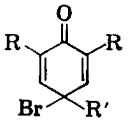
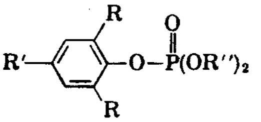
The Reactions of 4-Bromocyclohexadienones with Esters of Phosphorous Acids

Sir:

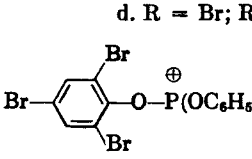
The reactions of quinones[1] and α-halocarbonyl compounds[2] with esters of phosphorous acid have recently attracted appreciable interest. We now wish to report that certain features of these two types of reactions have been combined to afford a novel synthetic route to the biologically active dialkyl aryl phosphates.

Dialkyl phosphonates react with 2,4,6-tribromo, 4-methyl-cyclohexadienone (Ia) in a manner similar to other reducing agents,[3] giving 2,6-dibromo, 4-methylphenol in high yield.





Ia. R = Br; R′ = CH_3 II a. R = Br; R′ = CH_3; R″ = Me
b. R = Cl; R′ = CH_3 b. R = Cl; R′ = CH_3; R″ = Et
c. R = R′ = Br c. R = R′ = Br; R″ = Et
d. R = Br; R′ = CH_3; R″ = Et



III

Trialkyl phosphites, however, react with Ia–c in benzene solution to give the dialkyl aryl phosphates IIa–d in quantitative yields. The reactions at room temperatures are apparently instantaneous, as judged by the disappearance of the yellow cyclohexadienone colors. Evaporation of the solvent leaves IIa–d in essentially pure states, as determined by comparisons of their vapor phase chromatograms with those of distilled products.

The structure of IId was confirmed by comparison of its infrared spectrum with that of a sample prepared by condensation of dry sodium 2,6-dibromo, 4-methyl phenoxide with *O,O*-diethylphosphorochloridate.

In contrast to the very rapid reactions of the 4-bromocyclohexadienones, neither 4-phenylamino, 2,6-dibromo, 4-methylcyclohexadienone nor 2,4,6-trimethyl, 6-acetoxy cyclohexadienone would react with trimethyl phosphite even on prolonged refluxing in benzene.

Triphenyl phosphite reacts with Ic to give the tetraäryloxy phosphonium salt III as a white, intensely hygroscopic solid which reacts rapidly with water or alcohols to give 2,4,6-tribromophenol and triphenyl phosphate.

Theoretical elementary analyses were obtained for all new compounds.

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(1) (a) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, 78, 5614 (1956). (b) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, 22, 857 (1957). (c) F. Ramirez and S. Dershowitz, 22, 1282 (1957). (d) F. Ramirez, E. Chen, and S. Dershowitz, *J. Am. Chem. Soc.*, 81, 4338 (1959). (e) B. A. Arbuzov, N. A. Polezhaeva, and V. S. Vinogradova, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk.*, No. 7, 1219 (1960).

(2) See B. A. Arbuzov, V. S. Vinogradova, and M. A. Zvereva, *Izvest. Akad. Nauk S.S.S.R. Otdel Khim. Nauk.*, No. 10, 1772 (1960), for leading references.

(3) K. Fries and G. Oehmke, *Ann.*, **462,** 1 (1928).

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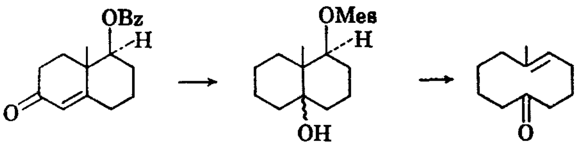
Stereospecific Synthesis of 6-Methyl-*trans*-5-cyclodecenone

Sir:

We wish to report the preparation of 6-methyl-*trans*-5-cyclodecenone (III) by a sequence of reactions which exemplifies an effective approach, of wide applicability, to the synthesis of various polyfunctional medium-sized carbocyclic ring systems of interest.[1] The key reaction of the sequence is the facile fragmentation of the 1,3-diol monomesylate II. Concomitantly, the ten-membered ring



I II III

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(1) The simplest systems, the *cis*- and *trans*-5-cyclodecenones and the corresponding alcohols have been synthesized and studied. See H. L. Goering and W. D. Closson, *J. Am. Chem. Soc.*, **83,** 3511 (1961), and ref. 9. See also D. J. Cram and L. K. Gaston, *J. Am. Chem. Soc.*, **82,** 6386 (1960). The more complex systems belong to a subgroup of the sesquiterpenes which continues to grow in number at a rapid rate. For leading references see the following: J. P. deVilliers, *J. Chem. Soc.*, 2049 (1961); J. Hochmannova, V. Herout, and F. Šorn, *Coll. Czech. Chem. Comm.*, **26,** 1826 (1961); M. Suchý, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, **26,** 1358 (1961); M. Souček, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, **26,** 803 (1961); D. H. R. Barton, O. C. Böckman, and P. de Mayo, *J. Chem. Soc.*, 2263 (1960); M. Suchý, V. Benešová, V. Herout, and F. Šorm, *Ber*, **93,** 2449 (1960); M. Suchý, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, **24,** 1542 (1959); S. C. Bhattacharyya, G. R. Kelkar, and A. S. Rao, *Chem. & Ind.*, 1069 (1959); V. Herout and F. Šorm, *Chem. & Ind.*, 1067 (1959); S. Dev, *Tetrahedron*, **9,** 1 (1960); S. Dev, *Chem. & Ind.*, **8,** 171 (1960); M. Holub, V. Herout, M. Horák, and F Šorm, *Coll. Czech. Chem. Comm.*, **24,** 3730 (1959). For a summary of the above, see F. Šorm, *Pure and Applied Chem.*, **2,** 533 (1961).