

TABLE V. EFFECT OF TEMPERATURE

Temp., ° C.	No. of Runs	Time, Hours	Fina		Fina pH
			Yeast Yield, %	Reducing Sugar Content, %	
25	3	24	0.30-0.47	7.4
28	6	23	0.30-0.33	0.23-0.32	7.5
32	4	22	0.33	0.20	7.4
34	11	22	0.30-0.31	0.18-0.20	7.4-7.9
C-Porosity Fritted-Glass Tubes					
30	3	18	0.31	0.20-0.21	7.8

SIZE OF INOCULUM. Studies made of the optimum yeast inoculum (Table IV) indicated that initial yeast concentrations of approximately 100,000,000 yeast cells per cc. were desirable. The experimental data further indicate that yeast concentrations considerably in excess of 100,000,000 cells per cc. did not increase the rate of sugar consumption.

DILUTION WITH WATER. The dilution of the still waste liquor with water speeded the removal of the sugar but had no apparent effect on the yield of yeast. The unconsumed residual reducing sugar content of 0.2 per cent was decreased proportionately with the amount of dilution.

TEMPERATURE. Studies were made between 25° and 34° C. The rate of sugar consumption increased with increase in temperature (Table V).

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Benzyl Benzoate from Benzyl Chloride and Sodium Benzoate

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AS A RESULT of wartime restrictions on the availability of toluene and, hence, benzaldehyde, production processes for the manufacture of the miticide benzyl benzoate other than by the Claisen condensation of benzaldehyde (4, 5) had to be investigated. Simultaneously, improved processes for production of benzyl chloride by chloromethylation of benzene and of benzoic acid through the aluminum-chloride-catalyzed reaction between benzene and phosgene were also studied in this laboratory (6).

These developments led to two methods for carrying out the double decomposition between benzyl chloride and sodium benzoate to form benzyl benzoate. One of them depends upon the presence of water as reaction solvent for sodium benzoate, as first described by Gomberg and Buchler (3); the other relies on the catalytic activity of a small amount of tertiary amine in the absence of any reaction solvent other than that supplied by the reacting materials (1).

Although the results in Table I and Figures 1 and 2 on the aqueous double decomposition between benzyl chloride and sodium benzoate generally agree with those of Gomberg and Buch-

ler (3), it should be noted that reaction times in excess of 6 hours tend to lower the yield of the ester. Also, Table I shows that 42% aqueous solutions of sodium benzoate may be employed in place of 22-27% solutions as used by Gomberg and Buchler without noticeably affecting the ester yield. Thus, much valuable reactor space is not surrendered to an inert solvent.

The amine-catalyzed reaction on a slurry of dry sodium benzoate in benzyl chloride is interesting. Despite the fact that practically quantitative yields of aromatic acid esters may be obtained easily, this method has strangely remained out of the chemical literature since its first appearance as a German patent in 1912 (1). Scelba (?) reports that dry sodium benzoate, heated with a slight excess of benzyl chloride at 170-175° C. for 24 hours, produces a 70-75% yield of benzyl benzoate. According to the German patent (1), a small quantity of triethylamine lowers the reaction temperature required for this same reaction to about 130-140° C., the reaction time to about one hour, and raises the ester yield to 95% or higher.

Volviler and Vliet (10) found that diethylamine possesses definite catalytic activity in the synthesis of benzyl salicylate and benzyl *p*-nitrobenzoate. Their data, as well as that presented

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TABLE I. FORMATION OF BENZYL BENZOATE FROM BENZYL CHLORIDE AND AQUEOUS SODIUM BENZOATE

Expt. No.	Benzyl Chloride, Moles	Sodium Benzoate, Moles	Reflux Period at 100-110° C., Hours	Benzoic Acid Recovered, Grams	Distillation, Grams			Benzyl benzoate residue	Cl, %	Free acid, %	Analysis of Stripped Benzyl Benzoate		M. P., ° C.	Yield, %
					Benzyl chloride	Benzyl alcohol	Benzyl benzoate				Esther, %	n _D		
1	1.5	1.0	8	52.0	54.6	18.8	118.0	0.18	<0.1	94.9	1.569	16.5	52.8	
2	1.5	1.0	6	Not detd.	67.0	12.8	121.4	0.09	<0.01	97.7	1.569	17.9	55.5	
3	1.5	1.0	4	55.8	73.7	11.7	119.7	0.33	<0.01	94.7	1.569	15.5	53.4	
4	1.5	1.0	2	65.6	89.0	About 8	103.3	0.28	<0.01	96.8	1.5675	15.9	47.1	
5	1.0	1.5	8	80.2	3.5	5.6	159.0	0.34	<0.01	94.0	1.5675	15.3	70.4	
6	1.0	1.5	6	104.5	5.0	5.6	157.0	0.11	<0.01	96.9	1.569	17.0	71.7	
7	1.0	1.5	4	93.1	5.8	0.6	148.6	0.11	<0.01	99.1	1.569	18.2	69.4	
8	1.0	1.5	3.25	93.9	5.8	0.9	159.2	0.15	<0.01	95.1	1.5675	13.4	68.4	
9	1.0	1.5	2	96.0	5.4	3.6	147.0	0.28	<0.01	96.8	1.5685	16.8	67.0	
10	0.5	1.0	6	75.4	About 0.5	0.5	80.9	0.06	<0.01	97.7	1.569	17.4	72.2	
11	0.5	1.0	4	85.1	1.6	0	77.7	0.16	<0.01	98.6	1.569	17.1	70.0	
12	0.5	1.0	2	76.1	1.9	0	76.1	0.15	<0.01	97.1	1.568	16.2	70.0	
13	0.25	1.0	4	96.8	0	0	41.8	0.28	<0.01	96.9	1.568	16.3	76.4	
14	0.25	1.0	2	103.0	0	0	40.9	0.07	<0.01	97.3	1.568	16.3	75.0	
Gomberg & Buehler (3)	0.25	0.38 ^d	4-5	20-22	37	70	
Gomberg & Buehler (3)	0.51	1.53 ^d	4-5	143	84	79	

^a Employed as a 42% solution by weight in water.^b Employed as a 22-27% solution by weight in water.^c Stated for comparison; dots indicate lack of information.^d Based on benzyl chloride.

A study was made to determine the optimum reaction conditions for two methods given in the literature for preparing benzyl benzoate from benzyl chloride and sodium benzoate. One of these methods consists in refluxing an aqueous solution of sodium benzoate with benzyl chloride, the other in the catalytic action of an amine on a slurry of dry sodium benzoate and excess benzyl chloride. The data indicate that in the aqueous method the yield of benzyl benzoate depends on the ratio of benzyl chloride to sodium benzoate and on the time of reflux. An excess of sodium benzoate, preferably 2 to 4 moles per mole of benzyl chloride, produces benzyl benzoate in yields above 70% in about 4-6 hours at about 110° C.; shorter or longer reaction times produce lower yields of ester. In the amine-catalyzed reaction between 1 mole of dry sodium benzoate and 1.4 moles of benzyl chloride, the results indicate that tertiary amines, such as triethylamine, will produce benzyl benzoate in yields of over 90% for a reaction period of about 1 hour at 110-140° C. The quantity of amine necessary ranges from 0.45 to 0.65% by weight based on the weight of the benzyl chloride-sodium benzoate reaction mixture. A probable reaction mechanism for the amine-catalyzed reaction is proposed.

in Table II, indicate that diethylamine does not exhibit the superior catalytic activity characteristic of some tertiary amines. The results of the present investigation (Table II) indicate that unsubstituted saturated *tert*-alkyl amines are the best catalysts in this type of double decomposition.

PROCEDURE

All materials were used as indicated without further purification.

BENZOIC ACID. Mallinckrodt's reagent grade.

BENZYL CHLORIDE. In the aqueous process a commercial grade was used throughout (chlorine: calculated for C₇H₇Cl, 28.01; found, 28.50; n_D²⁰, 1.5388). The amine-catalyzed nonaqueous procedures utilized a pure grade of benzyl chloride which had been prepared at Edgewood Arsenal by chloromethylation of benzene (6) (chlorine: calculated for C₇H₇Cl, 28.01; found, 27.98, 28.01; n_D²⁰, 1.5388).

HEXAMETHYLENE TETRAMINE. E. I. du Pont de Nemours and Company, Inc.

N-METHYLMORPHOLINE, MORPHOLINE, AND TRIETHANOLAMINE. Carbide and Carbon Chemicals Corporation.

PYRIDINE. City Chemical Corporation, c.p. grade.

SODIUM BENZOATE. The Coleman and Bell Company, U.S.P. grade.

TRIETHYL- AND DIETHYLAMINES. Eastman Kodak Company, White label grade.

AQUEOUS DOUBLE DECOMPOSITION. One mole of sodium hydroxide in the form of a 16.7% aqueous solution by weight (40 grams of NaOH pellets in 200 ml. H₂O) and one mole of benzoic acid are placed in a 1-liter, three-neck, round-bottom flask equipped with a mercury-seal stirrer, a thermometer, and a water-cooled reflux condenser. The reaction flask, immersed in an oil bath, is brought to reflux temperature (100-110° C.), and the desired amount of benzyl chloride (ranging from 0.25 to 1.5 mole of benzyl chloride per mole of sodium benzoate) is added through the condenser. The reaction mixture is stirred vigorously at reflux temperature for 2 to 8 hours.

At the end of the reaction period the product is transferred to a separatory funnel and the lower aqueous layer removed. The upper layer, containing the ester, is washed successively with several 200-ml. portions of 5% aqueous sodium hydroxide; two or three such washes usually suffice to extract all of the unreacted benzoic acid and are followed by two water washes of about 200 ml. each. The combined aqueous layers are extracted with 50 ml. of carbon tetrachloride or benzene, and this organic layer is added to the total organic product layer.

The combined organic product layers are then stripped of all volatile materials down to 5 mm. of mercury pressure, and the still residue, consisting almost entirely of the desired benzyl benzoate, is analyzed for ester content (by saponification), chlorine content, and amount of residual free benzoic acid. Its refractive index and melting point are also determined. The combined aqueous extracts are acidified by the addition of concentrated hydrochloric acid, whereupon unreacted benzoic acid is precipitated. It is filtered off with suction, dried in air, and weighed.

The reaction data obtained, together with any deviations from the general procedure given above, are found in Table I and Figures 1 and 2.

AMINE-CATALYZED NONAQUEOUS DOUBLE DECOMPOSITION. One half mole of dry sodium benzoate powder and 0.7 mole of benzyl chloride are placed in a 500-ml., three-neck, round-bottom flask, equipped with a thermometer, a mercury-seal stirrer, and a reflux condenser terminating in a calcium chloride trap. The mixture is stirred for a few minutes to a homogeneous slurry, and about 1 ml. or 1 gram of an amine is added. With constant and rapid stirring, this viscous mixture is brought to 90–130° C. (depending upon the catalytic activity of the amine used) in about 10 minutes by means of a Glas-Col electric heating jacket. Sufficient heat is generated, after the reaction begins, to raise the temperature of the reaction mixture to 140–155° C. This temperature rise continues for about 5 minutes. External heat is applied to the reaction flask so that the temperature is maintained somewhere between 100° and 140° C. The over-all reaction periods vary from 0.5 to 2.0 hours.

When the reaction is complete, the product is poured into 0.5–1.0 liter of water and is thoroughly shaken. The lower organic layer, after separation, is washed with two 250-ml. portions of water.

The combined aqueous washings are extracted with two 50-ml. portions of carbon tetrachloride, and the extract is added to the organic product layer. Without further treatment this product is stripped in vacuo. In some runs the stripped benzyl benzoate residue was distilled for purification. The results are given in Table II.

ASSAY OF ESTER BY SAPONIFICATION. Fifty milliliters of 0.25 *N* potassium hydroxide are pipetted into each of three 600-ml. Erlenmeyer flasks. To two of these flasks, 1.500 to 1.750 grams of the ester are added; the third flask remains for the blank determination. The flasks are fitted with air-cooled reflux condensers 90 cm. in length, and the contents are refluxed for 45 minutes on a steam bath. After refluxing, 125 ml. of carbon-dioxide-free distilled water are added to each flask, and the contents are immediately titrated with 0.3 *N* sulfuric acid, using 5 drops of phenolphthalein solution as indicator. The two determinations should check each other with a precision of 2%:

$$\text{percentage of ester} = (21.224 \times A \times B) / C$$

where *A* = (ml. of acid required for blank) minus (ml. of acid required for sample)
B = normality of acid
C = weight of sample

MELTING POINT OF BENZYL BENZOATE. The melting point of each sample is determined by the conventional method of allowing a solidified sample to warm up gradually in an air-jacketed tube. The time-temperature data obtained are plotted, the best straight lines are drawn through the two slopes of the curve, and the point of intersection is taken as the melting point of the product.

CHLORINE IN BENZYL BENZOATE. It was found that benzyl chloride gives lower values for chlorine by determination after refluxing with alcoholic sodium hydroxide than by determination after combustion in the Parr bomb. The values obtained for the total chlorine content of benzyl benzoate samples subjected to hydrolysis with alcoholic sodium hydroxide in pressure bottles are also consistently lower than those obtained by the Parr bomb method. Consequently, since the chlorine contents of the products are believed to arise mainly from traces of benzyl chloride and sodium chloride, the Parr bomb procedure was adopted for the determination of total chlorine in all benzyl benzoate samples.

YIELDS

Figures 1 and 2 show that the yield of benzyl benzoate depends upon two factors other than reaction temperature—namely, the ratio of benzyl chloride to sodium benzoate and the reaction time. An excess of sodium benzoate greatly reduces the formation of benzyl alcohol from the hydrolysis of benzyl chloride. This fact, together with the mass action effect imparted by an excess of sodium benzoates, favors higher yields of the ester. The optimum reaction period was found to be about 6 hours. As Figure 2 shows, refluxing of the reaction mixture for 8 hours results in lower yields of benzyl benzoate. This is probably caused by saponification of the ester after maximum yield has been reached. Benzyl alcohol produced through the hydrolysis of the chloride was identified, after isolation by fractionation, by its refractive index, (n_D^{20} 1.5392), and its urethan (melting point 76° C.) was prepared in the usual manner from phenyl isocyanate (8).

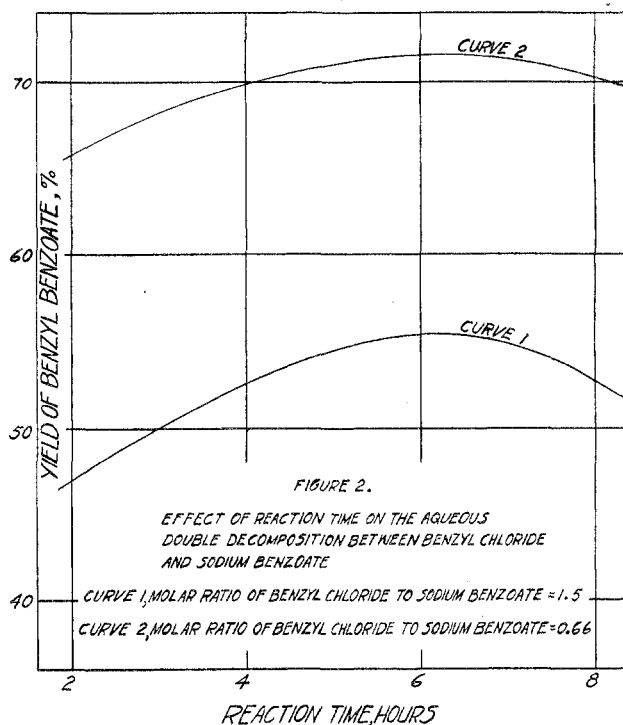
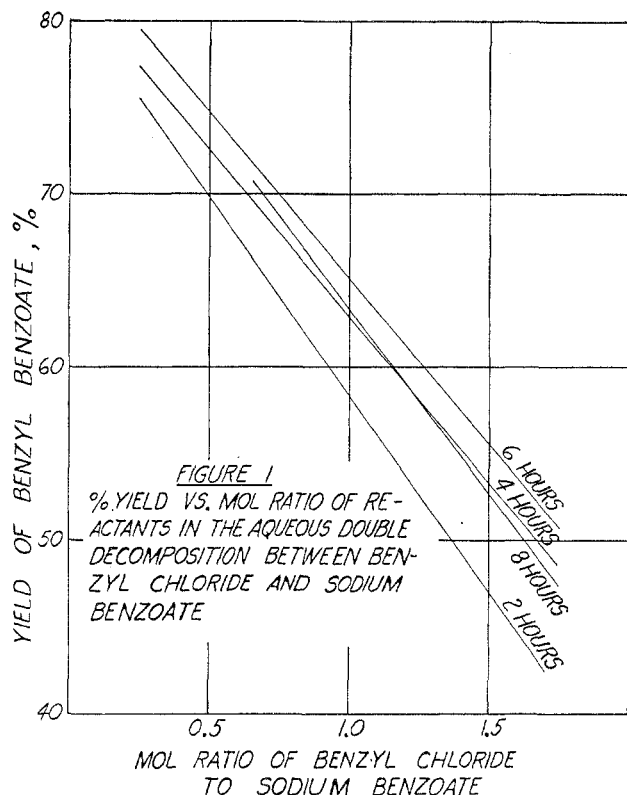
Tables I and II indicate that most of the benzyl benzoate samples prepared were not distilled but merely stripped in vacuo of all unreacted materials and by-products. This was done because the development was considered as preliminary to

TABLE II. REACTION DATA ON AMINE-CATALYZED NONAQUEOUS PREPARATION OF BENZYL BENZOATE FROM BENZYL CHLORIDE AND SODIUM BENZOATE

Expt. No.	Sodium Benzoate, Mole	Benzyl Chloride, Mole	Amine Added	Max. Temp. Reached, °C.	Av. Reaction Temp., Max. °C.	Total Reaction Period, Hours	Benzyl Chloride Recovered, Mole ^a	Benzyl Benzoate Obtained		Ester content by saponification, %	Refractive index, n_D^{20}	M. P., °C.	Chlorine content as Cl, %	Nitrogen content as N, %	Color of product
								Grams	Mole						
1	0.5	0.7	1 ml. triethylamine	125	110–115	1	Not measured	96.8 ^b	0.46	100.6	1.5685	18.6	0.24	..	Water white
2	0.5	0.7	Same	127	110–115	1	0.14	104.2 ^c	0.49	100.4	1.5685	18.3	0.38	..	Light amber
3	0.5	0.7	Same	145	130–140	0.5	0.18	103.2 ^c	0.49	100.5	1.5685	18.1	0.25	..	Light amber
4	0.5	0.7	1 g. hexamethylene tetramine	155	100–130	1	0.18	92.3 ^c	0.43	103.4	1.5675	16.4	0.20	..	Light amber
5	0.39	0.54	0.77 g. hexamethylene tetramine	143	130–140	1	0.15	76.9 ^e	0.36	101.8	1.567	13.6	0.32	..	Light amber
6	0.5	0.7	0.5 g. hexamethylene tetramine	144	120–130	2	0.18	97.5 ^c	0.46	101.6	1.568	16.5	0.14	..	Light amber
7	0.5	0.7	1 ml. <i>N</i> -methylmorpholine	130	120–130	1	0.20	98.1 ^c	0.46	100.5	1.5685	18.6	0.13	..	Very light amber
8	0.5	0.7	1 ml. pyridine	134	120–130	1	0.20	92.6 ^b	0.44	101.4	1.5685	18.5	0.35	..	Slightly yellow
9	0.5	0.7	Same	140	130–140	1	0.16	90.4 ^b	0.43	100.6	1.5685	18.4	0.57	..	Slightly yellow
10, 11	0.5	0.7	1 ml. triethanolamine	140	130–140	1	0.25	73.5 ^d	0.35	No appreciable	1.5685	18.0	Amber
12	0.5	0.7	1 ml. diethylamine	143	135–145	1	0.25	73.5 ^d	0.35	100.2	1.5683	18.0	Amber
13	0.5	0.7	1 ml. morpholine	135	125–135	1	0.51	22.3 ^d	0.11	100.2	1.5683	18.0	0.14	0.04	Dark amber

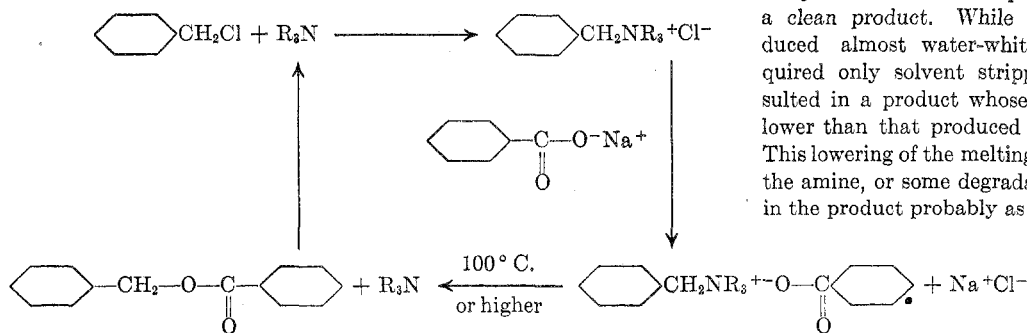
^a This fraction contains a small percentage of benzyl alcohol.

^b Of distilled product. ^c Of stripped residue. ^d Of stripped product.



larger-scale operation in which distillation of the final product would be undesirable because of the high boiling point of the product and unnecessary for the purposes of manufacture. One distillation of the combined stripped products (Table I) through a 6-inch unpacked column of 1-inch diameter produced a water-white grade of benzyl benzoate having the properties given in column 1 of Table III. When samples of the same stripped benzyl benzoate samples were washed twice before distillation with an equal volume of 5% aqueous sodium hydroxide, followed by two water washes of twice the ester volume, the resulting water-white benzyl benzoate was found to have somewhat superior properties (column 2).

It may be postulated that the amine-catalyzed formation of benzyl benzoate proceeds by formation of quaternary ammonium intermediates. Schematically, the course of the reaction may be written as follows:



This theory is based upon the fact that trialkyl benzyl ammonium salts thermally decompose contrary to Hofmann's rule (9) to produce a trialkyl amine and a benzyl derivative depending upon the negative ion in the parent salt.

Tertiary amines such as triethylamine, *N*-methylmorpholine, hexamethylenetetramine, and pyridine are all effective catalysts.

TABLE III. PROPERTIES OF DISTILLED BENZYL BENZOATE

	Without Caustic Wash	After Caustic Wash
Melting point, ° C.	18.5	18.7
Boiling range at 2.5 mm. Hg, ° C.	131-133	132
Refractive index, n_D^{20}	1.5687	1.5687
Specific gravity, d_4^{25}	1.113	1.114
Ester content, %	99.0	99.7
Chlorine content, %	0.28	0.00
Free benzoic acid, %	<0.01	<0.01
Odor	None	None

On the other hand, triethanolamine and secondary amines such as morpholine were found to be virtually inert, whereas diethylamine exhibited only moderate activity. While most of the tertiary amines tried gave good results, hexamethylenetetramine and pyridine were found to be less desirable than triethylamine or *N*-methylmorpholine. Pyridine consistently produced blackish, dirty materials which required distillation for isolation of a clean product. While hexamethylenetetramine produced almost water-white benzyl benzoate which required only solvent stripping, use of this catalyst resulted in a product whose melting point was decidedly lower than that produced by the other tertiary amines. This lowering of the melting point was undoubtedly due to the amine, or some degradation product thereof, included in the product probably as a quaternary ammonium salt.

Cooperative research has been carried out at the Pennsylvania State College with emphasis on reaction conditions using triethylamine as catalyst. If the sodium benzoate contained even small amounts of free benzoic acid, the catalyst was correspondingly neutralized and the reaction would not take place at steam bath temperature. More catalyst or a higher temperature (about 165° C.) was then needed. For the same reason the reagents had to be dry (11).

In the products from the amine-catalyzed reaction, the ester content, as determined by the saponification method described above, consistently exceeded 100%. This discrepancy was probably caused by the presence in the product of another neutralizable compound, which consumed an equivalent amount of sodium hydroxide and thus falsely appeared as ester in the results.

In the preparations presented in this paper, no attempts were made to produce a chlorine-free grade of benzyl benzoate. However, both the aqueous process as well as the amine-catalyzed nonaqueous process can produce a virtually chlorine-free product. It is necessary to use a grade of benzyl chloride free of nuclear chlorine—for example, that obtained from the chloromethylation of benzene (2, 6), and to include washing procedures which will remove all unused chloride as well as sodium chloride or nitrogen compounds present in the reaction product.

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PRODUCTION OF DDT . . .

Condensing Action of Chlorosulfonic Acid on Chloral Hydrate and Chlorobenzene

A new method of producing technical-grade DDT in 77% yield by the reaction of chlorosulfonic acid with chloral hydrate and chlorobenzene is presented. Although a yield of DDT greater than 90% is obtainable when chloral and chlorobenzene are condensed in an excess of sulfuric acid-oleum mixture, the process here described is carried out with the metathetical quantity of chlorosulfonic acid on chloral hydrate and chlorobenzene. Laboratory as well as best pilot plant procedures are outlined with a discussion of purification methods. The effects of reaction time and temperature on yield are shown. Since the process, on account of its low acid requirement, is apt to produce rather viscous products of DDT, a modification of the method using inert, recoverable solvents is described. Material costs for the chlorosulfonic acid and the conventional sulfuric acid-oleum processes, based on available published data, are compared.

AT PRESENT 1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, the insecticide commonly called DDT, is being produced in large quantities, both in this country and abroad, by condensing chlorobenzene with chloral in the presence of a large excess of concentrated sulfuric acid (2, 5, 7, 8). Inasmuch as some of the present commercial producers of DDT also possess facilities for the chlorination of ethanol, it has in some instances been found more economical to use chloral alcoholate, the end product of the ethanol chlorination, in place of chloral or its hydrate. This method of condensation and its many variations are based upon the work of Zeidler (10), who was the first to synthesize DDT.

For the manufacturer using chloral hydrate as a raw material, an alternate condensing agent was sought, in order to avoid the many troublesome operations connected with the handling of large volumes of sulfuric acid. It was found that halosulfonic acids of the type

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XSO_3H (where X = halogen) and, more specifically, chlorosulfonic acid, $ClSO_3H$, are excellent agents when used in metathetical quantities (2 moles) for the condensation of chloral hydrate (1 mole) with chlorobenzene (2 moles). Extensive laboratory and pilot plant investigations have proved the feasibility of the method.

Since halosulfonic acids, and specifically chlorosulfonic acid, are known to react with aliphatic alcohols (9) to form alkyl sulfates, the following over-all reaction mechanism for the condensation between chloral hydrate and chlorosulfonic acid is deemed likely:

