a particular parent peak to impurity X, it was evident that any of the peaks that were likely possibilities arose from impurities that were present at concentrations lower than 0.01% in the original sample of mesitylene I.

Further attempts to identify impurity X were abandoned upon exhaustion of the supply of mesitylene I.

It is interesting to compare the color reactions of impurity X with metal salts to the work of Walling.[3] This investigator has shown that indicators exhibiting color changes at low *p*H's in aqueous solutions give their acid colors when adsorbed on surfaces of iron, magnesium, silver and copper salts, and on other acidic surfaces. Since indicators are a class of substances having huge extinction coefficients and since it is likely that impurity X falls into such a class, it seems reasonable to postulate that impurity X is an indicator that exhibits a red-purple color on highly acidic surfaces.

Experimental

Mounted Salts.—Ten ml. of 0.5 *M* solutions of each of the four salts was added to 10-g. portions of pure silica gel, stirred on a hot-plate until the product seemed dry, and dried overnight in a 200° drying oven. Copper sulfate mounted on silica gel was used to follow the course of impurity (X) during the purification steps.

Mesitylene.—Both mesitylene I and mesitylene II were Eastman Kodak White Label products. Through the kind coöperation of the Eastman Kodak Company, it was learned that mesitylene I, which was distributed before about 1950, was most likely synthesized from acetone. Mesitylene II, the current Eastman Kodak product, probably was made from a coal tar distillate.

Color Tests.—The intense red-purple color could be brought about by the addition of a few drops of mesitylene I to *ca.* 0.1 g. of mounted salt on a spot plate. The full intensity developed in 5–10 minutes at room temperature, but could be greatly accelerated by warming 1–2 minutes at *ca.* 100°.

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[3] C. Walling, THIS JOURNAL, **72**, 1164 (1950).

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Polar Effects in N-Bromosuccinimide Brominations

BY ELIAS J. COREY

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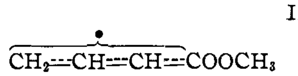
The reaction between N-bromosuccinimide and unsaturated compounds which results in the substitution of bromine for hydrogen is generally considered as involving free radical intermediates.[1] The allylic bromination of an olefin, for example, has been postulated to occur by dissociation of N-bromosuccinimide into bromine atoms and succinimide radicals, radical displacement on hydrogen by the succinimide radical to give a mesomeric radical and, finally, reaction of this radical with the reagent to give a succinimide radical and the allylic bromide.

According to this interpretation the reaction of N-bromosuccinimide with two isomeric substances which are converted by radical displacement on an allylic hydrogen to the same free radical should lead to the same product (or products).[2]

Methyl crotonate (I) and methyl vinylacetate (II) are such a pair of isomeric substances and their study seemed especially advantageous since only two allylic substitution products are possible and since, as Ziegler and co-workers have already reported, the reaction of methyl crotonate with N-bromosuccinimide produces methyl γ-bromocrotonate in good yield.[3] One might anticipate that methyl γ-bromocrotonate would also be formed from methyl vinylacetate.

$CH_3CH{=}CHCOOCH_3$ $CH_2{=}CHCH_2COOCH_3$

I II



$\overbrace{CH_2\text{---}CH\text{---}CH\text{---}COOCH_3}^{\bullet}$

III

We have found that under the same conditions which are favorable for the conversion of methyl crotonate to methyl γ-bromocrotonate, methyl vinylacetate reacts *more slowly* and yields chiefly methyl β,γ-dibromobutyrate (IV) along with an insignificant amount of monobrominated product. Some tarry material is also formed. The structure of IV was proved by debromination to methyl vinylacetate and by synthesis from methyl vinylacetate and bromine.

We and, very recently, others[4] have also observed that a similar situation exists with the corresponding nitriles, crotononitrile and vinylacetonitrile.

Regardless of what the mechanism of formation of dibromide is,[5] the relative inertness of the α-methylene group in methyl vinylacetate and vinylacetonitrile in succinimide radical displacements must still be explained. Since significant steric effects can hardly be operative in the case of vinylacetonitrile, it seems reasonable to suppose that the impediment to radical attack associated with the proximity of the cyano function (or in the case of II, the carbomethoxy group) is primarily electrical in nature.

Experimental

Reaction of Methyl Vinylacetate (II) with N-Bromosuccinimide.—Methyl vinylacetate, b.p. 107° (742 mm.), $n^{25}D$ 1.4060, was prepared by the action of diazomethane on pure vinylacetic acid,[6] b.p. 72.5–73.5° (14 mm.), $n^{25}D$ 1.4210. A mixture 10.0 g. (0.10 mole) of methyl vinylacetate, 17.8 g. (0.10 mole) of N-bromosuccinimide, 0.01 g. of benzoyl peroxide and 50 ml. of pure carbon tetrachloride was heated at reflux for 8 hours, after which time all of the N-bromosuccinimide had disappeared and a brown oil had settled out. The layers were separated by decantation and the oil extracted with two 10-ml. portions of carbon tetrachloride. The carbon tetrachloride solution (plus washings) was cooled to 0°, filtered to remove the precipitate of succinimide (7.2 g.) and concentrated. Distillation of the residual liquid through a semi-micro column yielded 6.14 g. (68.4% based on N-bromosuccinimide) of methyl β,γ-dibromobutyrate (IV), b.p. 70.5° (0.8 mm.), $n^{25}D$ 1.5114 and a small amount (0.48 g.) of a low-boiling fraction, b.p. 48–70°, which probably contained monobromide.

Anal. Calcd. for $C_5H_8O_2Br_2$: C, 23.10; H, 3.10; Br, 61.49. Found: C, 23.28; H, 3.28; Br, 61.78.

Debromination of IV.—A mixture of 3.30 g. of the dibromoester IV and 2 g. of zinc dust in 10 ml. of ether containing a few drops of methanol was heated to reflux for one hour. The resulting mixture was filtered and the filtrate

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[1] G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

[2] This point had apparently not been considered in connection with the reaction of N-bromosuccinimide with ketene dimer, A. T. Blomquist and F. H. Baldwin, THIS JOURNAL, **70**, 29 (1948).

[3] K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 118 (1942).

[4] P. Couvreur and A. Bruylants, *Bull. soc. chim. Belg.*, **61**, 253 (1952).

[5] See E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

[6] *Org. Syntheses*, **24**, 95 (1944).

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^{25}_{D} 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^{25}_{D} 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

BY DAVID CRAIG AND EARL C. GREGG, JR.

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Recently Johnson and Buell[1] 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 atom[2] 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 trimethyldihydroquinoline[3] (0.00625 g./l.) in methanol, 1,2 *N* in HCl, is shown in Fig. 1. The doublet at 259 and 255 mμ and *E* 53 (log ε 13.96) can be compared to the single band observed for α-methylstyrene at 242 mμ 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 Hoch[4] found to be at 259 mμ, log ε 3.8. Morton and de Gouveia[5] found 1,2-dihydronaphthalene to have a maximum at 262 mμ, log ε 4.0, and 1,4-dihydronaphthalene was found to have a doublet at 267 and 274 mμ, 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.

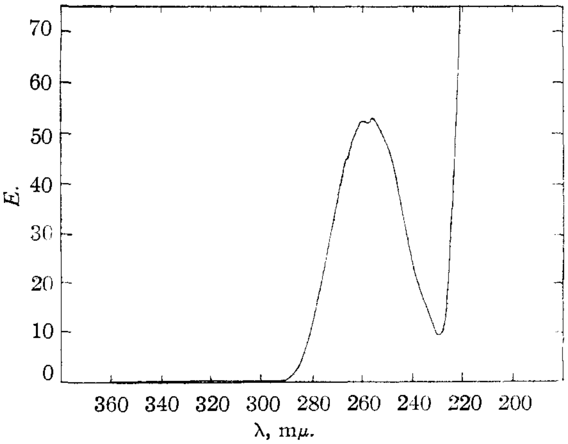

Fig. 1.

Since first submitting the present note, Dr. Paul Downey pointed out to us that Bohlmann[6] has recently reported 1,2-dihydroquinoline, m.p. 40–41° to result from the reaction of $LiAlH_4$ 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 PtO_2 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.

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(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 eneamines 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).

(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 $C^{13}H_3C^{14}OOH$ is administered as a substrate, the carboxyl group of histidine arises exclusively from the methyl carbon atom. This is in contrast to the high C^{14} (acetate carboxyl) incorporation into the carboxyl groups of the other amino acids.

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(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).