Synthesis of Aromatic Hydrocarbons

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Synthesis of Aromatic Hydrocarbons

A New Method for the Synthesis of Hydrocarbons of the Fluorene Series

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As we have shown previously ($^{1-6}$), the action of phosphorus pentoxide on tetrahydrophthalic anhydrides—adducts of diene hydrocarbons (alkylbutadienes and cycloalkenyls) with maleic anhydride, its homologs ($^{1-5}$), and cyclic analogs (^{6})—leads to the formation of aromatic hydrocarbons; the reaction proceeds with elimination of CO and H_2O:

$$\text{diene} + \text{maleic anhydride adduct} \xrightarrow{(P_2O_5)} \text{benzene} + 2CO + H_2O$$

In the present work we studied the action of phosphorus pentoxide on phenyltetrahydrophthalic anhydride (I)—the adduct of phenylbutadiene with maleic anhydride. It was found that in this case the reaction leads to the formation of fluorene (in 21% yield), and not diphenyl, as might have been expected. The reaction apparently proceeds through intermediate stages of intramolecular acylation of the benzene ring, leading to the formation of tetrahydrofluorenonecarboxylic acid (II), and subsequent decarboxylation of it to tetrahydrofluorenone (III); the latter, under the action of phosphorus pentoxide, is converted into fluorene*:

$$\text{phenylbutadiene} + \text{maleic anhydride} \longrightarrow I \xrightarrow{(P_2O_5)} II \xrightarrow{-CO_2} III \xrightarrow[-H_2O]{(P_2O_5)} IV$$

Subsequently we modified and simplified this reaction by using, as the starting substance, instead of phenyltetrahydrophthalic anhydride—

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* The possibility that each of the reactions indicated can occur under the action of phosphorus pentoxide is confirmed by literature data: the literature describes the use of this reagent for intramolecular acylation of a benzene nucleus (^{7,8}), for decarboxylation of acids or their derivatives (^{9}), and for the conversion of

tetrahydroaromatic ketones (with the carbonyl group in the ring or outside it) into aromatic hydrocarbons (^{10,11}).

phenyltetrahydrobenzoic acid—an adduct of divinyl with cinnamic acid (V). On heating this adduct with phosphorus pentoxide, fluorene was obtained in 63% yield:

$$\text{divinyl} + \text{cinnamic acid} \longrightarrow \text{V} \xrightarrow[(P_2O_5)]{-H_2O} [\text{ketone}] \xrightarrow[(P_2O_5)]{-H_2O} \text{IV}$$

From the adducts of cinnamic acid with isoprene and 2,3-dimethylbutadiene, 3-methylfluorene (yield 50%) and 2,3-dimethylfluorene (yield 53%) were obtained:

$$\text{diene} \ + \ \text{cinnamic acid} \longrightarrow \text{VI} \xrightarrow[(P_2O_5)]{-H_2O} [\text{ketone}] \longrightarrow \xrightarrow[(P_2O_5)]{-H_2O} \text{VII}$$

$$VIa \text{ and } VIIa: \ R = H,$$
$$VIb \text{ and } VIIb: \ R = CH_3.$$

The formation specifically of 3-methylfluorene, m.p. 87.5-88°, and not of its isomer 2-methylfluorene (m.p. 104°), from the adduct of isoprene with cinnamic acid confirms the structure of this adduct (VIa) as 4-methyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid.

From the adducts of cinnamic acid with dicyclohexenyl (VIII) and dicyclopentenyl (IX), 1,2,3,4-dicyclohexanofluorene (X) and 1,2,3,4-dicyclopentanofluorene (XI) were obtained; the yields were 83.5% and 73%:

$$\text{dicyclohexenyl} + \text{cinnamic acid} \longrightarrow \text{VIII} \xrightarrow[(P_2O_5)]{-H_2O} [\text{ketone}] \xrightarrow[(P_2O_5)]{-H_2O} \text{X}$$

$$\text{dicyclopentenyl} + \text{cinnamic acid} \longrightarrow \text{IX} \xrightarrow[(P_2O_5)]{-H_2O} [\text{ketone}] \xrightarrow[(P_2O_5)]{-H_2O} \text{XI}$$

Thus, the reaction of 2-aryl-1,2,3,6-tetrahydrobenzoic acids (adducts of diene hydrocarbons with cinnamic acid) with phosphorus pentoxide can be recommended as a new preparative method for the synthesis of hydrocarbons of the fluorene series.

Experimental Part

Fluorene (IV) from the adduct of 1-phenylbutadiene-1,3 with maleic anhydride. A mixture of 10 g of 1-phenylbutadiene-1,3 (b.p. 75-77°/6 mm; n_D^{20} 1.6088) and 7.5 g of maleic anhydride was carefully heated on a water bath until the reaction began; heating was then stopped, and after cooling the reaction mass was again heated for 10 min to complete the reaction. The adduct obtained—3-phenyl-1,2,3,6-tetrahydrophthalic anhydride (I; 12 g; 70%; m.p. 119-119.5° from petroleum ether; according to the literature (12), m.p. 120°)—was heated with phosphorus pentoxide (3.7 g) in a Würtz flask; after the vigorous reaction had ended and gas evolution had ceased, 1.92 g (21%) of fluorene was distilled off, which was further purified by sublimation in vacuum; m.p. 113.5-114° (from alcohol). A mixed sample with authentic fluorene melted without depression.

Found, %: *C* 93.67; 93.75; *H* 6.31; 6.21
$C_{13}H_{10}$. Calculated, %: *C* 93.97; *H* 6.03

Picrate: mp 80-81° (from alcohol). Literature data for fluorene: mp 116° (13); mp of the picrate 80-82° (14).

Hydrocarbons of the fluorene series from adducts of diene hydrocarbons with cinnamic acid

Fluorene. A mixture of cinnamic acid (mp 133°; 50 g; 0.33 mole), divinyl (100 ml; 1.4 mole), abs. benzene (50 ml), and hydroquinone (0.2 g) was heated in an autoclave for 25 hr at 140°. The crystallized reaction mass, after standing for 24 hr (in the cold), was shaken with a solution of soda; the soda solution was acidified, the reaction product was extracted with ether, and after removal of the ether was heated in vacuo at 140° for partial removal of cinnamic acid (sublimation); mp of the residue (20 g) 79-80°. However, the adduct V obtained (2-phenyl-1,2,3,6-tetrahydrobenzoic acid), judging by the melting point (literature data (15) mp 101°) and analytical data, nevertheless contained a considerable admixture of unreacted cinnamic acid (up to 40%).

$C_{13}H_{14}O_2$ (adduct). Found %: C 75.43; 75.56; H 6.66; 6.68
Calculated %: C 77.22; H 6.93
$C_9H_8O_2$ (cinnamic acid). Calculated %: C 72.96; H 5.44

Since the admixture of cinnamic acid could not interfere with the reaction of the adduct with P_2O_5 (a specially performed experiment showed that cinnamic acid, when heated with phosphorus pentoxide, is completely resinified), it was heated without further purification with phosphorus pentoxide (17 g) until foaming ceased (not above 300°); the fluorene formed was then distilled off in vacuo from the reaction mixture (6.2 g; yield 63%): mp 115° (after sublimation at 2 mm and crystallization from alcohol); a mixed sample with authentic fluorene melted without depression. Mp of the picrate 79-80°. 9-Benzalfluorene (the product of condensation of fluorene with benzaldehyde (16)) had mp 75-75.5° (from alcohol); mp of the picrate 113-114° (from alcohol). Literature data (16): mp 76°; mp of the picrate 115°.

3-Methylfluorene (VIIa). The reaction between isoprene (17 g; 0.25 mole) and cinnamic acid (14.8 g; 0.1 mole) was carried out in an autoclave in a solution of abs. benzene (20 ml), in the presence of hydroquinone (0.2 g), for 16 hr at 175–180°. After successive treatment with soda and acid, 15 g (70%) of 4-methyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid (VIa) was isolated: mp 125.5-126° (from petroleum ether). Literature data (17) mp 126°. The adduct obtained was heated with phosphorus pentoxide (9.9 g) until foaming ceased; the reaction product was distilled from the reaction mixture at 190-200°/10 mm. This gave 6.3 g (50%) of 3-methylfluorene, which, after washing with alkali and water, drying, distillation in vacuo, and recrystallization from alcohol, melted at 87.5-88°. Literature mp 88° (18) (2-methylfluorene melts at 104° (19)).

2,3-Dimethylfluorene (VIIb). The adduct from 2,3-dimethylbutadiene (68 g diene; 0.83 mole) and cinnamic acid (86 g; 0.58 mole) was obtained by the method described for the isoprene adduct, but in xylene (150 ml). After cooling of the reaction mass, a precipitate of the adduct separated (75 g) with mp 156-157°. From the residue, after removal of xylene, a further 10 g of adduct was isolated (by successive treatment with 5% potassium hydroxide solution and hydrochloric acid). The resulting 4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid (VIb; yield 55%) melted at 159-160° (from acetic acid). Literature data (20): mp 159-160°. Heating of the adduct obtained (15 g) with phosphorus pentoxide (9 g) and subsequent distillation of the hydrocarbon formed in vacuo gave 6.9 g (53%) of 2,3-dimethylfluorene with mp 123.5-124.5° (from alcohol). Literature data (21) mp 123-124°. Mp of the picrate (not described in the literature): 106° (from alcohol).

$C_{21}H_{17}O_7N_3$. Found %: N 10.05; 10.13
Calculated %: N 9.95

1,2,3,4-Dicyclohexanofluorene (X). The adduct of 1,1′-dicyclohexenyl with cinnamic acid [22] (2-phenyl-3,4,5,6-dicyclohexano-1,2,3,6-tetrahydrobenzoic acid; 7.5 g; m.p. 321.5–222°; literature data [22] m.p. 221°) was heated with phosphorus pentoxide (3.4 g); the reaction product was distilled off in vacuo at 210-220°/2 mm. The 1,2,3,4-dicyclohexanofluorene obtained (5.5 g; 83.5%) had m.p. 129-129.5° (from petroleum ether); not described in the literature.

Found, %:	C 92.10; 91.80; H 8.23; 8.31
$C_{21}H_{22}$. Calculated, %:	C 91.98; H 8.02

Dicyclohexanofluorene (3 g) was converted into dibenzofluorene by heating with selenium (3.4 g) for 7 hr at 340° (until evolution of hydrogen selenide had completely ceased). After extraction of the reaction mass with boiling butyl alcohol, 2.2 g (76%) of 1,2,3,4-dibenzofluorene, m.p. 159-159.5° (from butyl alcohol), was isolated; m.p. of the picrate 153-154° (from butyl alcohol). Literature data [23]: m.p. 158-159°; m.p. of the picrate 153-155°.

1,2,3,4-Dicyclopentanofluorene (XI). The adduct of 1,1′-dicyclopentenyl (16 g) with cinnamic acid (14.6 g) was obtained by the procedure described for dicyclohexenyl [22], with the difference that the temperature of the reaction mixture was maintained at 160°. After the reaction was complete, the adduct was extracted with boiling petroleum ether. The yield of the adduct–2-phenyl-3,4,5,6-dicyclopentano-1,2,3,6-tetrahydrobenzoic acid (IX) (not described in the literature)–was 53% (15 g); m.p. 144-145°.

Found, %:	C 80.87; 81.06;	H 7.97; 8.05
$C_{19}H_{22}O_2$. Calculated, %:	C 80.85;	H 7.80

By interaction of 5 g of the adduct obtained with 2.5 g of phosphorus pentoxide, 3 g (73%) of dicyclopentanofluorene, m.p. 135-136° (from alcohol), was obtained. Not described in the literature.

Found, %:	C 92.34; 92.64;	H 7.43; 7.32
$C_{19}H_{18}$. Calculated, %:	C 92.67;	H 7.33

M.p. of the picrate 176-176.5° (from acetone).

Found, %:	N 8.50; 8.43
$C_{25}H_{21}O_7N_3$. Calculated, %:	N 8.83

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