

was distilled carefully through a semi-micro column. The yield of the debromination product (II) was 0.98 g. (77%), b.p. 107° (746 mm.), n_D^{20} 1.4058.

The reaction of bromine (3 g.) with II (2.0 g.) in 10 ml. of carbon tetrachloride at -10° proceeded rapidly and afforded 4.85 g. (93.5%) of the dibromoester (IV), b.p. 70.5° (0.8 mm.), n_D^{20} 1.5112, which was identical with the product obtained by the action of N-bromosuccinimide on II.

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2,2,4-Trimethyl-1,2-dihydroquinoline

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Recently Johnson and Buell¹ prepared 1,2-dihydroquinoline. On the basis that its ultraviolet absorption spectrum, which had three peaks, was strikingly similar to that of the so-called "acetone anil," they opined that a 1,4-dihydro structure for the latter compound is eliminated. Incidentally, they also stated that 1,4-dihydroquinoline, unlike the 1,2-dihydroquinoline, should have a spectrum similar to that of 1,2,3,4-tetrahydroquinoline. On the contrary, the 1,4-dihydro derivative as a vinylamine has a double bond conjugated with the nitrogen atom² and hence its spectrum would not be like that of the 1,2,3,4-tetrahydroquinoline. Nevertheless, their assignment of structure is correct for the dihydroquinolines, in our opinion, not for other reasons given by them but for reasons set forth in the present note.

The spectrum of the trimethyldihydroquinoline³ (0.00625 g./l.) in methanol, 1,2 *N* in HCl, is shown in Fig. 1. The doublet at 259 and 255 m μ and *E* 53 (log ϵ 13.96) can be compared to the single band observed for α -methylstyrene at 242 m μ and log ϵ 4.03 or better still, since the open-chain methyl group here inhibits resonance, to the peak for the cyclic analog 1-methyl-3,4-dihydronaphthalene which Ramart-Lucas and Hoch⁴ found to be at

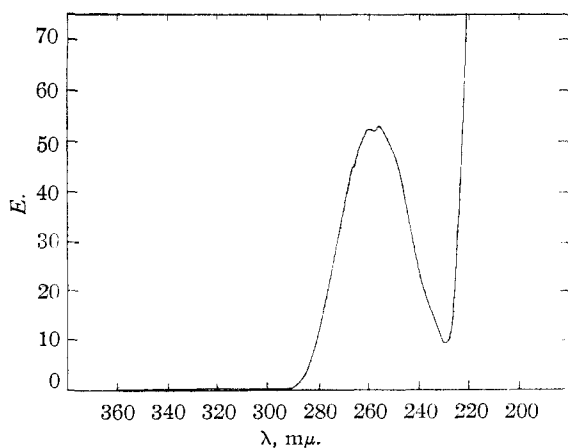


Fig. 1.

- (1) W. S. Johnson and B. G. Buell, *THIS JOURNAL*, **74**, 4518 (1952).
- (2) Compare the spectrum of an N-phenyl-1,2-dihydropyridine, D. Craig, L. Schaefgen and W. P. Tyler, *ibid.*, **70**, 1626 (1952); see also the spectra for enamines quoted by Johnson and Buell.
- (3) D. Craig, *ibid.*, **60**, 1458 (1938).
- (4) P. Ramart-Lucas and N. J. Hoch, *Bull. soc. chim.*, [5] **5**, 848 (1938).

259 m μ , log ϵ 3.8. Morton and de Gouveia⁵ found 1,2-dihydronaphthalene to have a maximum at 262 m μ , log ϵ 4.0, and 1,4-dihydronaphthalene was found to have a doublet at 267 and 274 m μ , log ϵ 2.9. It is thus apparent that the spectrum of the trimethyldihydroquinoline in acid solution (the acid is present in order to remove any ability of the nitrogen atom to conjugate with the benzene ring or double bond) requires that a double bond must be conjugated with the benzene ring, thus finally proving the structure of 2,2,4-trimethyl-1,2-dihydroquinoline.

Since first submitting the present note, Dr. Paul Downey pointed out to us that Bohlmann⁶ has recently reported 1,2-dihydroquinoline, m.p. 40–41° to result from the reaction of LiAlH₄ with quinoline. In our hands Bohlmann's directions gave a 90% yield of product which, if purified by extraction with cyclohexane, melted at 72–74°, and which had nearly the same absorption spectrum and other properties reported by Johnson and Buell for their dihydroquinoline. It was unstable in air and in acid solutions so that the absorption spectra in such solutions apparently could not be applied to the elucidation of the structure of the dihydroquinolines. Dr. Franz Widmer found in our laboratory that this compound, like N-phenyl-3,5-diethyl-2-propyl-1,4-dihydroquinoline,² evolves hydrogen (about one-third mole) when first contacted with reduced PtO₂ in acetic acid. Subsequently, hydrogen (a net amount of four moles) is absorbed by the acetic acid solution. This confirms Johnson and Buell's finding that their dihydroquinoline, which obviously is the same as Bohlmann's, readily undergoes dehydrogenation.

- (5) R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934).
- (6) F. Bohlmann, *Ber.*, **85**, 390 (1952).

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On the Origin of the Carboxyl Group of Histidine in Yeast^{1,2}

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Recently Ehrensvärd, *et al.*,^{3,4} have shown by isotopic studies in *Torulopsis utilis*, and Cutinelli, *et al.*,⁵ by similar studies in *Escherichia coli*, that when C¹³H₃C¹⁴OOH is administered as a substrate, the carboxyl group of histidine arises exclusively from the methyl carbon atom. This is in contrast to the high C¹⁴ (acetate carboxyl) incorporation into the carboxyl groups of the other amino acids.

- (1) This research was supported by contract number AT (45-1)-301 from the Atomic Energy Commission. Published with the approval of the Monographs Publications Committee, Research paper number 220, School of Science, Department of Chemistry. Presented before the Northwest Regional Meeting of the American Chemical Society, Corvallis, June, 1952.
- (2) Taken from a thesis presented by J. W. D. for the M.S. degree, Oregon State College, 1952.
- (3) G. Ehrensvärd, L. Reio and E. Saluste, *Acta Chem. Scand.*, **3**, 645 (1949).
- (4) G. Ehrensvärd, L. Reio, E. Saluste and R. Stjernholm, *J. Biol. Chem.*, **189**, 93 (1951).
- (5) C. Cutinelli, G. Ehrensvärd, L. Reio, E. Saluste and R. Stjernholm, *Acta Chem. Scand.*, **5**, 353 (1951).