SOME REACTIONS OF ALKYL 2-PHENOXYVINYL KETONES

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Alkyl 2-phenoxyvinyl ketones, which were prepared recently in our laboratory by the reaction of alkyl 2-chlorovinyl ketones with phenols [1], have received very little study. The readiness with which the phenoxy group undergoes exchange reactions is of interest: it is eliminated in treatments with acidic reagents and also in the formation of heterocyclic systems from 2-phenoxyvinyl ketones [1]. Apart from these reactions we have studied a peculiar rearrangement of 2-phenoxyvinyl ketones into pyrylium salts which is reminiscent of the Fries rearrangement [2].

The present paper is devoted to the further investigation of the chemical behavior of alkyl 2-phenoxyvinyl ketones. It was considered to be of interest to compare the reactivity of these substances with that of 2-dialkylaminovinyl ketones, which have been recently studied by one of us [3], and also with that of 2-chlorovinyl ketones. It would be expected that, with respect to the activity of the double bond and carbonyl group, 2-phenoxyvinyl ketones would occupy an intermediate position between these other two classes of compound. The conjugation of the free electron pair of the hetero-atom with the double bond and the carbonyl group, to which the deactivation found in aminovinyl ketones is to be attributed [3], will obviously be less effective when nitrogen is replaced by the oxygen of the phenoxy group, though in the phenoxyvinyl ketones this conjugation must be more marked than in 2-chlorovinyl ketones. These considerations lead us to suppose that in 2-phenoxyvinyl ketones the carbonyl group and, particularly, the double bond will be less reactive than in 2-chlorovinyl ketones, though this deactivation will not be as great as in 2-dialkylaminovinyl ketones. Our results confirm this view.

We first examined the catalytic hydrogenation of alkyl 2-phenoxyvinyl ketones at room temperature and normal pressure with the object of comparing them with 2-aminovinyl ketones, which are unable to undergo normal hydrogenation [3]. It was found that the hydrogenation of alkyl 2-phenoxyvinyl ketones (the methyl and propyl ketones were used) takes different courses according to which catalyst is used. Over palladium precipitated on barium sulfate the reaction goes normally, and the corresponding alkyl 2-phenoxyethyl ketones are formed in high yield, although it must be pointed out that the process is very slow, the hydrogenation of even very small amounts being complete only after 6-7 hours. On the other hand, hydrogenation over an Adams platinum catalyst does not give the expected reaction product. Instead, hydrogenolysis of the oxygen-carbon bond occurs, and only phenol and the corresponding saturated ketone can be isolated from the reaction mixture:

\[
\begin{align*}
R=CH_2CH_2O \rightarrow R=CH_2CH_2OH
\end{align*}
\]

The hydrogenation of alkyl 2-phenoxyvinyl ketones is, therefore, an example of a reaction in which catalysts as similar in character as platinum and palladium give completely different results. The observed behavior shows also that in alkyl 2-phenoxyvinyl ketones the double bond is indeed deactivated (slow hydrogenation over palladium: hydrogenolysis over platinum). This deactivation, however, is not as great as that found in 2-aminovinyl ketones, since the latter, unlike the phenoxy compounds, are unable to undergo normal hydrogenation.

From this point of view the observed behavior of alkyl 2-phenoxyvinyl ketones in a diene-synthesis reaction is particularly characteristic. It is known that 2-chlorovinyl ketones are active dienophiles [4, 5], whereas, owing to the complete deactivation of the double bond, 2-dialkylaminovinyl ketones do not condense with dienes [3]. It was found that neither at room temperature nor at 100° for several hours will methyl or propyl 2-phenoxyvinyl ketone condense with cyclopentadiene, which was selected as one of the most active dienes. This behavior sharply differentiates 2-phenoxyvinyl ketones from 2-chlorovinyl ketones, which react already in the cold with cyclopentadiene [4], forming adducts in high yield. However, under very vigorous conditions (145-155° for 15-16 hours) normal diene condensation occurs with formation of the corresponding phenoxy derivatives of bicyclo[2.2.1]hept-2-ene.
It must be pointed out, however, that under the severe conditions the condensation products are formed in moderate yields (30-50%). The structures of the resulting compounds were confirmed by tests for the double bond and the carbonyl group (formation of a dimethylphenylhydrazone) and by a positive iodoform test.

A confirmatory synthesis was carried out for 5-acetyl-6-phenoxybicyclo[2.2.1]hept-2-ene (methyl 3-phenoxybicyclo[2.2.1]hept-5-en-2-yl ketone), the starting point being 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene, which has been prepared previously [4]. As one of us and Karpinsky [6] have shown, the chlorine atom of this compound can readily be replaced by other nucleophilic groups. We found that treatment of 5-acetyl-6-chlorobicyclo[2.2.1]hept-2-ene with sodium phenoxide in molten phenol or with phenol in an aqueous medium gave a phenoxy derivative in high yield, and the product was found to be identical with the substance obtained by the direct condensation of cyclopentadiene and methyl 2-phenoxyvinyl ketone:

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\text{CH}_3 + \text{CH} = \text{COR} \rightarrow \text{CH}_2 = \text{OC}_6\text{H}_5
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Hence, the first stage of the reaction is probably the replacement of the phenoxy group, and not condensation at the carbonyl group. We cannot maintain that this is the only direction that reaction takes, for the yield of the