A yellow oil (10.7 Gm.) separated. (Increasing the reaction time to 1 min. gave only half this yield of yellow oil.) The infrared spectrum of this material was consistent with that expected for the nitro-alcohol condensation product, but this material was sufficiently labile that it was not convenient to purify a sample for analysis. This oil was dehydrated by mixing with 10.7 Gm. of powdered fused sodium acetate and 53.4 Gm. (0.523 mole) of acetic anhydride and boiling under reflux for 10 min. After cooling, the mixture was poured into 120 ml. of water. A yellowish brown solid was obtained, 8.25 Gm., m.p. 76–79°. Recrystallization from 95% ethanol gave 6.35 Gm. (51%) of yellow crystals, m.p. 83.5–84.5°.

Anal.—Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76; O, 30.89. Found: C, 58.12; H, 4.50; N, 6.82; O, 30.93.

N,O-Diacetyl-N-[β-(3-acetoxyphenyl-)α,β-bis(acetthio)ethyl]hydroxylamine (Ib)—3-Acetoxy-β-nitrostyrene (0.193 Gm.) was dissolved in 0.5 ml. of thiolacetic acid. Addition of 5 drops of tri-*n*-butylamine caused an exothermic reaction. The resulting solution was allowed to stand at room temperature for 20 hr. Upon addition of 1 ml. of 95% ethanol followed by cooling and scratching, there was precipitated 75 mg. of white solid, m.p. 110–111°. Recrystallization from ethanol did not raise the m.p.

Anal.—Calcd. for $C_8H_6NO_2S_2Ac_5$: C, 50.57; H, 4.95; N, 3.28; S, 15.00; acetyl, 50.3. Found: C, 49.76; H, 5.03; N, 3.39; S, 14.89; acetyl, 49.9.

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Oxidative Effect of Perbenzoic Acid on *N*-Methylated Pyrrole, Indole, and Carbazole

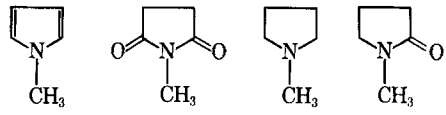
By I. NABIH and E. HELMY*

Perbenzoic has been shown to oxidize *N*-methylpyrrole to *N*-methylsuccinimide, *N*-methylpyrroline to *N*-methylpyrrolidone, and 2,3-dihydro-*N*-methylindole to *o*-dimethylaminobenzaldehyde. Under similar conditions *N*-methylcarbazole and 1,4-dihydro-*N*-methylcarbazole are not oxidized.

EXTENSIVE STUDIES have been carried out on the oxidation of pyrrole, indole, and carbazole using a variety of oxidizing agents (1–5).

In this work, the oxidative effect of perbenzoic acid on the *N*-methylated forms of pyrrole, indole, and carbazole is studied. Generally, peracids have been mostly used for the selective oxidation of the carbon-carbon double bond. As an electrophilic reaction, the rate is enhanced through the presence of an electron-donating group in the substrate (6). In systems where double bond is conjugated with other multiple bonds, this rate decreases since the delocalization of the π electrons reduces the electron density at all the double bonds.

Usually, the oxidation with peracids leads to the epoxide; however, the products may undergo subsequent rearrangements, as in the case of chloroolefins, where the over-all products are the chloroketones (7). Also, epoxidation of aliphatic enol-acetate leads after intermolecular rearrangements to α-acetoxy-ketones (8). By this route, the olefins *via* the epoxidation products can be converted after undergoing rearrangement to carbonyl compounds (9). In the present work, when *N*-methylpyrrole (I) was subjected to the oxidizing effect of perbenzoic acid in chloroform solution, the analytical measurements showed that two atoms of oxygen had been involved in the reaction. Preparative experiments showed that the reaction product was *N*-methyl succinimide (II) in 92% yield. It appears in this reaction that the initially formed epoxides at both double bonds, favored through the presence of the electron rich *N*-methyl group, undergo internal rearrangement to give the imide.



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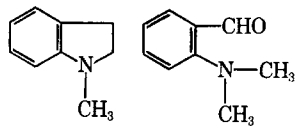

V VI

When *N*-methyl-3-pyrroline (III) was similarly treated, the product was *N*-methyl-α-pyrrolidone (IV) in 79% yield. The analytical data showed that only one oxygen atom had been consumed.

Under the same condition, 2,3-dihydro-*N*-methylindole (V) is oxidized with the fission of the pyrrole nucleus and *o*-dimethylaminobenzaldehyde (VI) is obtained in 81% yield. The analytical measurement indicated the consumption of one oxygen atom during the reaction.

N-Methylcarbazole and 1,4-dihydro-*N*-methyl carbazole could not be oxidized with the same oxidizing agent.

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EXPERIMENTAL

All melting points were taken in open capillaries and are uncorrected.

Determination of the Number of Oxygen Atoms Needed for a Known Weight of the Organic Substance (10).—The organic substance (0.2 Gm.) was added to a known volume of perbenzoic acid in chloroform with known normality. The mixture was left for 6 hr. in a dark place with occasional shaking. Five milliliters of 10% KI solution as well as 2 drops of concentrated H_2SO_4 were added to the mixture. The liberated iodine was then titrated against sodium thiosulfate (0.1 *N*).

With N-Methylpyrrole (I)—The determination showed two oxygen atoms to be involved in the reaction.

N-Methyl Succinimide (II)—*N*-Methylpyrrole (2.0 Gm.) was added to 190 ml. 0.54 *N* perbenzoic acid in chloroform. The reaction mixture was left in a dark place for 12 hr. Then it was neutralized by sodium bicarbonate solution. The chloroform layer was then isolated, washed with water several times, dried over calcium chloride, and finally evaporated.

Two and one half grams of *N*-methylsuccinimide was left. Yield 92%. Crystallization from acetone as white needles gave m.p. 67–68°. [Lit. m.p. 66° (11).]

Anal.—Calcd. for $C_5H_7NO_2$: C, 53.09; H, 6.29; N, 12.30; O, 28.31. Found: C, 53.00; H, 6.18; N, 12.30; O, 28.30.

With N-Methyl-3-pyrroline (III)—The determination showed that one oxygen atom was involved with each mole of the compound.

N-Methyl-α-pyrrolidone (IV)—*N*-Methyl-3-pyrroline (2.0 Gm.) was added to 120 ml. of perbenzoic acid in chloroform 0.4 *N* (one oxygen atom). The whole mixture was left for 3 hr. in a dark place at room temperature, then neutralized by sodium bicarbonate solution. The chloroform layer was then isolated, washed with water, dried over calcium chloride, and evaporated.

A 1.9-Gm. (79.1%) quantity of *N*-methyl-α-pyrrolidone was collected as a colorless oil, b.p. 201°/740 mm. [Lit. 202°/760 mm. (12).]

Anal.—Calcd. for $C_5H_9NO.HCl$: C, 44.40; H, 7.40; N, 10.36; O, 11.84. Found: C, 44.38; H, 6.99; N, 10.30; O, 11.81.

With N-Methylindoline (V)—The determination showed one oxygen atom was consumed in the reaction.

o-Dimethylaminobenzaldehyde (VI)—*N*-Methylindoline (2.0 Gm.) was added to 104 ml. 0.29 *N* perbenzoic acid in chloroform (one oxygen atom). The reaction mixture was left at room temperature in a dark place for 24 hr. with occasional shaking, then neutralized by solution of sodium bicarbonate. The chloroform layer was then separated, washed with water several times, dried over calcium chloride, and finally evaporated.

A 1.8-Gm. (81%) quantity of *o*-dimethylaminobenzaldehyde was collected at 141/30 mm. as yellow oil. [Lit. 142°/30 mm. (13).]

Anal.—Calcd. for $C_9H_{12}N_2O$: C, 60.10; H, 6.66; N, 15.55. Found: C, 59.87; H, 6.29; N, 15.49.

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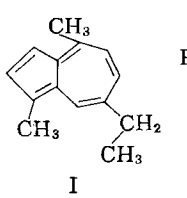
Isolation of Matricin from *Artemisia caruthii*

By JEFFREY C. SPITZER and CORNELIUS STEELINK

The sesquiterpene lactone, matricin, has been isolated from *Artemisia caruthii* and is shown to be the precursor of chamazulene, previously reported in the steam distillate of this species.

THE COMMON SAGE brush *Artemisia caruthii* Wood, var. *Wrightii* (A. Gray), yields a blue oil upon steam distillation or upon simple brewing as a "folk" tea. The oil has been identified (1) as chamazulene (I). Because of the occasional use of the plant as a folk medicine by the Indians of Northern Arizona, and because of the wide distribution of sesquiterpene lactones in the *Artemisia* species, the authors were prompted to investigate the sesquiterpene lactone precursors of chamazulene (pro-chamazulenogens) in this species.

The isolation and characterization of matricin (II) in *A. caruthii* is reported. This compound exists in low concentrations in the plant, and is readily converted to chamazulene (I) by simple steam distillation or by heating in the presence of



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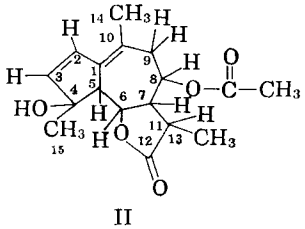

II

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