

Formation of a Semibenzene from Reaction of a 4-Trichloromethylcyclohexadienone
with Sodium Diethyl Phosphonate¹

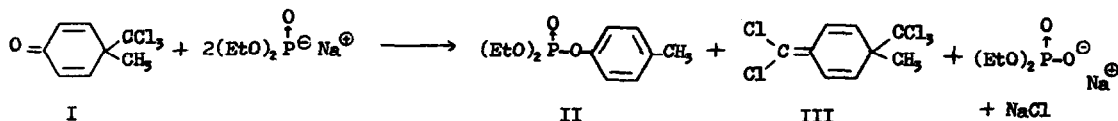
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Phosphines and aminophosphines react with 4-trihalomethylcyclohexadienones by nucleophilic attack at halogen atoms, giving the dihalomethyl derivatives.² In contrast, triethyl phosphite reacts very slowly with 4-methyl-4-tribromomethylcyclohexa-2,5-dien-1-one at 110° to form diethyl p-tolyl phosphate.³ Trialkyl phosphites do not react with 4-trichloromethylcyclohexadienones at all, even after prolonged heating at 150°.³

In view of the marked differences between the reactions of these dienones with oxygenated trivalent phosphorus derivatives and with phosphorus derivatives bearing alkyl and amino groups, I considered it of interest to examine the reactions of 4-trihalomethylcyclohexadienones with oxygenated phosphorus derivatives which would approximate the reactivity of phosphines and aminophosphines more closely than do trialkyl phosphites.

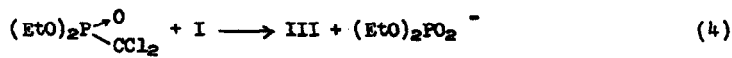
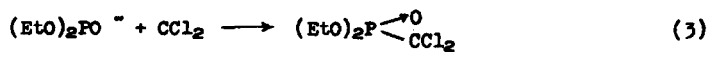
Reaction of one equivalent of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one (I) with sodium diethyl phosphonate in benzene gave a mixture of recovered I, diethyl p-tolyl phosphate (II) and a new compound, m.p. 91.5-92.5°, assigned the structure 1-dichloromethylene-4-methyl-4-trichloromethylcyclohexa-2,5-diene (III). Reaction of I with two equivalents of sodium diethyl



phosphonate resulted in complete disappearance of I and formation of II and III in 84% and 40% yield (based on the stoichiometry shown in the equation above) respectively. In contrast to the lack of reactivity of I with trialkyl phosphites, reaction of I with sodium diethyl phosphonate was highly exothermic, and appeared to be complete within a few seconds at 5°.

The structure of III was determined by its elemental analysis, which corresponded to the molecular formula C₉H₇Cl₅ (Found: C, 37.4; H, 1.78; Cl, 61.0), and its nmr spectrum (CCl₄ solution), which showed a singlet (3H) at δ 1.58 and doublets (2H each, J = 10.5 Hz) at δ 6.36 and δ 6.97. III showed unusual stability for a 4-trichloromethyl "semibenzene".⁴ It could be recovered unchanged after being held above its melting point for one hour, and showed no change after storage for nearly a year at room temperature. In contrast, other 4-trichloromethylsemi-

benzenes undergo 1,5 migration of the trichloromethyl group to give 2-aryl-1,1,1-trichloroethanes when heated slightly above room temperature.⁴ The stability of III is presumably due to the steric and polar effects of the vinyl chlorine atoms in inhibiting addition of a trichloromethyl radical⁵ to the exocyclic vinyl position. Formation of III can be accounted for by the reaction sequence shown below:



Two basic mechanisms could account for formation of II and a trichloromethyl anion in step (1) above: either the phosphonate anion could react directly with the carbonyl oxygen atom (either by nucleophilic attack or by electron transfer followed by radical combination) or the phosphonate anion could add to the carbonyl carbon, and then migrate to the oxygen atom. As yet, no decision can be made between these two possible paths.

References

- 1) Reactions of Cyclohexadienones, XXIX.
- 2) B. Miller, J. Am. Chem. Soc., 91, 751 (1969).
- 3) B. Miller, ibid., 88, 1841 (1966)
- 4) K. v. Auwers and W. Juehlicher, Chem. Ber., 55, 2167 (1922).
- 5) For evidence that the von Auwers rearrangement proceeds by a radical chain process, see M.S. Newman and R.M. Layton, J. Org. Chem., 33, 2338 (1968); also, H. Hart and J.D. DeVrieze, Tetrahedron Letters, 4259 (1968); B. Miller and K.-H. Lai, ibid., 1617 (1971).