IDENTIFICATION OF IMPURITIES IN BENZYL BUTYL PHTHALATE BY GAS-LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY

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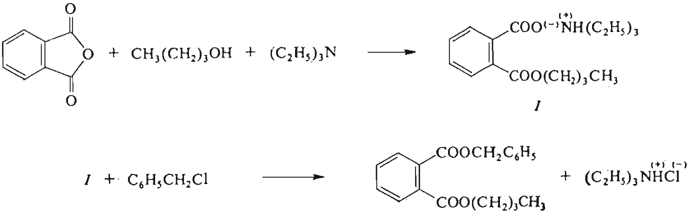
The impurities present in benzyl butyl phthalate of Monsanto, Belgium, and in benzyl butyl phthalate prepared by a modified procedure employing gaseous ammonia instead of triethylamine were identified by GLC-MS. Columns appropriate for the GLC analysis of this plasticizer were selected and their advantages and disadvantages discussed, and the optimum conditions for complete, rapid routine analysis of benzyl butyl phthalate were established. The side reactions proceeding during the preparation of benzyl butyl phthalate are discussed based on the identification of the impurities present.

Benzyl butyl phthalate (BBP) belongs to plasticizers employed for the plastification of PVC, polyvinyl acetate, and acrylic acid polyesters. Despite its importance, however, no studies could be found in the literature dealing in detail with the impurities present in BBP or discussing the potential side reactions occurring during its preparation. Cook and coworkers[1] confined themselves to tentative analysis of BBP, the determination of the contents of di-n-butyl phthalate and dibenzyl phthalate (GLC, column 0·23 m, Embacel wetted with 25% silicone grease, $t_{\mathrm{col}} = 235$°C). Esposito[2] employed for the separation of BBP and other phthalate type plasticizers also GLC (column 2·70 m, Chromosorb W, alkali-washed, wetted with 20% silicone grease, temperature program 120 to 290°C). The same technique was applied by Rapaport and coworkers[3] to the determination of phthalic acid esters with aliphatic alcohols C_4—C_{12} and with some cyclic alcohols (column 1·20, silanized Chromaton NAW, wetted with 5% XE-60).

BBP is being manufactured according to the following routine:[4–8]



The purity of the product obtained is at least 99%.

The aim of this work was to identify the impurities present in BBP prepared by a modified procedure (substitution of the organic base by ammonia)[9] and in the commercial chemical Santicizer 160 of Monsanto, Belgium, and to discuss the side reactions.

EXPERIMENTAL

Preparation of the Standards

The products obtained were analyzed by means of GLC (for the conditions see Table I). Their structure was confirmed by NMR or IR spectroscopy.

Tribenzylamine was prepared[10] and recrystallized from boiling diethyl ether (m.p. 90°C, ref.[10], 91°C), its purity was 99% (m/m). N-Benzyl phthalimide was prepared according to[11];

TABLE I

GLC Conditions of the Standards and Starting Components for the Preparation of Benzyl Butyl Phthalate

Argon flow rate 30—32 ml min^{-1}; numbering of the columns as in Table II.

Compound	Column	t_{col}, °C
Tribenzylamine	4, 7	220
N-Benzyl phthalimide	4, 7	210
Benzyl n-butyl ether	6, 7	180
Benzyl n-amyl ether	6, 7	180
Dibenzyl ether	4, 7	200
n-Butyl benzoate	6, 7	180
N-Butyl phthalimide	4, 7	200
N-Ethyl phthalimide	4, 7	180
Dibenzyl-n-butylamine	4, 7	190
Dibenzylamine	5, 7	200
Di-n-amyl phthalate	4, 7	220
Dibenzyl phthalate	4	240
Benzyl n-amyl phthalate	4, 7	220
Benzyl isoamyl phthalate	4, 7	220
Benzyl n-hexyl phthalate	4, 7	230
Benzyl butyl maleinate	4, 7	200
Triethylamine[a]	8	80
Benzyl chloride[b]	2	220
n-Butanol[c]	8[d]	90

[a] Contained 0·30% m/m ethanol; [b] contained 0·35% m/m $PhCH_2OH$; [c] contained 0·95% m/m di-n-butyl ether, 0·80% m/m isobutanol, 0·25% m/m other alcohols; [d] column 8 — length **1·0 m**, Chromosorb W wetted with 1·6% Carbowax 1500.

the excess benzyl chloride was distilled off, the product was extracted from the distillation residue with ethanol and recrystallized from the same solvent (m.p. 115°C, ref.[11] 115–116°C); purity 99% (m/m). Benzyl n-butyl ether was prepared[12] and purified by rectification (colum 0·20 m filled with Berl saddles, reflux ratio 1); the fraction 219–220°C was collected (ref.[12] 220·4°C) containing 99·1% (m/m) benzyl n-butyl ether. Benzyl n-amyl ether was prepared and purified in the same manner. Product b.p. 238–239°C was obtained (no reference concerning the b.p. is available from the literature) containing 99·0% (m/m) benzyl n-amyl ether. Dibenzyl ether was prepared by the same procedure as benzyl n-butyl ether and purified by vacuum rectification (column 1 m filled with Berl saddles, reflux ratio 5), the product boiling at 183·5°C/372 Pa (ref.[13] 184°C/372 Pa) contained 98·1% (m/m) of the main component. n-Butyl benzoate was obtained by esterification of benzoic acid with n-butanol catalyzed by sulfuric acid. The product boiling at 246·5°C (ref.[14] 247·0°C/0·101 MPa) contained 97·5% (m/m) of the main component. N-Butyl phthalimide was obtained in the same way as N-benzyl phthalimide from 1-butyl iodide and potassium phthalimide. The product after double recrystallization was contaminated with 5% (m/m) phthalimide (m.p. not determined). N-Ethyl phthalimide was prepared analogously as n-butyl phthalimide in the same purity, despite the fact that the starting potassium phthalimide was boiled and washed on a frit with hot anhydrous ethanol to free it from phthalimide. The m.p. of the product was not determined. Dibenzyl-n-butylamine was prepared by reaction of n-butylamine with benzyl chloride. From the alkalized reaction mixture the product was steam distilled. The content of the main component was 97·2% (m/m). Dibenzylamine was obtained as a mixed standard with tribenzylamine from the reaction of benzyl chloride with excess benzylamine. The hydrochloride mixture was alkalized with aqueous solution of sodium hydroxide, the free bases were extracted into diethyl ether, and the ether with the benzylamine was distilled off. The distillation residue containing 76·0% (m/m) dibenzylamine was employed as a mixed standard. Di-n-amyl phthalate was prepared by esterification of phthalic anhydride with n-amyl alcohol. The ester was vacuum distilled, b.p. 169–170°C/66·5 Pa (ref.[15] 170°C/66·5 Pa), the content of the ester in the product was 99·2% (m/m). Dibenzyl phthalate was prepared analogously, freed from volatile impurities, and decoloured with kieselguhr F-502 (Calofrig, Borovany). The content of dibenzyl phthalate in the product was 98·3% (m/m). Benzyl n-amyl phthalate was prepared according to[5] in 97·8% (m/m) purity. Benzyl isoamyl phthalate was prepared in the same manner as benzyl n-amyl phthalate in 98·0% (m/m) purity. Analogously were prepared benzyl n-hexyl phthalate (97·5%) and benzyl n-butyl maleinate (98·1%).

The other substances tested owing to their potential presence in BBP were commercial chemicals of sufficient purity. The content of the impurities in triethylamine, benzyl chloride, and n-butanol was determined by GLC (Table I).

Gas-Liquid Chromatography

A gas chromatograph Fractovap GV (Carlo Erba, Italy) equipped with an FID and a pressure and temperature programmer was used. The optimum working conditions and the phases and supports used are given in Table II.

Gas-Liquid Chromatography–Mass Spectrometry

The analyses were performed on a gas chromatograph Jeol JGC-20K interfaced to a mass spectrometer Jeol JMS 01S-2 (Jeol, Japan). The sample was analyzed on the column 7 (Table II) at the temperature 200°C, after 19 min the temperature was raised to 240°C applying the rate 20°C/min, $p_{\mathrm{He}} = 122$ kPa. The spectra were obtained using the ionizing energy 75 eV, accelerating voltage 10 kV, resolution $R_{10\%} = 700$, scanning rate 10 to 350 amu per 3 s, and chart speed 20 cm s^{-1}.

RESULTS AND DISCUSSION

Gas–Liquid Chromatography

The chromatographic system allowing the analysis of all the components in BBP on two columns built in a single chromatographic apparatus was chosen with regard to the wide span of the boiling points of the conceivable impurities in BBP and to their different polarities. Some columns did not yield the desired results (columns 1 to 3, Table II), as some of the components remained trapped in the system, other (mostly the lower-boiling ones) remained unseparated. The column 2 was only suited to analysis of the components present in the low-boiling distillates from the manufacturing of BBP (max. up to 230°C). The optimum conditions for these analyses were $t_{col} = 220°C$, carrier gas flow rate 30 ml min^{-1}. A good separation was achieved for triethylamine, n-butanol, toluene, benzyl chloride, and benzyl alcohol. Column 4 employed with the temperature and pressure program suited to the separation of medium polar higher-boiling impurities and dibenzyl phthalate (Fig. 1) whose content in BBP is significant from the point of view of the application of BBP as a plasticizer. Columns 5 and 6 were employed for additional identification of all impurities in BBP except dibenzyl phthalate. A shortcoming of the column 5 is the

TABLE II

Columns and Conditions Applied to the GLC Analysis of Benzyl Butyl Phthalate
Temperature rise 25°C min^{-1}, pressure rise discontinuous.

Column No	Stationary phase[a]	Length m	t_{col} °C	p_{Ar} kPa	Ar flow rate ml min^{-1}
1	10% SE-52	2	270	98	40
2	Chromosorb 101	1	220	78	31
3	8% Apiezon L	2	240	117	30
4	5% OV-17	1	200, 230[b]	78, 127[d]	30, 48[d]
5	4% Apiezon L + 1% Carbowax 20M	2	200, 230[c]	98, 127[d]	18, 32[d]
6	4% Apiezon L + 1% Carbowax 20M TPA	2	200, 230[c]	98, 180[e]	19, 33[e]
7	5% Apiezon L + 3% OV-17	2	200, 230[b]	78, 130[d]	18, 33[d]

[a] Chromosorb W served as the support in all cases except Column 2; [b] after 11 min; [c] after 17 min; [d] after 5 min; [e] after 4 min.

lower thermal stability of Carbowax 20M in the optimum experimental conditions, whereas in the column 6 impurities of basic nature were partly retained. Column 7 is the most appropriate for the separation of all the compounds eluted before BBP. It meets the requirement of thermal stability from 200 to 230°C. Like columns 5 and 6, it can be used in conjunction with column 4 incorporated in the same chromatograph. Almost simultaneous elution of dibenzyl phthalate from column 4 and of BBP from column 7 and accomplishing of the analysis in 40 min can be achieved by applying the same temperature and pressure program on the two columns (Figs 1 and 3). Another advantage is the possibility to compare the content of the impurities eluted in the region of elution of di-n-butyl phthalate based on the results obtained from two columns. A drawback of this connexion is the fact that dibenzyl phthalate remains trapped on column 7. This chromatographic system is the most suitable for routine analyses of technical BBP.

Gas–Liquid Chromatography–Mass Spectrometry

This technique served to confirm the structure of the following substances present in BBP in quantities exceeding 0·02% (m/m): N-Ethyl phthalimide – the nominal molecular weight 175 was determined and an odd number of nitrogen atoms was found. The spectrum agreed with that of N-ethyl phthalimide[16]. N-Butyl phthalimide – the nominal molecular weight 230 and an odd number of nitrogen atoms were established, the spectrum displayed fragments typical of N-alkyl phthalimides. The most intense ion of the spectrum, $m/e = 160$ (*i.e.* M – 43) corresponds to the cleavage of the C—C bond β with respect to the nitrogen and detachment of a propyl group. n-Butyl ethyl phthalate – the nominal molecular weight 250 was found, the spectrum exhibited ions characteristic of dialkyl phthalates. The diagnostic fragment M – R-2 H makes M – 55, and along with the ion M – 73 and $m/e = 56$ gives evidence that one of the substituents is a butyl group and the other substituent, with regard to the molecular weight, must be an ethyl group, as indicated also by the ion M – 45. Benzyl benzoate – the molecular weight found was 212, the spectrum showed intense peaks of the tropylium ion, $m/e = 91$, characteristic of the Ph—CH_2 grouping, and $m/e = 105$ typical for the benzoyl group. The spectrum is identical with that of authentic benzyl benzoate.

Side Reactions Occurring During the Preparation of BBP

A partial or complete replacement of the organic base by ammonia (or presence of ammonia in triethylamine) brings about a number of side reactions leading to the substances identified and described in Figs 1 and 2 and in Table III. Their presence implies that apart from the main reaction, several other reaction types occur as follows: *1*) reesterification leading to new phthalic acid esters, *2*) oxidation of the benzyl alcohol present in benzyl chloride or formed on its hydrolysis as far as benzoic acid and esterification of the latter to benzyl benzoate, *3*) formation of imides substituted at the nitrogen by an alkylene or benzyl group, *4*) nucleophilic substitution

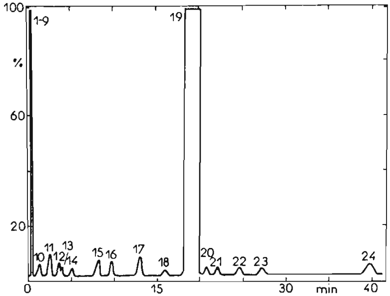


FIG. 1

Analysis of a BBP Sample Prepared in the Presence of Ammonia and Triethylamine

Conditions: Column 1 m, Chromosorb W + 5% OV-17, $t_{\text{col}} = 200°\text{C}$, after 11 min raised to 230°C, $p_{\text{Ar}} = 78$ kPa, after 5 min 127 kPa. The peak numbering conforms to the data of Table III.

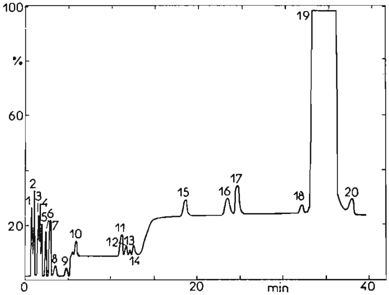


FIG. 2

Analysis of a BBP Sample Prepared in the Presence of Ammonia and Triethylamine

Conditions: Column 2 m, Chromosorb W + 5% Apiezon L + 3% OV-17, $t_{\text{col}} = 200°\text{C}$, after 11 min raised to 230°C, $p_{\text{Ar}} = 78$ kPa, after 5 min 127 kPa. The peak numbering conforms to the data of Table III.

involving benzyl chloride and a nucleophilic agent (ammonia, triethylamine, n-butanol, water).

The presence of other benzyl alkyl phthalates is accounted for by the other alcohols present in the starting n-butanol. The BBP contains also substances that do not take part in the reaction, which, however, are introduced into the system along with the starting reacting components (diphenylmethane in benzyl chloride, ethanol in triethylamine, di-n-butyl ether in n-butanol).

TABLE III

Contents of the Impurities in Benzyl Butyl Phthalate

No[a]	Substance	Content in BBP[b] % (m/m)	Content in Santicizer 160 % (m/m)	Response factor
1	n-Butanol	0·01	0·23	0·847
2	Di-n-butyl ether	0·02	0·17	0·963
3	Benzaldehyde	0·10	0·02	0·887
4	Benzyl chloride	0·11	0·00	0·668
5	Benzyl alcohol	0·10	0·00	0·871
6	Benzyl n-butyl ether	0·17	0·00	0·970
7	Benzyl n-amyl ether	addition	addition	1·000
8	n-Butyl benzoate	0·01	0·00	0·976
9	Diphenylmethane	0·01	0·00	1·236
10	N-Ethyl phthalimide	0·04	0·00	0·872
11	N-Butyl phthalimide	0·50	0·00	0·910
12	N-Butyl ethyl phthalate	0·20	0·15	1·232
13	Benzyl benzoate	0·10	0·09	1·862
14	Di-n-butyl phthalate	0·13	0·09	0·965
15	Di-n-amyl phthalate	addition	addition	1·000
16	N-Benzyl phthalimide	0·95	0·00	0·989
17	Tribenzylamine	1·10	0·00	0·716
18	Benzyl isobutyl phthalate	0·10	0·06	0·977
19	Benzyl n-butyl phthalate	96·28	98·87	not detd.
20	Benzyl isoamyl phthalate	0·12	0·00	0·990
21	Benzyl n-amyl phthalate	0·05	0·00	0·990
22	Benzyl n-hexyl phthalate	0·10	0·00	1·023
23	Benzyl alkyl phthalate	0·10	0·04	not detd.
24	Dibenzyl phthalate	0·80	0·28	0·660

[a] The sequence conforms to that in Figs 1 and 2. The content of the substances 1—9 was determined to an addition of benzyl n-amyl ether, that of the other impurities to an addition of di-n-amyl phthalate; [b] a representative sample from the chemical prepared by using ammonia and triethylamine.

On the other hand, etherification reactions do not occur (dibenzyl ether is absent and di-n-butyl ether is present only in low quantities). This can be explained in terms of the higher esterification rates, which bring about the formation of BBP and its reesterification to dibenzyl phthalate, and oxidation of benzyl alcohol. Benzyl butyl maleinate is absent from the product, although the starting phthalic anhydride contained 0·02% maleic anhydride (determined according to[17]). The presence of other maleinic acid esters therefore need not be dealt with. The absence of dibenzyl-n-butylamine indicates that either at the moment of the addition of benzyl chloride to the reaction mixture for the preparation all the n-butylamine is consumed in the reaction with phthalic anhydride, or it is not formed at all. N-Butylphthalimide would then form on the cyclization of n-butyl phthalate ammonium salt. The origination of N-ethylphthalimide and n-butyl ethyl phthalate can be ascribed to the presence of ethanol in triethylamine.

From the absence of phthalimide from BBP it follows that during the saturation of the phthalic anhydride solution with gaseous ammonia[9] the reaction leading to the n-butyl phthalate ammonium salt is markedly preferred. On the other hand, ammonium phthalate, which would afford phthalimide, is not found. The content of tribenzylamine and N-benzylphthalimide in BBP can be depressed down to 0·25 to 0·30% by an appropriate adjustment of the reaction conditions[9].

The application of triethylamine to the synthesis of BBP is associated with the formation of triethylbenzylammonium chloride, which for a great part separates in the crystal form[9]. It was identified by IR spectroscopy, by comparing with the spectrum of authentic triethylbenzylammonium chloride.

From a comparison of the results of analysis of Santicizer 160 and a sample of BBP prepared by the ammoniacal procedure it follows that decisive for the quality of the preparation are the composition of triethylamine (particularly the content of ethanol and ammonia), composition of the other starting materials, and the final treatment of the product by which the low-boiling impurities are removed.

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