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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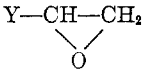
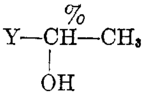
The hydrogenation of ethylene oxides is a reaction of considerable potential importance, but it has received surprisingly little systematic study. A number of monoalkyl- and arylethylene oxides have been hydrogenated,[1] and a primary alcohol has been obtained as the predominant product in every case, 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_2CH_2OH[a]	%  $Y—CH(OH)—CH_3$
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).

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(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.

The yield of products and recovered oxide accounted for 86 to 95% of the starting material except in the case of 4-bromostyrene oxide (55% yield) in which there was a large pot residue.

4-Bromoethylbenzene and 3,4-Dichloroethylbenzene. 4-Bromoacetophenone[10] and 3,4-dichloroacetophenone were reduced by the Clemmensen method. 3,4-Dichloroethylbenzene was distilled at 64° at 2 mm.; n_D^{34} 1.5363.

Anal. Calc'd for $C_8H_8Cl_2$: C, 54.9; H, 4.6. Found: C, C, 55.1; H, 4.6.

Hydrogenation of 2-(3,4-Dichlorophenyl)ethanol. A sample of 2-(3,4-dichlorophenyl)ethanol[5] was hydrogenated under the conditions used for the oxides. The product was 2-cyclohexylethanol, b.p. 50–57° at 0.5 mm. (reported[11] 88–90° at 7 mm.). The 3,5-dinitrobenzoate melted at 69.5–70.5° (reported[11] 70.5°).

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(10) Method of P. Karrer, E. Schlittler, K. Pfaehler, and F. Benz, *Helv. Chim. Acta*, **17**, 1516 (1934).

(11) R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

Alkaloids from *Rauwolfia Schueli*

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Rauwolfia schueli is the only species of this genus which grows in Argentina. It is a tree with roots of rather large diameter and the cortex of the root contains alkaloids which were found pharmacologically active in the ptosis test.[1]

An investigation of the alkaloids present in the bark revealed the presence of aricine, reserpiline, isoreserpiline, and reserpine and of the stronger base, ajmaline.

The amount of aricine found in several batches was around 0.5% of the cortex. It is very interesting to observe that the same alkaloid was found in another South American species, *Rauwolfia sellowii*,[2] but in larger amounts.

Reserpiline and isoreserpiline were both identified by Stoll, Hofmann, and Brunner[3] in the leaves of *R. canescens* and although reserpiline was first isolated from *R. serpentina* by Klohs, Draper, Keller, and Malesh,[4] the isomeric base was not found in this species.

EXPERIMENTAL

The cortex of the root was well ground and the bases were extracted with methanol. The solvent was evaporated and the residue extracted with 10% acetic acid. To the acetic acid solution 10% sodium hydroxide solution was added to bring it to *p*H 9, when most of the bases precipitated. The crude precipitate was extracted with chloroform and the solution was filtered. Practically all the sedative activity passed into the chloroform.

Ajmaline. The chloroform solution was then extracted with 10% acetic acid and the extract alkalinized to *p*H 9 and extracted with benzene. After washing with water and drying, the benzene solution was evaporated to dryness and the residue dissolved in methanol after which crystals soon appeared. Recrystallization from methanol yielded material melting at $[\alpha]_D^{21}$ +129.2° (chloroform). It was transformed into isoajmaline, m.p. 260–262°, $[\alpha]_D^{20}$ +71.4° (chloroform). These data agree substantially with the constants of ajmaline and isoajmaline.[5]

Aricine. The acid-washed chloroform solution was evaporated to dryness and the residue dissolved in ten times its weight of methanol containing 10% of acetic acid. A crystalline precipitate appeared in a few minutes. It was filtered and washed with the same solvent. Recrystallization from methanol containing 1% of acetic acid yielded rhombic plates melting at 148–149°, which contained about one mole of acetic acid.

Anal. Calcd. for $C_{22}H_{26}N_2O_4 \cdot C_2H_4O_2$: acetyl (1) 9.67. Found: 8.20.

From this acetate, aricine was prepared by shaking the crystals with a mixture of ether and dilute ammonium hydroxide, washing with water, evaporating the dried ether solution, dissolving the residue in ethanol, and seeding with a sample of the base. Recrystallization from the same solvent yielded long prisms melting at 189°. A mixed melting point with authentic aricine was unchanged. $[\alpha]_D^{25}$ $-58.6 \pm 1°$ (*c*, 0.54, ethanol). *Hydrochloride*, m.p. 255°; *hydrobromide*, m.p. 263–264°; *oxalate*, m.p. 243–245°; and *picrate*, m.p. 222–223°.

Isoreserpiline. The methanolic acetic acid solution remaining after the isolation of aricine was evaporated to dryness and the residue treated with chloroform and ammonia water, whereupon all the bases passed again into chloroform. This solution was washed, dried, and evaporated and the residue was dissolved in benzene. The solution was submitted to chromatography on a column of aluminium oxide. Elution with benzene and evaporation of the first fractions yielded a residue which was dissolved in 60% methanol. Dilute nitric acid (1:10) was added to the solution. The crystalline nitrate of the base precipitated in a few minutes. Upon recrystallization from methanol needles, m.p. 264–265° (vac.), $[\alpha]_D^{20}$ $-46.3 \pm 3°$ (*c*, 0.08, water) were obtained.

Anal. Calcd. for $C_{23}H_{28}N_2O_5 \cdot HNO_3$: C, 58.09; H, 6.15; N, 8.84. Found: C, 58.22; H, 5.93; N, 8.77.

The base was separated by dissolving the nitrate in water and adding sodium hydroxide solution to *p*H 10.5. The amorphous solid was collected, washed with water, and dried. It was dissolved in benzene-hexane and when the solution was evaporated, isoreserpiline crystallized in hexagonal plates, m.p. 208°, $[\alpha]_D^{20}$ $-84.7 \pm 2°$ (pyridine); $[\alpha]_D^{21}$ $-112.0 \pm 2°$ (chloroform); $[\alpha]_D^{21}$ $-84.2 \pm 2°$ (ethanol). Stoll *et al.*[3] give m.p. 211–212°.

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