Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61. Found: C, 65.46; H, 6.56.

1-Methyltryptophan (VII). The acetyl derivative V (3.0 g.) was refluxed with 20 ml. of 2*N* hydrochloric acid for 2 hr. The solution was evaporated to dryness *in vacuo* and the residue redissolved in water. The 1-methyltryptophan crystallized (1.8 g., 72% yield) on addition of 1.5 g. of sodium acetate dissolved in a little water. Recrystallization from aqueous ethanol (charcoal) yielded colorless plates of VII, m.p. 250–251°.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.87; H, 6.59; N, 12.82.

The infrared spectrum of VII, determined as a suspension in potassium bromide, had prominent maxima at 1623, and 735 cm.$^{-1}$

The picrate of the amino acid was obtained on admixture of methanolic solutions of VII and picric acid. Crystallization from water gave fine orange-red needles of the hydrated picrate, m.p. 142–143° (with dec.).

Anal. Calcd. for $C_{12}H_{14}N_2O_2.C_6H_3N_3O_7.H_2O$: C, 46.45; H, 4.11. Found: C, 46.31; H, 4.10.

The amino acid hydrochloride was obtained by addition of ethanolic hydrogen chloride to VII, refluxing, and allowing to cool. Recrystallization from ethanol gave colorless needles of 1-methyltryptophan hydrochloride, m.p. 235–236° (dec.) (lit.[3] 239–242°).

Anal. Calcd. for $C_{12}H_{14}N_2O_2.HCl$: C, 56.59; H, 5.94. Found: C, 56.50; H, 6.01.

1-Ethyltryptophan (VIII). The acetyl derivative VI was refluxed with 2*N* hydrochloric acid for 2 hr. and then evaporated to dryness *in vacuo*. The residue was dissolved in water and brought to a *p*H of 6 by the addition of sodium hydroxide. The 1-ethyltryptophan immediately crystallized in small prisms, m.p. 234–235° (dec.). Crystallization from aqueous ethanol yielded colorless plates, m.p. 225–226° (dec.).

Anal. Calcd. for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.07; H, 6.95; N, 11.89.

The picrate crystallized in short orange prisms from water as the monohydrate, m.p. 127–129° (dec.).

Anal. Calcd. for $C_{13}H_{16}N_2O_2.C_6H_3N_3O_7.H_2O$: C, 47.60; H, 4.42. Found: C, 47.61; H, 4.47.

Decarboxylation of the 1-alkylamino acids. (*a*) *1-Methyltryptamine.* 1-Methyltryptophan (1.0 g.) was added to molten fluorene (10 g.) heated on a metal bath at 270°. After 2–3 min. all evolution of carbon dioxide ceased and the mixture was cooled, diluted with benzene, and extracted with dilute hydrochloric acid. The aqueous extract was clarified by shaking with ether and then made basic with sodium hydroxide and extracted with ether. The dried ether extract was evaporated and the residue distilled (180°/0.1 mm.) to yield 1-methyltryptamine as a pale yellow oil (0.484 g., 64% yield). The picrate was obtained as yellow prismatic needles from ethanol, m.p. 183–184° (lit.[8] 180–181°). The hydrochloride was obtained as colorless plates from ether-ethanol, m.p. 205–206° (dec.) (lit.[3] 199–202°). The phthalimide was prepared by refluxing the amine with an equal weight of phthalic anhydride in acetic acid. Crystallization from the same solvent yielded pale yellow needles, m.p. 178–179° (lit.[3] 177–177.5°).

(*b*) *1-Ethyltryptamine.* The 1-ethyltryptophan was decarboxylated in molten fluorene at 240–250°. The amine was isolated as described in the previous preparation and was obtained as a pale yellow oil in 53% yield. The picrate was obtained as orange prisms from ethanol, m.p. 182.5–183° (lit[9] 180–181°). A large depression in melting point was observed on admixture with the picrate of N-ω-ethyltryptamine,[9] m.p. 186–187°. 1-Ethyltryptamine hydrochloride separated from a mixture of ethanol and ether in fine colorless needles, m.p. 193.5–194°.

Anal. Calcd. for $C_{12}H_{16}N_2.HCl$: C, 64.13; H, 7.63. Found: C, 64.20; H, 7.73.

1-Ethyltryptamine phthalimide was obtained as pale yellow prismatic needles from ethanol, m.p. 150–151°.

Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70. Found: C, 75.66; H, 5.78.

Paper chromatography of the amino acids. Chromatography was carried out on Whatman No. 1 paper using a mixture of 1-butanol (400 ml.), acetic acid (100 ml.), and water (250 ml.) as the developing solvent. The R_f values of tryptophan, 1-methyltryptophan, and 1-ethyltryptophan in this solvent were 0.63, 0.71, and 0.79, respectively. The amino acids appeared as brown spots on spraying with Millon reagent.

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(8) E. Späth and E. Lederer, *Ber.*, **63**, 2102 (1930).
(9) K. Eiter and O. Svierak, *Monatsh.*, **83**, 1453 (1952).

Anionic Exchange Resins as Catalysts in the Preparation of Fulvenes

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The preparation of fulvenes by the condensation of cyclopentadiene with aldehydes or ketones in the presence of bases, such as ammonia and the alcoholates or hydroxides of sodium and potassium,[1] has long been known.[2] Work in this laboratory has now demonstrated that ion exchange resins of either the high or medium base strength type also are capable of catalyzing this reaction, giving in many cases yields comparable to those obtained with more conventional catalysts. This system possesses an advantage in that the reaction time can be quite easily controlled simply by regulating the contact time of the reactants with the ion exchange resin. Thus it is possible to achieve some success in the preparation of sensitive monosubstituted fulvenes and of fulvene itself by simply stopping the condensation before the secondary, base-catalyzed reactions start. This also helps to avoid complications caused by the presence of a base during the isolation and purification of the product.

Several fulvenes were prepared using this method, including fulvene, methyl fulvene, ethyl fulvene, and dimethyl fulvene. Of these, only dimethyl fulvene was isolated. In spite of numerous attempts, the remainder of the fulvenes could not be purified due to their extreme instability. Attempts to react them with maleic anhydride in order to prepare their Diels-Alder adducts as derivatives were also unsuccessful because of both their thermal instability and the reactivity of the residual cyclopentadiene in this reaction. Thus it was necessary to depend on the intense color of the products and their characteristic ultraviolet absorption spectra for proof of their presence. This of course, makes it

(1) J. H. Day, *Chem. Revs.*, **53**, 167 (1953).
(2) J. Thiele and H. Balhorn, *Ann.*, **348**, 1 (1906).

impossible to determine yields of these sensitive fulvenes so that only these qualitative results can be given at this time. It is hoped that future refinements in technique may make a more quantitative treatment of this method possible.

EXPERIMENTAL

The ion exchange resins used in these reactions were prepared by first generating their basic forms with 20% aqueous potassium hydroxide, followed by thorough washing with distilled water. They were then washed well with methanol and dried under reduced pressure at room temperature. The dried resins were stored under nitrogen.

Dimethyl fulvene. Forty-four grams (0.67 mole) of cyclopentadiene was cooled to 0° in a 250 ml. glass-stoppered flask and 23 g. of Dowex 1-X10 (a strongly basic quaternary ammonium hydroxide type ion exchange resin) and 29 g. (0.5 mole) of acetone were added rapidly. The temperature of the mixture was permitted to rise slowly to room temperature and after 1.5 hr. a vigorous exothermic reaction commenced. The flask was shaken until the temperature began to fall and the reaction subsided (about 10 min. were required). The dark mixture was then allowed to stand at room temperature overnight. The Dowex 1-X10 was removed by filtration and thoroughly washed with ether, and the washings were combined with the original filtrate. The ether and unreacted starting materials were removed at 80 mm. pressure and the residue was kept at 30°/10 mm. for 1.5 hr. Fractionation of the residue through an 8 × 3/4 in. column packed with berl saddles gave 29.7 g. of the bright yellow dimethyl fulvene boiling from 41.5–45.5°/10 mm., yield 46.7%.

Methyl fulvene. A mixture of 22 g. (0.5 mole) of acetaldehyde and 44 g. (0.67 mole) of cyclopentadiene was introduced into the top of a 10 × 270 mm. column of Permutit A (an anionic exchange resin of medium base strength, consisting primarily of tertiary amine exchange sites) surrounded by a jacket containing circulating methanol cooled to −22 to −24° by an external Dry Ice–acetone bath. The rate of addition was adjusted so that the reactants were in contact with the resin for 1.25 hr., about 7 hr. being required to complete the reaction. The unreacted starting materials were removed at room temperature by distillation through a Dry Ice–cooled column at *ca.* 17 mm. The column was then permitted to warm to room temperature, the pressure was lowered to 0.75 mm. and the receiver was cooled in a Dry Ice–acetone bath. Under these conditions 16.3 g. of a bright yellow distillate (a solid at −70°) was collected without applying heat to the distilling flask. The ultraviolet absorption spectrum of this distillate in methanol showed a strong maximum at 255 mμ and a very weak one at 290 mμ. The absorption spectrum of dimethyl fulvene has a strong maximum at 265 mμ and a weak one a 357,[1] while that of fulvene is reported[3] to have maxima at 242 mμ (strong) and 362 mμ (weak). Thus the strong peak should be due to methyl fulvene.

Ethyl fulvene. In a 300-ml. three neck flask equipped with a stirrer, thermometer, reflux condenser, and addition funnel were placed 19.8 g. (0.30 mole) of cyclopentadiene and 10 g. of Dowex 1-X10. The mixture was cooled to 0° under nitrogen in an ice bath, and 14.5 g. (0.25 mole) of propionaldehyde was added over a 15-min. period while the temperature rose to 10–12°. After an additional 10 min. the mixture was warmed to 25° and the ion exchange resin was rapidly removed by filtration. The red-orange filtrate was transferred to a 50-ml. distilling flask, 3 g. of anhydrous magnesium sulfate was added, and the low-boiling material was removed at 20 mm., using a water bath at 40–50° for a heat source. After 3 hr. under these conditions no further boiling occurred and the orange oil was filtered to yield 14 g. of material. Its ultraviolet absorption spectrum showed a strong maximum at 256 mμ and a weak maximum at 360 mμ (see the previous section).

Fulvene. A mixture of 18.7 g. of 40% aqueous formaldehyde (equivalent to 0.25 mole of formaldehyde), 70 ml. of methanol, and 19.8 g. (0.3 mole) of cyclopentadiene was introduced into the top of a 20 × 150 mm. column of Amberlite IRA 400 (a strongly basic quaternary ammonium hydroxide type resin) at a rate such that the contact time with the catalyst was about 30 sec., 1 hr. being required to complete the reaction. The temperature of the column was maintained at *ca.* 5° throughout the reaction by circulating tap water. The orange oil which separated was removed and the aqueous layer was extracted 5 times with 10-ml. portions of ether. The extracts were combined with the original oil layer, dried over magnesium sulfate, and the solvent and other low boilers removed under reduced pressure as described in the previous sections. The yield of the orange product was 5.3 g. A single rather weak maximum occurred at 240 mμ in its ultraviolet absorption spectrum. This agrees quite well with the strong peak reported for fulvene[3] (see the preparation of methyl fulvene described previously). The absence of the second, weaker absorption at 362 mμ is probably due to the low concentration of the fulvene indicating a lack of purity in the product.

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Succinoylation of the Chloro- and Bromonaphthalenes

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Although the four halobenzenes have been converted to the corresponding β-(*p*-halobenzoyl)-propionic acids with succinic anhydride and aluminum chloride,[2] no successful succinoylation of the halonaphthalenes has been reported.[3] It is shown below that the chloronaphthalenes and 2-bromonaphthalene can be succinoylated, although the yields of pure products are low and the products are sometimes rearranged.

When 1-chloronaphthalene was treated with aluminum chloride and succinic anhydride in either tetrachloroethane or carbon disulfide solutions, an 87% and a 10% yield, respectively, of a mixture of difficultly separatable crude acids was obtained. Separation could best be effected by conversion of the acid mixture to the methyl esters and separation of the esters. From the mixture of methyl

(1) From the Senior Honors thesis of Y. Chu (Mrs. Y. C. Meinwald), 1952, and the M.A. thesis of N. Shieh, 1955.

(2) E. Berliner in *Org. Reactions*, V, Chapter 5 (1949).

(3) The succinoylation of 1-bromo-4-methylnaphthalene has been described as unpromising. R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 2720 (1932).