On the catalyst 0.5% RhNaX + 0.25% Fe_2O_3 the maximum yield of ethyl propionate of 50%, with an C_2H_5OH conversion of 98%, was obtained at 240°. Further increase in the temperature had little effect on the yield of $C_2H_5COOC_2H_5$ and alcohol conversion. Similar results were obtained when the catalyst 1% RhNaX + 0.5% Fe_2O_3 was used, where the maximum yield of ethyl propionate of 40-44% was obtained at 260°. From Fig. 1 it can be seen that the rate of forming $C_2H_5COOC_2H_5$ increased with decrease in the concentration of rhodium in the catalyst; this increase was greater, the higher the reaction temperature.

As a result, it was shown that in the presence of RhNaX catalyst, containing 0.1-1% of Rh and promoted with 0.05-0.5% of Fe_2O_3, ethanol is carbonylated to ethyl propionate at 240-260° and atmospheric pressure. However, due to the progress of the side reaction of C_2H_5OH dehydration to C_2H_4 the yield of $C_2H_5COOC_2H_5$ does not exceed 44-50%, with an alcohol conversion of 97-100%.

EXPERIMENTAL

The apparatus and experimental procedure are the same as described previously [1-3]. The catalysts were prepared as described in [3]. The liquid reaction products were analyzed by GLC on an LKhM-8MD chromatograph using a 3 m × 3 mm column packed with 10% polyethylene glycol 400 deposited on Celite-545 (30-60 mesh). The carrier gas was helium, and the flow rate was 40 ml/min.

CONCLUSIONS

By using as the catalyst the Rh form of type-X zeolite, promoted with Fe_2O_3, we were able to synthesize ethyl propionate in 44-50% yield by the carbonylation of EtOH with CO at 240-260° and atmospheric pressure.

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REACTION OF PHENYLPHOSPHINE WITH p-QUINONES

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UDC 542.91:547-1'118:547.567

This reaction was already studied on the example of secondary phosphines [1]. For primary phosphines of type $ArPH_2$, due to the slight increase in the nucleophilicity, a nearly complete retention of the basic features of the reaction of p-quinones with secondary phosphines was expected. However, instead of the expected addition products, compounds devoid of phosphorus are formed when phenylphosphine is reacted with brom- and chloranils, duroquinone, and p-benzoquinone. The elemental analysis data and IR spectra of these compounds indicate that they are the corresponding hydroquinones, which was confirmed by comparing the constants of the obtained compounds with those of the authentic compounds. Besides hydroquinones, an organophosphorus compound is formed in all of the reactions, which has a ^{31}P NMR spectrum (δ + 68 ppm, J_{PH} = 217 Hz) that resembles that of diphenyldiphosphine [2]. Due to the great tendency of this phosphine to be oxidized by atmospheric oxygen it was identified as phenylphosphonic acid and phenyldimethylphosphonium iodide (product of treating with CH_3I).

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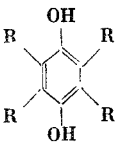
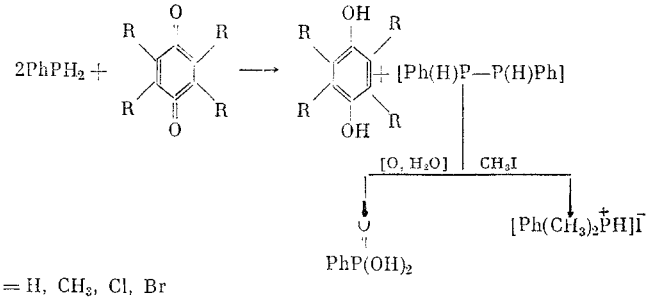
TABLE 1. Hydroquinones



R	Yield, %	mp, °C (solvent)	Found/calculated, %			Empirical formula	Infrared spectrum (ν_{OH}, cm^{-1})
			C	H	Hal		
H	73	170 [3] (ethanol–benzene)	65,48 / 65,45	5,61 / 5,45	–	$C_6H_6O_2$	3435
CH_3	87	232 [4] (acetonitrile–benzene)	72,19 / 72,29	8,45 / 8,43	–	$C_{10}H_{14}O_2$	3440
Cl	94	231 [5] (acetonitrile–benzene)	29,12 / 29,03	0,83 / 0,81	57,10 / 57,25	$C_6H_2Cl_4O_2$	3410
Br	92	246 [6] (acetonitrile–benzene)	16,88 / 16,90	0,49 / 0,47	75,18 / 75,12	$C_6H_2Br_4O_2$	3420



R = H, CH_3, Cl, Br

The formation of diphenyldiphosphine was observed previously in the reaction of phenylphosphine with tetraphenylcyclone [2].

EXPERIMENTAL

The reactions were run in an argon atmosphere in anhydrous solvents. The IR spectra were taken on a UR-20 spectrophotometer as Nujol mulls. The ^{31}P NMR spectra were recorded on a nonserial KGU-4 instrument (operating frequency 10.2 MHz, and 85% H_3PO_4 as the external standard).

Reaction of Phenylphosphine with Bromanil. To a solution of 4.24 g (0.01 mole) of bromanil in 50 ml of benzene at ~20°C was added a solution of 2.2 g (0.02 mole) of $PhPH_2$ in 20 ml of benzene. The reaction mixture was kept at ~20° for a day. Then a part of the solvent was removed in vacuo. The obtained crystals were filtered, washed with ether, and recrystallized from a 1:1 acetonitrile–benzene mixture to give 3.92 g (92%) of tetrabromohydroquinone.

The other reactions were run in a similar manner. The physical constants, IR spectra, and elemental analysis data are given in Table 1.

Preparation of Phenyldimethylphosphonium Iodide. A fivefold excess of MeI was added to the filtrate of the above-described reaction. The reaction mixture was heated for 1 h at 40-45°, cooled, a part of the solvent was removed in vacuo, and the obtained crystals were filtered, washed with ether, and recrystallized from a 1:1 methanol–ether mixture to give 0.89 g (40.5%) of phenyldimethylphosphonium iodide, mp 192°. Found: C 36.42; H 4.72; P 11.86%. $C_8H_{12}PI$. Calculated: C 36.09; H 4.51; P 11.65%. ^{31}P NMR spectrum (δ, ppm): −2.5 (ethanol), J^1_{PH} = 502 Hz.

Preparation of Phenylphosphonic Acid. The residual filtrate from the above-described reaction was kept for 2 h in the air and then most of the solvent was removed. The obtained crystals were filtered and recrystallized from benzene to give 1.98 g (62%) of phenylphosphonic acid, mp 162°(C_6H_6), cf. [7]. ^{31}P NMR spectrum (δ, ppm): −19 (acetonitrile), cf. [7].

CONCLUSIONS

The reaction of phenylphosphine with p-quinones gives the corresponding hydroquinones and diphenyldiphosphine.

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REACTIONS OF 2,6-DI-tert-BUTYLMETHYLENEQUINONE

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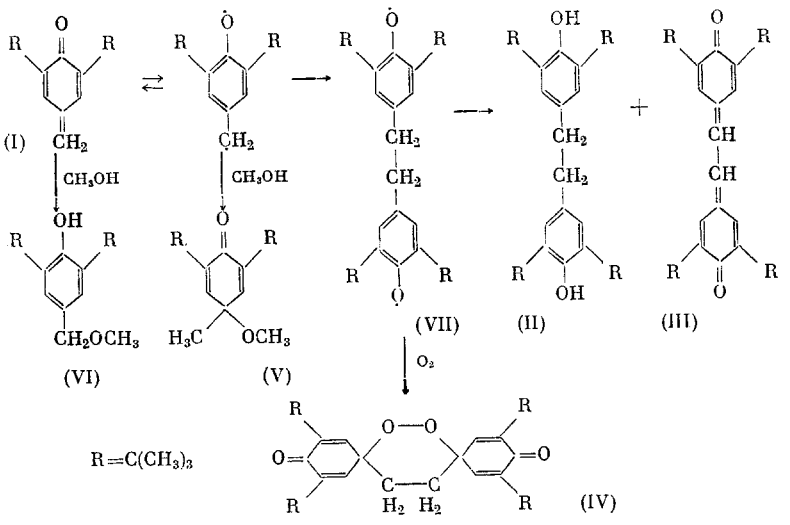
2,6-Di-tert-butylmethylenequinone (I) is the least stable of the sterically hindered methylenequinones, and the data on its properties are contradictory [1-4]. This circumstance is primarily related to the exceedingly easy transition of methylenequinone (I) to the biradical state, in view of which it can react either as a biradical or as a ketone vinylog.

Methylenequinone (I) in a benzene–methanol mixture, in the air, at 20°C, reacts predominantly to give 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxyphenylethane (II), 3,3',5,5'-tetra-tert-butylstilbenequinone (III), 6,8,11,13-tetra-tert-butylbisspiro[5.4.5]-1,2-peroxy-5,8,10,13-hexadecatetraene-7,12-dione (peroxide of the quinolide type) (IV), 4-methoxy-4-methyl-2,6-di-tert-butyl-2,5-cyclohexadien-1-one (V), and methyl (4-hydroxy-3,5-di-tert-butyl)benzyl ether (VI). The formation of quinol ether (V) is due to the unusual addition of the reactant to the double bond. Here (I) apparently reacts with CH_3OH as the biradical. The typical direction of the reaction of CH_3OH with methylenequinone (I) and its analogs [5] is 1,6-addition, which in the case of (I) leads to ether (VI). Ether (VI) is not formed when the studied reaction is run at 40°, but the yield of quinol ether (V) increases here.

The formation of dihydroxydiphenylethane (II), stilbenequinone (III), and peroxide (IV) is due to the transformations of the biradical methylenequinone (I). The bisphenoxyl radical (VII) is formed in the first step, which, depending on the concentration, either disproportionates to dihydroxydiphenylethane (II) and stilbenequinone (III) or reacts with oxygen.



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