

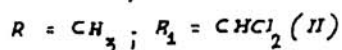
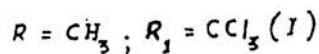
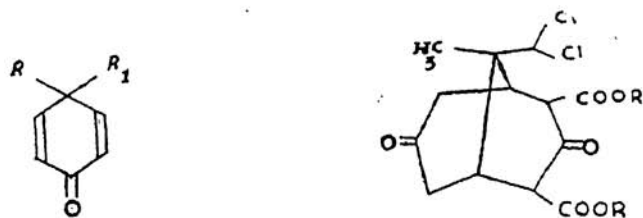
**AN INTERESTING OBSERVATION
ON THE REACTION OF
4-ALKYL-4 DICHLOROMETHYL-2,
5-CYCLOHEXADIENONE
WITH SODIUM ALKOXIDES**

DURING the course of our work¹ on 4-alkyl-4-trihaloalkyl-2, 5-cyclohexadienones, we investigated the reactions of 4-methyl-4-trichloromethyl (I) and 4-methyl-4-dichloromethyl (II) 2, 5-cyclohexadienones with acetone dicarboxylic ester in the presence of sodium alkoxides. Whilst the former dienone fails to react and is recovered unchanged, the latter has been reported by Stetter and Mayer² to yield the compound III.

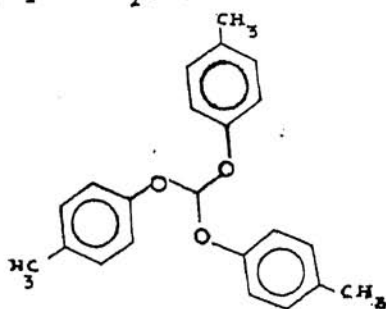
In our hands, however, instead of III, we obtained a neutral halogen free colourless crystalline compound, m.p. 109-110° (Found: C, 79.1; H 6.5%). In its mass spectrum, the molecular ion peak was obtained at 334, showing the compound to have the molecular

formula $C_{22}H_{22}O_3$. Its i.r. spectrum (KBr) showed bands at 1212, 1089 cm^{-1} (aryl ether), 1611, 1587, 1508 cm^{-1} (aromatic), 1381 cm^{-1} (methyl) and 815 cm^{-1} (*p*-disubstituted benzene). No band corresponding to ketone or ester carbonyl was observed. The n.m.r. spectrum ($CDCl_3$) showed signals δ 2.35 (9 H, s), δ 6.5 (1 H, s) and around 7.2 δ (12 H, m). In the mass spectrum, other peaks were observed at m/e 227 ($M - p\text{-Me-C}_6\text{H}_4 - \frac{1}{2}$), m/e 107 ($p\text{-CH}_3\text{-C}_6\text{H}_4 - \frac{1}{2}$) and at m/e 91 ($C_6H_5 - CH_2^+$).

Upon the basis of the analytical and spectral data the above compound was assigned the structure as an ortho ester IV.



III



IV

The above structure is consistent with the observation that II reacts with sodium alkoxides alone in alcohol solution to give IV. Further, the acid hydrolysis of IV affords *p*-cresol as would be expected.

The formation of a stable orthoester from II constitutes an interesting reaction of these types of compounds, and 4-ethyl-4-dichloromethyl-2,5-cyclohexadienone is also found to give an orthoester, m.p. 54–55°.

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1. Merchant, J. R. and Desai, V. B., *J. Chem. Soc.*, 1964, p. 2258; 1968, C, 499.
2. Stetter, H. and Mayer, J., *Chem. Ber.*, 1959, 92, 2664.