

spectrum showed the presence of the acid chloride carbonyl absorption (5.5μ) in addition to that of the ketene grouping. Further distillations of this material did not seem to lessen the amount of acid chloride present.

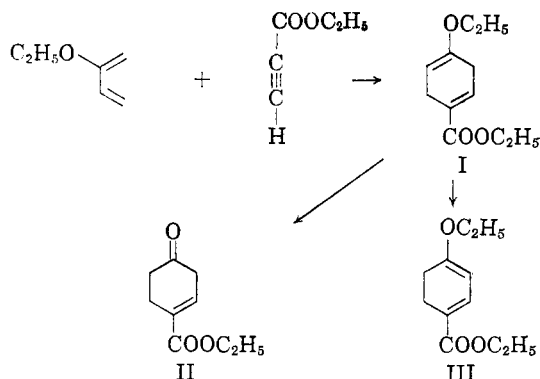
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Synthesis of 4-Carboethoxy-3-cyclohexenone

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On considering the facile alkylation of Hagemann's ester,² and hydrolysis and decarboxylation of the intermediate to give 2-alkyl-3-methyl-2-cyclohexenones, we became interested in the preparation and alkylation of 4-carboethoxy-3-cyclohexenone (II) as a possible route to 2-alkyl-2-cyclohexenones.



The Diels-Alder reaction of 2-ethoxy-1,3-butadiene and ethyl propiolate gave 70% of material that was chiefly ethyl 4-ethoxy-2,5-dihydrobenzoate (I). The structural assignment of this compound is based partly on the fact that dienes with substituents in the 2-position are known to yield exclusively 1,4-disubstituted adducts with monosubstituted dienophiles.³ Also when the product was treated with palladium-on-charcoal in refluxing xylene and then hydrolyzed, 4-ethoxybenzoic acid was obtained. The ultraviolet spectrum of the adduct, $\lambda_{max}^{C_2H_5OH}$ 256 $m\mu$ (ϵ 3640), 320 (sh) $m\mu$ (ϵ 1450), indicates that the product is chiefly the unconjugated diene I, with about 12% of the con-

jugated diene III. The absorption at 256 $m\mu$ is suggestive that some ethyl 4-ethoxybenzoate [$\lambda_{max}^{C_2H_5OH}$ 259 $m\mu$ (ϵ 10,500)] is present; however, that such is not the case was demonstrated by isomerization to ethyl 4-ethoxy-2,3-dihydrobenzoate (III), $\lambda_{max}^{C_2H_5OH}$ 322 $m\mu$ (ϵ 11,500), in 88% yield by the use of sodium ethoxide in ethanol at room temperature, with the concomitant loss of the absorption maximum at 256 $m\mu$.⁴ Selective hydrolysis of the Diels-Alder adduct with aqueous acid gave 4-carboethoxy-3-cyclohexenone II (71%) as a colorless liquid. The double bond has been assigned to the 3-position on the basis of the presence of only one carbonyl absorption peak in the infrared spectrum, $\lambda_{max}^{CCl_4}$ 1725 cm^{-1} , (conjugated ester and unconjugated ketone carbonyls),⁵ and the ultraviolet spectrum, $\lambda_{max}^{C_2H_5OH}$ 215 $m\mu$ (ϵ 8300) (typical of α,β -unsaturated esters).⁶ This compound (II) absorbed one mole of hydrogen on catalytic hydrogenation over 10% palladium-on-charcoal catalyst to give presumably 4-carboethoxycyclohexanone characterized as the 2,4-dinitrophenylhydrazone derivative. Attempts to isomerize II to 4-carboethoxy-2-cyclohexenone with sodium ethoxide have failed, the material being transformed instead into high molecular weight condensation products. Alkylation of 4-carboethoxy-3-cyclohexenone (II) with a variety of alkyl halides using sodium ethoxide in ethanol gave mixtures of difficultly separated mono- and dialkylated products in 35–45% yields, the rest of the material being resinous self-condensation products. Due to a pending change of laboratories, no further attempts were made to study other alkylation conditions and no further work in this area is anticipated.

EXPERIMENTAL⁷

Ethyl 4-ethoxy-2,5-dihydrobenzoate (I). A mixture of 63.5 g. of 2-ethoxy-1,3-butadiene,^{8d} 63.5 g. of ethyl propiolate,⁹ 650 ml. of anhydrous benzene, and 0.2 g. of hydroquinone was heated in an autoclave at 140° for 24 hr. Distillation of the mixture under reduced pressure gave 88.4 g.

(4) Ultraviolet spectra of similar systems for example, 2,5-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 245 $m\mu$ (ϵ 4000), 2,5-dihydro-6-methylacetophenone $\lambda_{max}^{C_2H_5OH}$ 245 $m\mu$ (ϵ 5000), 4-ethoxy-2,5-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 228 $m\mu$ (ϵ 11,500), and 4-ethoxy-2,3-dihydroacetophenone $\lambda_{max}^{C_2H_5OH}$ 336 $m\mu$ (ϵ 13,000), have been reported by E. A. Braude and co-workers.^{8d}

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(70%) of product as a colorless liquid, b.p. 88–89° (0.3 mm.), n_D^{20} 1.4848, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 256 μ (ϵ 3640) with a shoulder at 320 μ (ϵ 1450), $\lambda_{\text{max}}^{\text{CCl}_4}$ 1725 cm^{-1} (conj. ester C=O).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 67.32; H, 8.22. Found: C, 67.38; H, 8.16.

Ethyl 4-ethoxy-2,5-dihydrobenzoate (III). A solution of 3.05 g. of ethyl 4-ethoxy-2,5-dihydrobenzoate and 10 ml. of absolute ethanol was added with stirring to a solution of sodium ethoxide prepared from 0.3 g. of sodium and 15 ml. of absolute ethanol. The deep red solution was stirred at room temperature for 5 hr. before being diluted with water. The product was isolated by extraction with ether and distillation of the dried ether extract, under reduced pressure, gave 2.7 g. (88%) of a colorless liquid, b.p. 88–89° (0.3 mm.), n_D^{20} 1.5180, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 322 μ (ϵ 11,500) with no appreciable absorption in the 256- μ region. $\lambda_{\text{max}}^{\text{CCl}_4}$ 1727 cm^{-1} .

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 67.32; H, 8.22. Found: C, 67.00; H, 7.99.

4-Ethoxybenzoic acid. A mixture of 3.0 g. of 10% palladium-on-charcoal and 5.0 g. of ethyl 4-ethoxy-2,5-dihydrobenzoate in 75 ml. of xylene was refluxed for 6 hr. The catalyst was removed by filtration and the distillate was distilled to give 3.4 g. (68%) of ethyl 4-ethoxybenzoate as a colorless liquid, b.p. 82–87° (0.25 mm.), $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 259 μ (ϵ 10,500), $\lambda_{\text{max}}^{\text{CCl}_4}$ 1730 cm^{-1} . A small amount of ethyl 4-ethoxybenzoate was refluxed with 20 ml. of a 10% sodium hydroxide solution for 11 hr. On acidification with hydrochloric acid, 4-ethoxybenzoic acid precipitated, which after recrystallization from benzene-petroleum ether (b.p. 40–60°) melted at 194.5–196.5° (lit.,⁹ m.p. 195–196°), $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 254.5 μ (ϵ 16,500).

4-Carboethoxy-3-cyclohexenone (II). A solution of 66.6 g. (0.34 mole) of ethyl 4-ethoxy-2,5-dihydrobenzoate, 200 ml. of tetrahydrofuran, 35 ml. of concd. sulfuric acid, and 160 ml. of water was stirred at room temperature for 1 hr. before being diluted with more water. The product was isolated by extraction with ether, the ether extract washed with a saturated solution of sodium bicarbonate, dried, and distilled to give 40.5 g. (71.5%) of 4-carboethoxy-3-cyclohexenone as a colorless liquid, b.p. 83–84.5° (0.3 mm.), n_D^{20} 1.4789, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 215 μ (ϵ 8300), $\lambda_{\text{max}}^{\text{CCl}_4}$ 1725 cm^{-1} .

Anal. Calcd. for $\text{C}_9\text{H}_{12}\text{O}_4$: C, 64.27; H, 7.19. Found: C, 64.49; H, 7.38.

An orange-red *2,4-dinitrophenylhydrazone* was formed in ethanol solution, m.p. 124–124.5°, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 373 μ (ϵ 25,750). The orange-red color of this derivative and the suspiciously high wave length of the ultraviolet spectrum raise the possibility that it may actually be the 2,4-dinitrophenylhydrazone of 4-carboethoxy-2-cyclohexenone.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_6$: C, 51.72; H, 4.63; N, 16.08. Found: C, 51.68; H, 4.79; N, 15.83.

4-Carboethoxycyclohexanone. Hydrogenation of 1.16 g. of 4-carboethoxy-3-cyclohexenone in 15 ml. of ethanol with 0.07 g. of palladium-on-charcoal was completed in 2 hr. (one molecular equivalent of hydrogen was absorbed). The catalyst was removed by filtration, and the filtrate was added to a boiling ethanolic solution of 2,4-dinitrophenylhydrazine hydrochloride to give in essentially quantitative yield *4-carboethoxycyclohexanone 2,4-dinitrophenylhydrazone* which on recrystallization from ethanol melted at 121–122°, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 361 μ (ϵ 26,000).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_6$: C, 51.42; H, 5.18; N, 15.99. Found: C, 51.42; H, 5.29; N, 16.15.

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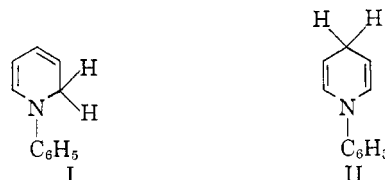
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The Preparation of *N*-Phenyl-1,2-dihydropyridine^{1,2}

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Pullman, San Pietro, and Colowick, and others, have shown that *N*-methyldihydropyridine and similar dihydropyridines have the 1,4-dihydro structure.^{3–9} In the present paper we wish to report the preparation, characterization, and unambiguous structural assignments of the *N*-phenyldihydropyridines I and II.



Although previous reports of reduction of simple *N*-alkylpyridinium salts with sodium or potassium borohydride¹⁰ indicate that only the tetrahydro compounds are formed, reduction of *N*-phenylpyridinium cation by sodium or potassium borohydride in alkaline aqueous solution gave a solid I, m.p. 82.5–83.5°, in 60% yield. The NMR spectrum clearly showed that this was the 1,2-isomer. Since the 1,2-isomer had previously been reported by Weitz¹¹ and subsequently by Karrer¹² who reported that it had been prepared by sodium amalgam reduction of the *N*-phenylpyridinium cation; we repeated this work and obtained compound II. The melting point and physical properties of II corresponded to those previously reported.

Even cursory examination of the NMR spectra

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