chem. Soc.*, **27**, 404 (1875).
- (6) Behrend, *Ann.*, **236**, 64 (1886).

Summary

The apparent error in the reported melting points for monochloroacetylurea is clarified, and the melting point for monobromoacetylurea is reported.

Dichloro-, dibromo-, diiodo-, and triiodo-acetylureas have been prepared, thus completing the series of halogenoacetyl-monosubstituted ureas.

SEATTLE, WASH.

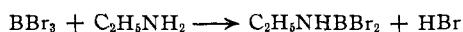
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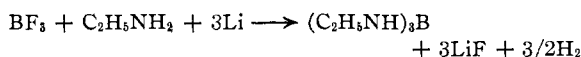
Organoboron-nitrogen Compounds. I. The Reaction of Boron Chloride with Aniline

BY REUBEN G. JONES AND CORLISS R. KINNEY

Two distinct types of organoboron-nitrogen compounds are known. One of these is the addition type in which the boron atom of a boron compound is attracted by the unshared pair of electrons belonging to a nitrogen atom in a molecule of ammonia, an amine, or a nitrile: $R_3B:NR_3$. Many of these compounds are surprisingly unreactive and thermally stable. The second type of boron-nitrogen linkage is the true covalent bond, known examples of which are very rare: $(R_2N)_3B$. The first of these was obtained by A. R. Johnson¹ in 1912, who found that boron bromide would form not only addition compounds with amines but also substitution products.



Recently, Kraus and Brown² have prepared the trisubstitution product by means of the reaction



Considering the work of Johnson and the reactivity of boron chloride and bromide, it appeared likely that the substituted amides of boric acid could be made directly from the halide and the various amines. Furthermore, Rideal³ in 1889 treated boron chloride with aniline and obtained a substance which he thought was $C_6H_5N=BCl$. This compound would be particularly interesting not only because of the possibilities for further synthesis but also because of the doubly bonded boron atom. With these points in view the study of the reaction of boron halides with amines was begun and in the present paper the work with aniline and boron chloride is presented.

The reaction of aniline with boron chloride is violent and it is desirable to moderate the reaction in some way. The first method tried was to depress the reactivity of the halide by converting it into an addition compound with a

tertiary amine. Upon treating dimethylaniline with boron chloride, the addition compound to be expected was obtained. This compound, however, did not yield the products desired when treated with aniline and the method was abandoned. The reaction rate is also lowered very markedly by using aniline hydrochloride instead of aniline; in fact, the reaction is too slow to be practicable. Thus, in one experiment, aniline hydrochloride and boron chloride were allowed to react at room temperature for a period of over three months. At intervals of two weeks the tube was opened and the hydrogen chloride produced allowed to escape, showing that a reaction was progressing. This procedure, while of interest in studying the reaction, also was abandoned. By far the best method is to dilute the reactants with an inert solvent such as benzene. Under these conditions no trouble was experienced in obtaining the addition compound of aniline and boron chloride and from that several other related derivatives. The reactivity of the addition compound was considerably greater and the thermal stability less than has been reported for many similar compounds. Thus, the substance reacts vigorously with water and readily with aniline, especially when heated in benzene, and, when heated alone in boiling benzene, decomposes into aniline and boron chloride.

Using the addition compound as a starting point, several substitution products were obtained by further reaction with aniline. The analysis of the simplest of these corresponded to that of the primary substitution product plus a molecule of aniline, $C_6H_5NHBCl_2 \cdot NH_2C_6H_5$. Unfortunately, this compound was isolated in very small yields only and was not readily purified. However, no difficulty was experienced in obtaining the compound having the composition reported by Rideal,³ and in good yields. Upon determining the molecular weight, the compound

(1) A. R. Johnson, *J. Phys. Chem.*, **16**, 1 (1912).

(2) Kraus and Brown, *THIS JOURNAL*, **52**, 4414 (1930).

(3) Rideal, *Ber.*, **22**, 992 (1889).