(paper chromatography). The mother liquor was evaporated to dryness to give 13.0 g. of a buff colored powder. This fraction was dissolved in 100 ml. of ether-benzene mixture (3:1) and chromatographed on 260 g. of deactivated acid-washed alumina. Elution with ether gave 350 mg. of crude ibogamine, which crystallized from methanol. When the solvent was changed to chloroform-ether mixtures, then to chloroform alone, 450 mg. of crude ibogaine were obtained. This fraction was followed by 520 mg. of a base which could not be induced to crystallize and gave a bright rose red color with Keller's reagent. The hydrochloride salt was prepared in the usual manner. After recrystallization from methanol-ether, 120 mg. of the hydrochloride were obtained, m.p. 264–266° (dec.).

Anal. Calcd. for $C_{21}H_{28}O_2N_2$.HCl: C, 66.91; H, 7.75; N, 7.43; Cl, 9.41; OCH_3(2), 16.47. Found: C, 66.58; H, 7.86; N, 7.39; Cl, 9.40; OCH_3, 16.75, 15.94.

The free base was liberated and crystallized from aqueous methanol, m.p. 141–143°. (The m.p. of the mixtures of ibogaline and ibogaine, and ibogaline and ibogamine were 112–119° and 113–123° respectively), $[\alpha]_D^{26} = -42.9°$ ($CHCl_3$, C = 1).

Anal. Calcd. for $C_{21}H_{28}O_2N_2$: C, 74.08; H, 8.29; N, 8.23; OCH_3 (2), 18.24. Found: C, 73.87, 74.30; H, 8.33, 8.48; N, 8.21, 8.23; OCH_3, 18.26. (The second analysis was obtained on material sublimed at 0.01 mm. pressure and 115°.)

The ultraviolet spectrum has the following bands: λ_{max}^{EtOH} 228 mμ (log a_M 4.43), 304 mμ (log a_M 4.01).

The infrared spectrum of ibogaline is characterized by the following prominent bands: $\lambda_{maax}^{CHCl_3}$ 2.91 (indole NH), 6.13,[13] 6.28,[13] 6.39,[13] 6.74,[13] 7.65, 8.64, 8.80, 9.79, and 11.96.[13]

ADDED IN PROOF: Since the submission of this paper, U. Renner, D. A. Prins and W. G. Stoll [*Helv. Chim. Acta*, **42**, 1572 (1959)] have reported the isolation of an alkaloid, conopharyngine, from the bark of *Conopharyngia durissima* Stapf. A direct comparison of descarbomethoxy conopharyngine with our ibogaline has shown that, although the two compounds have different X-ray patterns, they are identical in all other respects (mixture m.p., optical rotation, and infrared spectrum in chloroform solution); therefore, conopharyngine is carbomethoxy ibogaline. We should like to thank Dr. Prins for the sample of descarbomethoxy conopharyngine.

Acknowledgment. The author wishes to thank Dr. H. E. Boaz for the infrared data, L. G. Howard for the ultraviolet spectra, W. L. Brown, G. M. Maciak, H. L. Hunter, and Miss G. Beckmann for microanalyses.

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(13) These bands occur at the same wave lengths in the infrared spectrum in chloroform solution of 2,3-dimethyl-5,6-dimethoxyindole and are absent in the spectrum of ibogamine.

Epoxidation of Diethyl Ethylidenemalonate by Alkaline Hydrogen Peroxide

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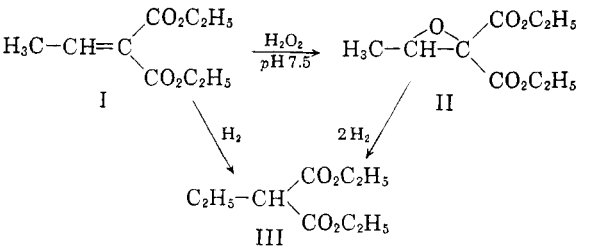
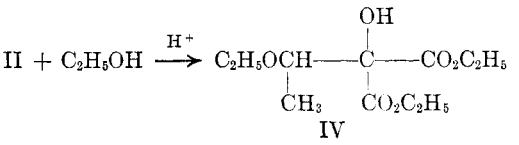
The technique recently employed for the epoxidation of acrolein to glycidaldehyde[1] has also been successfully applied to an α,β-unsaturated diester, diethyl ethylidenemalonate (I). A solution of this ester in methanol containing 1.1 mol. equiv. of



50% hydrogen peroxide was treated dropwise with 1*N* aqueous alkali to effect the reaction over a 2-hr. period at 35–40° and *p*H 7.5–8. The product, ethyl 2-carbethoxy-2,3-epoxybutyrate (II) was readily isolated in 82% yield.

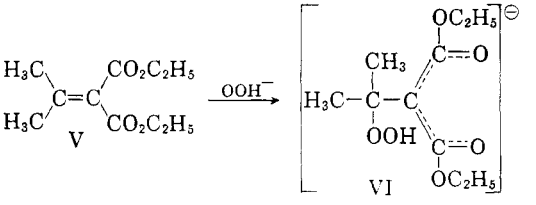
Hydrogenation of II proceeded with the absorption of 2 mol. of hydrogen to give diethyl ethylmalonate (III). The latter was also obtained from I to provide an authentic sample of ethylmalonic acid. When the hydrogenation of II was halted after 1 mol. uptake, only II and III were found.

Although II did not give the usual[2] titration for oxirane oxygen, the presence of that functional group was further indicated by reaction of II with hot acidic ethanol to give what was most likely the hydroxy ether IV, or the isomer having hydroxyl and ethoxyl groups reversed. The analysis of carefully fractionated IV was only fair; a low sapon-



ification equivalent, in particular, indicated the presence of an impurity.

The reaction of diethyl isopropylidenemalonate (V) with hydrogen peroxide proceeded to the extent of only 23% in 3 hr. at 45–50° and a higher *p*H (8–9) than used with I. Since alkali consumption was excessive during this period, the reaction was abandoned.



Failure of V to undergo epoxidation is in striking contrast to the facile reaction observed with I. This difference in reactivity is best rationalized on the basis of a steric inhibition of coplanarity

(1) G. B. Payne, *J. Am. Chem. Soc.*, **80**, 6461 (1958); **81**, 4901 (1959).

(2) J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

required for stabilization of the intermediate carbanion (VI).[3]

EXPERIMENTAL

Alkaline epoxidation of diethyl ethylidenemalonate. To a 1-l., five-neck, round-bottom flask equipped with stirrer, thermometer, *p*H electrodes and dropping funnel, were charged 400 ml. of methanol, 122 g. (0.656 mol.) of diethyl ethylidenemalonate[4] and 49 g. (0.72 mol.) of 50% hydrogen peroxide. To the dropping funnel was charged *N* sodium hydroxide.

The mixture was held at 35–40° by periodic cooling with an ice bath as alkali was added as needed to maintain a *meter* *p*H of 8.5–9.0; the true *p*H by indicator paper was about 7.5. At the end of 1 hr., 85% of the peroxide had been consumed (iodometric titration) along with 37 ml. of caustic. After an additional hour at meter *p*H 9–9.5, the reaction was essentially complete; 81 ml. of caustic had been consumed.

After dilution of the colorless reaction mixture with 1-l. of water, three 250-ml. portions of chloroform were used for extraction. The combined extract was washed, dried over anhydrous magnesium sulfate, and concentrated on the steam bath to a colorless residue. Distillation of the latter through a 0.7 × 50 cm. glass spiral packed column afforded 5 g. of pre-cut, b.p. 70–80° (1 mm.) and 99 ml., 109 g. (82% yield) of ethyl 2-carbethoxy-2,3-epoxybutyrate, b.p. 80–81° (1 mm.); n_D^{20} 1.4294.

Anal. Calcd. for $C_9H_{14}O_5$: C, 53.4; H, 7.0; O, 39.6; sapon. equiv., 101; mol. wt., 202. Found: C, 53.2; H, 6.9; O, 39.0; sapon. equiv., 100; mol. wt., 195 ± 10.

Hydrogenation of ethyl 2-carbethoxy-2,3-epoxybutyrate. To a 300-ml. capacity autoclave were charged 116 g. (0.57 mol.) of epoxy diester, 50 ml. of ethanol, and 2 teaspoons of Raney nickel catalyst. Hydrogenation was compete in 6 hr. at 100° and 300–900 lb. pressure; it was necessary to repressure three times. Exactly 2 mol. equiv. of hydrogen were consumed.

After cooling, venting, and filtration, the filtrate was distilled through the small spiral column to give 83 g. (77% yield) of diethyl ethylmalonate, b.p. 58–59° (2 mm.); n_D^{20} 1.4147 (lit.[5] b.p. 94–96° (13 mm.); n_D^{20} 1.4170).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.6; sapon. equiv., 94.1. Found: C, 56.9; H, 8.5; sapon. equiv., 93.5.

Saponification of 17 g. of this ester afforded 10 g. (83% yield) of ethylmalonic acid, m.p. 109–111°. Recrystallization from benzene gave 6 g. of pure acid, m.p. 112–113°; mixed m.p. with an authentic sample[6] of ethylmalonic acid (m.p. 112–113°) was not depressed.

Anal. Calcd. for $C_5H_8O_4$: equiv. wt., 66. Found: equiv. wt., 66.

Ethanolysis of ethyl 2-carbethoxy-2,3-epoxybutyrate. A solution of 16 g. (0.08 mol.) of epoxy diester in 100 ml. of ethanol containing 2 ml. of concentrated sulfuric acid was allowed to reflux overnight. The cooled solution was treated with 10 ml. of water and 10 g. of calcium carbonate to neutralize the catalyst. After filtration and concentration, the resulting residue was taken up in warm ether and filtered to remove 4.5 g. of insoluble material. Distillation of the filtrate through a 0.7 × 50 cm. spiral packed column gave 14.9 g. of material, b.p. 85–87° (0.3 mm.), n_D^{20} 1.4323, having an analysis in substantial agreement for ethyl 2-carbethoxy-2-hydroxy-3-ethoxybutyrate or its isomer, ethyl 2-carbethoxy-2-ethoxy-3-hydroxybutyrate.

Anal. Calcd. for $C_{11}H_{20}O_6$: C, 53.2; H, 8.1; sapon. equiv., 124; hydroxyl value, 0.40 equiv./100 g. Found: C, 52.6; H, 8.0; sapon. equiv., 116; hydroxyl value, 0.42 equiv./100 g.

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(3) See H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959) for a recent discussion of the stereochemistry of alkaline epoxidation.

(4) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 3343 (1923).

(5) V. H. Wallingford, A. H. Homeyer, and D. M. Jones, *J. Am. Chem. Soc.*, **63**, 2056 (1941).

(6) From diethyl ethylidenemalonate by hydrogenation followed by saponification.

Phosphonic Acids and Esters. I. Radical Initiated Addition of Phosphorous Acid to Olefins

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The generation of carbon-phosphorus bonds by addition to olefins of radicals produced by homolysis of phosphorus-hydrogen bonds has been investigated by a number of workers during the past decade. The following phosphorus compounds have been utilized: phosphine and alkyl phosphines, hypophosphorus acid, dialkyl phosphonates, alkyl and aryl phosphinates.[1,2] In conjunction with studies in progress on phosphonic acids containing acid labile groupings, it became important to investigate methods which would lead to the direct synthesis of free phosphonic acids, avoiding the hydrolytic step necessary in conventional synthetic methods. Toward this end, the reaction of phosphorous acid (I) with olefins was investigated. In analogy with previously investigated systems, it was expected that homolysis of the phosphorus-hydrogen bond in I would lead to a chain reaction with the over-all result:

$$RCH{=}CH_2 + HP(O)(OH)_2 \longrightarrow RCH_2CH_2P(O)(OH)_2$$

This expectation is borne out by the experimental results; however, the reaction does not constitute a practical approach to alkylphosphonic acids because of the meager yields obtained.

The reactions of three representative olefins (1-octene, cyclohexene, and indene) with I were investigated; in the absence of peroxides, no reaction occurred at reflux temperature in either aqueous dioxane or acetic acid. When the reactions were conducted in the presence of either dibenzoyl peroxide or di-*t*-butyl peroxide at 90° or ultraviolet irradiation at room temperature, the expected products were obtained. Reactant ratios, reaction conditions, and yields of the purified products are presented in Table I.

(1) P. C. Crofts, *Quarterly Revs.*, **12**, 363 (1958).

(2) L. A. Hamilton, paper presented at the 134th meeting of the American Chemical Society, Chicago, Ill., September 11, 1958; Abstracts, p. 69P.