EPOXIDATION OF CHALCONES

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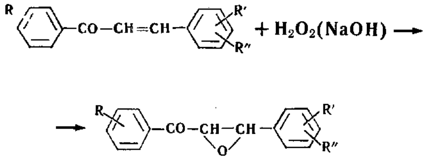
Previously undescribed aromatic α-keto oxides have been obtained by the epoxidation of chalcones with alkaline hydrogen peroxide in methanolic solution.

One of the methods for obtaining α-keto oxides is that based [1] on the oxidation of α,β-unsaturated ketones with hydrogen peroxide in an alkaline medium. A large number of α-keto oxides of the aliphatic and aliphatic-aromatic series has been obtained in this way. α-Keto oxides of the aromatic series are few in number and have been studied little [2], but they present considerable interest since they can be used widely in organic synthesis.

The present paper gives information on the epoxidation of the chalcones [3] I with alkaline hydrogen peroxide as a result of which six previously unknown aromatic α-keto oxides II (see table) was obtained.



II

The oxidation of the chalcones was carried out with concentrated solutions of hydrogen peroxide, since dilute solutions of the peroxide do not oxidize the double bond. For each chalcone there are optimum temperatures of oxidation, depending on the substituents (see table), and when these are exceeded oxidative cleavage of the chalcones takes place with the formation of the corresponding aromatic acids.

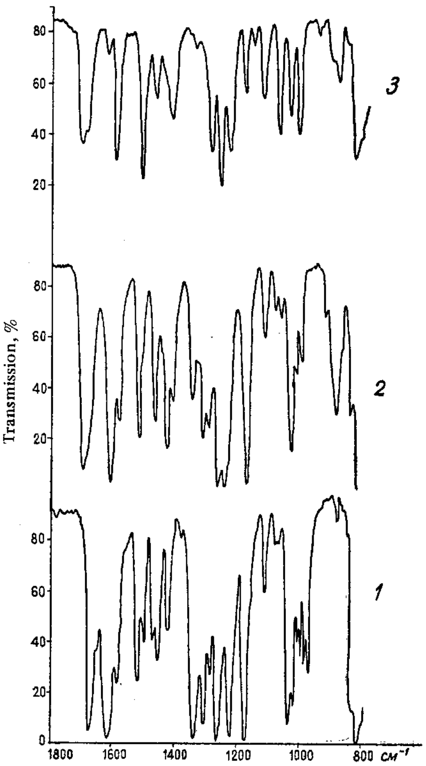
To prove the structue of the α-keto oxides obtained, the IR spectra of a chalcone and of chalcone oxides were recorded (see figure).

In the IR spectra of the chalcone (curve 1) and the chalcone oxides (curves 2 and 3) there is a clear shift in the absorption band of the carbonyl group with a maximum in the 1670 cm^{-1} region (chalcone) toward the high-frequency part of the spectrum with a maximum in the 1700 cm^{-1} region (chalcone oxide), which is satisfactorily explained by the destruction of the conjugation of the carbonyl group and the ethylenic bond on epoxidation [4]. The IR spectra of the α-keto oxides have absorption bands with maxima in the 800 cm^{-1} region which are absent in the chalcones. These absorption bands may be assigned to the epoxy group [4, 5] of an α-keto oxide.

EXPERIMENTAL

The epoxidation reaction was carried out with the chalcones that we obtained previously by ketovinylation [6, 7].

1-(p-Bromobenzoyl)-2-(2-methoxy-5-methylphenyl)ethylene oxide. A three-necked flask fitted with a stirrer, dropping funnel, and thermometer was charged with 3 g (0.009 mole) of p-bromophenyl 2-methoxy-5-methylstyryl ketone and 50 ml of methanol. With vigorous stirring and heating to 48° C, 6 g (0.018 mole) of 28.5% hydrogen peroxide and 3 ml of 4 N aqueous caustic soda were added dropwise over 15 min. The temperature rapidly rose to 59° C and the reaction mixture become lighter in color; the mixture was cooled to the initial temperature of oxidation, and stirring was continued for 40 min. White crystals of the α-keto oxide deposited which gave a red coloration with sulfuric acid and did not decolorize bromine water.

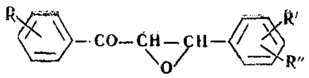


IR spectra: 1) o-chlorophenyl p-methoxystyryl ketone; 2) 1-(o-chlorobenzoyl)-2-(p-methoxyphenyl)ethylene oxide; 3) 1-(p-bromobenzoyl)-2-(2-methoxy-5-methylphenyl)ethylne oxide.

The **2,4-dinitrophenylhydrazone** was obtained in the usual way; bright red crystals with mp 248° C (from nitrobenzene). Found, %: N 11.06, 11.20. Calculated for $C_{23}H_{19}BrN_4O_6$, %: N 10.62.

The other α-keto oxides were synthesized analogously from the corresponding chalcones. Their physical constants, yields, and analytical data are given in the table.

The IR spectra of the chalcone and the α-keto oxides were recorded on a UR-10 spectrophotometer in the region of transmission of an NaCl prism (700–1800 cm^{-1}) at a layer thickness of 0.5 mm of a solution having a concentration of 0.1 M (in CCl_4).



R	R′	R″	Compound	Reaction conditions		Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
				temperature, °C	concentration of H_2O_2, %			C	H	Cl	C	H	Cl	
4-Br	2-OCH_3	5-CH_3	1-(p-Bromobenzoyl)-2-(2-methoxy-5-methylphenyl)ethylene oxide	50	28.5	118 (ethanol)	$C_{17}H_{15}BrO_3$*	58.99 59.15	4.74 4.79		58.80	4.35		83
2-Cl	2-OCH_3	5-OCH_3	1-(o-Chlorobenzoyl)-2-(2,5-dimethoxyphenyl)ethylene oxide	50	28.5	124 (ethanol)	$C_{17}H_{15}ClO_4$	63.94 64.15	4.88 4.92	11.05 11.20	64.05	4.71	11.13	64
2-Cl	3-OCH_3	4-OCH_3	1-(o-Chlorobenzoyl)-2-(3,4-dimethoxyphenyl)-ethylene oxide	50	28.5	94 (ethanol)	$C_{17}H_{15}ClO_4$	64.18 64.20	4.61 4.58	10.96 10.79	64.05	4.74	11.12	87
4-NO_2	4-OC_2H_5	H	1(-p-Ethoxyphenyl)-2-(p-nitrobenzoyl)-ethylene oxide	40	30.0	160 (toluene)	$C_{17}H_{15}NO_5$	65.36 65.27	4.97 5.06		65.17	4.82		57
2-Cl	4-OCH_3	H	1-(o-Chlorobenzoyl)-2(-p-methoxyphenyl)-ethylene oxide	40	28.5	86 (methanol)	$C_{16}H_{13}ClO_3$	66.49 66.37	4.78 4.64	12.57 12.32	66.55	4.54	12.28	70
2-Cl	4-OC_2H_5	H	1-(o-Chlorobenzoyl)-2-(p-ethoxyphenyl)-ethylene oxide	43	30.0	79 (methanol)	$C_{17}H_{15}ClO_3$	67.40 67.83	5.03 5.23	11.59 11.51	67.44	4.99	11.71	61

***Found, %: Br 23.09, 22.89. Calculated, %: Br 23.01.**

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