for synthesizing glycidyl nitrate in previous work.[3] It was not necessary to distil the 1-azido-3-chloro-2-propanol prepared by procedure A or B above before dehydrohalogenation with aqueous sodium hydroxide. The over-all yield of glycidyl azide based on epichlorohydrin was about 55%. Glycidyl azide may be nitrated to form 1-azido-3-nitrato-2-propanol by conventional procedures.[5]

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The Ultraviolet Absorption Spectrum of 1,4-Cyclohexadien-1-carboxylic Acid, an Intermediate in the Preparation of 1,4-Cyclohexadienyl Methyl Ketone

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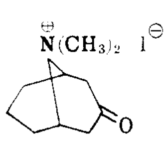
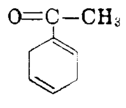
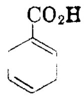
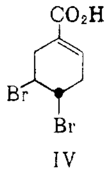
In connection with a study of the "dihydroacetophenone" reported to be formed by treatment of pseudopelletierine methiodide (I) with strong base,[1] we have had occasion to prepare 1,4-cyclohexadienyl methyl ketone (II) by a new route.


I


II


III


IV

Addition of butadiene to propiolic acid yielded 1,4-cyclohexadien-1-carboxylic acid (III), a compound previously isolated by Alder and Backendorf as a by-product arising from the addition of butadiene to acetylene dicarboxylic acid.[2] The desired ketone (II) was obtained by treatment of the Diels-Alder adduct (III) with lithiummethyl in the standard fashion.

It was of interest to examine the ultraviolet absorption spectrum of the diene acid III, in view of the considerable influence of the *nonconjugated* ethylenic linkage previously demonstrated in the case of II and some of its analogs. Thus, II has been shown to exhibit a $\lambda_{max.}$ at 245 mμ, ϵ 4,000, while 1-cyclohexenyl methyl ketone has a $\lambda_{max.}$ at 232 mμ, ϵ 12,500.[3] The isolated double bond in the carboxylic acid III has now been found to bring about a similar but somewhat larger shift in both wavelength and intensity of maximal absorption. A $\lambda_{max.}$ at 235 mμ, ϵ 2,500 was observed for this acid, while 1-cyclohexen-1-carboxylic acid[4] exhibits a $\lambda_{max.}$ at 212 mμ, ϵ 11,000. Thus in these closely related pairs of molecules, a shift of +23 mμ results from the nonconjugated unsaturation in the carboxylic acid, compared with a shift of +13 mμ in the case of the ketone. *trans*-4,5-Dibromo-1-cyclohexen-1-carboxylic acid (IV), readily produced by addition of bromine to III, showed the expected normal absorption ($\lambda_{max.}$ 212 mμ, ϵ 10,000).

EXPERIMENTAL

Ultraviolet spectra. The spectra were determined in ethanol solutions, using a Beckman DU spectrophotometer equipped with a photomultiplier.

1,4-Cyclohexadien-1-carboxylic acid (III). A solution of propiolic acid (7.5 g.) and butadiene (9.0 g.) in a sealed Pyrex bomb was maintained at 54° for 39 hours. The yield (6.0 g.) of white, crystalline adduct obtained after the usual work-up procedure could undoubtedly have been improved if an attempt were made to find the optimum reaction and isolation conditions. Alternate vacuum sublimation and recrystallization from heptane gave an analytical specimen, m.p. 121-122° (lit. m.p. 123°).

Anal. Calc'd for $C_7H_8O_2$: C, 67.7; H, 6.5. Found: C, 68.0; H, 6.4.

Light absorption. $\lambda_{max.}$ 235 mμ, ϵ 2,500.

1,4-Cyclohexadienyl methyl ketone (II). Following a classical example,[5] 1,4-cyclohexadien-1-carboxylic acid (III) (5.5 g.) and two equivalents of lithiummethyl in ethereal solution were allowed to interact, giving a lemon-colored liquid (4.7 g.) after the usual isolation procedure. Careful distillation yielded colorless 1,4-cyclohexadienyl methyl ketone (II) (2.1 g.), b.p. 71.5°/6.0 mm., n_D^{20} 1.5126 (lit. b.p. 80-81°/14 mm.; n_D^{16} 1.5135).

Light absorption. $\lambda_{max.}$ 245 mμ, ϵ 4,450.

trans-4,5-Dibromo-1-cyclohexen-1-carboxylic acid (IV). The Diels-Alder adduct (III) (0.10 g.) instantly decolorized bromine, added dropwise in carbon tetrachloride solution, giving rise to white crystals. Two crystallizations from carbon tetrachloride, followed by vacuum sublimation, gave the dibromo acid (IV) (0.18 g.), m.p. 152-154°.

Anal. Calc'd for $C_7H_8Br_2O_2$: C, 29.6; H, 2.8; Br, 56.3; Neut. equiv., 284. Found: C, 30.1; H, 3.1; Br, 55.7; Neut. equiv., 283.

Light absorption. $\lambda_{max.}$ 212 mμ, ϵ 10,000.

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