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## Abstract

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## AROMATIC HYDROCARBONS

## A NEW SYNTHESIS OF ANTHRACENES

*(Presented by Academician A. N. Nesmeyanov, March 13, 1962)*

In previous communications we described a method for the synthesis of fluorenes and 2-phenylfluorenes, as well as various polynuclear aromatic hydrocarbons containing the fluorene system; the method consisted in the action of phosphorus pentoxide on aryltetrahydrobenzoic acids—adducts of diene hydrocarbons with acrylic acids (cinnamic and *p*-phenylcinnamic) (1–3).

[reaction scheme]

$$R = H,\ C_6H_5$$

In the present work a new synthesis of hydrocarbons of the anthracene series is described, by the action of phosphorus pentoxide on benzyltetrahydrobenzoic acids.

It was found that 2-benzyl-1,2,3,6-tetrahydrobenzoic acids, like 2-phenyl- and 2-*p*-diphenylyl-1,2,3,6-tetrahydrobenzoic acids, under the action of phosphorus pentoxide undergo the so-called (4) aromatization of the second type, i.e., intramolecular acylation of the benzene ring by the carboxyl group takes place, with formation of hydroaromatic ketones, which then, with enolization, migration of the double bond, and dehydration, are converted into dihydroanthracenes; subsequent dehydrogenation of the dihydroanthracenes thus obtained (by heating with sulfur) leads to anthracenes.

Subsequently we simplified this route to the synthesis of anthracenes by carrying out the aromatization of benzyltetrahydrobenzoic acids by heating with phosphorus pentoxide in the presence of sulfur. As was to be expected, the dihydroanthracenes formed under these conditions are completely dehydrogenated to anthracene hydrocarbons of the corresponding structure.

[reaction scheme: benzyltetrahydrobenzoic acid $\xrightarrow[-H_2O]{P_2O_5}$ ketone intermediate $\rightarrow$ enol intermediate $\xrightarrow[-H_2O]{}$

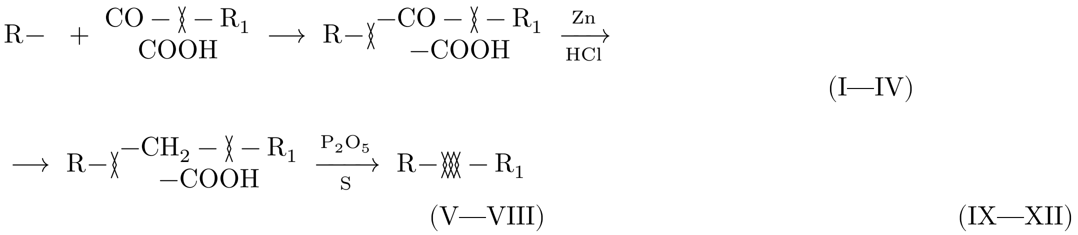
$\rightarrow$ dihydroanthracene $\xrightarrow[-H_2]{S}$ anthracene]

Benzyltetrahydrobenzoic acids—the starting substances in this reaction—were obtained by reduction of aroyltetrahydrobenzoic acids.

(adducts of diene hydrocarbons with aroylacrylic acids) with amalgamated zinc in hydrochloric acid; however, we were unable to isolate the benzyltetrahydrobenzoic acids obtained in this way in pure form: they were obtained as non-crystallizing oily liquids that decomposed on distillation in vacuum and, judging from analysis, contained an admixture of the starting aroyltetrahydrobenzoic acids.

Since specially designed experiments showed that the aroyltetrahydrobenzoic acids themselves resinify completely on heating with phosphorus pentoxide, it proved possible to introduce the benzyltetrahydrobenzoic acids into the aromatization reaction without subjecting them to further purification from admixtures of aroyltetrahydrobenzoic acids.

The benzyltetrahydrobenzoic acids (V—VIII), obtained by reduction of the adducts of divinyl and 2,3-dimethylbutadiene-1,3 with benzoyl- and *p*-toluylacrylic acids (adducts I—IV), were introduced into the aromatization reaction by heating with phosphorus pentoxide in the presence of sulfur; the yields of anthracene (IX), 2-methylanthracene (XI), 2,3-dimethylanthracene (X), and 2,3,6-trimethylanthracene (XII) were 48, 56, 51, and 49%, respectively.



$$\mathrm{R}- \quad + \begin{array}{c}\mathrm{CO}-\between-\mathrm{R}_1\\ \mathrm{COOH}\end{array} \longrightarrow \mathrm{R}-\between\begin{array}{c}-\mathrm{CO}-\between-\mathrm{R}_1\\ -\mathrm{COOH}\end{array} \xrightarrow[\mathrm{HCl}]{\mathrm{Zn}}$$

(I—IV)

$$\longrightarrow \mathrm{R}-\between\begin{array}{c}-\mathrm{CH}_2-\between-\mathrm{R}_1\\ -\mathrm{COOH}\end{array} \xrightarrow[\mathrm{S}]{\mathrm{P}_2\mathrm{O}_5} \mathrm{R}-\between\between\between-\mathrm{R}_1$$

(V—VIII) (IX—XII)

$$\mathrm{R} = \mathrm{R}_1 = \mathrm{H}\ (\mathrm{I},\ \mathrm{V},\ \mathrm{IX}),\quad \mathrm{CH}_3\ (\mathrm{IV},\ \mathrm{VIII},\ \mathrm{XII});$$
$$\mathrm{R} = \mathrm{CH}_3,\ \mathrm{R}_1 = \mathrm{H}\ (\mathrm{II},\ \mathrm{VI},\ \mathrm{X});$$
$$\mathrm{R} = \mathrm{H},\ \mathrm{R}_1 = \mathrm{CH}_3\ (\mathrm{III},\ \mathrm{VII},\ \mathrm{XI})$$

## Experimental Part

***β*-Benzoyl- and *β*-*p*-toluylacrylic acids.** To a suspension of finely powdered anhydrous aluminum chloride (2 mol) in tetrachloroethane (200 ml), with gradual stirring, powdered maleic anhydride (1 mol) was added; after half an hour of stirring at room temperature, anhydrous benzene (or, respectively, toluene, 1 mol)* was added, and after half an hour the reaction mixture was decomposed by addition of dilute hydrochloric acid; the acid obtained after the usual work-up of the reaction mixture and distillation of tetrachloroethane was recrystallized from benzene.

β-Benzoylacrylic acid (yield 80%), mp 96°; β-*p*-toluylacrylic acid (yield 92%), mp 138°. Literature data, respectively: 96–97° (5), 137–138° (6).

**2-Aroyl-1,2,3,6-tetrahydrobenzoic acids (I–IV).** 4 g of β-aroylacrylic acid, 4 ml of freshly distilled diene, and 4 ml of anhydrous ethyl alcohol were heated in an autoclave for 40 hr at 100–105°; the adduct obtained after distillation of the alcohol was an oily liquid, which crystallized on addition of petroleum ether (yield 3–4 g). An additional quantity of adduct (about 1 g) was isolated from the petroleum ether solution as follows: the solution was heated with alcoholic alkali for 3 hr on a water bath, diluted with water, boiled with activated charcoal, and acidified with hydrochloric acid. The preparations of each adduct obtained in this way were combined and recrystallized from a mixture of sulfuric and petroleum ethers.

* In the case of β-benzoylacrylic acid, after addition of benzene the reaction mixture was heated for 3 hr on a water bath.

2-Benzoyl-1,2,3,6-tetrahydrobenzoic acid (I, yield 98%), mp 129-130°. 2-*p*-Toluoyl-1,2,3,6-tetrahydrobenzoic acid (III, yield 95%), mp 150-151°. 4,5-Dimethyl-2-benzoyl-1,2,3,6-tetrahydrobenzoic acid (II, yield 85%), mp 142-143°. 4,5-Dimethyl-2-*p*-toluoyl-1,2,3,6-tetrahydrobenzoic acid (IV, yield 84%), mp 166-167°.

Literature data, respectively: mp 129-130° (7), 151.5°, 143°, 167.5° (8).

**2-Benzyl-1,2,3,6-tetrahydrobenzoic acids (V-VIII)—reduction of adducts (I-IV).** To 20 g of amalgamated zinc were added 8 ml of water, 18 ml of conc. hydrochloric acid, 20 ml of toluene, and 10 g of adduct* (I-IV), and the mixture was boiled for 30-40 hr (in the case of I, 48 hr); every 6 hr, 5 ml portions of conc. hydrochloric acid were added. The aqueous layer was separated, diluted with water (20 ml), and extracted with ether. The combined ethereal and toluene extracts were washed with a small amount of water, dried over calcium chloride, and the solvents (ether and toluene) were distilled off in vacuo; the resulting 2-benzyl-1,2,3,6-tetrahydrobenzoic acids (V-VIII; yield 8-6 g, oily liquids) were introduced without further purification (since on distillation in vacuo they decompose) into reaction with phosphorus pentoxide and sulfur.

**Reaction of 2-benzyltetrahydrobenzoic acid (V) with phosphorus pentoxide.** 2 g of V and 1.25 g of phosphorus pentoxide were heated (in a Claisen flask) for 40 min on a metal bath at 140-150°, and then in vacuo, with gradual raising of the temperature to 300°, the 9,10-dihydroanthracene formed was distilled off; it was purified by boiling with a 2 *N* alkali solution and recrystallization from ethyl alcohol: yield 1 g (60%), mp 106-108° (which corresponds to the literature data (9)); identified by conversion, on heating with sulfur, into anthracene with mp 216°.

**Reaction of benzyltetrahydrobenzoic acids V-VIII with phosphorus pentoxide and sulfur. Anthracenes IX-XII.** 2-Benzyltetrahydrobenzoic acids V–VIII (5 g) were heated with an equimolecular amount of phosphorus pentoxide and sulfur on a metal bath at 140–150° for 2–3 hr, until evolution of hydrogen sulfide ceased, and then in vacuo, with gradual raising of the temperature to 300°, the reaction product was distilled off. The hydrocarbons IX–XII obtained were boiled with sodium hydroxide solution (to remove admixture of the starting acid) and recrystallized 2–3 times from ethyl alcohol.

Anthracene (IX, 1.9 g, 48%), mp 216°; a mixed-melting sample with authentic anthracene melted without depression. 2-Methylanthracene (XI, 2.3 g, 56%), mp 207°. 2,3-Dimethylanthracene (X, 2.4 g, 51%), mp 250–251°. 2,3,6-Trimethylanthracene (XII, 1.9 g, 49%), mp 249–250°.

Literature data, respectively: mp 216.4–216.7° ($^{10}$), 206–206.5°, 250.5–251°, 249–249.5° ($^{11}$).

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named after M. V. Lomonosov

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* Preliminary recrystallization of them did not increase the yield of the reduction

products—benzyltetrahydrobenzoic acids.

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*