# Phenyl Isocyanate Derivatives of Certain Alkylated Phenols Melting Points and X-Ray Powder Diffraction Data

J. B. MCKINLEY, J. E. NICKELS, AND S. S. SIDHU Mellon Institute and University of Pittsburgh, Pittsburgh, Pa.

As positive means for identifying alkylated phenols, the authors have prepared phenyl isocyanate derivatives of a large number of phenols, and in this paper present tables of melting points and x-ray powder diffraction data.

P

A SA result of recent developments, considerable quantities of alkylated phenols are finding use in the preparation of synthetic plastics, rubber, germicides, fungicides, and related substances. Because of this increasing interest in alkylated phenols, the authors have undertaken to develop an easy and positive means for their identification. One widely used method for such purposes is the determination of the characteristic melting point of the aryl N-phenylcarbamate formed by the reaction of a phenol with phenyl isocyanate. As this procedure has been shown to be satisfactory, it was decided to prepare these derivatives of a large number of phenols which were available, and then to ascertain their melting points and also to obtain their x-ray powder diffrac-

tion data. Either the melting point or the x-ray powder diffraction pattern of the phenyl isocyanate derivative is usually sufficient for identification of the parent phenol, but a consideration of both determinations gives results which are unequivocal.

The melting points of a number of such phenolic derivatives have been listed by Morgan and Pettet (14) and by Steinkopf and Höpner (16); a few relevant supplemental data are given by other investigators. No previous publications have been found in which x-ray powder diffraction data are presented for these derivatives, although the value of such information for the identification of compounds possessing crystalline structure has been pointed out by Hanawalt and co-workers (7, 8), Davey (3), and others.

#### PROCEDURES

The method of preparation of the aryl N-phenylcarbamates was based upon the procedures given by Steinkopf and Höpner (16) and Weehuizen (21). A small quantity of the phenolic substance (ca. 1 gram) was mixed with a slight molar excess of phenyl iso-cyanate in a 20-cm. (8-inch) test tube fitted with a reflux condenser and to this reaction mixture were added 8 to 10 ml, of a petroleum distillate (b.p. 170-200° C.) previously fractionated from kerosene. The reaction was completed by gently refluxing for 1 to 4 hours (usually 4). After product was cooled, the crystals which formed were recovered by filtration and purified by recrystallization from petroleum ether, benzene, or a mixture of these solvents. The purified derivative was dried under room conditions and its melting point was determined using a cali-brated Anschütz thermometer.

The x-ray diffraction patterns of the aryl Nphenylcarbamates were secured by the usual Debye-Scherrer-Hull method. A small portion of the material was finely powdered, packed into a short length of 19-gage stainless steel hypodermic needle tubing of 0.7-mm. internal diameter, compressed with a plunger, and finally extruded as a cylinder of the same diameter. The steel tubing was mounted in a camera of 57.3-mm. effective diameter in such a manner that only the extruded part of the specimen appeared in the x-ray beam. The photograms were made with filtered  $CuK_{\alpha}$  radiation having an effective wave length of 1.539 A. A camera of 171.9-mm. effective diameter was employed to obtain better resolution of the diffraction patterns of some of the samples.

The diffraction patterns obtained were, in general, sharply defined and the measurement of them could be duplicated satisfactorily. In a few instances, however, two or more diffraction lines representing different interplanar spacings merged, making exact interpretation of a specific portion of a pattern uncertain. When this was the case, the merged lines were considered as a group and measured as a single line. The interplanar spacing calculated from such a measurement represents the shortest inter-

#### Table I. Melting Points

X-Ray Diffrac- tion Pattern No.	Empirical formula	Phenols Used Name	M.P. of N- Observed by authors	Phenylcarbamates, ° C. Literature values and references
$\frac{1}{2}$	CsHsClO CsHsNOs	4-Chlorophenol 2-Nitrophenol (m.p.	148.5	
3 4	CaHaNOa CaHaO	4-Nitrophenol Phenol	$\substack{156\\126.5}$	126 (6, 14), 125.5 (13),
5 6	CeHeS C7HeO	Thiophenol 2-Methylphenol	$\begin{array}{c} 128.5\\ 142.5\end{array}$	125 (16) 145 (18, 17), 122 (10) 145 (18, 17), 144.5 (16), 144 (14), 143
7	C7H8O	3-Methylphenol	124.5	$(\delta), 141 (20)$ 125-6 (17), 125 ( $\delta, 14$ ), 124.5 (16), 121-2
8	C7HaO	4-Methylphenol	113	(50) 115 (5, 14), 114 (18, 18, 17), 112–13 (80)
9 10	C7H0S C8H10O	4-Methylthiophenol 2-Ethylphenol	$\substack{132\\143.5}$	141 (16, 19), 140-1 (2),
11 12 13 14	CaH100 CaH100 CaH100 CaH100 CaH100	3-Ethylphenol 4-Ethylphenol 2,3-Dimethylphenol 2,4-Dimethylphenol	1376 120.5 173.5 103¢	138.8 (16), 138 (11) 120 (11, 16, 19) 176 (16) 112 (14, 16), 111.8-
15	CsH18O	2,5-Dimethylphenol	166	122.2 (4), 102 (6, 17) 162 (5, 14, 16), 160-1
16 17 18	CaH10O CaH10O CoH12O	3,4-Dimethylphenol 3,5-Dimethylphenol 2,4,6-Trimethylphenol	$119.3 \\ 149.5 \\ 143$	$\begin{array}{c} 120 \\ 14, 16) \\ 151 \\ (5, 16), 148 \\ 142 \\ (16), 141-2 \\ (9), \\ 140-2 \\ (1) \end{array}$
19	$C_{10}H_{10}ClO$	2-tert-Butyl-4-chloro-	133	
20 21	$C_{10}H_{14}O$ $C_{11}H_{16}O$	4-tert-Butylphenol 4-Methyl-2-(8-methyl- allyl)phenol	$\substack{148.5\\98.5}$	· · · · · · · · ·
22 23	C11H16O C11H16O	4-tert-Amylphenol 4(or 6)-tert-Butyl-2- methylphenol (b.p. 135% C at 20 mm)	108 139.5	
24	$C_{11}H_{16}O$	6(or 4)-tert-Butyl-2- methylphenol (b.p.	189	
25	C11H16O	123° C. at 20 mm.) 4(or 6)-tert-Butyl-3- methylphenol (b.p. 129° C at 20 mm)	133	
26	$C_{11}H_{16}O$	2-tert-Butyl-4-methyl-	155	* ,
27 28	C12H10O C12H14O3	4-Phenylphenol 2,6-Diacetyl-3,5-di- methylphenol (m.p. 109° C.)	167.5 a	

These phenols did not form phenyl isocyanate derivatives.
 This value was had only after thorough drying of the sample. Without drying, value of 124° C, was obtained consistently.
 This value was found consistently even after several recrystallisations and drying.

planar spacing of the group considered and is followed by the letter D in Table II.

Certain flaky organic crystals tend to pack anisotropically, which results in preferred orientation of the crystallites in the extruded specimen when prepared in the manner employed in this work. Since it is necessary that the powdered specimen employed for a Debye-Scherrer-Hull diffraction photogram contain crystallites randomly oriented, diffraction data were secured for a number of the compounds studied, using a rotating powdered sample loosely packed in a thin-walled nylon tube in order to determine whether anisotropic packing of the extruded specimens occurred. Patterns obtained with loosely packed specimens checked those secured with extruded specimens, and inasmuch as all the compounds studied were similiar, these data were taken to indicate that there was no preferred orientation of crystallites in the extruded specimens examined.

#### DISCUSSION

The phenols studied were mainly of the alkylated type, where the alkyl groups were methyl, ethyl, isopropyl, *tert*-butyl, and *tert*-amyl, although a few contained other substituents. In Table I is set forth a complete list of these phenols along with the melting points of their phenyl isocyanate derivatives. In the first column of this table are also listed the diffraction pattern numbers for cross reference to Table II, which contains the x-ray diffraction data of the phenyl isocyanate derivatives.

In certain cases no reaction between the phenol and phenyl isocyanate occurred even after as much as 15 hours of refluxing. In

Table I. Melting Points (Cont'd)

X-Ray Diffrac-		N	M.F -Phenvicarb	. of amates. ° C.
tion		Phenols Used	Observed	Literature
No.	formula	Name	authors	references
29	C12H16O	2-Cyclohexylphenol	111.5	
30	C12H10	4-Cyclohexylphenol	145.5	
31	CiaHisO	2-tert-Amyl-4-methyl-	124	•••••
32	C12H18O	4(or 6)-tert-Butyl-3- ethylphenol (b.p.	156	•••••
33	$C_{12}H_{18}O$	2-tert-Butyl-4-ethyl- phenol	134	•••••
34	C12H18O	4(or 6)-tert-Butyl-2,3- dimethylphenol (b.p.	216	•••••
35	$C_{12}H_{18}O$	6-tert-Butyl-2,4-di- methylphenol	173	•••••
36	$C_{12}H_{18}O$	4-tert-Butyl-2,5-di-	144	• • • • • • • • •
37	C12H12O	4-tert-Butyl-2.6-di-	160	
	~ ~ ~	methylphenol		
38	C12H18O	6-tert-Butyl-3,4-di-	142	• • • • • • • •
39	C12H18O	2,6-Diethyl-3,5-di-	226	• • • • • • • •
40	CuHmO	methylphenol 3.5-Dijsopropyl-2-meth-	198 5	
		ylphenol	100.0	
41	C12H20O	3,5-Diisopropyl-4-meth-	256	•••••
42	C14H22ClO	2,6-Di-tert-butyl-4- chlorophenol (m.p.	a	•••••
43	$C_{15}H_{24}O$	4,6-Di-tert-butyl-2-meth	- 163.5	
44	ClsHMO	ylphenol 4,6-Di- <i>tert</i> -butyl-3-meth ylphenol	- 171.5	
45	C18H24O	2,6-Di-tert-butyl-4-meth ylphenol (m.p.	- a	
46	$C_{16}H_{24}O$	2-tert-Butyl-4-cyclo- hexylphenol	170	•••••
47	$C_{16}H_{26}O$	4,6-Di-tert-butyl-3-	182.5	• • • • • • • • • • • • • • • • • • • •
48	C16H26O	ethylphenol 2,6-Di-tert-butyl-4- ethylphenol (m.p.	a	•••••
49	C18H26O	4,6-Di-tert-butyl-2,3-	216	• • • • • • • • • •
50	C18H30O	2,4,6-Tri-tert-butyl-	a	
51	C20H82O	phenol (m.p. 131° C.) 2,6-Di-tert-butyl-4-cy- clohexylphenol (m.p.	a	•••••
4 These		110,0° (,)		





<sup>a</sup> d = interplanar spacing in Ångstroms; I/I<sub>1</sub> = estimated relative intensity; S = strong; M = medium; W = weak; V = very. Three strongest lines indicated in decreasing order of intensity by (1), (2), and (3). For explanation of Dese text.
 <sup>b</sup> Data obtained using a camera of 171.9-mm. effective diameter.

						Table II	. Po	wder Dif	fraction D	ataª (C	ont'd)						
d $I/I_1$ d $I/I_1$ 10. 2-Ethylphenyl 11. 3-Ethylphenyl N-phenylcarbamate N-phenylcarbamate		I/I1 nenyi mate	d 12. 4- N-pher	Ethylpl lylcarb	I/I1 henyi amate	I/I1 thyl-	d 14. 2,	4-Dime henyl	I/I1 thyl-	d I/Ii 15 <sup>b</sup> . 2,5-Dimethyl- phenyl N-phenylcar-							
7.9 5.3 4.71 4.22 4.07 3.67 2.98 2.77 2.259 2.41 3.20D 2.98 2.77 2.28 2.13 1.98 1.98 1.98 1.51 1.51 1.44 1.37 1.25 1.17	(2) (1) (3)	SMS SMS VS SS SWMMWWWWW VWW VVVVVVVVVVVV	$\begin{array}{c} 1 & -9 \\ -6 & -2 \\ -5 & -3 \\ -4 & -63 \\ -4 & -18 \\ -3 & -62 \\ -5 & -3 \\ -4 & -3 \\ -4 & -3 \\ -5 \\ -4 & -2 \\ -5 \\ -4 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5 \\ -5$	(2) (3) (1)	S MSSSVS SS MM S W W W W W W W W W W W W W W	7.3 6.5 5.5 4.732 4.32 4.32 4.32 2.50 2.43 2.55 2.45 2.25 2.25 2.05 1.88 1.79 1.65 1.47	(2) (1) (3)	M W 8 V 8 M W W W W W W W V V V V V	N-phe: 7.8 6.2 5.4 4.24 3.68 3.21D 3.68 3.21D 2.75 2.58 2.40 2.22 2.12 2.68 2.40 2.22 2.12 1.95 1.78 1.70	(3) (2) (1)	amate M W S VS VS S S W W W W W VW VW VW VW VW VW	N-phe: 5.6 5.1 4.52 4.05 3.31 3.02 2.76 2.57 2.43 2.28 2.16 2.04 1.96 1.86 1.66	(1) (3) (2)	amate M M VS W W W VW VW VW VW VW VW VW V	$\begin{array}{c} 7.7\\ 7.2\\ 6.6\\ 5.0\\ 4.33\\ 4.05\\ 3.80\\ 3.60\\ 3.50\\ 3.44\\ 3.25\\ 3.34\\ 3.25\\ 3.34\\ 3.25\\ 3.34\\ 2.99\\ 2.93 \end{array}$	(3) (1)	SWMWWSS SSWWMMMWMW
16. 3,4 pl	-Dimet henyl	hyl-	17. 3,5 phenyl	-Dime N-phen	thyl- aylcar-	18. 	2,4,6-1 hylphe	Cri- nyl	19. 2- chle	-tert-Bu orophen	tyl-4- lyl	4-tert-	20. Butylph	nenyl	21. 4 methy	-Methy lallyl)pl	l-2(β- henyl
N-phen 8.2 6.7 5.5 4.83 4.30 3.70 3.73 2.71 2.53 2.00 1.82 1.66 1.58 1.22	(3) (2) (1)	mate M M S S VS S M W W W W W W W V V W V V W V V W	7.7 5.7 4.76 4.76 4.76 3.70 3.38 3.20 2.55 2.40 2.55 1.89D 1.72 1.63 1.43 1.08	amate (3) (2) (1)	S S S VS M M W W M W W W W V W V V W	N-phe 8.1 7.1 6.3 5.8 4.83 4.03 3.59 2.91D 2.74 2.68 2.59 2.37 2.23 2.23 2.23 2.11 1.83 1.76	(2) (1) (3)	amate S M S S S S S S S M W W W W W W W W W W	N-phe 8.55 5.5 4.83 3.65 3.02 2.68 2.26 2.289 2.268 2.268 2.268 2.268 2.268 2.268 2.268 2.268 2.268 1.92 1.81 1.52	(3) (2) (1)	amate S VS VS VS VS VS VS VW M VW VW VW VW VW VW VW	N-phe 7.8 6.2 4.56 3.98 3.68 3.04 2.88 2.71 2.34 2.31 1.98 1.87 1.55	(1) (2) (3)	amate M W VS S W S M W W W W W W W W W W W W V W	N-914 6.4 4.28 3.84 4.28 3.34 3.18 2.96 2.67 2.51 2.23 2.00D 1.92 1.81 1.66 1.59	(1) (2) (3)	S S S W W W W W W W W W W W W W W W
22. 4 phenyl	-tert-A1 N-phen	nyl- ylcar-	23, 4(or 2-m	r 6)- <i>tert</i> ethylph	-Butyl- enyl	24. 6(or 2-me	4)-tert thylph	-Butyl- enyl	25 <sup>b</sup> . 4( tyl-3-r	(or 6)- <i>te</i> nethylp	ert-Bu- henyl	26. 2 me	-tert-Bu thylphe:	ityl-4- nyl	27. 4- N-ph	Phenyl; enylcari	henyl amate
b 8.1 6.5 4.59D 3.379D 3.35 2.83 2.83 2.47 2.31 2.19 1.99 1.86 1.74 1.65	(2) (1) (3)	W S VS M M M M W W W VW VW VW VW VW	N-ph 6.6 4.78D 4.28 3.94 3.51 2.86 2.86 2.39 2.29 1.82 1.62	(1) (2) (3)	bamate M VS M S S M W W W W W W W W W W	N-phe 7.7 6.4 6.2 5.6 4.86 3.94D 3.40 3.14 2.82 2.82 2.82 2.07 1.96 1.77 1.61	nylcāri (1) (2) (3)	pamate VW VS VW VS VS S M M M M M W W W W VW VW VW	N-phe 12.0 8.1 7.3 5.9 5.2 4.82 4.19 3.71 3.54 3.21 2.89	(3) (1) (2)	ann àte S M W W V V V V S S M W W W W W W W	N-phe 8.6 7.5 6.4 4.81 4.28D 3.63 3.27 2.89 2.68 2.23 2.11 1.80 1.63 1.53 1.43 1.36	(3) (1) (2)	94mate M W VS S S W M M W VW VW VW VW VW VW VW VW VW VW VW	8 4 6.9 5.8 5.0 4.38 4.18 3.98 3.57 3.14 2.33 2.64 2.33 2.64 2.33 1.84 1.63	(1) (2) (3)	MMMS SSSSMMW₩₩ VW
28. 2,6- dime	-Diacety thylphe	yl-3,5- enol	29. 2 phenyl	2-Cyclol N-phe	hexyl- enylcar-	30. 4 phenyl	-Cyclo N-phe	hexyl- nylcar-	31. 2 me	2-tert-An thylphe	myl-4- myl	32. Butyl-	4(or 6) 3-ethyl	-tert- phenyl	33. e N-ph	2- <i>tert</i> -Bi	utyl- <b>4-</b> nyl bamate
6.7D 5.7D 4.78 4.28 3.39 3.28 3.39 3.28 3.12 2.87 2.587 2.41 2.26 2.15 1.89 1.84 1.71 4.71	(3) (2) (1) - interj	S M M VS VS W M M M M W W W W W W W W W W W W W W	6.6 6.1 4.94 4.26D 3.55 3.26 3.10 2.92 2.61 2.47 2.31 2.13 2.03 1.84 1.62 1.62 pacing in . M - medi	(2) (1) (3)	- M M S VS M W W VW VW VW VW VW VW VW VW	7.8 6.7 3.98 3.67 3.207 2.70 2.53 2.41 2.12 2.22 2.22 2.22 1.66 1.61 1.53 1.47	(1) (2) (3) ted rel Thre	S S VS W S S M W W W V V W V V W V V W V W V V W	$\begin{array}{c} \mathbf{x} - \mathbf{y} \\ 8 & 6 \\ 6 & 5 \\ 5 & $	(3) (1) (2)	M S S VS VS M M M M M M M M M W W VW VW VW	7.2 7.2 7.4 4.59 3.99 3.57 3.37 3.68 2.47 2.25 2.25 2.25 2.25 1.91 1.55	(3) (1) (2)	S W VS M S M M W VW VW VW VW VW VW VW	- , 3 5, 7 4, 636 3, 81 3, 62 2, 86 2, 69 2, 55 2, 30 2, 22 2, 03 1, 96 1, 78 1, 63	(3) (1) (2)	M S S S S V W M V W V W V W W W W W V W V W V W
est line explans b Da	s indication of ta obta	D see t ined us	lecreasing text. ing a came	order of ra of 17	f inténsity 71.9-mm. e	by (1), (2 effective d	), and ( iameter	3). For	1.00		,						

						Table	ll. Po	wder Di	ffraction D	)ataª ((	Cont'd)						
d 34. Butyl- 6.7 6.7 6.7 6.7 2.4.81 3.481 2.864 2.864 2.61 2.433 2.12 2.433 2.12 2.433 2.12 1.965 1.877 1.671 1.490 1.35 1.491 1.491 1.495	4(or 6)-/ 2,3-dime N-phen, samate (2) (1) (3)	1/I1 iert- ithyl- ylcar- VS S S M VW VW VW VW VW VW VW VW VW VW VW VW VW	d 35. 6 2,4-dim N-pher 8.0 6.6 5.8 4.16 3.26 3.09 2.62 2.19 2.62 2.19 2.92 2.62 2.19 2.92 2.62 1.90 1.78 1.64 1.26 1.17 1.08	-tert-Bi lethylpl ylcarb (1) (2) (3)	I/I1 ittyl- henyl amate W VS M VS VS S S S W W VS S S S W W W VS VS VS VS VS VS VS VS VS VS VS VS VS	d 36. N-pho 8.4 6.5 5.5 4.71 4.32 3.86 3.52 3.32 3.04 2.63 2.05 1.87	4-tert-B methylp nylcarb (2) (3) (1)	I/I1 iutyl henyl M W W S S M W W W W W W W W W W W W W W	d 37. 4 2,6-6 17. 5-9 18 9,4 6,6 10 5,8 4,26 3,84 4,26 3,84 4,26 3,84 4,26 3,84 4,26 3,84 4,26 3,50 2,76 2,17 2,76 2,17 2,05 1,96 1,88	4-tert-B nethylp nylcart (3) (2) (1)	I/I, utyl- henyl samate S VS VS VS VS VS VS VS VS VS VS VS VS V	d 38. 3.4-din N-pbs 8.9 7.5 5.5 4.89 4.34 4.00 3.40 4.62 3.40 2.82 2.52 2.31 2.52 2.21 2.52 2.39 2.21 1.96 1.81 1.63	6-tert-B nethylp inylcarb (2) (1) (3)	<i>I/I</i> <sub>1</sub> utyl- begyl semate M S M W W W W W W W W W W W W W	d 39 jir N-phe 6.2 5.7 4.94 4.441 3.62 3.62 2.46 2.46 2.17 1.98 1.98 1.98 1.60 1.60 1.24	<pre>?,6-Dieti hethylph mylcarbi (2) (1) (3)</pre>	I/I1 hyl- henyl amate S W VS W W VS W W W W W W W W W W W W W
<b>40. 3</b> pyl-2- <i>X</i> - pho 5.7 4.97 4.38 3.95 3.13 2.70 2.23 1.95 1.84 1.63 1.58	3,5-Diiso methylpi enylcarb (2) (1) (3)	pro- tenyl amate M VS M M M M W W W W W W VW VW VW VW	<b>41.</b> 3,5 <b>4-me</b> <i>N</i> -phen 8.6 7.6 6.4 <b>4.89</b> <b>4.66</b> <b>4.16</b> 3.811 3.54 3.16 2.72 2.24 2.24 2.24 2.24 1.97 1.84 1.56 1.47	-Diisop thylphe aylcarb (1) (3) (2)	ropyl- nyl M M S VS S S W S V W W W W W W W W W V W W V W V	<b>42.</b> <b>buty1-4</b> 7.5 6.4 4.78 4.22 3.82 3.23 3.01 2.80 2.66 2.51 2.39 2.20 1.92 1.66	2,6-Di- -chloro (2) (1) (3)	tert- phenol 8 WVS 8 M W W W W W W W W W W W V W V W V W V W	<b>43.</b> 4, tyl-2-r <i>N</i> -phen 6. 4 5.7 4.86 3.98 3.78 3.27 2.67D 2.30 2.19 2.09 1.94 1.81 1.66 1.60 1.48	6-Di-ter nethylp nylcarb (2) (1) (3)	t-bu- benyl amate M S M VS S M M W W W W W W VW VW VW VW VW VW VW	<b>44. 4,</b> tyl-3-1 N-phe 7.8 7.1 6.5 5.3 4.47 4.16 3.79 2.88 2.76 2.23 2.23 2.23 2.23 2.23 2.23 1.91 1.79 1.67 1.55	6-Di-ter nethylp nylcarb (2) (1) (3)	r-bu- henyi amate M M VSS VS W M S S W W M M W W VW VW VW	45 <sup>5</sup> . butyl-4 8.5 7.6 6.7 5.8 4.52 4.28 4.08 3.865 3.327 3.10 2.92 2.81 2.81 2.81 2.81 2.81 2.81 2.81 2.8	2,6-Di- -methylg (3) (1) (2)	tert- phenol S W VS W VS W V W S W M M W W W W W W W W W W W W
46. 2 cyclo 7.5 7.1 5.7 4.71 4.71 4.70 3.70 4.10 3.70 3.286 2.47 2.32 2.32 2.32 2.32 1.88 1.66 1.08	2-tert-But hexylph enylcarba (1) (2) (3)	yl-4- snyl amate M W W W W W W W W W W W W W V W V W V W	47. 4,6- 3-et N-phe: 8.6 7.4 6.1 5.1 4.54D 4.24 3.86 3.48 3.25 2.79 2.54 2.41 2.06 1.85 1.75 1.75 a d = tensity; lines ind planatio b Dat	Di-tert- hylphen nylcarb (3) (1) (2) (2) (2) (2) (3) (2) (2) (3) (2) (3) (2) (3) (2) (3) (3) (2) (3) (2) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3	butyl- amate S S M W VS S S S S V W W W W W W W V W V W V	48. 2, 4-e 8.3 5.2 4.63 4.34 3.73 3.44 3.22 2.93 2.28 2.10 2.20 1.87 1.87 xeing in Å = medium sing order	6-Di-ter thylphe (1) (3) (2) (2) (2) (2) (2) (3) (2) (2) (3) (2) (3) (4) (4) (5) (4) (5) (5) (5) (5) (5) (5) (5) (5) (5) (5	t-butyl nol S S VS S VS M M M W W W W W W W S S S S S S S S S	49. 4,6 2,3-di: N-phe: 8.0 7.2 5.4 4.32 3.71 3.39 3.16 2.88 2.48 2.24 2.24 2.24 2.24 1.92	-Di-tert methylr nylcarb (3) (1) (2) ed rela (2) ed rela three sti d (3). meter.	-butyl- ohenyl amate VS M VS VS VS M W VW VW M M M M tive in- rongest For ex-	50. jp 8.0 6.6 5.1 4.49 3.68 3.29 2.26 2.76 2.76 2.76 2.27 2.29 2.18 2.02 1.95 1.81 1.68 1.60 1.26 1.16	2,4,6-Tr tylphen (3) (1) (2)	i-tert- kol S S M W W M W W M W W W W W V V W W V V W	2.16 2.10 2.05 1.88 1.82 1.70 1.59 1.59 1.59 1.59 1.59 1.59 1.59 51. 51. 51. 51. 52 51. 51. 52 52 51. 52 52 52 52 52 52 52 52 52 52 52 52 52	2,6-Di- buty1-4- hexylph (2) (1) (3)	W W W W W V W V W V W V W W V W W M W W W W

such instances the pertinent data in Tables I and II refer to the phenol itself and a footnote to Table I points out these exceptions. In a very few cases, the specific structure of the phenol was not known, and for these compounds an alternative structure is given in parentheses and the boiling point of the compound is indicated. For example, two mono-tert-butyl derivatives of ocresol are probable in which the tert-butyl radical is in either the 4 or 6 position. To the isomer boiling at 135° C. at 20 mm., the formula 2-methyl-4(or 6)-tert-butylphenol was assigned, while to the one boiling at 123° C. at 20 mm. was given the formula 2methyl-6(or 4)-tert-butylphenol.

Phenols which would not form aryl N-phenylcarbamates by reaction with phenyl isocyanate were, in general, of the type in

which both positions ortho to the hydroxyl were occupied by large groups which hindered the activity of the hydroxyl hydrogen. Specifically, these were 2,6-diacetyl-3,5-dimethylphenol, 2,6-di-tert-butyl-4-cyclohexyl-2,6-di-tert-butyl-4-chlorophenol, phenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, and 2,6-di-tert-butyl-4-ethylphenol. 2-Nitrophenol reacts only to a very limited extent with phenyl isocyanate (6) and for this reason the properties of its derivative are not included in this paper.

The nonreactivity of 2,6-di-tert-butyl substituted phenols is interesting in that it makes possible the removal of admixed 2tert-butyl substituted phenols upon treatment of such mixtures with phenyl isocyanate. Advantage of this fact was taken

in the preparation of 2-tert-butyl-4-cyclohexylphenyl-N-phenylcarbamate from a mixture of 2-tert-butyl-4-cyclohexylphenol and 2,6-di-tert-butyl-4-cyclohexylphenol. The aryl N-phenylcarbamate obtained had a sharp melting point indicating its purity, and its elementary analysis (calculated: C, 78.59; H, 8.32; found: C, 78.54; H, 8.19) indicated that only the mono-tertbutyl derivative reacted with the phenyl isocyanate.

#### ACKNOWLEDGMENT

The authors are indebted to Roger Adams of the University of Illinois for the 4-methyl-2(8-methylallyl)phenol and to Givaudan-Delawanna, Inc., New York, N. Y., for the 2-methyl-3,5-diisopropylphenol and 4-methyl-3,5-diisopropylphenol used in this work.

### LITERATURE CITED

(1) Auwers, K., Ber., 32, 17 (1899).

(2) Baeyer, A., and Seuffert, O., Ibid., 34, 40 (1901).

- (3) Davey, W. P., Gen. Elec. Rev., 25, 565 (1922).
- (4) Fichter, F., and Schetty, G., Helv. Chim. Acta, 20, 150 (1937).
- (5) Fromm, E., and Eckard, H., Ber., 56, 948 (1923).
  (6) Gumpert, F., J. prakt. Chem., 32, 278 (1885).
- (7) Hanawalt, J. D., and Rinn, H. W., IND. ENG. CHEM., ANAL. ED., 8,244 (1936).
- (8) Hanawalt, J. D., Rinn, H. W., and Frevel, L. K., Ibid., 10, 457 (1938).
- (9) Hey, D. H., J. Chem. Soc., 1931, 1581.
- (10) Hofmann, A. W., Ber., 4, 246 (1871).
- (11) Kruber, O., and Schmitt, A., Ibid., 64, 2270 (1931).
- (12) Leuckart, R., J. prakt. Chem., (2) 41, 301 (1890).
- (13) Morel, A., Bull. soc. chim., (3) 21, 823 (1899).
- (14) Morgan, G. T., and Pettet, A. E. J., J. Chem. Soc., 1931, 1124.
- (15) Snape, H. L., Ber., 18, 2428 (1885).
- (16) Steinkopf, W., and Höpner, T., J. prakt. Chem., 113, 137 (1926).
- (17) Stoermer, R., and Boes, J., Ber., 33, 3013 (1900).
- (18) Stoermer, R., and Kahlert, B., Ibid., 35, 1630 (1902). (19)Vavon, G., and Mitchovitch, V. M., Bull. soc. chim., (4) 45, 961
- (1929).
- (20)Weehuizen, M. F., Rec. trav. chim., 37, 266 (1918).
- (21) Ibid., 37, 355 (1918).

## Bomb Furnace for Carius Digestion

LEON A. GREENBERG, Laboratory of Applied Physiology, Yale University, New Haven, Conn.

THE oxidation of organic material in a sealed glass tube at The oxidation of organic matters as first used by Carius for high temperatures and pressures, as first used by Carius for the determination of halides (1), is still used for the determination of halides, sulfur, and nitrogen. The pressure tubes are made of heavy Jena glass or Pyrex; they are carefully flame-sealed, avoiding any strain in the glass, and are heated to temperatures as high as 300° C. in a bomb furnace. The pressure developed within the tubes is so great that they frequently explode, causing considerable damage (2). In carrying out halide determinations in this laboratory, there have been several such explosions. The author has therefore devised a bomb furnace in which the danger of explosion is eliminated.

In principle, the glass pressure tube is heated in an atmosphere whose pressures approximate the pressure developed within the tube. A diagram of the furnace (built by the Bigelow Boiler Works, New Haven, Conn.) is shown in Figure 1. It consists of a steel tube 70 cm. in length, 4 cm. in diameter, and closed at one end. The wall of the steel tube is 3 mm. thick. The open end has a flange measuring 13 cm. in diameter and 3 cm. in thickness, to which a cap of similar dimensions can be bolted. The cap has attached to it a steam pressure gage read-ing up to 910 kg. (2000 pounds), a safety valve, and a manual valve. The furnace is built to operate safely up to 910 kg. (2000 pounds) and the safety valve is adjusted to open at 700 kg. (1500 pounds). The steel tube is supported in a vertical po-tion of the steel tube is supported in a vertical position by a metal frame and is heated at its lower end by vertical gas burners.

To use the furnace, water is placed in the vertical steel tube to a depth of about 20 cm. The sealed glass bomb, about 25 cm. in length, is suspended by a short piece of cord tied at one end to a hook drawn out at the sealed end of the tube, and at the other end to a short metal bar laid across the mouth of the steel tube. The glass bomb must not dip into the water and must not come into contact with the wall of the steel tube. This is not come into contact with the wan of the steer tube. This is easily accomplished if the furnace is perfectly vertical. A gasket is placed on the flanged open end of the furnace and the cap is bolted into position. With the manual valve open, the gas burn-ers are lighted and when the vapor starts to escape from this valve, it is closed. Heating is continued until the desired tem-perature is reached as estimated by the pressure on the gage. The flame is then adjusted to maintain this pressure. At the end, the flame is started of and the furnace is allowed to cod until end, the flame is turned off and the furnace is allowed to cool until the pressure reading is not more than a few pounds. The manual the pressure reading is not more than a few pounds. valve is then opened and the cap is removed.

The author has carried out many Carius digestions with this furnace, using Pyrex tubes of ordinary thickness, without losing one. Although the unit illustrated holds only 1 pressure tube, a multiple unit can be easily constructed. Besides the determina-



Figure 1. Diagram of Furnace

tions of halides, sulfur, and nitrogen, many other procedures used in laboratories, such as aminization, must be carried out in glass bombs at high temperatures. For such purposes, the type of furnace described here is useful in eliminating the danger of explosion.

#### LITERATURE CITED

- Carius, L., and Houben, J., "Die Methoden der organische Chemie", Vol. 1, pp. 59-63, Leipzig, G. Thieme, 1925.
- (2) Gordon, C. L., J. Research Natl. Bur. Standards, 30, 107 (1943).