CXLV.—*The Use of Arylcarbimides in identifying Hydroxylic Compounds.*

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PHENYLCARBIMIDE has been employed in separating and characterising phenols from tar and tar products; thus Fromm and Eckard (*Ber.*, 1923, **56**, 948) have identified *m*-cresol in lignite tar, and Steinkopf and Höpner (*J. pr. Chem.*, 1926, **113**, 148) have identified *o*-3- and *m*-5-xylenols in producer-gas tar from Bohemian lignite. Phenylcarbimide has also served to isolate several dihydric phenols from the aqueous liquors of low-temperature carbonisation (Morgan and Pettet, *J. Soc. Chem. Ind.*, 1931, **50**, 72T), but the method is not generally applicable, particularly to the less volatile phenols of low-temperature tar, since mixtures of these compounds yield oily products.

French and Wirtel (*J. Amer. Chem. Soc.*, 1926, **48**, 1736) suggested the use of α-naphthylcarbimide, but its combinations with phenols offer little advantage as regards diminished fusibility over the phenylcarbamates.

We have now found a more satisfactory alternative reagent in p-*xenylcarbimide*, which is readily obtained from *p*-xenylamine, itself prepared from diphenyl (Morgan and Walls, *J. Soc. Chem. Ind.*, 1930, **49**, 15T). This carbimide has been mentioned by Zimmerman (*Ber.*, 1880, **13**, 1965), but its analysis and physical properties were not recorded. The p-*xenylcarbamates*, $C_6H_5{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2R$, are considerably less fusible than the corresponding phenylcarbamates, so that phenolic fractions, which yield only oily mixtures of the latter, provide crystalline *p*-xenyl derivatives and, in addition, solubility relationships are modified.

Moreover, as shown in the appended table, the *p*-xenylcarbamates of many alcohols have convenient melting points, higher than those of their phenylcarbamates and lower than those of the carbamates obtained from 4′-iodoxenylene-4-carbimide (Kawai and Tamura, *Proc. Imp. Acad. Japan*, 1930, **6**, 198).

In general the carbimide process of separating phenols and alcohols has the advantage that the original hydroxylic compound is readily regenerated from the purified arylcarbamate by boiling with dilute aqueous or aqueous-alcoholic ammonia.

Phenylcarbimide.—Phenylcarbimide is readily prepared in 100 g. batches by Hentschel's method (*Ber.*, 1884, **17**, 1284; Houben, "Die Methoden der Organische Chemie," 3rd edition, **3**, 11) when carbonyl chloride is passed over aniline hydrochloride fused in a retort with wide outlet tubes and receiver. The neck of the retort is preferably lagged with asbestos to avoid accumulation of carbanilide and solid phenylcarbamyl chloride. This intermediate carbamyl chloride decomposes on subsequent heating into hydrogen chloride and phenylcarbimide, the latter being purified by repeated distillation (yield, 42% of the theoretical).

p-*Xenylcarbimide.*—Carbonyl chloride was passed into a solution of *p*-xenylamine (60 g.) in 1500 c.c. of warm toluene, which was then brought to boiling point during the course of 2 hours and maintained at this temperature till no more hydrogen chloride was evolved. Toluene was distilled from the hot filtrate, and the residual p-*xenylcarbimide* recrystallised from petroleum (b. p. 40—60°) (yield, 54 g.); m. p. 56°, b. p. 283° (decomp.) (Found : C, 80·0; H, 4·9. $C_{13}H_9ON$ requires C, 80·0; H, 4·7%); 13·5 g. of s-*di*-p-*xenylcarbamide*, m. p. 312°, were also obtained (Found: C, 82·4; H, 5·5. $C_{25}H_{20}ON_2$ requires C, 82·4; H, 5·5%).

p-*Xenylcarbamates.*—The hydroxyl compound under examination is heated at 100° for 1 hour with a slight excess of *p*-xenylcarbimide, and the cooled solid mass of p-*xenylcarbamate* crystallised from alcohol, benzene, or benzene–petroleum. Any *s*-di-*p*-xenylcarbamide which may be formed is readily separated, since it is almost insoluble in the ordinary organic media.

In the following table the melting points of the *p*-xenylcarbamates are compared with those of the already known phenylcarbamates.

Hydroxyl compound.	Phenyl-carbamate, m. p.	*p*-Xenyl-carbamate, m. p.	Found. C.	Found. H.	Required. C.	Required. H.
Methyl alcohol	47°	127°	74·1	5·8	74·0	5·8
Ethyl alcohol	51	119	74·6	6·3	74·7	6·3
n-Propyl alcohol	57	129	75·3	6·7	75·3	6·7
*iso*Propyl alcohol	90	138	75·4	6·7		
n-Butyl alcohol	55	109	75·8	6·9	75·8	7·1
n-Amyl alcohol	—	99	76·1	7·5	76·3	7·5
*cyclo*Hexanol	82	166	77·3	7·4	77·2	7·2
Phenol	126	173	79·1	5·2	78·9	5·2
o-Cresol	144	151	79·6	5·9	79·2	5·7
m-Cresol	125	164	78·9	5·6		
p-Cresol	115	198	79·3	5·5		
Benzyl alcohol	78	156	79·3	5·7		
o-4-Xylenol	120	183	79·3	6·1	79·4	6·0
m-2-Xylenol	133	198	79·3	5·9		
m-4-Xylenol	112	184	79·6	5·9		
m-5-Xylenol	148	150	79·4	6·0		
p-Xylenol	162	162	79·1	5·9		
Pseudocumenol	110	196	79·6	6·3	79·7	6·3
Thymol	106	194	80·2	6·6	80·0	6·7
Carvacrol	135	166	79·7	6·8		
α-Naphthol	178	190	81·4	5·1	81·4	5·1
Catechol	169	decomp.	—			
Resorcinol	164	decomp.	—			
Quinol	224	decomp.	—			
Homocatechol	166	193	76·9	5·4	77·0	5·1
Orcinol	154	196	77·3	5·2		

In general, the *p*-xenylcarbamates are well-crystallised substances, but those derived from methyl and ethyl alcohols have the peculiar property of separating in gelatinous condition from saturated solutions, the crystalline form being subsequently developed.

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