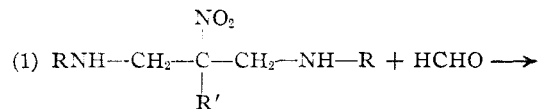


is noteworthy in view of reported debenzylations of compounds like 2-benzylamino-2-methyl-1-propanol⁴ and benzylethylmethylamine.⁵

5-Amino-1,3-dibenzyl-5-methylhexahydropyrimidine was allowed to react with aqueous formaldehyde in an attempt to prepare a derivative of this compound. Distillation of this reaction mixture gave 5-methyl-5-methyleneimino-1,3-dibenzylhexahydropyrimidine. Some properties of this compound are listed in Table I.

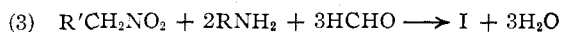
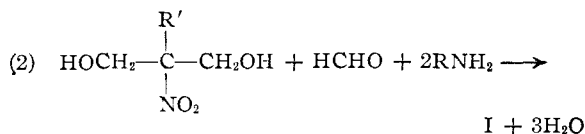
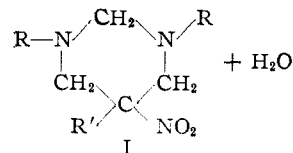
Summary

The preparation of a number of 5-nitrohexahydropyrimidines by one or more of the three following procedures is described:



(4) Senkus, *THIS JOURNAL*, **67**, 1515 (1945).

(5) Baltzy and Buck, *ibid.*, **63**, 1964 (1941).



The hydrogenation of some of the 5-nitrohexahydropyrimidines to the corresponding 5-amino-hexahydropyrimidines is also reported.

TERRE HAUTE, IND.

RECEIVED MAY 16, 1946

[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

The Preparation of DDT Using Hydrogen Fluoride as the Condensing Agent

By J. H. SIMONS,¹ J. C. BACON, C. W. BRADLEY,² J. T. CASSADAY, E. I. HOEGBERG AND PAUL TARRANT

Hydrogen fluoride has been found to be a good condensing agent for a number of different reactions catalyzed by reagents such as sulfuric acid or aluminum chloride.³ It was hoped that one of the particular advantages of the use of hydrogen fluoride in the preparation of DDT would be the elimination of side reactions usually encountered in the use of the other catalysts. For example, in a recent article Haller⁴ states that thirteen impurities are present in technical DDT made by condensing chloral and chlorobenzene in the presence of sulfuric acid. Four of these compounds are formed directly in side reactions involving the sulfuric acid.

As soon as sufficient information was available from the early experiments to show the possibilities of the condensation, the scale of the experiments was increased and the conditions of the reaction and the nature of the product were examined more accurately. Table I shows the various conditions under which the reaction was run and the results obtained.

Discussion

The results show that a large excess of chlorobenzene did not alter the reaction appreciably. A very great excess of hydrogen fluoride is necessary to complete the condensation, and lower temperatures with slower reaction rates are desirable.

Preliminary work in the laboratory and pilot plant on the production of chloral from alcohol

indicated a probable yield of about 75%. On the basis of the alcohol used in the preparation of the chloral and chloral alcoholate, respectively, the yield of refined DDT was 58% in both cases. These results indicate that it might be advantageous to use crude chloral alcoholate as the starting material, thus eliminating the conversion to chloral. The quality of the product from the condensation of crude chloral alcoholate with chlorobenzene needs further investigation.

Investigations on the By-products and Impurities.—An investigation of the oily by-products was undertaken in an attempt to clarify the course of the reaction and to determine the probable impurities in the product.

The residual oil isolated during purification of the crude DDT, as described in the experimental section, probably contained some of the by-products obtained in the sulfuric acid process⁴ as well as certain fluorine derivatives. In an effort to identify one of the more probable fluorine derivatives, a sample of 2-trichloro-1-*p*-chlorophenylethanol⁵ was treated with hydrogen fluoride. A 50% yield of product, b. p. 94.5 to 96.5° at 1.5 mm., *n*²⁵_D 1.5463, was obtained which had the same physical properties as a material isolated from the by-product oils both by direct fractionation and steam distillation. Analysis of the latter material for fluorine and chlorine agrees closely with that for 2-trichloro-1-*p*-chlorophenyl-1-fluorethane (CCl₃CHFC₆H₄Cl). *Anal.* Calcd. for C₈H₅Cl₃F: Cl, 54.16; F, 7.26; mol. wt., 262. Found: Cl, 54.77, 54.96; F, 6.54; mol. wt., 262.

(1) Pennsylvania State College, State College, Pennsylvania.

(2) Deceased.

(3) Simons and Archer, *THIS JOURNAL*, **60**, 2953 (1938).

(4) Haller, *et al.*, *ibid.*, **67**, 1591 (1945).

(5) Prepared by the method given in British Patent 460,647; see also J. W. Howard, *THIS JOURNAL*, **57**, 2317 (1935).

TABLE I

Run	Reactor	Reagents, g.			Molar ratio	Time, hr.	Temp., °C.	Crude product		Purified product		Residual oil, %	
		Chloral	Chloro-benzene	HF				Yield, %	S. p., °C.	Yield, %	M. p., °C.	S. p., °C.	Yield
1	Black iron	34	62	100	1:2:20	0.5	110	12					
2		37	62	96	1:2:20	3.5	110	45					
3	Cu lined Autoclave	18.5	31	50	1:2:20	0.5	110	52					
4		18.5	32	62	1:2:24	2.0	110	74					
5	Stainless	37	63	111	1:2:21	0.5	110	71	34	92-95			
6	steel	37	63	101	1:2:20	2.0	110	73					
7	Rocking	41.4 ^a	62	112	1:2:21	2.0	110	63					
8	Autoclave	37	62	112	1:2:21	0.5	150	75					
9		37	62	60	1:2:12	2.0	110	64					
10		37	84	101	1:2:20	0.5	110	59	42	82-90			
11		37	62	98	1:2:20	41	25	61					
12		18	32	107	1:2:40	5.5	60	75					
13		48.4 ^b	62	120	1:2:24	1.0	110-130	74					
14	Stainless	147.5	246	470	1:2:24	0.5	105-110	72	54	82-92			
15	steel stir-	147.5	787	450	1:7:23	.5	105-110	65	36	98-100			
16	rer type	165.5 ^a	450	640	1:4:32	.5	105-110	71	29	95-98		49	
17		147.5	450	450	1:4:23	.5	105-110	73	49	88-94			
18		147.5	450	450	1:4:23	.5	90-95	56	39	85-95			
19		147.5	450	850	1:4:43	.5	105-110	92	71	85-90		21.5	1.25
20		147.5	450	815	1:4:41	1.5	90-95	91	82	85-97	93	20.7	
21		147.5	450	815	1:4:41	0.5	115-120	94	66	80-85		16	1.41
22		147.5	456	850	1:4:41	5.0	70-80	95	81 ^g	92-96	91.5	16.4	1.58
23		147.5	450	890	1:4:45	43	25	24					
24		147.5	250	850	1:2.2:43	5.0	70-80	"	88		84		
25		147.5	450	900	1:4:45	3.0	70-80	91 ^g	84	73	92-94		
26		147.5	335	800	1:3:40	11	25 ^e	91	69	58	78-79		22
27		180 ^b	450	935	1:4.3:50	1.75	90-105	92	46	44	82-91	87	48
28		193.5 ^c	335	1087	1:3:54	4.75	70-80	80	78	58	93-95		26
29	^d	147.5	335	885	1:3:44	4.75	70-80	84	80	64	98-100		21

^a Chloral hydrate used. ^b Chloral alcoholate used. ^c Crude chloral alcoholate used. ^d A copper liner was used. ^e Autoclave heated to 115° and then allowed to cool to room temperature. ^f Theoretical yield based on chloral. ^g The washed product or a portion of it was steam-distilled for two hours. In 22 the loss was about 2% and the dried product had a setting point of 89°. ^h Setting point determined as outlined in "Joint Army-Navy Specification JAN-D-56," June 30, 1944.

Replacement of the hydroxyl group by fluorine in the intermediate product, 2-trichloro-1-*p*-chlorophenylethanol, would account for its formation. Since, according to the literature, high temperatures are required to replace a hydroxyl group with fluorine, lower temperatures in the preparation of DDT may reduce the amount of oily by-product. Analysis of the DDT for fluorine showed 0.6% fluorine present, indicating that there may be as much as 5 to 10% of the fluorine by-product present in a material having a setting point of 90°. By repeated recrystallization from ethanol and from heptane a fluorine-free material has been obtained.

Fluorine free DDT was heated for several hours with hydrogen fluoride. The resulting product contained 0.3% fluorine. The fluorine was probably introduced by the exchange of the fluorine of hydrogen fluoride for chlorine in the CCl₃ group.

Corrosion and Metals in the Product.—The wash liquors amounting to one liter per run from some of the larger experiments were analyzed

spectrophotometrically for iron, chromium and nickel.

TABLE II

Run	Fe, g./l.	Cr, g./l.	Ni, g./l.
19	0.33	0.099	0.041
21	.187	.144	.042

Slight corrosion of the stainless steel vessel was apparent; however, the amount of iron retained in a washed product from the same reactor was of the order of one p.p.m.

Experimental

Reaction Vessels.—The first two experiments were run in a one-inch black iron pipe equipped with a condenser, pressure gage and valve. Further exploratory work was done in a stainless steel rocking autoclave of about 300-ml. capacity. A copper liner was used in this autoclave in some instances as noted in Table I. The large runs were made in a two-quart, stainless steel autoclave equipped with a propeller type agitator.

Procedure.—The usual procedure was to charge the reaction vessel with a solution of chloral in chlorobenzene. The reaction vessel and contents were cooled in an ice-bath and hydrogen fluoride added.

In the case of the two small vessels, the hydrogen fluoride was poured from a small copper transfer vessel. At first the larger autoclave was filled by distillation of the hydrogen fluoride from a commercial cylinder. Later a blow case of about ten pounds capacity and operating under a few pounds of air pressure was used to blow the hydrogen fluoride into the reactor, thus eliminating the necessity for cooling.

Since both chloral and hydrogen fluoride are highly hygroscopic, it is essential that exposure to atmospheric moisture be kept to a minimum.

After the reaction mixture was heated for the specified time, the hydrogen fluoride was vented while the vessel and contents were still warm. Then water was added and the mixture poured from the reaction vessel and washed with water. In most of the experiments, the product solidified on cooling. The addition of a solvent such as chloroform or methylene chloride was desirable to facilitate further handling. The solution was washed with water and dilute potassium bicarbonate until free of hydrogen fluoride, dried over anhydrous sodium sulfate and the solvent evaporated. The residual material was further heated under vacuum on a steam-bath until essentially constant weight was reached. This crude product on cooling varied from a brown, viscous oil to a cream-colored solid. In several cases, noted in Table I, the washed product was stripped of volatile material by a steam distillation.

In the exploratory runs in the smaller vessels, this crude product was generally not investigated further.

The crude product from the larger runs solidified on cooling, but was generally low melting. In order to get an estimate of the DDT and oily by-products present, a simple refinement procedure was adopted. The crude molten product was poured rapidly into an approximately equal weight of methanol. A homogeneous solution was formed for a short time but DDT crystallized rapidly, and, after being cooled to 20°, the solid was filtered and air dried. The mother liquor was then freed of solvent leaving an oily residue.

Acknowledgment.—We are indebted to Mr. A. Struck for the spectrophotometric determination and to Messrs. F. J. Frere, I. D. Carter and J. R. Newsome for the analytical data.

Summary

Chloral and chlorobenzene have been condensed in the presence of hydrogen fluoride to give good yields of DDT. Copper and stainless steel equipment were used successfully with slight corrosion in the latter case. Results in a black iron vessel were less favorable. The use of chloral hydrate and chloral alcoholate in place of chloral has been investigated to a limited extent.

STAMFORD, CONN.

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[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT CO.]

Catalytic Synthesis of Hydrocarbons and Oxygenated Compounds from Ketene and its Relation to the Fischer-Tropsch Synthesis

BY B. R. WARNER, M. J. DERRIG AND C. W. MONTGOMERY

It was early proposed by Fischer and Tropsch¹ that the catalytic synthesis of hydrocarbons from hydrogen and carbon monoxide proceeds through the polymerization of methylene radicals, the latter being formed by the reduction of metallic carbide produced from the metal and carbon monoxide. Craxford and Rideal² in a later investigation also postulated the formation and utilization of carbides in the Fischer-Tropsch reaction. As Bahr and Jessen³ showed, precipitated and reduced cobalt reacts with carbon monoxide at 230° to yield the carbide, Co₂C. While these carbides are reduced in acid solution to give gaseous, liquid and solid hydrocarbons,⁴ the reaction with hydrogen yields methane almost exclusively.³

It is perhaps significant that in the Fischer-Tropsch synthesis oxygenated compounds are generally produced along with the hydrocarbons¹ even at low pressures. It is possible that oxygenated compounds either are actual intermediates in the synthesis or are produced in side reactions. That the formation of oxygen-containing compounds is an intermediate step in the formation of hydrocarbons was first suggested by Elvins and

Nash.⁵ The possibility that acetone is an intermediate was investigated by Smith⁶ but the hydrocarbons obtained with acetone, and acetone and hydrogen, over a cobalt-copper-manganese oxide catalyst, were different in character from those usually obtained from hydrogen and carbon monoxide. Recently Eidus⁷ investigated the reactions of methyl alcohol, ethyl alcohol and formic acid on a cobalt-thoria-kieselguhr catalyst with the view that these compounds might be intermediates. Although hydrocarbons were obtained, the conclusion reached was that these were formed from the secondary reaction between hydrogen and carbon monoxide, the primary reaction being the decomposition of the alcohols and formic acid into hydrogen and carbon monoxide. With the use of Balandin's multiplet theory of catalysis,⁸ Eidus postulates the intermediate formation of methylene radicals without assuming the intermediate formation of carbide.

A direct test of the methylene theory would be to supply the catalyst with methylene radicals. It was thought that ketene might possibly func-

(5) Elvins and Nash, *Nature*, **118**, 154 (1926).

(6) Smith, Hawk and Golden, *THIS JOURNAL*, **52**, 3331 (1930).

(7) Eidus, *Bull. acad. sci. U. R. S. S.*, 65-72 (1943); *Natl. Petroleum News*, **37**, No. 14, R 302, G (1945).

(8) Balandin, *J. Russ. Phys.-Chem. Soc.*, **61**, 909 (1929); *Acta Physicochim. U. R. S. S.*, **2**, 177 (1935).

(1) Fischer and Tropsch, *Ber.*, **59**, 830 (1926).

(2) Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).

(3) Bahr and Jessen, *Ber.*, **63**, 2226 (1930).

(4) Fischer and Tropsch, *Brennstoff-Chem.*, **9**, 21 (1928).