sibly, the base strength) of the borohydride ion by the addition of triethylamine.[3]

Unfortunately, the latter premise could not be verified, because the produce of reduction of *p*-nitrostyrene oxide with lithium borohydride and triethylamine detonated during distillation.

Reduction of *p*-nitrostyrene oxide at room temperature in the presence of magnesium bromide afforded mixtures of the isomeric *p*-nitrophenylethanols which contained 16 and 7% 2-(*p*-nitrophenyl)ethanol. The product contained 62% of this component[1] in the absence of magnesium bromide. Reductions of *p*-methylstyrene oxide yield mixtures of the isomeric *p*-tolylethanols, which were 84 and 93% 2-(*p*-tolyl)ethanol in the presence of, and 67%[2] in the absence of magnesium bromide.

Other possible explanations of the change in product ratios will be considered. If magnesium borohydride were the reducing agent the steric requirement might be greater. This would lead to a smaller amount of attack at the benzyl atom of both oxides, which is not observed. A more serious consideration is the possible magnesium bromide-catalyzed isomerization[4] of *p*-methylstyrene oxide to *p*-tolylacetaldehyde, and of *p*-nitrostyrene oxide to *p*-nitroacetophenone, followed by borohydride reduction of the carbonyl compounds. Isomerization experiments with *p*-nitrostyrene oxide at room temperature in the absence of lithium borohydride yielded mainly non-distillable materials. At 0° the products were unchanged oxide and *p*-nitrostyrene bromohydrin. The latter compound was unaffected by treatment with lithium borohydride and magnesium bromide under the conditions used for the oxide. In the lithium borohydride–magnesium bromide reduction of the oxide little bromohydrin was formed, so the rates of the several possible reactions of *p*-nitrostyrene oxide are: reduction > bromide attack > isomerization. Isomerization cannot be an important influence on the product composition.

Treatment of *p*-methylstyrene oxide at 0° with magnesium bromide yielded an oil which polymerized when distillation was attempted at a bath temperature of 40° Partial isomerization to *p*-tolylacetaldehyde cannot be ruled out in the reduction with lithium borohydride and magnesium bromide, particularly in the light of the observation[5] that the reduction of styrene oxide with lithium aluminum deuteride and aluminum chloride gives 2-phenylethanol-1-*d*, presumably through phenylacetaldehyde as an intermediate.[6] The magnesium bromide used in the present study would be expected to be a less effective isomerization catalyst than aluminum chloride, but lithium borohydride is also a weaker reducing agent than lithium aluminum hydride. It is therefore, difficult to predict how the ratios of $k_{isomerization}/k_{reduction}$ should compare for the two reducing mixtures. It is probable that the ratio is larger for *p*-methylstyrene oxide than for *p*-nitrostyrene oxide.

Electrophilic catalysis probably causes the increased reactivity of sodium borohydride in the presence of aluminum chloride,[7] lithium halides,[3,8] and magnesium halides.[3] In all cases borohydride ion could be the reducing agent, which is, however, insufficiently nucleophilic to react with any but highly polarized carbonyl bonds, or bonds which are polarized by coordination of a metal cation or metal halide at the oxygen atom.

(3) Brown, Mead, and Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(4) The isomerization of styrene oxide to phenylacetaldehyde has been reported by Tiffeneau and Tchoubar, *Compt. rend.*, **207**, 918 (1938).

(5) Ernest L. Eliel, private communication.

(6) The reduction of a number of oxides with lithium aluminum hydride and aluminum chloride has been reported by Eliel and Delmonte, *J. Am. Chem. Soc.*, **78**, 3226 (1956).

EXPERIMENTAL

Reduction of oxides. *p*-Nitrostyrene oxide[1] or *p*-methylstyrene oxide[2] (0.10 mole) was added to a solution of magnesium bromide[9] (0.05 mole) and lithium borohydride (0.20–0.25 mole) in ether at room temperature. The products were isolated and analyzed by the methods previously reported.[1,2] The yields were 75–80%, which included 17–20% of unchanged oxide in the experiments with *p*-nitrostyrene oxide.

Isomerization of p-nitrostyrene oxide. A mixture of 0.075 mole of oxide and 0.05 mole of magnesium bromide stood in ether solution for 2 hours at 0°. After hydrolysis with dilute acid, 8.8 g. of the oily product was distilled, giving 2.7 g. of oxide, m.p. 78–82°, 5.7 g. of *p*-nitrostyrene bromohydrin, and 0.4 g. of residue. Similar treatment of *p*-methylstyrene oxide yielded an oil which polymerized when low temperature distillation was attempted.

p-Nitrostyrene bromohydrin (214 mg.) was treated with lithium borohydride and magnesium bromide under the conditions used for the reduction of the oxides. The product (115 mg., 54%) had the same melting point as the original bromohydrin (80–84°) as had a mixture of the two.

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(7) Brown and Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

(8) Kollenitsch, Fuchs, and Gabor, *Nature*, **173**, 125 (1954).

(9) Prepared in ether solution from bromine and magnesium.

The Aconite Alkaloids. XXXIII. The Identity of γ-Oxodelphinine

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Early in the study of delphinine,[1] the action of hot, dilute nitrous acid upon this alkaloid was in-

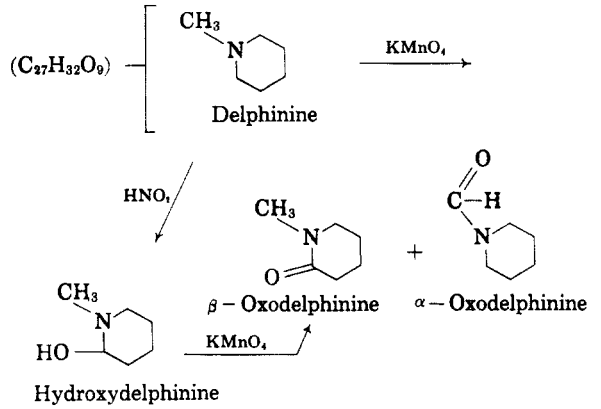
* Dr. Rathgeb's participation occurred in 1950–1951.

(1) W. A. Jacobs and S. W. Pelletier, *J. Am. Chem. Soc.*, **78**, 3542 (1956).

vestigated.[2] The main product of the reaction was a $C_{33}H_{45}NO_{10}$ base which proved to be a hydroxydelphinine. That the new hydroxyl group was secondary and situated on a carbon adjoining the nitrogen was demonstrated by oxidation in acetone with permanganate to a neutral oxodelphinine. Since this substance appeared to differ from β-oxodelphinine[3,4] in rotation and in the formation of a methylbenzoyloxodelphonine[2] whose rotation differed from the corresponding derivative obtained from β-oxodelphinine, it was provisionally designated "γ-oxodelphinine."

Recently we have had occasion to reexamine the identity of γ-oxodelphinine. Oxidation of a sample of hydroxydelphinine which had been recrystallized to constant melting point and rotation, m.p. 190–194°; $[\alpha]_D^{29}$ −0.8° (EtOH)[5] has given a product in 86% yield which is identical in every respect (mixture m.p., optical rotation in ethanol and acetic acid and infrared spectra) with β-oxodelphinine. The designation γ-oxodelphinine should therefore be discarded.

The partial formulae[1] below summarize the relationship between these simple oxidation products of delphinine.



EXPERIMENTAL[6]

Hydroxydelphinine. Crude hydroxydelphinine[2] was recrystallized four times from absolute ethanol, m.p. 190–194°, $[\alpha]_D^{29}$ −0.8° (*c*, 2.5 in ab. EtOH).

β-Oxodelphinine. A solution of 485 mg. of the above hydroxydelphinine in a mixture of 50 ml. of dry acetone and 0.5 ml. of acetic acid was treated with 300 mg. of finely powdered potassium permanganate and allowed to stand at 30° overnight. To the mixture was added an equal volume of water and 5 ml. of 10% sulfuric acid. After decomposing the manganese dioxide with sulfur dioxide the mixture was extracted with ether. The washed and dried extract was taken to dryness *in vacuo* and evaporated repeatedly with methanol to remove acetic acid. Crystallization of the residue from acetone gave 412 mg. (86%) of neutral product, m.p. 227–229°. Recrystallization from acetone gave four-sided platelets and prisms, m.p. 228–229°; $[\alpha]_D^{29}$ +24° (*c*, 2.6 in ab. EtOH); $[\alpha]_D^{29}$ +30° (*c*, 3.0 in AcOH). An authentic sample of β-oxodelphinine[3] did not depress the melting point and showed $[\alpha]_D^{29}$ +23.5° (*c*, 2.4 in EtOH); +30° (*c*, 2.0 in AcOH). The infrared spectra in Nujol were identical.

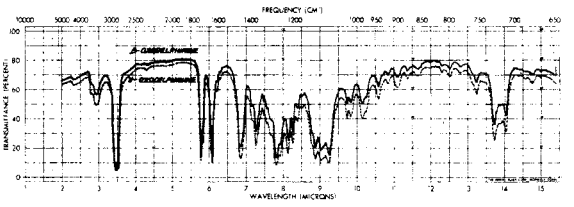


FIG. 1. INFRARED ABSORPTION SPECTRA IN NUJOL MULLS. ————, β-Oxodelphinine; ------, γ-Oxodelphinine.

Anal. Calc'd for $C_{33}H_{43}NO_{10}$: C, 64.58; H, 7.06. Found: C, 64.46; H, 7.23.

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(2) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **136**, 303 (1940).

(3) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **128**, 431 (1939).

(4) W. A. Jacobs and S. W. Pelletier, *Chemistry & Industry*, 948 (1955).

(5) The value reported previously (+7°) was probably due to contamination of the hydroxydelphinine with delphinine (+25°).

(6) Melting points are corrected and were taken on a hot-stage under a microscope equipped with a polarizer. Samples were placed on the stage about 15° below the melting point and the temperature was raised rapidly to within 5° of the melting point. The temperature then was raised 2° per minute.

Trinitrobenzene Adducts of Various Indole Compounds[1]

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Recently Redemann, *et al.*[2] and Weller, *et al.*[3] have reported a method for characterizing micro quantities of indole compounds by forming the 1,3,5-trinitrobenzene adducts. These complexes crystallize readily, have distinct melting points, and are sufficiently insoluble in cold ethanol to permit ready purification of small quantities of this derivative by recrystallization from this solvent. The ease of preparation makes these derivatives a convenient method to identify indole compounds occurring in natural products.

(1) Journal Article No. 1933 from the Michigan Agricultural Experiment Station, East Lansing. This work was supported by the Horace H. Rackham Research Endowment of Michigan State University.

(2) C. T. Redemann, S. H. Wittwer, and H. M. Sell, *J. Am. Chem. Soc.*, **73**, 2957 (1951).

(3) L. E. Weller, T. L. Rebstock, and H. M. Sell, *J. Am. Chem. Soc.*, **74**, 2690 (1952).