REACTION OF o-BENZOQUINONES WITH BENZYLIDENETRIPHENYLPHOSPHORANE UNDER THE CONDITIONS OF THE COMMON EFFECT OF HIGH PRESSURE AND SHEAR DEFORMATION

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It was shown that the effect of high pressure (HP) and shear deformation (SD) causes the rates of reactions to increase substantially. In certain cases it was established that, depending on the pressure, the direction of the chemical transformations can change [1]. The effect of HP + SD causes an efficient mixing of the reactants [2, 3], which eliminates the need of using a solvent and permits observing processes that are not complicated by the effect of the medium.

One of the more interesting aspects of studying organic chemical transformations under HP + SD conditions is a study of the steric effects, which can be especially manifested in the reactions of sterically hindered compounds. In view of this it seems of interest to study under HP + SD conditions the behavior of sterically hindered hydroxyaromatic compounds, and specifically phenols and pyrocatechols and their derivatives, the quinones, quinomethides, etc. These compounds possess a complex of practically valuable properties and are widely used in the national economy.

The reaction of the isomeric 3,5-(I) and 3,6-di-tert-butyl-o-benzoquinones (II) with benzylidenetriphenylphosphorane (III) under HP + SD conditions was studied in the present paper.

EXPERIMENTAL

The work was carried out on a forged apparatus of the Bridgman type at a pressure of 2000 MPa and ∿20°C. The reaction products were analyzed by TLC on Silufol UV-254 employing standardization. Products (VI)-(VIII) were isolated by preparative TLC.

Compound (VI), 77% yield, mp 112°, corresponds to the data of [4], and does not depress the mixed melting point with an authentic sample.

Compound (VII), 70% yield, mp 91°. Found: C 81.20; H 8.42%. $C_{21}H_{26}O_2$. Calculated: C 81.29; H 8.38%.

Compound (VIII), 93% yield, mp 123°, and does not depress the mixed melting point with a sample that was obtained by reacting (II) with triphenylphosphine in acetone. Found: C 80.24; H 6.48%. $C_{32}H_{35}O_2P$. Calculated: C 80.63; H 6.89%.

Ylide (III) was generated in situ by the action of HP + SD on a three-component mixture of reactants composed of either quinone (I) or (II), benzyltriphenylphosphonium chloride (IV), and NaOH in ratios of 1:1:1 and 1:2:2. The obtained results were compared with the data for ylide reactions of (I) and (II) with (III) under atmospheric conditions in a two-phase catalytic system [4], according to which the behavior of the isomeric quinones toward the ylide differs and depends on the steric situation of the quinone carbonyl groups: Quinone (I) enters into the Wittig reaction at the open carbonyl group to give the corresponding o-quinomethide, the reaction of which with a second equivalent of the ylide leads to the substituted dihydrobenzofuran (V).

In the case of (II) the shielding of both carbonyl groups by the tert-butyl substituents suppresses the Wittig reaction. The reaction product of (II) with the ylide is the cyclic ether (VI).

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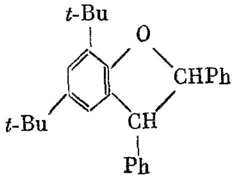
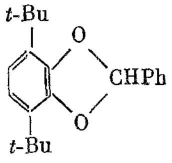
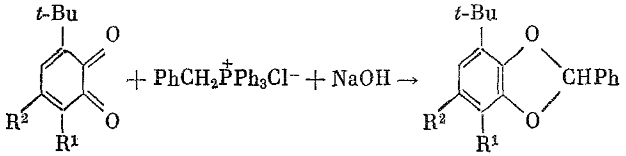

(V)


(VI)

Compounds (V) and (VI) were used as standards in the present study.

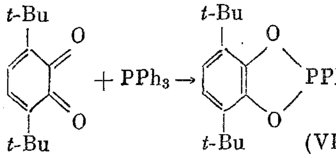
DISCUSSION OF RESULTS

Under HP + SD conditions the effect of the character of the substitution in the quinone is counterbalanced and, independent of the structure of the starting quinone, the reaction with ylide (III) gives cyclic ethers (VI) and (VII), respectively.


(I), (II) (VI), (VII)

$R^1 = H$, $R^2 = t\text{-Bu}$(I); $R^1 = t\text{-Bu}$, $R^2 = H$(II); $R^1 = t\text{-Bu}$, $R^2 = H$(VII); $R^1 = H$, $R^2 = t\text{-Bu}$(VI).

The structural identity of the formed products testifies to a change in the mechanism of the ylide reactions of (I) and (II) under HP + SD conditions and the realization of a single reaction path under these conditions. On the example of quinone (II), together with cyclic ether (VI), the formation of a certain amount of phosphorane (VIII) was observed, apparently via the successive reaction of quinone (II) with the triphenylphosphine liberated in the first step. This supposition was confirmed by the independent reaction of (II) with Ph_3P, which leads to phosphorane (VIII) in quantitative yield.


(VIII)

One of the possible effects of HP + SD is the formation and subsequent transformation of the excited states of the reactants, which is related to a change in their electronic structure [5]. The C—P bond in the ylide can be especially sensitive to a change in the pressure, since a possible decrease in the diffusivity of the d orbitals of P with increase in the pressure improves the conditions for overlap with the p orbital of the adjacent C atom [6]. Within the framework of the concepts of the resonance theory this can be reflected by an increase in the contribution of the canonical structures (IX) and (X) to the resonance hybrid.

$$Ph\bar{C}H{-}\overset{+}{P}Ph_3 \leftrightarrow \underset{(IX)}{PhCH{=}PPh_3} \leftrightarrow \underset{(X)}{Ph\ddot{C}H :: PPh_3}$$

The carbenoid character of (X) apparently determines the reactivity of the ylide under the discussed conditions. Indirect proof for the carbenoid mechanism of the ylide reaction of (I) and (II) under HP + SD conditions is the fact that cyclic ethers of the (VI) type are the usual reaction products of o-quinones with the donors of carbenes [7]. Taking into account the nature of the reactants, and also the increasing role of donor-acceptor interactions with increase in the pressure [8], it is possible to consider two alternate mechanistic schemes for the formation of (VI) and (VII). Scheme A* corresponds to a coordinated cheletropic process, while scheme B* includes the formation of a bipolar intermediate. The scheme for the formation of (VIII) is apparently analogous to scheme A, with the involvement of triphenylphosphine as the cheletropic component.

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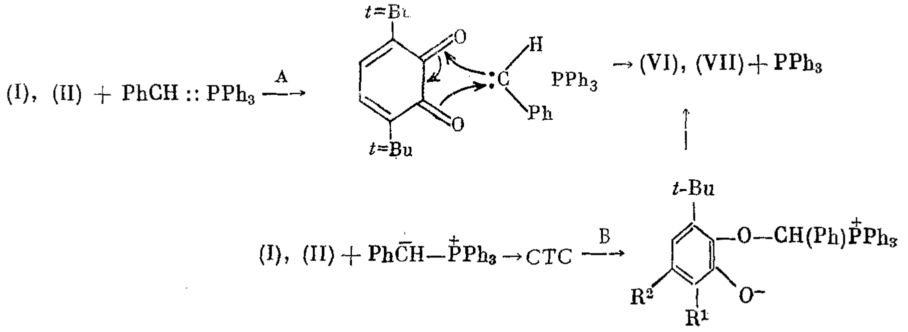

CONCLUSIONS

When the isomeric 3,5- and 3,6-di-tert-butyl-o-benzoquinones are reacted with benzylidenetriphenylphosphorane under the combined effect of high pressure and shear deformation the benzylidene ethers of the corresponding pyrocatechol are formed, in contrast to the analogous reactions of the indicated o-quinones in a two-phase catalytic system at atmospheric pressure. The observed change in the composition of the transformation products is related to a change in the electron distribution of the C—P bond of the ylide under the effect of HP + SD.

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