EPOXIDE COMPOUNDS OF β,β-DIALKYL DIVINYL KETONES AND UNSATURATED β-METHOXY KETONES

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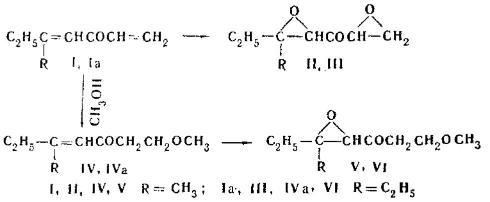
By the epoxidation with alkaline hydrogen peroxide of 5-methylhepta-1,4-dien-3-one and 5-ethylhepta-1,4-dien-3-one and the 3-methyl-7-methoxyhept-3-en-5-one and 3-ethyl-7-methoxyhept-3-en-5-one formed from them, we have obtained the mono- and diepoxy ketones corresponding to them with yields of 48–65%. It has been shown that under the influence of zinc chloride 4,5-epoxy-3-methyl-7-methoxyheptan-5-one forms 3-methyl-7-methoxyheptane-4,5-dione and 3-methylhept-1-ene-3,4-dione. Under the same conditions, 4,5-epoxy-3-ethyl-7-methoxyheptan-5-one is converted into 3-ethyl-7-methoxyheptane-4,5-dione and 3-ethylhept-1-ene-3,4-dione. 3-Methyl- and 3-ethylheptene-3,4-diones are also formed in the distillation of the methyl and ethyl methoxy diketones in the presence of p-toluenesulfonic acid. The IR spectra of the compounds synthesized have been recorded.

It is known [1–3] that divinyl and vinyl propenyl ketones of the aliphatic series, and also the unsaturated β-methoxy ketones corresponding to them, are oxidized by alkaline hydrogen peroxide to mono- and diepoxy ketones with high yields of the latter. Because of the incomplete hybridization of the C—O bond of an epoxy ring conjugated with a carbonyl group, these compounds possess a definite tendency to undergo various reactions and therefore form an interesting group of substances for the purposes of organic synthesis. In this work we have studied the epoxidation by hydrogen peroxide in an alkaline medium [4] of 4-methylhepta-1,4-dien-3-one (I) and 5-ethylhepta-1,4-dien-3-one (Ia) and of the 3-methyl-7-methoxyhept-3-en-5-one (IV) and the 3-ethyl-7-methoxyhept-3-en-5-one (IVa) formed from the divinyl ketones mentioned by the addition of methanol to their vinyl groups. This reaction yielded 3,4:6,7-diepoxy-3-methylheptan-5-one (II), 3,4:6,7-diepoxy-3-ethylheptan-5-one (III), 3,4-epoxy-3-methyl-7-methoxyheptan-5-one (V), and 3,4-epoxy-3-ethyl-7-methoxyheptan-5-one (VI) with yields of 48–65%:



I, II, IV, V R = CH_3; Ia, III, IVa, VI R = C_2H_5

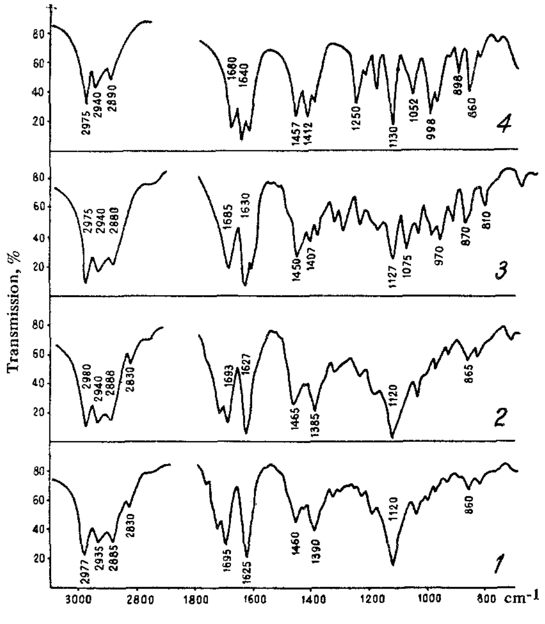


Fig. 1. IR spectra (liquid film): (1) 3-methyl-7-methoxyhept-3-en-5-one (IV); (2) 3-ethyl-7-methoxyhept-3-en-5-one (IVa); (3) 5-methylhepta-1,4-dien-3-one (I); (4) 5-ethylhepta-1,4-dien-5-one (Ia).

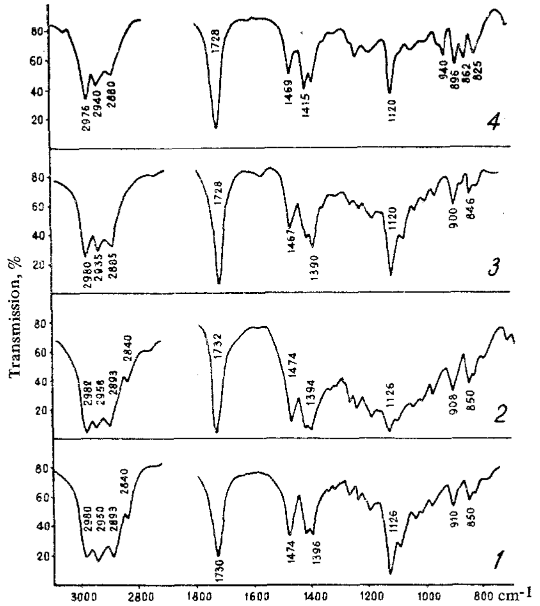
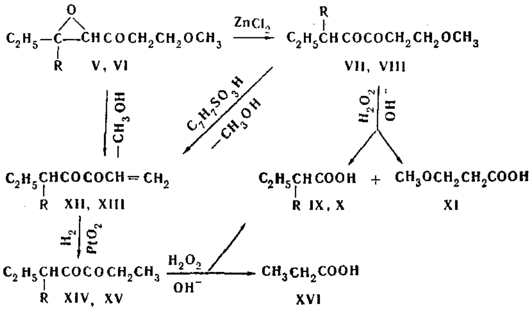


Fig. 2. IR spectra (liquid film): (1) 3,4-epoxy-3-methyl-7-methoxyheptan-5-one (V); (2) 3,4-epoxy-3-ethyl-7-methoxyheptan-5-one (VI); (3) 3,4:6,7-diepoxy-3-methylheptan-5-one (III); (4) 3,4:6,7-diepoxy-3-ethylheptan-5-one (III).

On being heated with zinc chloride, the methoxylated epoxy ketones V and VI isomerized into 3-methyl-7-methoxyheptane-4,5-dione (VII) and 3-ethyl-7-methoxyheptane-4,5-dione (VIII), respectively, the structures of these compounds being shown by the cleavage of the C—C bond between the neighboring carbonyl groups under the action of an excess of alkaline hydrogen peroxide [4] to give, in the one case, methylethylacetic acid (IX) and β-methoxypropionic acid (XI) and, in the other case, diethylacetic acid (X) and β-methoxypropionic acid, and also by their IR absorption spectra. In addition to the methoxylated α-diketones (VII and VIII) the reaction concerned also yielded 5-methylhept-1-ene-4,5-dione (XII) and 5-ethylhept-1-ene-3,4-dione (XIII), formed by the simultaneous cleavage of the C—O bond of the epoxy ring and the splitting off of methanol. Compounds XII and XIII were also obtained in good yield by the distillation of the methoxy diketones VII and VIII in the presence of p-toluenesulfonic acid. The diketones XII and XIII were reduced over platinum oxide to 3-methyl- and 3-ethylheptane-4,5-diones (XIV, XV) which were cleaved by oxidation with hydrogen peroxide in an alkaline medium to form, in the one case, methylethylacetic acid (IX) and propionic acid (XVI) and, in the other case, diethylacetic acid (X) and propionic acid:



V, VII, IX, XII, XIV R=CH$_3$; VI, VIII, X, XIII, XV R=C$_2$H$_5$

In the IR absorption spectra of the mono- and diepoxy ketones II, III, V, and VI obtained, a strong absorption band in the 1732–1728 cm^{-1} region corresponds to the stretching vibrations of the C═O group. In the initial divinyl ketones, the absorption maxima for this band were at 1685 cm^{-1} (I) and 1680 cm^{-1} (Ia). In the unsaturated β-methoxy ketones IV and IVa, it is split into two well-defined bands with maxima at 1695 and 1720 cm^{-1} and at 1693 and 1715 cm^{-1}. This splitting is probably connected with the presence of geometrical or rotational isomers, the time of existence of which is increased because of the presence of fairly large groups "hindering" the rotation about the single C—C═O bond. It is characteristic that in the divinyl ketones I and Ia the band of the double bond is split into bands 15–21 cm^{-1} distant from one another. This splitting is evidently due to a change in the nature of the vibrations of two identical bonds because of the branching of the chain and the simultaneous appearance of syn-phase and anti-phase vibrations. We have observed a similar phenomenon previously [5]. In the epoxidation of the ketones I, Ia, IV, and IVa, in addition to the disappearance of the band of the double bond, the splitting of the carbonyl absorption also disappears. Under these conditions, the frequency of the vibrations of the C═O group of the epoxy ketones is displaced in the high-frequency direction by from 10 to 48 cm^{-1} and becomes comparable with the frequency of the carbonyl vibrations of saturated acyclic ketones, which shows the absence in the epoxy ketones formed of appreciable conjugation between the C═O group and the epoxy ring. The bands of the epoxy ketones II, III, V, and VI and of the unoxidized ketones I, Ia, IV, and IVa in the 2962–2885-cm^{-1}, 1474–1382-cm^{-1}, and 2840–2830-cm^{-1} (IV–VI) regions are due, respectively, to the stretching and deformation (symmetrical and antisymmetrical) vibrations of the methyl and methylene groups and the stretching vibrations of the the methoxy group. The characteristic band in the 1130–1120-cm^{-1} region probably relates to the stretching vibrations of the C═O bond of the chain. In the epoxy ketones V and VI, in contrast to the unoxidized ketones, there is a band in the 910–908-cm^{-1} region apparently due to the asymmetric stretching vibrations of the epoxy ring [5–7]. Bands in the 1728–1726-cm^{-1}, 2980–2793-cm^{-1}, 1494–1380-cm^{-1}, 2840-cm^{-1}, and 1129–1127-cm^{-1} regions in the case of the α-diketones VII, VIII, XIV and XV are due to the vibrations of the C═O groups, the methyl and methylene groups, the CH$_3$O group and, apparently, the stretching vibrations of the C═O skeleton, respectively. The bands at 1718 cm^{-1} and 1630 cm^{-1} in the unsaturated diketones XII and XIII are due to the C═O and C═C groups. The IR spectra of the initial ketones and of the mono- and diepoxy ketones obtained are shown in Figs. 1 and 2.

EXPERIMENTAL

The divinyl ketones and unsaturated β-methoxy ketones used for epoxidation were obtained by isomerizing the corresponding ethyl vinyl carbinols under the action of mercury salts in methanolic solution [8, 9]. The epoxidation reaction was carried out with alkaline hydrogen peroxide [4] as described previously [3].

3,4:6,7-Diepoxy-3-methylheptan-5-one (II). With stirring at 0–10° C, 310 ml of an 18% solution of hydrogen peroxide and 45 ml of a 4 N aqueous solution of caustic soda were added to 100 g of 5-methylhepta-1,4-dien-3-one (I, bp 59–60° C at 10 mm, n_D^{20} 1.4725) in 500 ml of dioxane. After the addition of the oxidizing agent, the reaction mixture was stirred at room temperature for 3 hr. This yielded 53 g (48%) of II in the form of a colorless liquid with a faint odor, bp 75° C (1 mm), (n_D^{20} 1.4507; d_4^{20} 1.0584; $\nu_{C=O}$ 1730 cm^{-1}). Found, %: C 61.74; 61.60; H 7.98; 7.86; mol. wt. 158, 156 (in benzene); MR$_D$ 39.67. Calculated for ($C_8H_{12}O_3$), %: C 61.49; H 7.74; mol. wt. 156; MR$_D$ 39.46.

3,4:6,7-Diepoxy-3-ethylheptan-5-one (III). 119 g of 5-ethylhepta-1,4-dien-3-one (Ia, bp 63–64° C at 9 mm, n_D^{18} 1.4725) in 500 ml of dioxane was oxidized by the addition of 345 ml of 18% hydrogen peroxide solution and 45 ml of a 4 N aqueous solution of caustic soda at a temperature not exceeding 10° C. This yielded 71 g (53%) of III in the form of a colorless liquid with a faint odor, mp 80° C (1 mm), (n_D^{20} 1.4548; d_4^{20} 1.0465; $\nu_{C=O}$ 1728 cm^{-1}). Found, %: C 63.33; 63.34; H 8.23; 8.29; mol. wt. 164, 166 (in benzene); MR$_D$ 44.17. Calculated for ($C_9H_{14}O_3$), %: C 64.49; H 8.29; mol. wt. 170; MR$_D$ 44.09.

3,4-Epoxy-3-methyl-7-methoxyheptan-5-one (V). At a temperature not exceeding 15° C, 370 ml of 15% hydrogen peroxide and 60 ml of a 4 N aqueous solution of caustic soda were added to 234 g of 3-methyl-7-methoxyhept-3-en-5-one (IV, bp 56° C at 0.75 mm, n_D^{20} 1.4510) in 1200 ml of methanol. After the addition of the oxidizing agent, the solution was left at room temperature for 3 hr. By the usual treatment (the methanol was distilled off in vacuum), 169 g (65.5%) of V was obtained in the form of a colorless liquid with a characteristic odor, bp 72–73° C (1 mm); (n_D^{20} 1.4417; d_4^{20} 0.9771; $\nu_{C=O}$ 1730 cm^{-1}). Found, %: C 62.57; 62.64; H 9.39; 9.47; mol. wt. 174, 168 (in benzene); MR$_D$ 46.41. Calculated for ($C_9H_{16}O_3$), %: C 62.75; H 9.31; mol. wt. 172; MR$_D$ 46.17. The epoxy ketone V is sparingly soluble in water and readily soluble in the usual organic solvents.

5-Methylhept-1-ene-3,4-dione (XII) and 3-methyl-7-methoxyheptane-4,5-dione (VII). A mixture of 20 g of V and 0.7 g of zinc chloride was heated in a small flask with a reflux condenser at 100° C for 5 hr. The isomerization product was distilled with steam, giving 300 ml of a yellow distillate on the surface of which there was a layer of oily liquid with a stronger yellow coloration. The solution was saturated with sodium chloride, the product was extracted with ether, the extract was dried with magnesium sulfate, the ether was driven off, and the residue was distilled in vacuum to give 7.5 g of **XII** (1-st fraction) in the form of a yellow-green liquid with a rather pungent smell, bp 44–45° C (1 mm); (n_D^{20} 1.4470; d_4^{20} 0.9376; $\nu_{C=O}$ 1718 cm^{-1}). Found, %: C 68.29; 68.36; H 8.91; 8.73; mol. wt. 145, 148 (in benzene); MR_D 38.89; double bonds (Kaufmann) 0.95, 0.96. Calculated for ($C_8H_{12}O_2$), %: C 68.72; H 8.63; mol. wt. 140; MR_D 38.90; double bonds 1.

The 2-nd fraction (2.8 g) was **VII**, a yellow liquid with an odor resembling that of biacetyl; bp 73–74° C (1.5 mm); (n_D^{20} 1.4521; d_4^{20} 1.0191; $\nu_{C=O}$ 1727 cm^{-1}). Found, %: C 63.19; 63.21; H 9.11; 9.04; mol. wt. 175, 174 (in benzene); MR_D 45.60. Calculated for ($C_9H_{16}O_3$), %: C 62.75; H 9.31; mol. wt. 172; MR_D 45.43.

3-Methylheptane-4, 5-dione (XIV). Seven grams of **XII** was hydrogenated in 25 ml of ethanol in the presence of 0.08 g of platinum oxide. After the absorption of 1090 ml of hydrogen (normal conditions), hydrogenation practically ceased. The catalyst was filtered off, the ethanol was driven off in vacuum, and the product was distilled, giving about 6.5 g (91%) of **XIV** in the form of a light yellow liquid with an odor resembling that of α-diketones; bp 65–67° C (10 mm); (n_D^{20} 1.4285; d_4^{20} 0.9319; $\nu_{C=O}$ 1727 cm^{-1}). Found, %: C 67.24; 67.42; H 10.13; 10.27; mol. wt. 145, 147 (in benzene); MR_D 39.19. Calculated for ($C_8H_{14}O_2$), %: C 67.55; H 9.93; mol. wt. 142; MR_D 39.16.

Cleavage of XIV. Four grams of XIV in 15 ml of water was treated with 8 ml of 28% hydrogen peroxide and 3 g of caustic soda in 10 ml of water. After the solution had stood for a short time, the neutral products were extracted with ether and the aqueous residue was extracted almost to dryness. The usual treatment of the salts obtained yielded 0.5 g each of propionic and ethylmethylacetic acids.

The cleavage of **VII** was carried out similarly. Four grams of **VII** in 15 ml of water was treated with 6 ml of 28% hydrogen peroxide and 15 ml of 18% caustic soda, giving 0.5 g each of ethylmethylacetic and β-methoxypropionic acids.

Splitting off of methanol from VII. A mixture of 3 g of **VII** and about 0.1 g of p-toluenesulfonic acid was heated for a short time and was then distilled in vacuum, giving 2.1 g (81%) of **XII**.

3, 4-Epoxy-3-ethyl-7-methoxyheptan-5-one (VI). With stirring, 265 ml of 15% hydrogen peroxide and 40 ml of 4 N caustic soda were added to a solution of 179 g of **III** in 850 ml of methanol cooled to 0° C. During the oxidation, the temperature was not allowed to rise above 15° C. After 3 hr, the solution was worked up in the usual way, to give 120 g (61.2%) of **VI**, bp 78° C (1 mm), (n_D^{20} 1.4460; d_4^{20} 0.9825; $\nu_{C=O}$ 1726 cm^{-1}). Found, %: C 64.48; 63.97; H 9.85; 9.73; mol. wt. 189, 189 (in benzene); MR_D 50.31. Calculated from ($C_{10}H_{18}O_3$), %: C 64.45; H 9.74; mol. wt. 186; MR_D 50.19.

5-Ethylhept-1-ene-3, 4-dione (XIII) and 3-ethyl-7-methoxyheptane-4, 5-dione (VIII). When the products of the isomerization of 20 g of **VI** in the presence of 0.7 g of zinc chloride were vacuum-distilled, two fractions were isolated:

(1) 7.5 g of **XIII** as a yellow-green liquid with a rather pungent odor, bp 55–56° C (1.5 mm); (n_D^{20} 1.4510; d_4^{20} 0.9351; $\nu_{C=O}$ 1720 cm^{-1}). Found, %: C 69.89; 69.85; H 9.29; 9.31; mol. wt. 155.5, 157 (in benzene); MR_D 44.49; double bonds (Kaufmann) 0.91, 0.95. Calculated for ($C_9H_{14}O_2$), %: C 70.08; H 9.16; mol. wt. 154; MR_D 43.32; double bonds 1.

2. A 3 g quantity of **VIII** in the form of a yellow liquid with an odor resembling that of α-diketones, bp 79° C (1 mm); (n_D^{20} 1.4564; d_4^{20} 1.0062; $\nu_{C=O}$ 1726 cm^{-1}). Found, %: (C 63.02; 62.61; H 9.82; 9.36); mol. wt. 190, 191 (in benzene); MR_D 50.32. Calculated for ($C_{11}H_{18}O_3$), %: (C 62.85; H 9.74; mol. wt. 186; MR_D 50.04).

3-Ethylheptane-4, 5-dione (XV). Compound XIII (5.5 g) was hydrogenated in 20 ml of ethanol in the presence of 0.06 g of platinum oxide. The amount of hydrogen absorbed was 695 ml, as compared with the calculated 706 ml (normal conditions). The catalyst was filtered off, the ethanol was driven off in vacuum, and the residue was distilled to give 4.8 g (88%) of **XV** in the form of a light yellow liquid with a pleasant smell, bp 53° C (1 mm); (n_D^{20} 1.4345; d_4^{20} 0.9266; $\nu_{C=O}$ 1728 cm^{-1}). Found, %: C 69.51; 69.43; H 10.52; 10.64; MR_D 43.80. Calculated for ($C_9H_{16}O_2$), %: C 69.62; H 10.40; MR_D 43.78.

Cleavage of the diketone **XV** was carried out in a similar manner to the preceding experiments. Four grams of **XV** in 10 ml of water was treated with 7 ml of 28% hydrogen peroxide and 3 g of caustic soda in 15 ml of water. This gave 0.5 g each of propionic and diethylacetic acids. The cleavage of **VIII** was carried out similarly. With shaking and cooling in running water, 7 ml of 28% hydrogen peroxide and 3.5 g of caustic soda in 10 ml of water were added in two portions to 7 g of the diketone in 15 ml of water, and then the mixture was left at 20° C for 2 hr. The neutral products were extracted with ether, and the aqueous residue was evaporated almost to dryness and was treated with 10% sulfuric acid, after which the organic acids were extracted with ether. This yielded 1.1 g of diethylacetic and 0.8 g of β-methoxypropionic acids.

Splitting off of methanol from VIII. A mixture of 6 g of **VIII** and 0.1 g of p-toluenesulfonic acid was heated in a small Claisen flask in the boiling water bath for 35 min. The methanol was driven off in vacuum and the residue was distilled, giving 4.6 g (92%) of **XIII**.

The infrared spectra of pure liquid samples were taken on a UR-20 spectrophotometer with prisms of LiF (3700–2700 cm^{-1}) and NaCl (1800–700 cm^{-1}).

REFERENCES

1. I. N. Nazarov and A. A. Akhrem, Izv. AN SSSR, OKhN, 621, 1950.
2. I. N. Nazarov and A. A. Akhrem, ZhOKh, **20**, 2188, 1950.
3. I. N. Nazarov, A. A. Akhrem, and I. G. Tishchenko, ZhOKh, **25**, 708, 725, 1955.
4. E. Weitz and A. Scheffer, Ber., **54**, 2327, 1921.
5. I. G. Tishchenko, I. P. Zyat'kov, and V. M. Yazychenko, collection: Heterogeneous Reactions and Reactivity [in Russian], Minsk, p. 274, 1964.
6. K. Nakanishi, Infrared Absorption Spectroscopy [Russian translation], Mir, Moscow, p. 43, 1965.
7. S. S. Skorokhodov, Vestn. LGU, **16**, 110, 1950.
8. I. N. Nazarov, Izv. AN SSSR. OKhN, 545, 1940.
9. A. N. Elizarov and I. N. Nazarov, Izv. AN SSSR, OKhN, 223, 1940; 423, 1941.

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