for the preparation of dimethyl 4,6-dinitroisophthalate. No precipitate formed on cooling the reaction mixture so the solution was diluted with ether and shaken out three times with water to remove sulfuric acid and most of the methanol. The ether was then shaken out with 1% aqueous sodium carbonate; 20 ml. was required. The carbonate extract freed of ether was acidified and furnished the crude acid methyl ester IV in 43% yield. The poor yield is probably a result of the high solubility of the acid ester. No attempt was made to obtain more of the acid ester from the water washings or the acidified carbonate extract. The ether solution that had been extracted with sodium carbonate left no residue on evaporation showing that no neutral ester had been formed. The acid methyl ester is too soluble in aqueous methanol to permit crystallization from that solvent. For analysis, the material was crystallized from ether–petroleum ether (b.p. 60–90°). The pure methyl acid ester IV melts at 184–185°.

Anal. Calcd. for $C_9H_6N_2O_8$: CH_3O, 11.1. Found: CH_3O, 11.44.

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Reaction of Hydrogen Bromide with Conjugated Dienols[1]

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Dimorphecolic acid, the major fatty acid of *Dimorphotheca aurantiaca* seed oil, rapidly consumes essentially one molar equivalent of hydrogen bromide in the Durbetaki titration for oxirane oxygen.[2] Formulation of this acid as 9-hydroxy-*trans,trans*-10,12-octadecadienoic acid indicated no grouping known to consume hydrogen bromide in this manner. We report here a comparison of the behavior of dimorphecolic acid with that of two model compounds, 2,4-hexadiene-1-ol (sorbyl alcohol) and 4,6-octadiene-3-ol, when treated with hydrogen bromide in nonaqueous media.

Although several aliphatic compounds with a secondary hydroxyl group in α-position to a conjugated diene are known, their behavior toward hydrogen bromide has not been examined. Kuhn and Grundmann[3] showed that 4,6-octadiene-3-ol is readily dehydrated by *p*-toluenesulfonic acid to 2,4,6-octatriene. Heilbron and co-workers,[4] as well as Braude and co-workers,[5] examined the effect of acid catalysts on related unsaturated alcohols. They found that compounds containing the system —CH=CH—CHOH—CH=CH— showed a pronounced tendency to rearrange to secondary conjugated dienols (—CHOH—CH=CH—CH=CH—) which were readily dehydrated to trienes. Heilbron examined the action of hydrochloric acid on the closely related hex-4-ene-1-yne-3-ol and similar compounds. Rearrangement similar to that of the dienols was observed, accompanied by replacement of hydroxyl by chlorine. However, the action of hydrobromic acid led to "unstable heterogeneous products."

2,4-Hexadiene-1-ol does not consume hydrogen bromide under the conditions of the Durbetaki[6,7] titration, but 4,6-octadiene-3-ol behaves in a manner analogous to that of dimorphecolic acid. It rapidly consumes a like amount of hydrogen bromide. Ultraviolet absorption studies indicate that essentially all the dienoid absorption is preserved immediately after titration, but triene is then formed at a slower rate. Appearance of triene is accompanied by disappearance of diene, suggesting that an initially formed bromodiene is dehydrobrominated. Similar results are obtained when a chloroform solution of hydrogen bromide is used rather than an acetic acid solution. Hydrogen chloride in acetic acid is not consumed rapidly.[8] Treatment of the octadienol with two thirds the titrimetric amount of hydrogen bromide results in eventual turning of the indicator. This observation supports the interpretation of replacement followed by elimination. The presence of free acid in mixtures that had stood some time after Durbetaki titration was confirmed by the rapid neutralization of sodium carbonate dissolved in acetic acid.

Although consumption of hydrogen bromide appears to be stoichiometric or nearly so, formation of triene is not. Diene and triene are in equilibrium (Fig. 1). The molar sum of conjugated diene and triene is 75–80% of that expected. The fate of the remainder is not known, but a possibility exists that in the equilibrium reaction some of the hydrogen bromide is added to yield a nonconjugated bromodiene that would not be estimated by the spectral method used. Conversion of diene to triene is reminiscent of the results Bergström and Hansson[9] obtained by treating linoleate with *N*-bromosuccinimide. The initially formed conjugated dienoid bromide lost hydrogen bromide to form a conjugated triene. They also observed that about 30% of the bromide was not eliminated, even after prolonged refluxing.

The mechanism sequence may resemble that proposed by DeWolfe and Young[10] for the reaction of

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[1] This is a contribution from the laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

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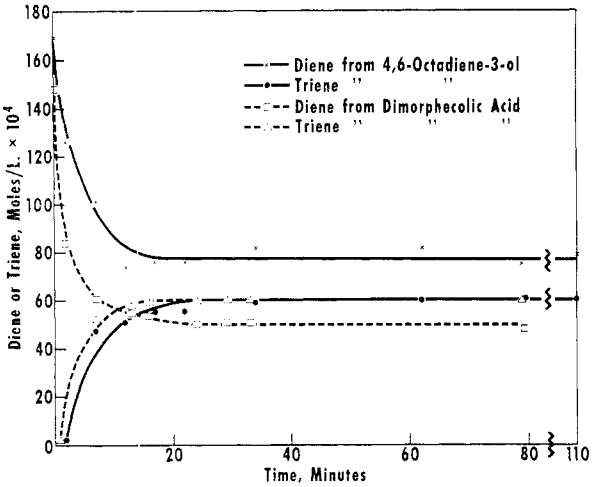

Fig. 1. Effect of hydrogen bromide on 4,6-octadiene-3-ol and on dimorphecolic acid

monoethenoid allylic alcohols with hydrogen bromide, followed by elimination to form triene. Interpretation of the initial substitution as an S_N2 mechanism is favored by the similar uptake of hydrogen bromide in either acetic acid or chloroform solution, by the slower uptake of the more weakly nucleophilic hydrogen chloride, and by the appearance of triene only after the uptake of hydrogen bromide, rather than concurrently as would occur from a carbonium ion intermediate in an S_N1 scheme. However, an S_N1 route is strongly supported by the lack of uptake of hydrogen bromide by the primary alcohol, 2,4-hexadiene-1-ol, which should have a lesser tendency toward carbonium ion formation than the secondary dienols.[11]

EXPERIMENTAL

Dimorphecolic acid. An analytically pure sample was prepared by chromatographing acid isolated by solvent partitioning of mixed acids from *Dimorphotheca aurantiaca* seed oil.[12] A benzene solution of acid (0.5 g.) was added to a silica gel column (5 g.) pretreated with 80% aqueous methanol:-hexane (1:1). The pure acid (0.22 g.) was eluted by benzene under nitrogen. It was a semisolid at room temperature. $\lambda_{max}^{C_2H_5OH}$ 231, ϵ 28,800.

Anal. Calcd. for $C_{18}H_{32}O_3$: C, 73.0; H, 10.8. Found: C, 73.3; H, 10.9.

Trans,trans-2,4-hexadiene-1-ol. Ethyl sorbate was reduced by lithium aluminum hydride by a slight modification of the method of Nystrom and Brown.[13] The alcohol was obtained as a colorless mobile liquid. Its 3,5-dinitrobenzoate, prepared according to Reichstein and co-workers,[14] melted at 82–84° (Fisher-Johns[15] block) (lit. m.p., 85°).

Trans,trans-4,6-octadiene-3-ol. Technical grade hexadienal[16] was purified by distillation at 65.5–66°/18 mm., $\lambda_{max}^{C_2H_5OH}$ 271, ϵ 28,700. Hausser, *et al.*[17] reported ϵ 26,500. The distilled hexadienal was condensed with ethylmagnesium bromide according to Kuhn and Grundmann[3] to give the octadienol (78%) $\lambda_{max}^{C_2H_5OH}$ 229, ϵ 24,200. Distillation at 77–79°/20 mm. gave a product having $\lambda_{max}^{C_2H_5OH}$ 229, ϵ 28,400, n_D^{18} 1.4895 (lit., 1.4892).

Hydrogen bromide consumption. Uptake of hydrogen bromide by the unsaturated alcohols was determined by Durbetaki titration[6,7] in benzene–acetic acid solution. For spectral studies, acetic acid only was used as solvent. This solvent change reduced the molar hydrogen bromide uptake to 0.77 (from 0.9 or higher).

Hydrogen bromide reactions. The unsaturated alcohols (0.15–0.2 mmole) were dissolved in 5–10 ml. of glacial acetic acid and were treated with a volume of 0.03–0.05*N* hydrogen bromide in acetic acid found, by prior titration, to be rapidly consumed. At intervals, 0.1-ml. aliquots were removed and diluted to 100 ml. with absolute ethanol. Conjugated diene was determined in 1-cm. cells in a Beckman Model DU spectrophotometer, using the experimentally determined extinction coefficients given above. A molecular extinction of 59,200 at 264 mμ[18] was used for conjugated triene. Data in Fig. 1 are from one of several similar experiments.

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(15) Mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

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Specificity of the Phenolic Component for Sakaguchi Reaction[1]

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In 1925, Sakaguchi observed that an intense red color was produced when arginine was treated in alkaline solution with 1-naphthol and hypohalite[2]; it was found later that the reaction was specific for a class of monosubstituted guanidines.[2,3] The specificity of the phenolic component for this reaction has not, however, been studied adequately

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(1) (a) This constitutes Paper V in a series *Studies on Sakaguchi Reaction;* for Paper IV, see K. R. Bhattacharya, *Ann. Biochem. Exptl. Med.*, **20**, 57 (1960). (b) Presented in part by K. R. Bhattacharya and J. Datta before the 46th session of the Indian Science Congress Association, Delhi, January 21–28, 1959.

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