

TABLE I. SOLUBILITY OF SILVER SELENIDE AND TELLURIDE IN AMMONIA

Temp., ° C.	NH ₄ OH Concentration	Time of Contact, Min.	Soly., Gram/100 Ml. of Solvent	
			Ag ₂ Se	Ag ₂ Te
23 (room)	Concd.	30	0.0247	0.0004
		60	0.0261	0.0008
		240	0.0260	0.0008
23	1:1	30	0.0242	0.0005
		60	0.0262	0.0007
		240	0.0262	0.0007
34 (b.p.)	Concd.	2	0.0232	0.0012
		5	0.0249	0.0024
		20	0.0250	0.0025
64 (b.p.)	1:1	2	0.0202	0.0009
		5	0.0239	0.0020
		20	0.0240	0.0020

ence of time on the solubility of silver selenide and telluride is illustrated by Table I.

After boiling for 5 minutes, the ammonia content had decreased to 8.4% by weight with the concentrated solution, and 3% by weight with the 1:1 solution. Determinations of silver, selenium, and tellurium were made on the filtrate of the filtered samples. Silver was determined gravimetrically as chloride; selenium and tellurium were determined gravimetrically in the elemental state after precipitation by means of sulfur dioxide in accordance with the following procedures.

Selenium was precipitated, after removal of silver as chloride, by addition at 20° C. of 80% by volume of concentrated hydrochloric acid saturated with sulfur dioxide, stirring, allowing the red selenium to settle overnight, and filtering on a Gooch crucible.

The precipitate was washed thoroughly with cold concentrated hydrochloric acid and in succession with cold water, alcohol, and ether. The selenium was dried at 40° C. for 3 hours and at 120° C. for 2 hours.

Tellurium was precipitated, after the removal of silver as chloride, by heating the solution containing 25% by volume hydrochloric acid to boiling, adding 15 ml. of a saturated solution of sulfur dioxide, 10 ml. of a 15% solution of hydrazine hydrochloride, and another 25 ml. of the saturated sulfur dioxide solution. Boiling was continued for 5 minutes; the tellurium was allowed to settle 15 minutes and was then filtered on a tared Gooch crucible. The precipitate was washed quickly with hot water and finally with alcohol, dried at 105° C., and weighed.

The following results indicate the degree of precision experienced in this work (in grams per 100 ml. of solvent):

AgCl	Se	Te
0.0506	0.0140
0.0509	0.0141
0.0070	0.0031
0.0066	0.0029

In all cases the combination of silver, selenium, and tellurium determinations gave the theoretical composition of silver selenide and silver telluride within the limits of experimental error. From these results the solubilities of silver selenide and telluride (Table I) were determined.

It is obvious that silver selenide is only sparingly soluble in ammonium hydroxide solutions, and increase of ammonia concentration or of temperature does not increase the solubility of this compound. Silver telluride is virtually insoluble in either cold or hot ammonia solutions, although the percentage increase of solubility with temperature is appreciable.

Production of Benzyl Benzoate

LABORATORY AND PILOT PLANT STUDIES

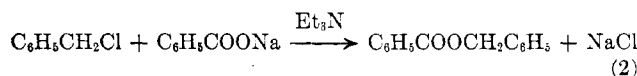
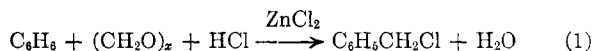
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INVESTIGATIONS have been in progress for the preparation of benzyl benzoate, a miticide, by means other than its standard preparation from compounds derived from toluene. The most promising process has been the conversion of benzene to benzyl chloride by chloromethylation (Equation 1) and the dry esterification of the latter with sodium benzoate in the presence of triethylamine (Equation 2).



The first step in this process has been reported (5). Rueggeberg, Ginsburg, and Frantz (3) have reported some laboratory results on the dry esterification step. It is the purpose of this report to

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give additional laboratory data and also pilot plant data for this reaction.

Considerable work has been done on the preparation of benzyl esters under anhydrous conditions. The methods have been reviewed by Gomberg and Buchler (2). For the most part long periods of heating at high temperatures were required, and in many cases low yields of the esters were obtained. Preparation of the benzyl esters in the presence of organic bases is first described in a patent assigned to the Badische Anilin- & Soda-Fabrik (1), and Volwiler and Vliet (4) have prepared certain benzyl esters using diethylamine as a catalyst.

LABORATORY STUDIES

In the laboratory, the procedure for the dry esterification of benzyl chloride was modified to allow a study of the following: (a) reaction using either an excess of benzyl chloride or sodium benzoate; (b) reaction using slightly acid (benzoic acid) or alkaline (sodium hydroxide) sodium benzoate; (c) reaction in the presence of iron filings; (d) reaction in the presence of dried and undried benzene; and (e) reaction using a chloromethylation reaction mixture as the source of benzyl chloride.

The general procedure is illustrated by the following typical run:

In a 500-ml., round-bottomed, three-necked flask equipped with a water-cooled condenser, mercury-sealed stirrer, and thermometer were placed 79.2 grams (0.55 mole) of dry sodium benzoate (slightly alkaline), 63.3 grams (0.50 mole) of benzyl chloride, and 0.8 gram of triethylamine. With vigorous stirring the mixture was warmed on the steam bath, which allowed the temperature to rise to the maximum (about 110° C.). When the temperature rose to about 95°, the reaction took place. The mixture became more fluid, and finer particles of sodium chloride appeared. Eventually the mixture became a gel. Stirring and heating were continued for a total of 60 minutes.

The reaction mixture was washed with 500 ml. of water, and the benzyl benzoate layer was allowed to settle and was separated. The water layer was then extracted with a small volume of benzene or carbon tetrachloride to collect small amounts of benzyl benzoate adhering to the walls of the vessel. The benzene (or carbon tetrachloride) extraction also facilitated breaking the interfacial emulsion which was sometimes troublesome. An alternative procedure to benzene extraction was the addition of the interfacial material to the still. Usually 2 to 5% of the reaction product remained in the water layer.

The combined product layer and benzene wash were distilled without drying in a four-plate fractionating column (1.8 × 68 cm. packed with single-turn 1/4-inch glass helices) to remove the benzene (and excess benzyl chloride when this was used). The benzyl benzoate distilled at 187° C. at 20 mm. and had a refractive index n_D^{20} of 1.5687. Acidification of the original water wash yielded the excess benzoic acid.

Other experimental data and results are summarized in Table I.

DISCUSSION OF RESULTS. The reaction of dry sodium benzoate with excess benzyl chloride in the presence of triethylamine gives a 94% yield of distilled benzyl benzoate [boiling point 187° C. at 20 mm., melting point 20° C., n_D^{20} 1.5687, saponification number 213, negative test for chlorine (Table I, run 1)]. When the catalyst is omitted, the reaction does not take place (run 2).

Using an excess of sodium benzoate, the reaction product, after washing with water and drying (no distillation), is practically pure benzyl benzoate (b.p. 187° C. at 20 mm., m.p. 19° C., n_D^{20} 1.5686) having a slight straw color (run 3).

The sodium benzoate in the esterification reaction must be alkaline. Reactions with the use of sodium benzoate having slight amounts of benzoic acid are troublesome. The catalyst is

Anticipated large scale production of benzyl benzoate coupled with the shortage of toluene derivatives for this purpose during the war led to the investigation of the dry esterification of sodium benzoate and benzyl chloride, the latter from the chloromethylation of benzene (5). The reaction of benzyl chloride and sodium benzoate is carried out at a moderate temperature in the presence of triethylamine. Results show that benzyl benzoate can be prepared in yields of 90% or better in a relatively short time.

correspondingly neutralized. Under these conditions the reaction requires a higher temperature or more catalyst. Furthermore, free benzoic acid distills during the fractionation of the product and causes considerable difficulties (runs 6, 7, 8, and 9). This could be avoided by an alkaline water wash.

In a single run (run 10), the esterification reaction was carried out in the presence of iron filings. This was done to determine if condensation would occur before esterification in case metal equipment were used. The reaction proceeds equally well. However, the results do not fully support the use of metal equipment, since here only a short time is needed to bring the reactants to reaction temperature, whereas, in large scale production the longer heating period may give some condensation.

Benzene can be used as a partial solvent to facilitate agitation, temperature control, and subsequent washing of the product. The proportions of benzene and benzyl chloride are important, since too large a volume of the former will prevent the temperature rise necessary for the reaction (runs 11 to 15).

The use of dry and wet benzene is illustrated by runs 12, 14, and 15. Although the yield is not affected much, benzoic acid accompanies the use of wet benzene in clogging the receiver upon distillation. The benzoic acid could be removed by an alkaline wash of the reaction mixture prior to distillation.

The reaction mixture from the chloromethylation of benzene (5) can be used directly for the preparation of benzyl benzoate without isolating the benzyl chloride. Thus, the troublesome

TABLE I. STUDIES ON DRY ESTERIFICATION OF BENZYL CHLORIDE

Run No.	ϕCOONa		$\phi\text{CH}_2\text{Cl}$		Et_3N , Grams	C_6H_6 , Ml.	Max. Temp., ° C.	Total Run, Min.	Variable Studied	Yield of Benzyl Benzoate, %	Recovery of Reactants, %	
	Grams	Moles	Grams	Moles							ϕCOOH^a	$\phi\text{CH}_2\text{Cl}$
WITHOUT BENZENE												
1	80	0.56	96	0.76	0.8	...	110	30	Test run	94
2	80	0.56	96	0.76	None	...	143 ^b	60	No catalyst	0	100	89
3	79	0.55	63	0.50	0.8	...	112	60	Excess ϕCOONa	94	10	None
4	144	1.00	173	1.36	1.4	...	105	30	Large run	85	None	22
5	144	1.00	173	1.36	1.4	...	103	60	As in 4 with longer stirring	93	None	21
6	79	0.55	63	0.50	0.8	...	92	60	Presence of small amt. ϕCOOH	0	100	98
7	79	0.55	63	0.50	0.8	...	165 ^b	90	As in 6 using higher temp.	64	20	22
8	79	0.55	63	0.50	2.3	...	107	60	As in 6 using more catalyst	88	10	None
9	79	0.55	63	0.50	0.8	...	114	60	Using ϕCOONa slightly alkaline	94	6	0.5
10	79	0.55	63	0.50	0.8	...	128	60	In the presence of 5 g. Fe filings	92	11	0.5
WITH BENZENE												
11	79	0.55	63	0.50	2.3	100	93	90	As in 6 using benzene and more catalyst	84	16	None
12	79	0.55	63	0.50	0.8	100	95	60	Effect of solvent benzene not dried	67	29 ^c	36
13	79	0.55	63	0.50	0.8	100	25	240	Effect of low temp. and solvent	0	100	100
14	79	0.55	63	0.50	0.8	50	106	60	Effect of less benzene (not dried)	91	10 ^c	None
15	79	0.55	63	0.50	0.8	50	105	60	As in 14 using dry benzene	95	7	None
WITH REACTION MIXTURE FROM CHLOROMETHYLATION OF BENZENE												
16	72	0.55	60	0.47	0.7	34	100	45	Crude reaction mixture from chloromethylation	83	Trace ^c	None
17	65	0.45	54	0.43	0.6	40	103	60	Same as 16	99	None	None
18	86	0.60	64	0.50	0.8	45	109	80	Same as 16	86	Trace ^c	Trace
19	86	0.60	64	0.50	0.8	45	100	60	Same as 16	86	Trace	Trace

^a Recovered by the acidification of water wash.

^b Heated with a Glas-Col heating mantle. Other runs were heated on a steam bath.

^c Trace of benzoic acid in column during distillation.

TABLE II. REACTION DATA ON DRY ESTERIFICATION OF SODIUM BENZOATE AND BENZYL CHLORIDE

Run No.	C ₆ H ₅ CH ₂ Cl		C ₆ H ₅ COONa		(C ₂ H ₅) ₃ N		C ₆ H ₆ lb.	Max. Temp., °C.	Total Run, Hr.	Variables Studied	Yield of Benzyl Benzoate	
	Lb.	Mole	Lb.	Mole	Lb.	Mole					Lb.	%
1	57.5	0.455	47	0.326	0.56	0.0056	50	96	5	Excess benzyl chloride	62	90.2
2	86	0.68	108	0.75	0.56	0.0056	0	124	5	Excess sodium benzoate	138	95.8
3	95 ^a	0.75	108	0.75	1	0.01	0	130	5	Mol. equiv. of reactants	154	96.8
4	86 ^a	0.68	108	0.75	1	0.01	0	126	2	Excess sodium benzoate and reaction time	134	93.2
5	86	0.68	108	0.75	1	0.01	0	127	2	Excess sodium benzoate and reaction time	134	93.2

^a Prepared by chloromethylation of benzene.

TABLE III. EFFECT OF REACTION TIME ON YIELD OF BENZYL BENZOATE

Run No.	Reaction Time, Hr.	Ester in Mix, %	Theory of Ester in Mix, %	Yield by Anal., %
1	1	43.4	44.6	97.4
	2	45.6		102
	3	44.5		99.7
	4	46.6		104
	5	47.2		106
2	1	73.6	74.2	99.2
	2	73.6		99.2
	3	74.5		100
	4	73.7		99.3
	5	75.8		102
3	1	74.7	78.4	95.3
	2	74.8		95.4
	3	77.2		98.4
	4	78.3		99.9
	5	79.1		101
4	1/4	73.4	74.2	98.9
	1/2	74.2		100
	3/4	74.7		101
	1	74.6		101
	2	75.1		101
5	1/4	73.2	74.2	98.6
	1/2	73.7		99.4
	3/4	74.3		100
	1	74.2		100
	2	74.8		101

washing and distillation procedures for the purification of the benzyl chloride are avoided. However, the subsequent esterification mixture must be distilled to yield the pure ester.

In using the chloromethylation reaction mixtures, the catalyst layer is separated, and the benzene layer is aerated and concentrated to remove hydrogen chloride gas and any water present. It is then ready for the esterification reaction. Yields of 83 to 99% are obtained, based on the sodium benzoate used. The esterification product is distilled and leaves 6 to 14% (by weight) residue (runs 16 to 19).

It is necessary to use dry sodium benzoate in these reactions for the same reasons given for the use of dry benzene.

PILOT PLANT STUDIES

As a result of the laboratory work, a number of the conclusions reached were accepted as a basis for pilot plant work. Those conclusions accepted were as follows: (a) The reaction does not take place at a moderate temperature without a catalyst; (b) the sodium benzoate used in the reaction must be alkaline and dry; and (c) dry benzene can be used as a solvent to facilitate agitation.

Benzyl chloride and triethylamine were charged to a 50-gallon glass-lined reactor equipped with a 45-r.p.m. glass-coated anchor-type agitator, a glass-coated thermometer well, and a glass-lined reflux condenser. To this mix was added about one third of the sodium benzoate to be charged, and the mix was allowed to react by being heated to about 95° C. When the reaction had started, the remaining two thirds of the sodium benzoate was charged. The reaction is mildly exothermic for a short period at the start of the reaction, and a reactor-jacket steam pressure of 1 pound per square inch gage is sufficient to maintain the mix above 95° C.

At the end of the reaction period the mix was cooled and washed twice with water. Emulsions which may form during washing

are readily broken with a small amount of a wetting agent. The washed product layer was then subjected to a vacuum distillation and stripped of volatile matter to a final absolute pressure of 50 mm. of mercury at 130° C. The residue from the stripping operation was the product and was either dropped to storage or filtered through activated carbon to storage.

The reaction data for runs made by the dry esterification of sodium benzoate and benzyl chloride are given in Table II.

In run 1 benzene was used as a solvent to facilitate agitation. This was necessary when all of the sodium benzoate was charged to the reactor before the reaction was started. In the remaining runs this was not necessary when the sodium benzoate was charged as described.

DISCUSSION OF PILOT PLANT RESULTS. The investigation of optimum reaction time was carried out by sampling of the reaction mix at varied time intervals and subsequent laboratory analysis of the samples for their ester content. The analyses thus obtained are given in Table III. In runs 1, 2, and 3 the reaction was virtually completed at the end of 1 hour. In runs 4 and 5 reaction time investigation was made to determine the completeness of the reaction at intervals of less than 1 hour. These results show that the reaction was complete in 30 to 45 minutes.

QUALITY OF BENZYL BENZOATE PRODUCED

The benzyl benzoate produced was submitted to the laboratory for determination of the per cent ester content, specific gravity, refractive index, per cent free acid, and the melting point. Table IV gives the results of such analyses.

TABLE IV. PURITY OF BENZYL BENZOATE PRODUCED

Run No.	Ester, %	Sp. Gr., d ₄ ²⁵	Refractive Index, n _D ²⁰	Free Acid as Benzoic, %	M.P., °C.
1	97.0	1.113	1.5683	0.22	17.6
2	97.3	1.115	1.5693	0.31	17.8
3	98.8	1.114	1.5699	0.05	18.0
4	99.8	1.116	1.5700	0.25	18.0
5	98.4	1.115	1.5696	0.45	17.8

CONCLUSIONS

Benzyl benzoate may be produced by the esterification of benzyl chloride and sodium benzoate in the presence of triethylamine with yields of about 95%. Expenditures for raw materials and handling of materials would be low. Processing time is short, and adaptability to a continuous method may prove advantageous. Washing and stripping operations may be eliminated by filtering the salts from the mix at the end of the reaction period. To improve the color of the product, filtration through activated carbon is noteworthy.

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