

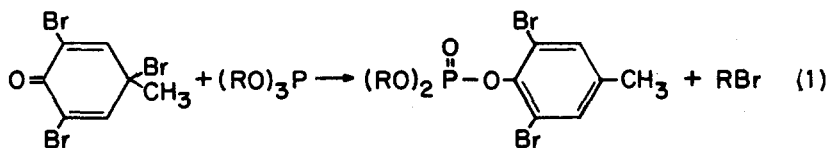
ALKYLATION OF A HINDERED PHENOXIDE ION BY BROMOPHOSPHONIUM IONS<sup>1</sup>

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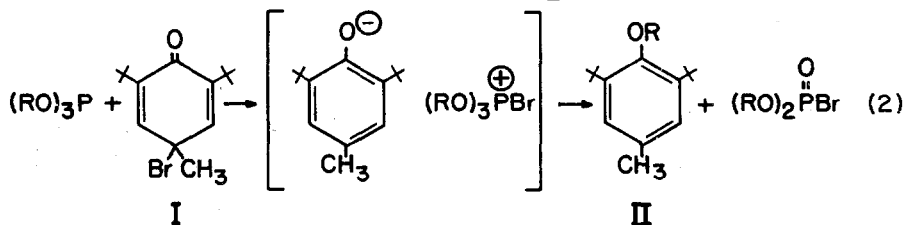
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It was previously reported that trialkyl phosphites react with 4-bromocyclohexadienones to give high yields of dialkyl aryl phosphates (eq. 1)<sup>2,3</sup>.



It was suggested<sup>3</sup> that the reaction proceeds by initial attack of the phosphorus atom at the "positive" bromine atom of the dienone. The possibility of direct attack by the phosphite upon the carbonyl oxygen could not, however, be completely discounted.

To obtain further information about this point, the reactions of phosphites with 2,6-di-*t*-butyl-4-bromo-4-methylcyclohexadienone (I) have now been examined, since the presence of the two *t*-butyl groups should



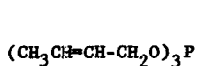
markedly decrease the rate of any reaction at the carbonyl group.

Trimethyl and triethyl phosphite reacted rapidly with I in benzene, ether, or methylene chloride solutions to give the corresponding ethers (II) in 70-80% yield. The reaction of I with trimethyl phosphite gave,

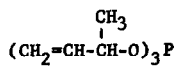
in addition, dimethyl phosphorobromidate, which was identified as its anilide<sup>4</sup>.

The isolation of ethers and phosphorobromidates from these reactions clearly demonstrates that the phosphites attack the bromine atom, rather than the oxygen atom, of I, as is shown in equation (2). The assumption that reaction (1) also proceeds by attack at the allylic bromine is supported by the observation that reaction (1) proceeds only slightly more rapidly than reaction (2). The small difference can readily be accounted for by the expected inductive effects of the substituents on the reaction rates. If reactions (1) and (2) proceed by completely different mechanisms, a greater difference in reaction rates might be expected.

Phosphites of allylic alcohols gave more complex reactions with I than did simple trialkyl phosphites. Reaction of I with triallyl phosphite or tri-3-methylallyl phosphite (III) gave approximately equal

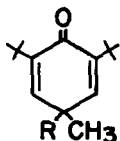


III

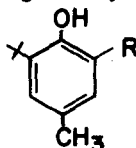


IV

amounts of ethers (II, R = CH<sub>2</sub>-CH=CH<sub>2</sub> and R = CH<sub>2</sub>-CH=CHCH<sub>3</sub>) and of cyclohexadienones (Va and Vb). Unexpectedly, somewhat greater yields of

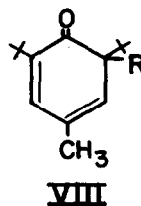
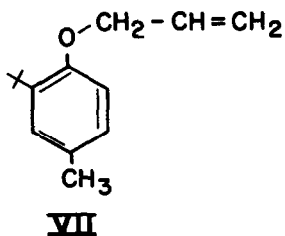


V a, R = CH<sub>2</sub>-CH=CH<sub>2</sub>  
b, R = CH<sub>2</sub>-CH=CH-CH<sub>3</sub>



VI a, R = CH<sub>2</sub>-CH=CH<sub>2</sub>  
b, R = CH<sub>2</sub>-CH=CH-CH<sub>3</sub>

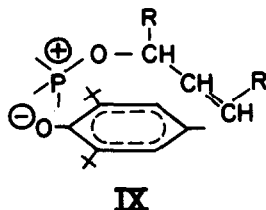
phenols VIa and VIb were also obtained. The structures of the phenols were assigned on the basis of their elementary analyses and IR and NMR spectra, and the structure of VIa was confirmed by its synthesis by a Claisen rearrangement of the allyl ether VII.



VIIa and VIIb are undoubtedly formed from the *o*-cyclohexadienone VIII. Such cyclohexadienones have been found to lose *t*-butyl groups under very mild conditions<sup>5</sup>.

Reaction of tri-*l*-methylallyl phosphite (IV) with I did not give any ortho-alkylated products similar to VI. An ether and a ketone were obtained in the ratio of 1:3. While the NMR of the ether showed that it had the expected structure II ( $R = \text{CH}_3\text{CH}-\text{CH}=\text{CH}_2$ ), the ketone had the same structure (Vb) as that obtained from reaction of I with III.

Formation of the ketone with allylic rearrangement and of the ether with retention of the *l*-methylallyl system may be ascribed to the orientation of the components of the ion-pair prior to alkylation of the phenoxide ion. Location of the positively charged phosphorus atom close to the oxygen atom of the phenoxide ion (structure IX) will place the para-position of the aromatic ring roughly equidistant from the  $\alpha$  and  $\gamma$  carbons of the allylic chain. The location of substituents on the chain



should therefore determine whether reaction of the para-position will proceed by an  $\text{S}_{\text{N}}2$  or an  $\text{S}_{\text{N}}2'$  reaction. The oxygen atom (or the ortho-carbon atoms), however, can react only at the  $\alpha$ -carbons.

Alternative explanations (such as formation of allylic isomers from free carbonium ions) appear to require *ad hoc* hypotheses to account for the various results.

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