

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

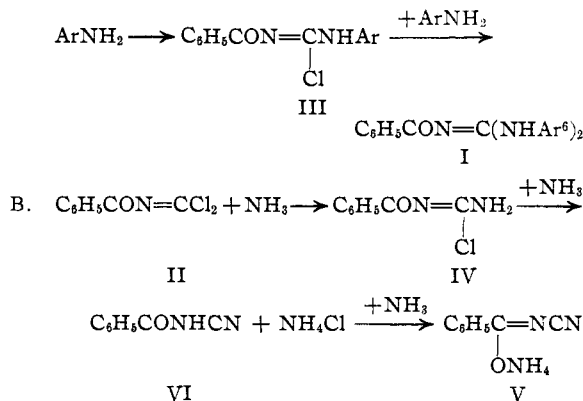
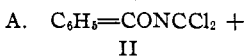
On the Ammonolysis of Benzoylisocyanidichloride

BY JOSEPH C. AMBELANG¹ AND TREAT B. JOHNSON

Benzoyldiarylguanidines (I) have been prepared by Johnson and Chernoff² by interaction of benzoylisocyanidichloride (II) and aromatic amines. Douglass and Johnson³ later applied this reaction successfully for the identification of benzoylisocyanidichloride (II) which they obtained by chlorination of ethyl benzoyldithiocarbamate in aqueous solution. The authors attempted through this same general procedure to synthesize monobenzoguanidine which was required in quantity for an investigation now in progress in this Laboratory. They were also interested in comparing the product of such interaction with the benzoylguanidine previously obtained by Traube⁴ by the action of ethyl benzoate on guanidine.

It has now been found that the interaction of benzoylisocyanidichloride (II) with an excess of ammonia in ether or alcohol solution leads not to the production of the desired benzoylguanidine, but to the formation of the isomeric ammonium salt of benzoylcyanamide (V). This salt has previously been described by Buddeus,⁵ who prepared it by the action of ammonia on benzoylcyanamide (VI) in ether solution. Acidification of this reaction product (ammonium salt (V)) with hydrochloric acid yielded a halogen-free substance, which was identified as benzoylcyanamide (VI). Benzoylguanidine, if present, would give according to the same treatment its characteristic hydrochloride.

This difference in behavior between aromatic amines and ammonia may be explained by assuming that their reaction with benzoylisocyanidichloride (II) proceeds in two steps with formation of the intermediates (III) and (IV), respectively; and that the latter compound (IV), in the presence of ammonia, undergoes dehydrohalogenation more readily than ammonolysis. These changes are expressed in the equations A and B below.



Experimental Part

Benzoylisothiocyanate, C₆H₅CONCS.—Forty-five grams of potassium thiocyanate, finely pulverized and thoroughly dried at 110° for ten hours, was suspended in 100 cc. of dry benzene containing 56.5 g. of benzoyl chloride. After refluxing this mixture for six hours at 110–120°, the odor of the acid chloride could not be detected. The salt was removed by filtration, the excess of benzene evaporated *in vacuo* and the reaction product purified by distillation. It boiled at 133–137° at 18 mm.; yield, 64%.

Benzoylisocyanidichloride, C₆H₅CON=CCl₂.—This reagent was prepared from benzoylisothiocyanate according to the directions of Johnson and Chernoff.² A nearly colorless oil was obtained in a yield of 73%. It distilled at 131–132° at 17 mm. This oil retained its original appearance when stored in a sealed ampoule.

Ammonium Salt of Benzoylcyanamide.—Sixty cc. of anhydrous ether was cooled in an ice-bath and saturated with ammonia. A solution of 5.2 g. of benzoylisocyanidichloride in 40 cc. of dry ether was then added slowly with shaking. Since the odor of ammonia was not apparent at the end of the addition, ammonia gas was passed into the suspension until an excess was in evidence. The reaction mixture was allowed to stand for several hours in an ice-bath. The solid was then filtered off and dried *in vacuo*; 6.3 g. of reaction product was obtained. This material was extracted with boiling absolute alcohol to remove ammonium chloride, and the alcohol extract freed from any dissolved ammonium chloride by dilution with ether. Evaporation of the filtered extract yielded 3.7 g. of nearly colorless needles. This product was recrystallized from absolute alcohol or a mixture of alcohol and ethyl acetate. It melted at 184°,⁷ and was identified as the ammonium salt of benzoylcyanamide. *Anal.* Calcd. for C₈H₉O₂N₃: N, 25.76. Found: N, 25.91, 25.74. The addition of benzoylisocyanidichloride to an excess of alcoholic ammonia led to the formation of the same substance.

(6) Ar = Aryl.

(7) Hantzsch and Dollfus, *Ber.*, **35**, 256 (1902).

(1) Sterling Professorship of Chemistry Research Assistant, 1938–1939.

(2) Johnson and Chernoff, *This Journal*, **34**, 164 (1912).(3) Douglass and Johnson, *ibid.*, **60**, 1486 (1938).(4) Traube, *Ber.*, **43**, 3589 (1910).(5) Buddeus, *J. prakt. Chem.*, [2] **42**, 84 (1890).

Benzoylcyanamide.—The ammonium salt obtained from 9.6 g. of benzoylisocyanidchloride (above) was dissolved in 30 cc. of warm water, and the solution poured with shaking into 40 cc. of hot 3 *N* hydrochloric acid. An immediate precipitate of benzoylcyanamide was formed in a yield of 85%. It was purified by crystallization from water followed by drying *in vacuo* over concentrated sulfuric acid; m. p. 140°. ^{7,8} *Anal.* Calcd. for C₈H₈ON₂: N, 19.17. Found: N, 19.03.

(8) Diels and Wagner, *Ber.*, **45**, 876 (1912).

Summary

1. Benzoylisocyanidchloride and ammonia do not interact to yield Traube's benzoylguanidine formed by the action of ethyl benzoate on guanidine.

2. It reacts with ammonia in both ether and alcohol solutions to form the ammonium salt of benzoylcyanamide in excellent yield.

NEW HAVEN, CONN.

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Catalytic Oxidations. II. Oxidations in the Cycloparaffin Series

BY NICHOLAS A. MILAS AND WILLIAM L. WALSH¹

In a previous paper² a technique was developed for the catalytic oxidation of compounds which readily polymerize on heating, of solids which decompose at their melting point and in general of compounds of low volatility. Inasmuch as very little work of this type has been done in the cycloparaffin series,³ we undertook to investigate the catalytic oxidation of cyclohexane and cyclopentane and some of their derivatives. We have found that in all cases the chief solid products were maleic acid and its anhydride. Table I summarizes some of our typical runs in this field together with the optimum conditions used. These results may be contrasted with those obtained when cyclohexene⁴ and cyclohexanol⁵ are oxidized in solution in which case adipic acid

inter alia is the chief product formed. However, at higher temperatures and under the conditions of our experiments adipic acid itself goes over to maleic acid. Apparently at relatively high temperatures maleic acid is one of the most stable products formed in catalytic oxidations of substances of four or more carbon atoms joined in a chain or a ring. This generalization is amply confirmed by the patent literature in this field.

Experimental Part

Apparatus and the Catalyst.—The apparatus was the same as that previously described² except for the addition of an extra spiral trap immersed in a carbon dioxide freezing mixture. This modification was found to trap completely all products condensable at the temperature of solid carbon dioxide. In various runs passage of the exit gases through two calcium chloride drying towers and a final weighed U-tube filled with silica gel showed no increase in weight of the latter.

The catalyst used throughout this work was vanadium pentoxide deposited on pumice. Its preparation and activation were also described in our first paper.

Organic Materials.—Most of the materials were those of the purest quality supplied by the Eastman Kodak Company, but further purified when their physical properties failed to agree with those recorded in the literature.

The cyclopentadiene was made by fractionating several times the technical grade cyclopentadiene through a 23-inch (58-cm.) Fenske column and the fraction boiling at 40–44° was collected and used in our experiments. To prepare cyclopentane, 80 g. of the purified cyclopentadiene was reduced in an Adams apparatus using 2 g. of platinum oxide catalyst. The product from this reduction was fractionated through a column and the fraction boiling at 48–50° showed no unsaturation and was therefore collected and used in our experiments.

Analytical Procedure.—To determine the unoxidized hydrocarbons the condensates in the various traps were combined into a special volumetric flask the neck of which

TABLE I
SUMMARY OF TYPICAL EXPERIMENTS

Substance	Optimum <i>t</i> , °C.	Molal ratio air/substance	Time of contact, sec.	% Yield of maleic acid	
Cyclohexane	350	205	3.6	19.7	19.78
Cyclohexene	410	109	1.6	30.94	30.89
Cyclohexanone ⁶	328	17	
Cyclohexanol ⁶	365	14.8	
Cyclopentane	410	135	1.6	25.46	25.50
Cyclopentadiene	410	126	1.6	32.4	
Adipic acid	410	...	1.6	15.64	

(1) Abstracted from Part II of the Ph. D. Dissertation of William L. Walsh, M. I. T., June, 1936.

(2) Milas and Walsh, *THIS JOURNAL*, **57**, 1389 (1935).

(3) Cf. Wilken-Jorden, *J. Chem. Met. Mining S. Africa*, **32**, 283 (1932); *C. A.*, **26**, 5406 (1932).

(4) Willstätter and Sonnenfeld, *Ber.*, **46**, 2952 (1913); Schrauth, U. S. Patent 1,921,101 (1933); Milas and Sussman, *THIS JOURNAL*, **59**, 2345 (1937).

(5) Ellis, "Organic Syntheses," Coll. Vol. 1, 1932, p. 18; Foster, *ibid.*, Vol. XIII, 1933, p. 110.

(6) Brooks, B. S. Thesis, M. I. T., June, 1935.