the usual manner and the mixture was heated for an additional forty minutes. After separation of the product from the catalyst by means of hot benzene, the latter was removed and the residue was evaporatively distilled at 175° (0.01 mm.). The orange-yellow hydrocarbon (0.450 g.; m. p. 166–168°) was converted into its picrate in benzene–petroleum ether and the picrate was recrystallized once from benzene–petroleum ether; m. p. 148.5–150° (vac.).

Anal. Calcd. for $C_{21}H_{16} \cdot C_6H_3O_7N_3$: N, 8.5. Found: N, 8.4.

A benzene solution of the regenerated hydrocarbon was passed through a tower of alumina, the solvent was evaporated in the usual manner and the residue was recrystallized from acetone–alcohol from which the hydrocarbon separated in the form of orange-yellow cubes; yield 0.355 g. (67% based on the ketone (VII)); m. p. 169–170°. A mixed melting point of 1-methylcholanthrene and cholanthrene (169–170°) was 144–155°.

Anal. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.8; H, 6.1.

Summary

The synthesis of 5-methyl-6,7-dimethylenechrysene, a structural isomer of the methylcholanthrenes, is described. The preparation of 1-methylcholanthrene is also reported.

The new hydrocarbons will be tested for carcinogenic activity.

ANN ARBOR, MICHIGAN RECEIVED JULY 25, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation of Some *p*-Dialkylbenzenes[1]

BY CHARLES E. WELSH AND G. F. HENNION

Introduction

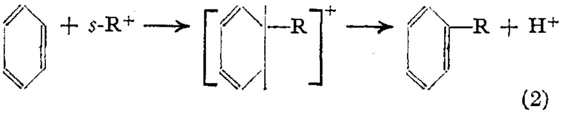
The alkylation of monoalkylbenzenes by the alcohol–boron fluoride–phosphorus pentoxide method, previously described,[2] has now been found to be an excellent method for the preparation of certain *p*-dialkylbenzenes. Toluene and ethylbenzene have been so alkylated and give excellent yields with normal alcohols, particularly in the range C_4 to C_{12}. The advantage of the use of co-condensing agents with boron fluoride in certain cases has again been noted. *n*-Butyl alcohol does not alkylate toluene under the influence of boron fluoride alone, but when phosphorus pentoxide is used also, a 90% yield of *p*-*s*-butyltoluene is obtained. It has been found better to omit the phosphorus pentoxide, however, when the same alkylation is performed with *s*-butyl alcohol. In general the normal primary alcohols give the best yields, apparently because they react more slowly and do not give the olefin polymer and high boiling residues so often obtained with the easily dehydrated alcohols.

The direct dialkylation of benzene was studied with *n*-butyl and *n*-amyl alcohols. These gave 68% and 40% yields, respectively, of the *p*-di-*s* products, somewhat less satisfactory than the two step processes.

With one exception all of the alkylations resulted in selective para substitution, as shown by the fact that products distilled over narrow temperature ranges, with substantially constant refractive indices, and oxidized to terephthalic acid. Samples of the latter gave only faint fluorescein tests and yielded dimethyl terephthalate of correct melting point. The ethylation of toluene gave material boiling over a two degree range with continuous drift in the refractive index, approximately from the para to the ortho values. The diacid obtained on oxidation gave a pronounced fluorescein test.

The reaction products are those which would be obtained by dehydration of the alcohol to olefin with para addition of the latter. Thus the normal primary alcohols introduce the corresponding secondary alkyl group. Actually the olefin mechanism[3] is no longer tenable as shown by the work of Whitmore[4] and Price[5] as well as recent experiments in this Laboratory,[1] all of which favor the positive fragment theory.

$$n\text{-ROH} + BF_3 \longrightarrow s\text{-R}^+ + (HO \longrightarrow BF_3)^- \quad (1)$$



(2)

The experimental conditions and products are described in Tables I, II and III.

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[1] Paper XXV on organic reactions with boron fluoride; previous paper, THIS JOURNAL, **63**, 1722 (1941).

[2] Toussaint and Hennion, *ibid.*, **62**, 1145 (1940).

[3] Sowa, *et al.*, *ibid.*, **57**, 709 (1935); **59**, 470, 1204 (1937); **60**, 125, 654 (1938).

[4] Whitmore, *ibid.*, **54**, 3274 (1932).

[5] Price *et al.*, *ibid.*, **60**, 2499 (1938); **61**, 1595 (1939); **62**, 3105 (1940).

TABLE I

EXPERIMENTAL DATA, PREPARATION OF p-DIALKYLBENZENES

Moles						
R-OH	Hydrocarb.	BF$_3$	P$_2$O$_5$	Temp., °C.^{a}	Time, hr.	Yield, %
			A. From Toluene			
1.0 C$_2$	4	1.2	0.25	90–115	22	70
0.5 n-C$_3$	2	0.5	.125	70	9	76
.5 n-C$_4$	2	.5	.125	70	3	90
.5 s-C$_4$	2.5	.5		75	4.5	65
.5 i-C$_4$	2	.5		75	4	85
.5 t-C$_4$	2	.5		75	5	67
.5 n-C$_5$	2	.5	.125	75	6	81
.5 n-C$_8$	2	.5	.125	75	2	81
				90	2	
.5 n-C$_{12}$	2	.5	.125	80	2	81
				95	8	
.5 n-C$_{18}$	2	.5	.125	85	12	17
.5 cyclo-C$_6$	2	.5		75	1.5	81
			B. From Ethylbenzene			
.5 n-C$_3$	2	.5	.125	80	4	81
.5 n-C$_4$	2	.5	.125	75	4	96
.5 n-C$_5$	2	.5	.125	75	5	79
.5 n-C$_8$	2	.5	.125	75	8	64
.5 n-C$_{12}$	2	.5	.125	95	10	80
			C. From Dialkylation of Benzene			
2.0 n-C$_4$	1	2.0	.25	75	6	68
2.0 n-C$_5$	1	2.0	.25	75	9	40

^{a} Plus or minus 5°.

TABLE II

PHYSICAL CONSTANTS OF p-DIALKYLBENZENES, R—C$_6$H$_4$—R′

		B. p.,				Mol. wt.	
R	R′	°C.	Mm.	n^{20}_D	d^{20}_4	Calcd.	Obsd.
C	i-C$_3$	175	740	1.4933	0.8644	134	133
C	s-C$_4$	193	732	1.4930	.8658	148	147
C	t-C$_4$	188–189	740	1.4929	.8641	148	147
C	s-C$_5$	95	20	1.4920	.8631	162	159
C	s-C$_8$	116	7	1.4877	.8607	204	202
C	s-C$_{12}$	167	8	1.4841	.8594	260	256
C	s-C$_{18}$	234–237	8	1.4798	.8563	344	338
C$_2$	i-C$_3$	193	744	1.4927	.8625	148	150
C$_2$	s-C$_4$	86	16	1.4921	.8629	162	164
C$_2$	s-C$_5$	97	11	1.4910	.8626	176	172
C$_2$	s-C$_8$	126	7	1.4874	.8609	218	215
C$_2$	s-C$_{12}$	171–173	7	1.4852	.8586	274	278
C	cyclo-C$_6$	117	10	1.5253	.9353	174	173
s-C$_4$	s-C$_4$	104	10	1.4879	.8686	190	183
s-C$_5$	s-C$_5$	127–128	14	1.4880	.8619	218	212

Experimental

Alkylation of Toluene.—The reactor consisted of a one-liter three-necked flask equipped with an efficient sealed stirrer, a reflux condenser and a gas inlet tube. Two moles (184 g.) of toluene and 0.5 mole (37 g.) of n-butyl alcohol were weighed into the flask. A cold water-bath was placed around the flask, the stirrer started and boron fluoride bubbled rapidly beneath the surface of the liquid until 0.5 mole (34 g.) had been absorbed. The flask was now cooled with ice, the gas inlet removed and 0.125 mole (17.5 g.) of phosphorus pentoxide added. A thermometer was fixed to the open neck and the combined reagents heated to 75 ± 5° for three hours. The phosphorus pentoxide dissolved on heating with the formation of an appreciable lower liquid layer. The lower layer decreased in volume as the reaction progressed. On completion of the heating period the contents of the reactor were transferred to a separatory funnel and the lower layer drawn off. The hydrocarbon layer was washed twice with water, with dilute sodium carbonate solution, again with water, dried over calcium chloride and distilled twice through an efficient column. The yield of p-s-butyltoluene was 90%.

TABLE III

ANALYSES OF p-DIALKYLBENZENES, R—C$_6$H$_4$—R′

		% Carbon		% Hydrogen	
R	R′	Calcd.	Obsd.	Calcd.	Obsd.
C	s-C$_5$	88.9	88.7	11.1	11.0
C	s-C$_8$	88.3	87.8	11.7	11.7
C	s-C$_{12}$	87.7	87.6	12.3	12.2
C	s-C$_{18}$	87.2	87.6	12.8	12.9
C$_2$	s-C$_4$	88.9	88.5	11.1	11.1
C$_2$	s-C$_5$	88.7	88.4	11.3	11.3
C$_2$	s-C$_8$	88.1	88.5	11.9	11.7
C$_2$	s-C$_{12}$	87.6	87.5	12.4	12.5

Dialkylation of Benzene.—One mole (78 g.) of benzene and one mole (74 g.) of n-butyl alcohol were weighed into a 500-ml. three-necked flask fitted as described above. One mole (68 g.) of boron fluoride was admitted, followed by 0.25 mole (35 g.) of phosphorus pentoxide. The mixture was heated at about 75° for two and one-half hours, cooled and a second mole (74 g.) of n-butyl alcohol added. After resaturating with boron fluoride, the mixture was heated for another three and one-half hours and treated as previously described.

Oxidation of Dialkylbenzenes.—A 2-g. sample of each of the dialkylbenzenes was oxidized to the diacid with sodium dichromate and sulfuric acid, using glacial acetic acid as a diluent. A portion of each oxidation product was esterified with methanol and hydrogen chloride. The ester melted at 144–145° in practically all cases. A further portion of each acid was treated with resorcinol and sulfuric acid. Only one sample, that obtained from ethyltoluene, gave a deep fluorescein color in this manner.

Summary

1. The reaction between alcohols and aromatic hydrocarbons in the presence of boron fluoride and phosphorus pentoxide has been applied to the preparation of p-dialkylbenzenes.

2. Dialkylbenzenes have been prepared by the monoalkylation of toluene and ethylbenzene and by the direct dialkylation of benzene. The former method gave the higher yields.

3. The normal primary alcohols from about C$_4$ to C$_{12}$ are best suited for these reactions.

NOTRE DAME, IND.

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