isolation of 2,5-dimethoxyaniline in 12% yield indicated that a "benzyne" intermediate had indeed formed. To minimize the competing reaction, sodium amide in liquid ammonia[13] was used in subsequent experiments in slight molar excess to the bromo compound plus nucleophile.

An attempt to use ethyl acetate as a potential nucleophile was also unsuccessful. Examination of Fisher-Hirschfelder-Taylor models suggested that the formation of the products expected from reaction with diethyl malonate or ethyl acetate would be unlikely for steric reasons.

α-Sodio sodium acetate[14] was also tried as a nucleophile at the boiling points of the inert solvents *p*-xylene and tetrahydrofuran as well as at room temperature with 2,5-dimethoxybromobenzene itself as a suspending medium. The α-sodio sodium acetate appeared to be partially soluble in each of these reaction media but in no case could the product of interest be isolated.

When acetonitrile was tested as a potential nucleophile, the reaction mixture after work-up yielded 2,5-dimethoxyphenylacetic acid. While synthesis of this compound *via* the nitrile results in yields of approximately 10%, the reaction takes little time and work-up procedures are short. Thus the synthesis appears to hold promise for the synthesis of homogentisic acid labeled in the side chain for metabolic studies. In addition the reactions constitute a novel route to 2,5-dimethoxyphenylacetic acid.

EXPERIMENTAL

Materials. 2,5-Dimethoxybromobenzene (I) was prepared in approximately 60% yield by the methylation of bromohydroquinone employing conventional reaction conditions with dimethyl sulfate and sodium hydroxide. The product was obtained as a colorless oil which was identified by boiling point, analysis for C, H, and Br, and infrared analysis.[15]

Attempted reaction of I with diethyl malonate. Isolation of 2,5-dimethoxyaniline (II). To approximately 300 ml. of liquid ammonia (−77°) and 0.28 g. of ferric nitrate·9 H_2O, approximately 2 g. of potassium was added and the mixture stirred for 15 min. to form the catalyst (metallic iron) for the preparation of potassium amide. Additional potassium (43.4 g., 1.14 mol.) was then added with stirring. After evolution of hydrogen was complete, 19.2 g. of diethyl malonate (0.12 mol.) was added dropwise with stirring, followed by 21.7 g. of 2,5-dimethoxybromobenzene (0.1 mol.) and the temperature of the reaction mixture raised to approximately −30° for 1 hr. Enough 10% ammonium chloride was then carefully added to convert amide ion to ammonia and the ammonia was then distilled out of the reaction mixture at reduced pressure. The reaction mixture was extracted with diethyl ether, and the ether removed by distillation to leave a dark brown oil. The oil was fractionated by distillation under reduced pressure and partial characterization of minor fractions gave no indication that diethyl(2,5-dimethoxyphenyl)malonate had been formed. The major fraction which distilled at about 1 mm. from 80–90° and crystallized in the condenser was collected. This solid was further purified by sublimation to yield 1.8 g. (12%) of white, crystalline II, which melted at 74–76° (literature m.p. 80°[16]) and behaved as a typical amine.

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.15. Found: C, 62.59; H, 7.23; N, 9.27.

The infrared spectrum supported the structure of the product.

Reaction of I *with acetonitrile. Preparation of 2,5-dimethoxyphenylacetic acid* (III). Reaction conditions were similar to those described above except that to one flask (−30°) containing 150 ml. of ammonia and 3.84 g. of sodium (0.17 mol.), 6.93 g. of acetonitrile (0.17 mol.) was added followed by the addition of 17.8 g. of 2,5-dimethoxybromobenzene (0.083 mol.). The contents of a second flask (−30°) containing initially 250 ml. of ammonia, 3.84 g. of sodium (0.17 mol.), and a catalytic amount of ferric nitrate·9 H_2O were then slowly flushed into the first flask. After complete transfer, which took approximately 30 min., the reaction mixture was covered with anhydrous diethyl ether and ammonium chloride added to liberate ammonia. To the reaction mixture more diethyl ether was added, and the ether was then removed from the ether extract by distillation, leaving a brown oil. This oil was then submitted to hydrolysis in twice its volume of concentrated hydrochloric acid for 4 hr. During hydrolysis a viscous oil separated, and after hydrolysis this oil was dissolved in 10% sodium carbonate. Acidification of the bicarbonate solution to *p*H 2 yielded a tan crystalline compound which was isolated in 15% yield (2.38 g). Purification of the tan product by sublimation and recrystallization resulted in 50–70% recovery of the tan product as a white, crystalline compound (III). III melted at 121.0–121.5° (literature m.p., 122–123°[12]) and the infrared spectrum supported the proposed structure.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.19; H, 6.13.

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[13] Sodium amide is less soluble in ammonia at −30° than is potassium amide.

[14] We wish to thank Ethyl Corp., New York, for a generous gift of this compound.

[15] Elemental analyses were performed by Weiler and Strauss, Microanalytical Laboratory; infrared analyses were made by the Division of Industrial Research, Washington State University.

[16] A. Blackhall and R. H. Thomson, *J. Chem. Soc.*, 3916 (1954).

Epoxidation of Cinnamaldehyde by Alkaline *tert*-Butyl Hydroperoxide

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An attempt was made to form an epoxide of cinnamaldehyde with alkaline hydrogen peroxide using the technique recently described for the epoxidation of acrolein and α-methylacrolein.[1] As the

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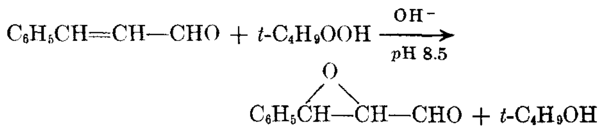
[1] G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959); E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921) obtained only acidic product from the attempted alkaline epoxidation of cinnamaldehyde.

major product appeared to be an organic peroxide rather than the desired epoxy aldehyde, the reaction was carried out with *tert*-butyl hydroperoxide as oxidant rather than hydrogen peroxide.


I

Cinnamaldehyde and *tert*-butyl hydroperoxide were allowed to react in *methanol* solution at 35–40° for five to six hours while dilute sodium hydroxide was added continuously to neutralize acidic by-product and maintain a *p*H of about 8.5. β-Phenylglycidaldehyde (I) was readily obtained in 73% yield by Claisen-distillation of the crude product.

While this epoxidation of cinnamaldehyde by means of alkaline *tert*-butyl hydroperoxide appears to be the first such reaction with an α,β-unsaturated aldehyde, the corresponding reaction with α,β-unsaturated ketones has recently been described.[2] In that work, *benzene* was the solvent and no attempt was made to operate with controlled *p*H. When such a procedure was used with cinnamaldehyde, the crude product was mainly an organic peroxide (possibly *via* Michael addition); it was not further investigated.

EXPERIMENTAL

Epoxidation of cinnamaldehyde. To a 1-l., 5-neck, round bottom flask equipped with mechanical stirrer, dropping funnels, thermometer, and standard electrodes connected to a Beckman *p*H meter, were added 400 ml. of methanol and 71.2 g. (0.60 mol.) of *tert*-butyl hydroperoxide (Lucidol, 75.9% by iodometric titration). The meter *p*H was adjusted to 10.5 ± 0.2 (true *p*H of about 8.5 by indicator paper) by the addition of *N* sodium hydroxide and maintained there as 66 g. (0.50 mol.) of freshly distilled cinnamaldehyde was added at 35–40° over 1 hr. After another 4.5 hr., iodometric titration indicated that 0.48 mol. of hydroperoxide had been consumed and the reaction had essentially stopped; 20 ml. of alkali (4 mol. %) was utilized in maintaining the desired *p*H.

After dilution with 1.5 l. of water and extraction by three 200-ml. portions of chloroform, the combined extracts were washed, dried, concentrated to low volume under vacuum and finally Claisen-distilled. There was thus obtained 54 g. (73% yield) of β-phenylglycidaldehyde, b.p. 66–68° (0.2 mm.), n_{D}^{20} 1.5447. The infrared spectrum showed aldehyde carbonyl absorption at 5.76 μ and epoxide absorption at 8.14 and 11.50 μ.

Anal. Calcd. for $C_9H_8O_2$: C, 73.0; H, 5.4; carbonyl value, 0.68 equiv./100 g.; oxirane oxygen, 10.8. Found: C, 72.9; H, 5.7; carbonyl value, 0.69 equiv./100 g.; oxirane oxygen, 6.7.[3]

The *2,4-dinitrophenylhydrazone* was prepared from 3.0 g. of epoxy aldehyde by adding the latter to a hot solution of 4.0 g. of 2,4-dinitrophenylhydrazine and 2 ml. of acetic acid in 300 ml. of ethanol. After boiling for 1 min., the solution was cooled quickly to 60° and filtered. After standing overnight at room temperature, the derivative was recovered by filtration and washed well with ethanol. The weight of material melting at 138–139° was 3.3 g.

Anal. Calcd. for $C_{15}H_{12}N_4O_5$: N, 17.0. Found: N, 16.9.

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[2] N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, **80**, 5845 (1958).

[3] Hydrochloric acid in dioxane; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, "Organic Analysis, Vol. 1," Interscience Publishers, Inc., New York, 1953, p. 135; in a blank experiment, styrene oxide itself gave an oxirane oxygen value of only 88% of theory.

Diels-Alder Diene Synthesis With 1,1,1-Trichloro-3-nitropropene[1]

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Although many examples of the Diels-Alder reaction for aromatic substituted nitroolefins, such as β-nitrostyrene and substituted β-nitrostyrenes, have been published,[2] few have been reported for non-aromatic nitroolefins. Nitroethene,[3,4] 1-nitro-1-propene,[3] 1-nitro-1-pentene,[3] 1-nitro-1-heptene,[5] 1-nitro-1-octene,[5] 2-nitropropene,[6,7] 2-nitro-1-butene[6] and 2-nitro-2-butene[7] react with cyclopentadiene to yield the normal Diels-Alder adduct in 33 to 72% yield. Both aromatic and non-aromatic nitroolefins react with anthracene[8] in yields up to 62%. Substituents on the nitroolefins reduce the yield[8] or appear to cause the reaction to proceed with greater difficulty.[5]

The present study was undertaken to learn the effect of the sterically bulky, electron attracting trichloromethyl group in 1,1,1-trichloro-3-nitropropene[9] (I) upon the Diels-Alder reaction. The dienes used were butadiene-1,3 (IIa), isoprene (IIb), pentadiene-1,3 (IIc), 2,3-dimethylbutadiene-1,3 (IId), cyclopentadiene (IIe), 2-chlorobutadiene-1,3,furan and 2,5-dimethylfuran. The latter two compounds were chosen because they react with less facility or fail to react in the Diels-Alder re-

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[1] Supported in part by a grant from Research Corporation to whom the authors are grateful. Taken in part from the Masters thesis of W. W.

[2] For example: W. C. Wildman, R. B. Wildman, W. T. Norton, and J. B. Fine, *J. Am. Chem. Soc.*, **75**, 1912 (1953).

[3] K. Alder, H. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938).

[4] W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952); J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

[5] W. E. Noland, R. E. Counsell, and M. H. Fisher, *J. Org. Chem.*, **21**, 911 (1956).

[6] D. V. Nightingale, M. Maienthal, and J. A. Gallagher, *J. Am. Chem. Soc.*, **75**, 4852 (1953).

[7] W. E. Noland and R. E. Bambury, *J. Am. Chem. Soc.*, **77**, 6386 (1955).

[8] W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956).

[9] F. Brower and H. Burkett, *J. Am. Chem. Soc.*, **75**, 1082 (1953).