pentoxide[1] in 68 ml. of methylene chloride was added over 15 min. while the temperature of the reaction mixture was maintained between −15° and −10°. After addition of the dinitrogen pentoxide the solution was allowed to warm to 3° and stirred for 15 min. The reaction mixture was then quenched with aqueous sodium bicarbonate. The organic layer was washed with water, combined with the organic extracts of the neutralized aqueous washes, and dried over magnesium sulfate. Removal of the methylene chloride at reduced pressure left 15.5 g. of residue. A 3.1-g. portion of this residue was extracted with hot ligroin and the cooled extract was chromatographed on a silica acid–Celite (1:1) column packed in ligroin. Elution of the column with ligroin-ether (30:1) gave 0.43 g. (12%) of 10-nitro-2-nitratocamphane, m.p. 95–97°. Recrystallization of this material from ligroin gave white crystals, m.p. 98–99°.

Anal. Calcd. for $C_{10}H_{16}NO_5$: C, 49.18; H, 6.59; N, 11.47. Found: C, 49.38; H, 6.70; N, 11.14.

From the ligroin-ether (9:1) eluate was obtained 0.35 g. (10%) of the carboxylic acid (II or VIa), m.p. 138–140° reported 140–141°.[3]

The ligroin filtrate from the recrystallization of the nitronitrate was chromatographed on silicic acid–Celite and yielded ω-nitrocamphene, 0.12 g. (4.5%), m.p. 60–62°, m.p. 64–65° after recrystallization from aqueous ethanol, reported 64–65°.[5]

The addition of dinitrogen pentoxide to camphene in the manner described above except that an equivalent of tetraethylammonium nitrate was present[1] led to the isolation of 29% of 10-nitro-2-nitratocamphane and 12.4% of ω-nitrocamphene.

Rearrangement of 10-nitro-2-nitratocamphane. To 10 ml. of 50% ethanol containing 1.2 g. of potassium hydroxide was added 2.30 g. of 10-nitro-2-nitratocamphane. The mixture was warmed and swirled until solution occurred. On cooling in ice, a red salt separated and was removed by filtration. This red salt was suspended in a mixture of 25 ml. of water and 25 ml. of ether and acidified with aqueous hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether. Evaporation of the ether left 1.97 g. of a solid, m.p. 155–156°. Two recrystallizations from ligroin gave 10,10-dinitro-2-hydroxycamphane (V) as white needles, m.p. 157–158°, reported 158.5°.[5]

Anal. Calcd. for $C_{10}H_{16}N_2O_5$: C, 49.18; H, 6.59; N, 11.47. Found: C, 49.56; H, 7.11; N, 11.14.

pK determinations. The *p*K's of the nitratoacid (II or VIa) and of VIb were estimated from the titration curves of the acids in 50% ethanol–water at 25°. Under these conditions benzoic acid was found to have a *p*K of 4.50.

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2-Nitro-6-methoxybenzaldehyde[1]

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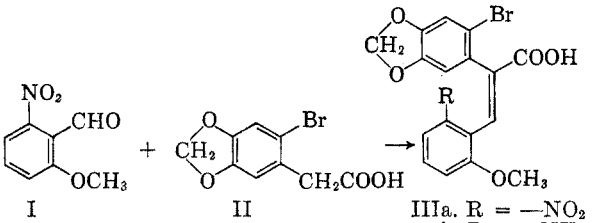
Incidental to another study, it was necessary to prepare *trans*-2-amino-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIb) from 2-nitro-6-methoxybenzaldehyde (I). Synthesis of I from *m*-nitrophenol by means of a Reimer-Tiemann reaction followed by methylation had already been described by Ashley, Perkin, and Robinson.[2] However, conclusive evidence for the assigned orientation of the formyl group was unavailable since the original structural assignment was made on the basis of color reactions and a physical property.[2,3]

In order to remove any doubt concerning the reliability of the Reimer-Tiemann route to I, a sample for comparison purposes was obtained by the following unequivocal procedure. Conversion of 2,6-dinitrotoluene to 2-methyl-3-nitrophenol was accomplished as previously described.[4,5] Methylation of the phenol followed by chromyl chloride oxidation[6] of the methyl ether afforded an authentic specimen of the aldehyde (I) which was found to be identical with the compound described by Ashley.[2] Reaction of *m*-nitrophenol with chloroform in the presence of sodium hydroxide does indeed yield some 6-nitrosalicylaldehyde.

Condensing[7] I with 6-bromohomopiperonylic acid (II)[8−10] in the presence of triethylamine and acetic anhydride led to *trans*-2-nitro-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIa). Reduction of IIIa with ferrous sulfate gave the required amino acid (IIIb).



(1) The author is pleased to acknowledge the financial assistance provided by the Coe Research Fund of the University of Maine.

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(3) The corresponding phenol, 6-nitrosalicylaldehyde, which was obtained in 3% yield, was shown to be steam volatile and therefore the product of *p*-formylation was excluded as a possible structure. After completion of the present investigation, it was found that additional experimental evidence favoring the 6-nitrosalicylaldehyde structure has been presented by H. Shirai and N. Oda, *Bull. Nagoya City Univ. Pharm. School* No. 4, 30 (1956); *Chem. Abstr.*, **51**, 9522 (1957).

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EXPERIMENTAL[11]

2-Nitro-6-methoxytoluene. A solution of 2-methyl-3-nitrophenol[4,5] (73 g.) in 400 ml. of water containing 19 g. of sodium hydroxide was cooled and treated with 60 g. of dimethylsulfate. The mixture was then stirred and heated on the steam bath for 2 hr. before subjecting the crude reaction mixture to a steam distillation. The cream colored product was collected with *ca.* 6 l. of water; yield 42 g. (53%), m.p. 55–57.5°. Simonsen and Nayak[12] report a melting point of 52–53°.

2-Nitro-6-methoxybenzaldehyde (I). A solution of 2-nitro-6-methoxytoluene (40 g.) in 250 ml. of carbon disulfide was added over a 30 min. period to a stirred solution of chromyl chloride (70 g.) in the same solvent (150 ml.). After 72 hr. at room temperature, the dark colored crystalline intermediate was collected and washed with carbon disulfide. After adding the solid to water, the aqueous mixture was extracted with chloroform and the combined chloroform extracts washed with saturated sodium bicarbonate solution and water. Removal of solvent afforded 15 g. (35%) of crude red colored crystalline product. Four recrystallizations from carbon tetrachloride gave an analytical sample as colorless needles, m.p. 110–111°, λ^{CHCl_3} 5.85 μ.

Anal. Calcd. for $C_8H_7NO_4$: C, 53.04; H, 3.90; N, 7.73. Found: C, 53.44; H, 4.23; N, 7.87.

The product was found to be identical (mixture melting point and infrared comparison) with a specimen prepared by Ashley's[2] procedure.

Trans-2-nitro-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIa). A mixture of 2-nitro-6-methoxybenzaldehyde (2.0 g.), 3.06 g. of 6-bromohomopiperonylic acid (II),[8–10] acetic anhydride (10 ml.), and triethylamine (1 ml.) was heated at reflux for 15 min. before cautiously treating the hot reaction mixture with 10 ml. of water. After cooling, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with chloroform. Acidification of the aqueous solution with dilute hydrochloric acid yielded 0.87 g. (17%) of crude pale yellow product, m.p. 200–230°. Three recrystallizations from acetic acid–water afforded a pure sample as pale yellow crystals, m.p. 264–265° (dec.), λ^{KBr} 5.95 μ.

Anal. Calcd. for $C_{17}H_{12}BrNO_7$: C, 48.36; H, 2.87; N, 3.32. Found: C, 48.48; H, 3.03; N, 3.53.

Trans-2-amino-6-methoxy-α-(3′,4′-methylenedioxy-6′-bromophenyl)cinnamic acid (IIIb). A suspension of IIIa (0.55 g.) in a solution composed of ferrous sulfate (3.3 g.), hydrochloric acid (0.2 ml.), and water (5 ml.) was heated to 90–95° before adding 3 ml. of 28% ammonium hydroxide. Heating on the steam bath and intermittent stirring were continued for 45 min. The hot reaction mixture was then filtered through Norit-A and after washing the filter cake with water the combined filtrate was acidified to *p*H 4.5 with hydrochloric acid. The gray colored crystalline product weighed 0.41 g. (81%) and melted at 160–164°. Three recrystallizations from methanol-water gave a pure sample of the amino acid as yellow needles, m.p. 205–206°, λ^{KBr} 5.95 μ.

Anal. Calcd. for $C_{17}H_{14}BrNO_5$: C, 52.07; H, 3.60; N, 3.57. Found: C, 52.04; H, 3.58; N, 3.62.

The amino acid was found to be virtually insoluble in dilute hydrochloric acid.[13]

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(11) All melting points were taken in open Kimble glass capillaries and are uncorrected. Elemental analyses were derformed by The Microanalytical Laboratory of Dr. A. Bernhardt, Mülheim, Germany. The infrared spectra were peterminated by Mr. Evan Thomas of this department.

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Preparation of α,β-Unsaturated Sulfones

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In earlier papers[1,2] from these laboratories it was reported that β-amino and α,β-unsaturated sulfones are formed when aryl- or alkyl-sulfonylacetic acids are condensed with aromatic aldehydes in the presence of ammonia in glacial acetic acid. The yields of the α,β-unsaturated sulfones in such condensations were found to be generally very low. Being engaged in studies on α,β-unsaturated sulfones we were interested in getting increased yields of these compounds. It has been found that the use of benzylamine in place of ammonia and refluxing the reaction mixture for a longer period reduce the β-amino sulfone in the product to a negligible amount and greatly increase the yield of the α,β-unsaturated sulfone. Even with catalytic amounts of benzylamine excellent yields of the unsaturated sulfones were obtained. Using this procedure many new unsaturated sulfones have been prepared (see Table I). In the same Table are shown the increased yields of the previously reported α,β-unsaturated sulfones.

EXPERIMENTAL

General procedure for the preparation of α,β-unsaturated sulfones. A mixture of the sulfonylacetic acid (0.1 mole), the aldehyde (0.1 mole), glacial acetic acid (25 ml.) and benzylamine (0.1–0.2 g.) was refluxed on a hot plate for 50 min. The product was cooled, mixed with 100 ml. of dry ether and set aside for 1 hr. In most cases the α,β-unsaturated sulfone, being sparingly soluble in ether, partly crystallized out. It was removed by filtration and dry hydrogen chloride was passed into the ether solution. The precipitated β-amino sulfone hydrochloride, if any, was filtered off. Evaporation of the ether from the filtrate gave a mixture of the unreacted aldehyde, acetic acid, and unsaturated sulfone. Treatment of this mixture with a few ml. of methanol or isopropyl alcohol precipitated the unsaturated sulfone in many cases. In other cases the unchanged aldehyde had to be removed with sodium bisulfite before the unsaturated sulfone could be separated. The relevant data on the compounds prepared are given in Table I.

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