

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, KYUSHU UNIVERSITY]

Eight-membered Ring Compounds. I. Reaction of Cyclooctatetraene with Ethyl Diazoacetate

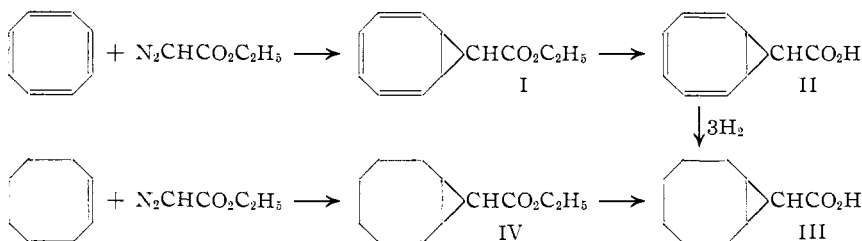
BY SABURO AKIYOSHI AND TSUTOMU MATSUDA

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Evidence is presented to show that the addition product of ethyl diazoacetate and cyclooctatetraene retains the eight-membered ring system.

A bicyclic or aromatic product usually is obtained by the halogenation or oxidation of cyclooctatetraene; chlorination of cyclooctatetraene yields a dichlorobicyclo(4,2,0) compound.¹ However, the products of catalytic hydrogenation or peroxidation are exceptions in that the original eight-membered ring probably is retained.¹⁻³

We have studied the addition of ethyl diazoacetate to cyclooctatetraene, an example of the latter type of addition reaction. The adduct of cyclooctatetraene and ethyl diazoacetate (I) was saponified and hydrogenated to yield the saturated acid III. Saponification of the adduct of cyclooctene and ethyl diazoacetate also gave III, as is shown by the mixed melting point of the two products and the coincidence of their infrared absorption spectra.



Since it is unlikely that the eight-membered ring of cyclooctene is changed under these conditions, adducts I and IV in all probability retain this structure. The ultraviolet absorption spectrum of II also favors this conclusion⁴; λ_{\max} 244 μ , $\log \epsilon$ 3.56; λ_{\min} 226 μ , $\log \epsilon$ 3.45 in ethanol.

Experimental

Cyclooctene was prepared according to Cope, *et al.*⁵; b.p. 79–80° (100 mm.), n_D^{25} 1.4678. Its purity was 100 \pm 0.5%, as estimated by the bromate–bromide method for the determination of double bonds.

Ethyl diazoacetate, which had been purified by steam distillation followed by vacuum distillation [b.p. 39–40° (10 mm.)] was used for the reaction with cyclooctatetraene. The ester obtained by evaporating the ether extract of the steam distillate was used for cyclooctene.

Reaction of Cyclooctatetraene with Ethyl Diazoacetate.—In a 200-ml. four-necked flask, a mixture of 30 g. of cyclooctatetraene and 0.5 g. of copper powder was heated at 80°; a mixture of 15 g. of ethyl diazoacetate and 15 g. of cyclooctatetraene was added dropwise with vigorous stirring during one-half hour, while the temperature was maintained at 80–85°. Vigorous evolution of nitrogen was ob-

served during the reaction. The mixture was stirred for another hour and then filtered to separate the copper, which was washed three times with ether. The combined filtrate and washings was distilled immediately into fraction 1, 33.0 g. of recovered cyclooctatetraene, b.p. 40–43° (30 mm.); fraction 2, 1.1 g., b.p. 77–85° (2 mm.); and fraction 3, 10.0 g., b.p. 85–98° (2 mm.). Fraction 3 was redistilled through a 15-cm. concentric tube column as follows: fraction 4, 2.5 g., b.p. 70–87° (1 mm.), n_D^{20} 1.4864; fraction 4.5 g., b.p. 87–89° (1 mm.), n_D^{20} 1.5160; and fraction 6, 1.5 g., b.p. 89–90° (0.8 mm.), n_D^{20} 1.5222. Fraction 5 which was supposed to be compound 1, was not analytically pure as shown below.

Anal. Calcd. for C₁₂H₁₄O₂: C, 75.74; H, 7.42; sapon. equiv., 190.1. Found: C, 73.73; H, 7.68; sapon. equiv., 168.

The crude ester I (1.3 g.) was saponified with 15 ml. of 5% aqueous sodium hydroxide at 80–90° for 1 hour. After cooling, it was acidified carefully with 10% sulfuric acid, with the formation of a needle-like precipitate. It was extracted three times with 30-ml. portions of ether. The combined extracts, evaporated under vacuum, yielded 0.8 g. of a residue which, after three recrystallizations from ethyl acetate, gave 0.5 g. of white needles (II), m.p. 162–163° dec.

Anal. Calcd. for C₁₀H₁₀O₂: C, 74.04; H, 6.23. Found: C, 73.80; H, 6.33.

Reaction of Cyclooctene with Ethyl Diazoacetate.—A mixture of 10 g. of cyclooctene and 15 g. of

ethyl diazoacetate was added to a stirred mixture of 35 g. of cyclooctene and 0.5 g. of copper powder at 100–105° under the conditions described above. During the reaction 2940 ml. of nitrogen was evolved, which corresponds to 70% of the diazoacetate used. The product was treated as above and the following fractions obtained: fraction 1, 27.6 g. of recovered cyclooctene, b.p. 70–73° (86 mm.); fraction 2, 1.1 g., b.p. 90–99° (3 mm.); fraction 3, 8.4 g., b.p. 99–105° (3 mm.); and fraction 4, 1.4 g., b.p. 110–125° (3 mm.). Fraction 3, fractionated through a 15-cm. concentric tube column, yielded fraction 5, 0.6 g., b.p. 85–97° (3 mm.); fraction 6, 0.4 g., b.p. 97–100° (3 mm.); and fraction 7, 7.6 g., b.p. 100–105° (3 mm.), n_D^{25} 1.4798. The last fraction is assumed to be mainly IV. The crude ester (IV, 1.3 g.) was saponified with a mixture of 4 g. of NaOH, 20 ml. of methanol and 10 ml. of water at 70° for 3 hours. After acidification and extraction, 1.0 g. of the crude acid was recrystallized three times from petroleum ether to give 0.6 g. of white crystal (III), m.p. 113.5–114.8°.

Hydrogenation of II.—To 10 ml. of ethanol and 0.5 g. of Raney nickel, saturated with hydrogen in a hydrogenation vessel, was added 0.382 g. (2.35 mmoles) of the unsaturated acid II which was hydrogenated with vigorous shaking at ordinary pressure and temperature. After one hour hydrogenation was completed, 147 ml. of hydrogen (93% of the theoretical amount) having been absorbed. After purification, 0.30 g. of white crystals (III) was obtained, m.p. 111.2–113.0°. The mixed melting point of the two samples (III) was 111.2–113.6°; the infrared absorption spectra of the compounds coincided almost perfectly.

Anal. Calcd. for C₁₀H₁₀O₂: C, 71.42; H, 9.52; neut. equiv., 168. Found: C, 71.32; H, 9.59; neut. equiv., 167.

FUKUOKA, JAPAN

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(3) O. H. Wheeler, *ibid.*, **75**, 4858 (1953).

(4) O. H. Wheeler, *ibid.*, **75**, 4858 (1953).

(5) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950).