

Liquid-phase Catalytic Oxidation of 2,5-Dimethylbiphenyl

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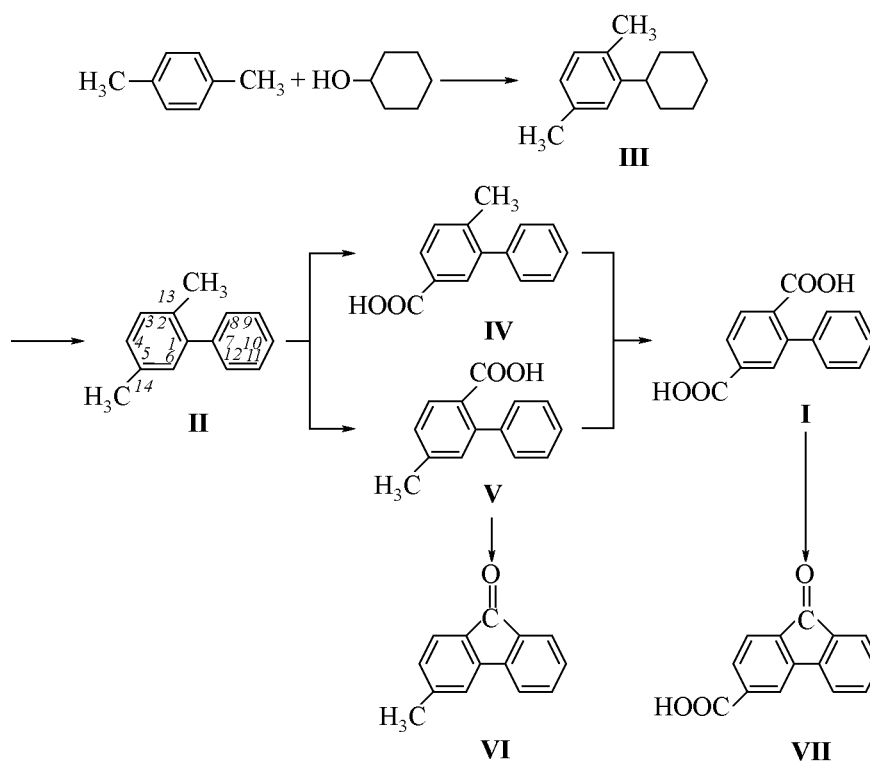
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Abstract—Liquid-phase catalytic oxidation of 2,5-dimethylbiphenyl provided 2,5-biphenyldicarboxylic acid. The effect on reaction of temperature, catalyst type, and reagents concentration was investigated.

Biphenylcarboxylic acids are promising monomers for preparation of composite and mesomorphic thermotropic materials. For instance, mesomorphic polymers based on 2,5-biphenyldicarboxylic acid (**I**) possess extremely high strength and heat resistance. At the same time they have lower (by about 100°C) melting point that is favorable for processing [1]. However acid **I** is not produced in Russia or abroad,

and all the known methods of its synthesis are multistage and reagents-consuming and afford the target product in low yield [2].

We developed a procedure for acid **I** preparation by oxidation of 2,5-dimethylbiphenyl (**II**). The latter is synthesized by alkylation of p-xylene with cyclohexanol followed by dehydrogenation of the arising 1,4-dimethyl-2-cyclohexylbenzene (**III**) [3].



The oxidation of hydrocarbon **II** was carried out at the atmospheric pressure in acetic acid in the presence of a catalytic system cobalt(II) acetate–manganese(II) acetate–sodium bromide. We established that at a high initial concentration of compound **II** ($c_0 > 1.5 \text{ mol l}^{-1}$) and at a high relative concentration in the catalytic system of promotor (NaBr) only one methyl group underwent oxidation. We isolated from the reaction mixtures compounds that by their elemental analysis, GLC, and ^1H NMR spectra corresponded to monocarboxylic acids of methylbiphenyls **IV** and **V**.

Further oxidation of separated compounds **IV** and **V** at 95°C and the following concentrations of the catalyst components: cobalt(II) acetate 0.1 mol l^{-1} , sodium bromide 0.1 mol l^{-1} , manganese(II) acetate 0.005 mol l^{-1} resulted in formation of acid **I** that was isolated from the reaction mixture and identified. Similar result was obtained at the liquid-phase oxidation of hydrocarbon **II** at its initial concentration 0.75 mol l^{-1} . Under these conditions the reaction occurs as successive oxidation of the methyl groups into carboxyls first with formation of monocarboxylic acids **IV**, **V** and then of dicarboxylic acid **I** through the corresponding intermediate methylformylbiphenyls. The presence of the latter in the reaction mixture was proved by polarographic method.

The most reactive bonds in molecule **II** are presumably C–H bonds of the methyl group in the *ortho*-position to the benzene ring caused by its $-I$ -effect $\{\sigma^+(\text{C}_5\text{H}_5)\}$ according to Taft is equal to $+0.60$ [4]. This assumption is in agreement with the accumulation of the monocarboxylic acids **IV** and **V** in the process of hydrocarbon **II** oxidation (Fig. 1).

During the investigation of hydrocarbon **II** oxidation into acid **I** we separated from the reaction mixture side oxidation products identified as 3-methyl-9-fluorenone (**VI**) and 9-fluorenone-3-carboxylic acid (**VII**), and therewith the concentration of compound **VI** in the course of the process went through a maximum. It is presumable that ketone **VI** forms from acid **V**: It is known that biphenylcarboxylic acids with a carboxy group in the *ortho*-position with respect to the second benzene ring are capable to yield fluorenones in acidic media [5]. During the reaction ketone **VI** is apparently oxidized into 9-fluorenone-3-carboxylic acid (**VII**).

We carried out a series of one-factor experiments in order to elucidate the effect on the oxidation rate of compound **II** of temperature within 80 – 105°C range, concentration of the substrate **II** in 0.1 – 1 mol l^{-1} range, and the concentrations of the cata-

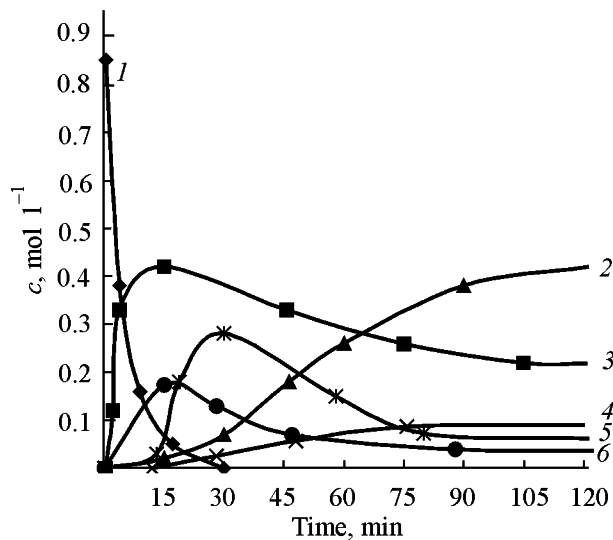


Fig. 1. Kinetic curves of compound **II** consumption and accumulation of oxidation products. (1) 2,5-dimethylbiphenyl (**II**); (2) 2,5-biphenyldicarboxylic acid (**I**); (3) 5-methyl-2-biphenylcarboxylic acid (**V**); (4) 9-fluorenone-3-carboxylic acid (**VII**); (5) 3-methyl-9-fluorenone (**VI**); (6) 2-methyl-5-biphenylcarboxylic acid (**IV**).

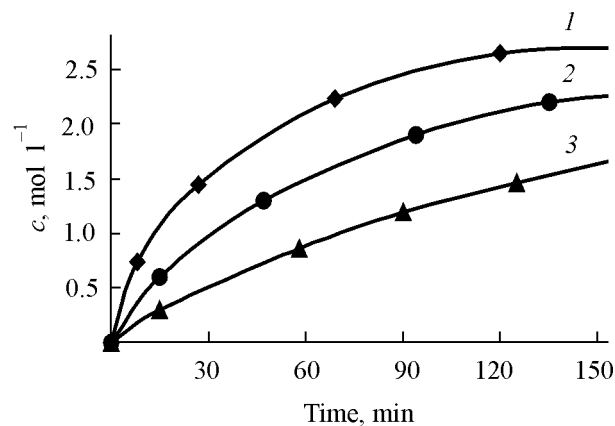


Fig. 2. Temperature effect on accumulation of 2,5-biphenyldicarboxylic acid (**I**) during the liquid-phase oxidation of 2,5-dimethylbiphenyl (**II**) ($c_{\text{II}}^0 1$, $c_{\text{Co(OAc)}_2}^0 0.05$, $c_{\text{NaBr}} 0.05$, $c_{\text{Mn(OAc)}_2}^0 0.005 \text{ mol l}^{-1}$). (1) 105°C , (2) 95°C , (3) 80°C .

lytic system components in the following intervals, mol l^{-1} : cobalt(II) acetate, 0.005 – 0.5 ; manganese(II) acetate, 0 – 0.1 ; sodium bromide, 0.01 – 0.1 . The reaction rate was measured by oxygen consumption. The kinetic curves of hydrocarbon (**II**) oxidation in the temperature range 80 – 105°C are presented in Fig. 2. It was established that within this temperature interval the reaction rate grew fivefold. From the experimental data on the initial reaction rates we determined

Effect of catalyst composition and of its amount on the yield of 2,5-biphenyldicarboxylic acid (**I**) (95°C)

Molar ratio hydrocarbon II : catalyst	Molar ratio cobalt(II)acetate: sodium bromide	Reaction time, min	Yield, %	
			acid I	acids IV, V
7.14	1	160	48	10
0.95	1	60	18	48
9.50	1	160	51	33
3.66	1	160	78	20
6.52	10	200	9	32
2.94	0.67	180	46	9
0.88	0.13	185	51	18
3.61	1	150	52	43
6.82	1.05	135	9	88
4.84	2	180	68	25
2.11	6	130	74	11

graphically the apparent activation energy of oxidation equal to 50 ± 5 kJ mol.

Note that at increased temperature the selectivity of compound **I** formation is reduced, and the reaction product contains up to 5% of acid **VII**. The latter spoils the consumers' quality of acid **I**. The best temperature for attaining relatively high reaction rate and the good quality of the target acid **I** is 95°C. The treatment of the kinetic curves obtained was carried out along the method of initial rates.

The experiments show that the conversion of hydrocarbon **II** in oxidation process reaches 100%, the selectivity depends on the ratio of the hydrocarbon and catalyst and on the ratio of the components of the catalytic system (see table).

The results of experiments evidence that the best yield of acid **I** (~80%) is obtained at oxidation of compound **II** in acetic acid in the presence of cobalt-manganese-bromide catalyst at the molar ratio cobalt and manganese acetates to sodium bromide equal to 1:1, and the molar ratio hydrocarbon to catalyst 3-4:1.

EXPERIMENTAL

IR spectra were recorded on Specord 75IR instrument from mulls in mineral oil. ^{13}C NMR spectra were registered from 10% solutions in DMSO- d_6 on spectrometer Tesla BS-567A (25.142 MHz) in Fourier-transform mode at wide-band decoupling from protons (band width 900 Hz); pulse width 8 μs , response collection time 1.069s, pulse interval 100 s, scan number 160-2200; stabilization on ^2H nuclei

from the solvent DMSO- d_6 (99% ^2H enriched); internal reference TMS.

GLC analysis was carried out on a chromatograph LKhM-8 MD equipped with a flame-ionization detector, a steel column 1000×3 mm, stationary phase 4.8% of methylvinylsilicone on Chromosorb G-AW; carrier gas nitrogen, flow rate 30 ml min^{-1} , programmed heating from 100 to 240°C at a rate 8 deg min^{-1} .

Analysis of the oxidation product for methylformyl-biphenyl content was performed with the use of polarograph LP-7 with a dropping mercury electrode relative to saturated calomel electrode. Aldehyde concentration was determined from a calibration plot measured with benzaldehyde as standard.

***p*-Xylene alkylation with cyclohexanol.** To a mixture of 234 g of *p*-xylene and 217.12 g of sulfuric acid at 5-8°C was added within 1 h 74.61 g of cyclohexanol. The reaction mixture was kept for 3 h at the same temperature. Then the hydrocarbon layer was separated and washed in succession with water, concn. aqueous alkali, and again water till pH 7. Then the solution was dried with calcium chloride, and the excess *p*-xylene was distilled off in a vacuum. We obtained 86.6 g (62%) of 1,4-dimethyl-2-cyclohexylbenzene (**III**) as a clear colorless liquid, bp 135°C (16 mm Hg), d_4^{20} 0.9375, n_D^{20} 1.5267.

Dehydrogenation of 1,4-dimethyl-2-cyclohexylbenzene (III**).** The dehydrogenation of 86.8 g of hydrocarbon **III** was performed in the presence of 43 g of palladium catalyst (Production standard TU 0-02-974-74) at 300°C for 5-6 h. On completion of

the process the catalyst was filtered off, and the filtrate distilled in a vacuum. We obtained 82.3 g (95%) of 2,5-dimethylbiphenyl (**II**) as a colorless liquid, bp 123°C (9 mm Hg), n_D^{20} 1.5790. ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 19.0 (C^{13}), 19.9 (C^{14}), 125.0–128.9 ($\text{C}^{3,4,6,8-12}$), 130.3 (C^5), 133.2 (C^2), 138.7 (C^1), 139.2 (C^7). Found, %: C 92.47, 92.66; H 8.35, 8.10. $\text{C}_{14}\text{H}_{14}$. Calculated, %: C 92.26; H 7.74.

Oxidation of 2,5-dimethylbiphenyl (II). Through a solution of 1.092 g of compound **II** in 6.93 ml of acetic acid in the presence of 199.3 mg of cobalt(II) acetate, 82.4 mg of sodium bromide, and 9.8 mg of manganese(II) acetate at 95°C was passed an oxygen flow at a rate $\sim 1.5 \text{ l h}^{-1}$ for 1–2 h. The reaction was monitored by an amount of oxygen consumed. The content in the reaction mixture of the initial hydrocarbon **II**, intermediate compounds **IV**, **V**, and the final reaction product **I** was determined by GLC. The duration of the process was 1–3 h. On completion of the reaction the mixture was cooled, the separated precipitate of acid **I** was filtered off, washed with water, and dried in air at room temperature. The yield of acid **I** was 1.089 g (75%), colorless crystals, mp 277°C. ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 125.4–129.1 ($\text{C}^{3,4,6,8-12}$), 131.1 (C^5), 135.6 (C^2), 138.9 (C^1), 139.9 (C^7), 165.7 (C^{14}), 168.1 (C^{13}). Found, %: C 69.42; H 4.16. Acid number 469. $\text{C}_{14}\text{H}_{10}\text{O}_4$. Calculated, %: C 69.30; H 4.21. Acid number 463.

Monocarboxylic methylbiphenyl acids IV, V. Through a solution of 40.95 g of compound **II** in 110 ml of acetic acid in the presence of 3.74 g of cobalt(II) acetate, 2.32 g of sodium bromide, and 18.4 mg of manganese(II) acetate at 95°C was passed an oxygen flow at a rate $\sim 1.5 \text{ l h}^{-1}$ for 4 h. On completion of the reaction the mixture was cooled, the separated precipitate of the monocarboxylic acids **IV**, **V** was filtered off, washed with water, and dried.

2-Methyl-5-biphenylcarboxylic acid (IV), colorless crystalline compound, mp 206–207°C. ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 19.7 (C^{13}), 124.6–131.5 ($\text{C}^{3,4,6,8-12}$), 139.8 (C^2), 149.2 (C^1), 141.1 (C^7), 167.0 (C^{14}). Found, %: C 79.03; H 5.81. Acid

number 262. $\text{C}_{14}\text{H}_{12}\text{O}_2$. Calculated, %: C 79.20; H 5.70. Acid number 264.

5-Methyl-2-biphenylcarboxylic acid (V), colorless crystalline compound, mp 156–157°C. ^{13}C NMR spectrum (DMSO- d_6), δ_{C} , ppm: 22.2 (C^{14}), 124.0–128.2 ($\text{C}^{3,4,6,8-12}$), 130.0 (C^2), 130.2 (C^5), 138.6 (C^1), 139.4 (C^7), 171.2 (C^{13}). Found, %: C 79.03; H 5.81. Acid number 266. $\text{C}_{14}\text{H}_{12}\text{O}_2$. Calculated, %: C 79.20; H 5.70. Acid number 264.

3-Methyl-9-fluorenone (VI). In 50 ml of concn. sulfuric acid 5 g of compound **V** was heated to 55°C at stirring for 10 min. The reaction mixture was poured on ice, the separated precipitate was filtered off, washed with water, and dried in air at room temperature. We obtained 4.65 g of compound **VI**. Yellow crystalline substance, mp 163–165°C. 165°C. IR spectrum (ν , cm^{-1}): 860 (1,2,4-substituted benzene ring), 1376 and 1465 (CH_3), 1735 ($>\text{C}=\text{O}$ in a five-membered ketone).

9-Fluorenone-3-carboxylic acid (VII). From 5 g of compound **I** along procedure similar to that of compound **VI** preparation we obtained 4.23 g of compound **VII**. Yellow crystalline substance, mp 283–284°C. IR spectrum, ν , cm^{-1} : 835 (C–H of a monosubstituted benzene ring), 860 (1,2,4-substituted benzene ring), 1590–1610 (COO^- in the spectrum of acid **VII** potassium salt), 1720 ($>\text{C}=\text{O}$ in a five-membered ketone). Found, %: C 74.89; H 3.62. $\text{C}_{14}\text{H}_9\text{O}_3$. Calculated, %: C 75.00; H 3.57.

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