Decomposition of Quaternary Hydroxides. (a) *α-dl*-**Methadol.**—To a solution of 5 g. of *α-dl*-methadol methiodide in aqueous ethanol was added 3 g. of silver oxide. The mixture was stirred vigorously until the presence of iodide ion could no longer be detected. The mixture was filtered and the precipitate was washed with ethanol and water. The filtrate and washings were combined and concentrated at reduced pressure. The residue was transferred to a Claisen flask (using a minimum amount of ethanol) and the material was pyrolyzed under 15–20 mm. pressure. The distillate was dissolved in ethanol and cooled. The crystals which separated were recrystallized from ethanol; m.p. 88–89°.

(b) *α-d*-**Isomethadol.**—This was run as above using 10 g. of *α-d*-isomethadol methiodide. The yield was 3.9 g. of material melting at 63–64.5°.

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Bromohydrins from Olefins and N-Bromosuccinimide in Water

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The reaction of olefins with N-bromoacetamide in water to form bromohydrins has been known and used for many years.[2,3] It might be assumed that N-bromosuccinimide would behave similarly. Results have verified this assumption; for several years we have employed the latter reagent for the preparation of bromohydrins, and thence, olefin oxides. The availability and stability of this reagent, the ease of reaction and the yields obtained make this method superior, in many instances, to alternative methods. Some of the results that illustrate the scope of this method are summarized in Table I to supplement those already reported.[4]

Experimental

The general procedure used can be illustrated by the reaction of styrene (26.0 g., 0.25 mole), NBS (47 g., 95% purity, 0.25 mole) and water (100 ml.). These were stirred together vigorously at room temperature until the solid NBS disappeared (35 minutes). In all experiments, the disappearance of the NBS was a good criterion of the progress of the reaction. The styrene bromohydrin layer was separated and the aqueous layer extracted with benzene. Distillation of the combined product gave 41.0 g. (81.6%) of styrene bromohydrin, b.p. 120–123° (5 mm.), $n^{19}\mathrm{D}$ 1.5785; lit.[5] b.p. 109–110° (2 mm.), $n^{17}\mathrm{D}$ 1.5800.

In a similar run the styrene bromohydrin was taken up in ether and, after removal of the ether, was converted to styrene oxide by stirring for one-half hour with sodium hydroxide (15 g.) in water (75 ml.) at 60°. Extraction with ether and distillation gave 25.6 g. (85.3%) of styrene oxide, b.p. 65° (5 mm.), $n^{20}\mathrm{D}$ 1.5340; lit.[6] b.p. 87–88° (23 mm.), $n^{20}\mathrm{D}$ 1.5331. α-Methylstyrene gave equally good results.

The aqueous solution of succinimide from the separation of the bromohydrin was treated with sodium hydroxide (10 g.), cooled to 0°, and then bromine (13.6 ml.) was added. The mixture was shaken for two minutes, and the NBS filtered off, washed with cold water and dried to give 23.5 g. (50% recovery by reconversion) of NBS of 95% purity.

It was found that the bromohydrin could often be converted to the oxide by adding sufficient aqueous sodium hydroxide without separating the bromohydrin from the NBS–olefin mixture.

Tetrachloroethylene, crotonaldehyde, cinnamaldehyde and benzalacetophenone were used in this reaction without success.

TABLE I

BROMOHYDRINS FROM OLEFINS AND NBS IN WATER

Olefin	Time	Yield,[a] % Bromohydrin	Oxide
Cyclohexene[b]	10 min.	79.3[c]	81.2[d]
Trimethylethylene[b]	25 min.	76.5[e]	78.2[f]
Allylbenzene[g]	48 hr.[h]		56.3[i]
1,4-Dihydronaphthalene[g]	12 hr.	30.0[j]	
Indene[k]	3 hr.	59.1[l]	
Mesityl oxide[g]	15 min.		56.1[m]
Fumaric acid[g] (Na salt)	48 hr.		60.6[n]
Cinnamic acid[g,o] (K salt)	2 hr.	35.0[p]	

[a] The oxides usually were obtained by taking the bromohydrins up in ether and then converting the crude material directly to the oxide. [b] 0.25 mole of olefin, 0.25 mole of NBS and 100 ml. of water. [c] B.p. 73–75° (5 mm.), $n^{20}\mathrm{D}$ 1.5180; lit.[3b] b.p. 86.6–88.4° (10 mm.), $n^{25}\mathrm{D}$ 1.5184. [d] B.p. 129–130°, $n^{20}\mathrm{D}$ 1.4528; "Organic Syntheses," Coll. Vol. 1, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 185, gives b.p. 129–134°. [e] B.p. 49–51° (10 mm.), $n^{20}\mathrm{D}$ 1.4723; lit.[4] b.p. 48–51° (10 mm.), $n^{25}\mathrm{D}$ 1.4712. Comparable results were obtained by Winstein and Ingraham[4] in this same reaction. [f] B.p. 72–74°, $n^{18}\mathrm{D}$ 1.3885; lit.[4] b.p. 73–73.3°, $n^{25}\mathrm{D}$ 1.3822. [g] 0.125 mole of olefin in 100 ml. of ether stirred with 0.125 mole of NBS in 100 ml. of water. [h] A 50% yield of the oxide was obtained when the ether was omitted and a 4-hour reaction time used. [i] B.p. 72–75° (3 mm.); E. Fourneau and M. Tiffeneau, *Compt. rend.*, **140**, 1596 (1905), report b.p. 94–98° (15 mm.). [j] M.p. 106–106.5°; E. Bamberger and W. Lodter, *Ber.*, **26**, 1833 (1893), report the same value. [k] 0.063 mole of olefin, 0.063 mole of NBS and 50 ml. of water. [l] M.p. 130–131°, lit.[2] m.p. 131–132°. [m] B.p. 61–63° (20 mm.), $n^{17}\mathrm{D}$ 1.4290; E. Weitz and A. Scheffer, *ibid.*, **54**, 2327 (1921), report b.p. 44–48° (15 mm.). [n] M.p. 212–213°; W. Lossen, *Ann.*, **348**, 299 (1906), reported m.p. 203° and R. Kempf, *J. prakt. Chem.*, **83**, 388 (1911), reported m.p. 215°. These references describe the isolation method used. [o] 200 ml. of water used and reaction flask cooled in ice-bath during reaction. [p] M.p. 124–125°; E. Erlenmeyer, *Ber.*, **39**, 788 (1906), reported m.p. 125°.

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The Oxygenation of the Tri-(*p*-nitrophenyl)-methide Ion. A Novel Oxidation–Reduction Reaction[1]

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Tri-(*p*-nitrophenyl)-methane (I) is a pseudo-acid probably having a pK_a near 13[3] and its solution in alcoholic alkali exhibits the deep purple color of the highly resonance stabilized anion II.

Previously, it was reported that the air oxidation of the anion II in alcoholic alkali gave high yields of tri-(*p*-nitrophenyl)-carbinol (III) as well as traces of *p*-nitrophenol and 4,4′-dinitrobenzophenone.[4] This nearly exclusive production of carbinol III seemed anomalous to us in view of the ease of

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