When addition was complete (1 hr.), the reaction mixture was allowed to stand at room temperature for 4 hr., and then poured into 500 ml. of ice water containing 50 g. of NH_4Cl. The aqueous layer was separated and extracted with 60 ml. of ether. The combined ethereal layers were washed with two 100 ml. portions of 20% NH_4Cl and then with brine. After drying over $MgSO_4$, the ether was removed and the product was distilled through an 8 cm. helix-packed column. The fraction boiling 99–100°/30 mm. was collected; 50.5 g. (81%). A sample which had been redistilled twice through a 20 cm. Widmer column had the following physical properties: b.p. 99–100°/30 mm., 85–85.5°/15 mm.; n_D^{25} 1.4837; d^{25} 0.9669. The I.R. spectrum in CCl_4 solution showed strong absorption at 2.95 μ and weak absorption at 4.5 μ.

Anal. Calc'd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.52; H, 9.80.

The other yields listed in column 4 of Table I were obtained by a similar procedure.

Acknowledgment. We are indebted to the Research Corporation for financial assistance during this investigation.

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Preparation of Alkyl Vinyl Ketones

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In connection with another problem the need arose for some alkyl vinyl ketones. The procedure devised by McMahon *et al*[1] is unsuitable for larger scale work due to the violence of the dehydrohalogenation. Woodward[2] recommended that several small scale experiments (39 g.) be run to obtain sizable amounts of ethyl vinyl ketone.

We have found that the dehydrohalogenation of 1-chloro-3-pentanone proceeds smoothly when an intimate mixture of the haloketone and anhydrous sodium benzoate is stirred and heated. In this way it is possible to obtain the desired unsaturated ketone in 78% crude yield on mole scale runs. The two disadvantages of the method, namely, the poorer yields that resulted in the preparation of higher homologs and the mechanical difficulties in handling the cooled cement-like residues, were overcome by employing Dowtherm as a diluent in the reaction. In this way the yield of butyl vinyl ketone was increased from 30% to 58%, and the nonvolatile material remained fluid throughout.

In our preferred method we found it expedient to use the crude undistilled chloroketone. The over-all yield based on the acid chloride was at least as good as that obtained when distilled ketone was used. It was possible to obtain the higher alkyl vinyl ketones in approximately 30% over-all yield with a minimum of manipulation.

EXPERIMENTAL[3]

Ethyl vinyl ketone. A 500-ml. three-necked flask was equipped with a Hershberg stirrer and a still-head connected to a condenser set for downward distillation. The receiver, containing 0.1 g. of hydroquinone, was immersed in ice. A mixture of 90 g. of 1-chloro-3-pentanone and 0.5 g. of hydroquinone was placed in the flask and the stirrer was started. Anhydrous sodium benzoate (120 g.) was added portionwise over a 10-min. period. A second 90-g. portion of the chloroketone was added followed by a second 120-g. portion of sodium benzoate.

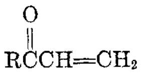
After the reagents were thoroughly mixed the flask was heated by means of a heating mantle. After a few minutes the contents solidified but after about 10 minutes the whole liquefied, allowing the stirrer to function. Within the next hr. and one-half the entire distillate, b.p. 100–135°, was collected.

The apparatus was dismantled while still hot and the residue immediately was emptied into a stone crock (hood). The distillate was separated from a small amount of water and dried. The crude ethyl vinyl ketone weighed 99 g. (78%).

A small portion reacted with aniline to furnish 1-phenylamino-3-pentanone, m.p. 56.2–57.2° after two crystallizations from absolute ethanol. McMahon[1] reported m.p. 56.5–57°.

General method for the preparation of the alkyl vinyl ketones. One and one-half moles of the acid chloride was treated with ethylene in chloroform as described by Woodward.[2] The crude chloroketone was obtained after removal of the solvent and was weighed and used directly in the next step.

TABLE I

Alkyl Vinyl Ketones 
$RC(=O)CH{=}CH_2$

R	Yield[a]	B.P., °C. (mm.)	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found
n-Propyl	27	25-26 (11)	$C_6H_{10}O$	73.43	73.28	10.27	10.52
n-Butyl	34	44-45 (11)	$C_7H_{12}O$	74.95	74.50	10.79	10.66
n-Amyl	26	58-61 (11)	$C_8H_{14}O$	76.14	76.00	11.18	11.60

Analyses

[a] Yield based on the acid chloride used to prepare the β-chloroketone. In the case of propyl vinyl ketone distilled 1-chloro-3-hexanone furnished the desired product in 82% yield. However there was no gain in over-all yield.

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(1) E. M. McMahon, J. N. Roper, W. P. Utermohlen, R. H. Hasek, R. C. Harris and J. H. Brant, *J. Am. Chem. Soc.*, 70, 2971 (1948).

(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

(3) Analyses were carried out by Mr. K. D. Fleischer and his staff of this Institute.

The residual haloketone, two volumes of Dowtherm, sodium benzoate (10% molar excess) and a pinch of hydroquinone were placed in a flask equipped as described above in the ethyl vinyl ketone experiment. Heating and stirring were continued until the distillation temperature reached 210°. The crude ketone was dried over Drierite and then distilled.

The contents of the flask remained fluid throughout and could be removed from the flask readily. The properties of the ketones thus prepared are described in Table I.

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Substituent Effects in the Catalytic Hydrogenation of Styrene Oxides

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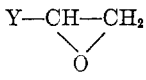
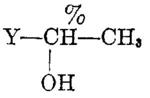
The hydrogenation of ethylene oxides is a reaction of considerable potential importance, but it has received surprisingly little systematic study. A number of monoalkyl- and arylethylene oxides have been hydrogenated,[1] and a primary alcohol has been obtained as the predominant product in every case, in the absence of added acid or base. Only a few oxides with electron-withdrawing groups have been hydrogenated, and a secondary alcohol is always produced. Glycidol,[2,3] epichlorohydrin,[3,4] and butadiene dioxide[3] are reduced to 1,2-propandiol, 1-chloro-2-propanol, and 2,3-butandiol, respectively, as the main product. Two possible factors might determine the direction of ring opening of epoxides by hydrogen, the orientation of the molecules at the catalyst surface, and the electronic effects of substituents. In the present work the electronic influences have been studied in a series of *m*- and *p*-substituted styrene oxides which presumably are similarly oriented on the platinum catalyst surface. The results appear in Table I.

TABLE I

HYDROGENATION OF SUBSTITUTED STYRENE OXIDES

 $Y{-}CH{-}CH_2$ (epoxide, O)	% $Y{-}CH_2CH_2OH$[a]	%  $Y{-}\underset{\displaystyle OH}{CH}{-}CH_3$
Y = *p*-CH_3-C_6H_4	100	0
C_6H_5[b]	100	0
m-CH_3O-C_6H_4[c]	88	12
p-Br-C_6H_4	82	18[d]
3,4-dichlorophenyl	35	65[e]

[a] The percentages listed refer to the composition of the material which actually underwent hydrogenation. [b] Reference 1. [c] A small amount of a low boiling substance was formed. [d] Isolated as 4-bromoethylbenzene. [e] Isolated in part as 3,4-dichloroethylbenzene.

It may be seen that the Hammett *rho* value for the reaction would be negative, as in the reaction of the same oxides with lithium borohydride.[5] The data are not considered sufficiently accurate to obtain a significant value of *rho*, because of the experimental difficulties in removing contaminants such as starting material from the desired products. The secondary alcohols 1-(4-bromophenyl)ethanol and 1-(3,4-dichlorophenyl)ethanol formed by hydrogenation of the corresponding styrene oxides, underwent hydrogenolysis to 4-bromoethylbenzene and 3,4-dichloroethylbenzene, respectively. The hydroxyl group of the primary alcohol 2-(3,4-dichlorophenyl)ethanol, as expected, did not undergo hydrogenolysis. A pure sample of the substance was hydrogenated to 2-cyclohexylethanol, although this product was not obtained from the hydrogenation of 3,4-dichlorostyrene oxide under similar conditions. It is apparent that only the secondary (benzyl) alcohols undergo hydrogenolysis to ethylbenzene derivatives, and this has been taken into account in the calculation of the amount of secondary alcohols initially formed.

The considerable substituent effect militates against a mechanism which involves the simultaneous addition of hydrogen atoms to the oxygen and carbon atoms. It is not possible to decide definitely between two alternative mechanisms[6,7] which involve the addition of a proton or hydrogen atom to the oxygen atom, with formation of a (bound) carbonium ion or radical, followed by addition of a hydride ion or a hydrogen atom to the carbon atom. It is known[8] that electron-donating substituents may facilitate both carbonium ion and radical reactions at the benzyl carbon atom, presumably by stabilization of the intermediate benzyl carbonium ion or radical.

EXPERIMENTAL[9]

Hydrogenation of the Oxides. A solution of 0.10 mole of each oxide in 100 ml. of 95% ethanol was shaken with 0.15 g. of platinum oxide catalyst for about 24 hr., or until hydrogen uptake had completely ceased. In all cases the initial pressure was about 45 lbs., and the uptake was 0.09 to 0.10 mole.

Low boiling ethylbenzene derivative and unchanged oxide were separated by fractional distillation, and the mixture of 1- and 2-arylethanol was analyzed by infrared absorption, with reference to spectra of known mixtures.[5]

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[1] See, for example, O. Loehr, U. S. Patent **1,787,205**; *Chem. Abstr.*, **25**, 963 (1931); M. S. Newman, G. Underwood, and M. Renoll, *J. Am. Chem. Soc.*, **71**, 3362 (1949).

[2] A. Kötz and K. Richter, *J. prakt. chem.*, [2] **111**, 373 (1925).

[3] R. Fuchs, Thesis, University of Kansas, 1953.

[4] S. Searles and C. F. Butler, *J. Am. Chem. Soc.*, **76**, 56 (1954).

[5] F. Fuchs, *J. Am. Chem. Soc.*, **78**, 5612 (1956).

[6] Mechanisms have been proposed for the hydrogenation of ethylene: L. Hernandez and F. F. Nord, *J. Colloid Sci.*, **3**, 363 (1948).

[7] R. K. Greenhalgh and M. Polanyi, *Trans. Faraday Soc.*, **35**, 520 (1939).

[8] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[9] The preparation of the oxides and the reference samples of the arylethanols was described in ref. 5.