SYNTHESIS AND SOME PROPERTIES OF \( \alpha, \beta \)-EPOXY ALDEHYDES

L. A. Yanovskaya, B. I. Kozyrkin, and V. F. Kucherov

One of the possible routes to the synthesis of various types of polyfunctional compounds is based on the use of starting compounds containing two or more groups of different reactivities. This route requires the initial conversion of the more reactive group into the first desired function and the further use of the second, less reactive group for the introduction of the second desired function. As such starting compounds we have previously [1, 2] made successful use of dialdehyde monoacetals \( \text{HOC} \cdots \text{R} \cdots \text{CH(OC}_2\text{H}_5\text{)}_2 \) and synthesized a number of bifunctional compounds.

Our attention was attracted by other types of possible starting compounds of promise for the synthesis of polyfunctional compounds. Epoxy aldehydes may present interest in this respect, and this paper is devoted to their use for this purpose. As Payne showed [3-5], simple \( \alpha, \beta \)-unsaturated aldehydes can be epoxidized with hydrogen peroxide in aqueous or methanolic solution at a certain optimum pH. The same author showed [4, 6] that glycidaldehyde is capable of reactions at the carbonyl group (with preservation of the epoxide ring) with hydroxylamine, cyanoacetic, acetoacetic, and malonic esters, primary amines, ethyl chloroacetate, orthoformic ester, ketene, and hydrocyanic acid.

It was of interest to study the possibility of using Payne's method for the epoxidation of \( \beta \)-functionally substituted \( \alpha, \beta \)-unsaturated aldehydes. It was found that \( \alpha, \beta \)-unsaturated aldehydes with electron-donor substituents in the \( \beta \)-position [3-(diethylamino)acrolein, 3-ethoxyacrolein, and 3,3-dichloroacrolein], and also sorbaldehyde, do not give epoxy aldehydes under the usual conditions of the Payne reaction. Also unsuccessful were attempts to epoxidize sorbaldehyde acetal with 60% hydrogen peroxide in acetonitrile [7] and sorbic acid in aqueous solution in presence of ammonium tungstate [8].

On the other hand, under the action of hydrogen peroxide in aqueous-alcoholic solution at pH 8-8.5, \( \alpha,\beta \)-unsaturated aldehydes with electron-acceptor substituents in the \( \beta \)-position [fumaraldehyde mono(dimethyl acetal) (Ia) and ethyl malealdehydate (Ib)] gave good yields of the corresponding \( \alpha,\beta \)-epoxy aldehydes. In this way we prepared 2,3-epoxysuccinaldehyde mono(dimethyl acetal) (IIa), ethyl 2,3-epoxysuccinaldehydate (IIb), and also 2,3-epoxybutyraldehyde (IIc) [from trans-crotonaldehyde (Ic)].

\[
\begin{align*}
R-\text{CH} = \text{CHCHO} & \xrightarrow{\text{H}_2\text{O}_2 \ \text{pH} \ 8-8.5} R-\text{CH} \cdots \text{CHCHO} \\
\text{O} & \overset{(\text{IIa,b,c})}{\downarrow} \\
R-\text{CH} = \text{CHCH(OC}_2\text{H}_5\text{)}_2 & \xrightarrow{\text{O}} \overset{(\text{IIa,b,c})}{\downarrow} \\
\text{a) } & R = (\text{CH}_2\text{O})_2\text{CH; } \text{b) } R = \text{C}_3\text{H}_7\text{OOC; } \text{c) } R = \text{CH}_3
\end{align*}
\]

The acetalization of the epoxy aldehydes (IIa), (IIb), and (IIc) went smoothly under the action of an alcoholic solution of orthoformic ester in presence of ammonium nitrate. We obtained high yields of the corresponding diethyl acetals: 2,3-epoxysuccinaldehyde diethyl acetal dimethyl acetal (IIIa), ethyl 2,3-epoxysuccinaldehydate diethyl acetal (IIIb), and 2,3-epoxybutyraldehydate diethyl acetal (IIIc). We also verified the possibility of synthesizing the acetal (IIIc) by the direct epoxidation of trans-crotonaldehyde di-ethyl acetal with 60% hydrogen peroxide in acetonitrile, as proposed by Payne [7] for acrolein acetal, but in this case the yield of (IIIc) was low.

For the epoxy aldehydes (IIa) and (IIc) we studied a number of reactions at the aldehyde group. We showed that the condensation of the aldehyde (IIc) with nitromethane in aqueous media in presence of potassium carbonate is accompanied by cleavage of the epoxy ring, while the condensation in alcohol in...
presence of sodium ethoxide is accompanied by much resinification. We succeeded in bringing about the condensation of (IIC) with nitromethane in presence of catalytic amounts of triethylamine at room temperature. Under these conditions the reaction goes smoothly with formation of 3,4-epoxy-1-nitro-2-pentanol (IV) in satisfactory yield. Triethylamine also proved to be the best catalyst for the condensation of (IIC) with acetone cyanohydrin, which led to 3,4-epoxy-2-hydroxyvaleronitrile (V). (IV) and (V) are thick yellowish oils, readily soluble in water, but even in a high vacuum they are distilled with difficulty and with considerable resinification. When left in air, (IV) and (V) are gradually transformed into clear sticky masses. Study of the IR spectra of the epoxides (IV) and (V) showed the presence of a strong intramolecular hydrogen bond; this gives grounds for the view that the hydroxy group and the oxygen of the epoxide ring in these compounds have the erythro configuration.

Attempts to bring about selective Grignard reaction at the aldehyde group of the epoxy aldehyde (IIC) were not successful. Even under mild conditions reaction is accompanied by opening of the epoxide ring, which leads to the formation of a complex mixture of products. It was found that the epoxy aldehydes (IIA) and (IIC) are able to react with chloroacetic esters in presence of sodium methoxide, and this enabled the ready preparation of ethyl 2,3 : 4,5-diepoxypentanal dimethyl acetal (VII) and methyl 2,3 : 4,5-diepoxypentanoate (VI). As we have shown previously [9], the epoxy aldehydes (IIA) (IIB), and (IIC) can undergo Wittig reaction with stable phosphoranes and phosphonates with formation of products of condensation at the aldehyde group with preservation of the epoxide ring.

\[
\begin{align*}
\text{CHNO}_2 & \quad \text{R} - \text{CH} - \text{CH} - \text{CH}_2\text{NO}_2 \\
\text{O} & \quad \text{R} = \text{CH}_3 \quad \text{(IV)} \\
\text{O} \quad \text{R} = \text{CH}_3 \quad \text{(V)} \\
\text{H} & \quad \text{R} = \text{CH}_3 \quad \text{(V)} \\
\end{align*}
\]

Results of interest from the point of view of synthesis were obtained in the Payne epoxidation of ethyl 5-formyl-2,4-pentadienoate (VIII) and ethyl 7-formyl-2,4,6-heptatrienoate (IX). It was found that in this case oxidation goes at the double bond adjacent to the aldehyde group with formation of the corresponding monoepoxides (X) and (XI) in satisfactory yields; the structures of the latter were proved by their IR spectra.

\[
\begin{align*}
\text{C}_2\text{H}_4\text{OOC} & \quad \text{CH} = \text{CH}_n\text{CH} = \text{CHO} \quad \text{C}_2\text{H}_4\text{OOC} \quad (\text{VIII}, \ n = 1); \ (\text{IX}, \ n = 2) \\
\text{O} & \quad \text{C}_2\text{H}_4\text{OOC} \quad (\text{X}, \ n = 1); \ (\text{XI}, \ n = 2) \\
\text{Pb}_3\text{P} & \quad \text{CHCOOC}_2\text{H}_3 \\
\text{C}_2\text{H}_4\text{OOC} & \quad \text{CHCH} - \text{CH} - \text{CH} = \text{CHO} \quad \text{C}_2\text{H}_4\text{OOC} \\
\text{O} & \quad \text{C}_2\text{H}_4\text{OOC} \quad (\text{XII}) \\
\text{O} & \quad \text{C}_2\text{H}_4\text{OOC} \quad (\text{XIII}) \\
\end{align*}
\]

We studied the reactions of the epoxy aldehyde (X) with ethyl (triphenylphosphoranylidene)acetate and with (triphenylphosphoranylidene)acetone, which enabled us to obtain the dienic epoxides (XII) and (XIII), the UV and IR spectra of which were in accord with their structures.

**EXPERIMENTAL**

For the gas-liquid chromatography of the compounds obtained we used a 2-m column containing 1% of silicon elastomer on NaCl. For thin-layer chromatography we used plates covered with unbound alumina of activity II.