slurry of 2.77 g. (7.11 mmoles) of the perchlorate **6a** in benzene. The mixture was then filtered and the precipitate was washed with fresh benzene. The combined benzene solutions were evaporated on a steam bath to assure complete removal of ammonia, and the residue was again dissolved in benzene. Gaseous hydrogen chloride was bubbled through the solution for 15 min.; then the resulting precipitate was collected by filtration, washed with benzene, and air dried. The crude product (2.22 g., 96% yield), when recrystallized from methanol and dried at 137° and 0.05 mm., yielded 1.78 g. (77%) of pure **6b** as brown-orange needles, which gradually darkened and decomposed above 280°.

Anal. Calcd. for $C_{19}H_{16}ClNS$: C, 70.03; H, 4.95; Cl, 10.88; S, 9.84. Found: C, 69.80; H, 4.65; Cl, 10.89; S, 9.74.

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A New Synthesis of *o*-Nitrophenylacetaldehyde

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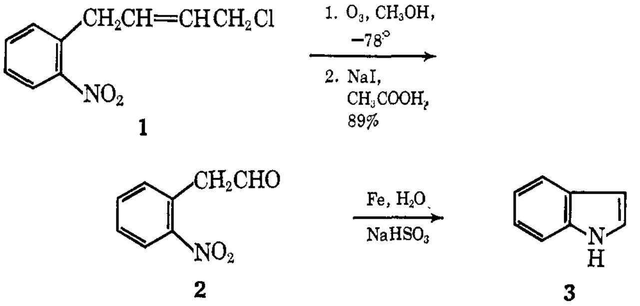
o-Nitrophenylacetaldehyde (**2**) is the key intermediate in the synthetic proof of structure of triindole,[2,3] indole–di-2-methylindole mixed trimer,[2–4] indole–di-1,2-dimethylindole mixed trimer,[2,3] indole–di-2,5-dimethylpyrrole mixed trimer,[2,3] and tri-1-methylindole.[3] It has also been used in a synthesis of indole (**3**), by reduction with iron powder and aqueous sodium bisulfite.[5] The previously reported route[5,6] to **2** gives only a 21% yield[3] from *o*-nitrocinnamamide. Nitration of phenylacetaldehyde at −10 to −15° did not give **2**.[5,7]

The present procedure for the synthesis of **2** involves ozonolysis of 1-chloro-4-(*o*-nitrophenyl)-2-butene[8–11] (**1**), the product of the Meerwein reaction of diazotized *o*-nitroaniline and 1,3-butadiene. The procedure is simpler, shorter, and proceeds in much higher yield (72%) from the more readily available *o*-nitroaniline than does the older method[5] starting from *o*-nitrocinnamic acid.



Application of the Meerwein reaction to diazotized readily available *o*-nitroaniline derivatives and appropriate 1,3-dienes, followed by ozonolysis of the products according to the procedure illustrated here and subsequent reductive cyclization, should greatly increase the usefulness of the Baeyer–Jackson synthesis[12] of indoles.

Experimental Section

1-Chloro-4-(*o*-nitrophenyl)-2-butene (1).—The procedure is essentially that of Braude and Fawcett[8] and Goldberg and Scott.[9] A solution was prepared by adding solutions of sodium acetate trihydrate (80 g., 0.59 mole) in water (100 ml.) and cupric chloride dihydrate (38 g., 0.22 mole) in water (42 ml.) to acetone (1 l.) in a 3-l., three-necked, round-bottomed flask equipped with a mechanical stirrer and a Dry Ice–acetone condenser set up for reflux. The resulting solution was cooled in an ice–salt bath. 1,3-Butadiene (125 ml., 1.44–1.50 moles) was condensed in a precalibrated 250-ml. erlenmeyer flask cooled in a Dry Ice–acetone bath. The butadiene was then poured into the cooled acetone solution. An aqueous suspension of diazotized *o*-nitroaniline [from *o*-nitroaniline (140 g., 1.01 moles), concentrated hydrochloric acid (240 ml.) in water (200 ml.), and sodium nitrite (70 g., 1.01 moles) in water (120 ml.)] kept at −2 to 0°[13] was then siphoned slowly over about 1 hr. into the mechanically stirred, cooled butadiene solution. The liquid mixture was stirred for 6 hr. (or overnight), during which the ice in the bath melted and the solution warmed to room temperature.

The resulting dark brown supernatant oil was separated. The light green, aqueous lower layer was diluted with water (1 l.), and the resulting solution (about 2.7 l.) was extracted with ether (two 500-ml. portions). The ether extracts were combined with the oil, shaken gently (to avoid an emulsion, which separates only slowly) with water (two 500-ml. portions) and saturated salt solution (two 250-ml. portions), and dried over anhydrous sodium sulfate. The ether was then evaporated at aspirator pressure with a rotary evaporator, leaving a brown oil (201 g., 94%), $n^{24}\text{D}$ 1.5657, lit.[8] 75%. Vacuum distillation, without significant forerun,[13] gave a brown oil (173 g., 81%): b.p. 108–118° (0.35 mm.), $n^{25}\text{D}$ 1.5662; lit. 66%,[10,11] b.p. 126° (0.005 mm.),[8] 155–156° (3 mm.),[10,11] $n^{20}\text{D}$ 1.5653,[8] 1.5692[10,11]; ν 1660 (w), 1610 (m), 1580 (mw) (C=C), 1530 (vs), 1350 (s) (NO_2) cm.$^{-1}$ on the oil. The n.m.r. spectrum of a 60% (w./v.) solution in deuteriochloroform contains (with areas relative to 10 protons given in parentheses; δ scale, 1 p.p.m. = 60.00 c.p.s.) an extensively split doublet (1.1) centered at about 7.97 (J = 7 c.p.s., proton *ortho* to the nitro group), a complex multiplet (3.4) from 7.75 to 7.25 with a strong peak at 7.50 (remaining three aromatic protons), a complex multiplet (1.9) centered at 5.87 (two vinyl protons), a doublet (1.8) centered at 4.05 (J = 5.4 c.p.s., methylene group attached to chlorine), and another doublet (1.8) centered at 3.71 (J = 5.4 c.p.s., methylene group attached to the phenyl ring).

***o*-Nitrophenylacetaldehyde (2).**—A solution of 1-chloro-4-(*o*-nitrophenyl)-2-butene (25 g., 0.118 mole) in technical grade methanol[14] (180 ml.) in a 500-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer, a gas inlet tube extending below the surface of the solution, and a gas exit tube, was cooled in a Dry Ice–isopropyl alcohol bath until extensive precipitation of the starting material occurred as a yellow precipitate.

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[13] On one occasion, during distillation of the product, a significant amount (~5 g.) of forerun, b.p. 105° (0.4 mm.), was encountered, which solidified in the condenser and receiver. This by-product may have resulted from allowing the temperature of the diazotized *o*-nitroaniline solution to rise as high as 5–7°.

[14] When absolute methanol was used, the yellow precipitate did not form on cooling, and the resulting product did not seem to be so pure as when ordinary hydrous methanol was used.

The stirrer was started, and a 4–5% mixture of ozone in dry oxygen (generated in a Welsbach Corp. ozonator, Style T-23, with the voltage set at 120 and the oxygen pressure at 8 p.s.i.) was passed in through the gas inlet tube at a rate of about 500 cc./min. The yellow precipitate dissolved completely after about 2.5 hr. and, when the solution turned dark after a total of 3.25 hr., the ozonizer was turned off, but the stirring was continued and the stream of oxygen was passed through the solution for an additional 0.5 hr. Then sodium iodide (70 g., 0.47 mole) and glacial acetic acid (70 ml.) were added simultaneously all at once, and the cooling bath was removed. Stirring was continued while the mixture was allowed to warm to room temperature over a period of 0.5 hr.

Saturated aqueous sodium thiosulfate (about 250 ml.) was then added immediately after the 0.5-hr. warming period to the resulting very dark brown, iodine-containing solution until the color of the solution turned from dark brown to yellow. The solution was diluted with water (300 ml.) and extracted with ether (three 200-ml. portions). The ether extracts were washed with water (200 ml.) and then with saturated aqueous sodium bicarbonate until carbon dioxide was no longer evolved. The ether solution was then washed with saturated salt solution (two 50-ml. portions), dried over anhydrous sodium sulfate, and evaporated at aspirator pressure with a rotary evaporator. The residual oil was then evacuated further with a rotary evaporator and a vacuum pump at 60° (1mm.), leaving **2** as a light orange oil[15] (17.3 g., 89%), $n^{25}\mathrm{D}$ 1.5602. The oil obtained at this stage is nearly pure, as shown by the identity of the infrared spectrum with that of the distilled sample, except for a band at 1105 (mw) cm.$^{-1}$. This preparation has been carried out on three times the scale described, without difficulty, and in the same yield.

When subjected to ordinary vacuum distillation, *o*-nitrophenylacetaldehyde undergoes extensive decomposition, even when pure, with formation of black, tarry undistillable material. Thus, distillation of a 15.5-g. sample of the crude oil at 100–110° (0.25 mm.) gave 10.2 g. (66% recovery) of pure *o*-nitrophenylacetaldehyde as a yellow oil, $n^{25.5}\mathrm{D}$ 1.5634. Subsequent redistillations at the same pressure gave about a 70% recovery, leaving in each case a black tar as a residue in the distillation flask. Purification was best effected by molecular distillation of the crude oil in a Hickman still at 90° (5×10^{-4} mm.) until distillation stopped, which gave the product without forerun as a yellow oil (16.7 g., 86%), $n^{25.5}\mathrm{D}$ 1.5634. Alternatively, the oil can be subjected to rapid short-path (7 cm.) distillation[16] at a pot temperature up to 185° (0.05–0.02 mm.) until distillation stops. Again, there was no forerun, and the pure *o*-nitrophenylacetaldehyde was obtained as a yellow oil (15.8 g., 81%): $n^{25}\mathrm{D}$ 1.5639; reported[5] as a light yellow oil, b.p. 133–135° (5 mm.); ν 2710 (mw) (H—C═O), 3400 (w) (overtone), 1725 (s) (C═O), 1525 (s), 1350 (s) (NO_2) cm.$^{-1}$ on the oil. The n.m.r. spectrum of a 60% (w./v.) solution in deuteriochloroform contains (with areas relative to 7 protons given in parentheses; δ scale, 1 p.p.m. = 60.00 c.p.s.) a hyperfinely split triplet (1.0) with the high-field member further split into a doublet centered at 9.95 ($J = \sim 0.5$ c.p.s., aldehyde proton), an extensively split doublet (1.1) centered at 8.12 (J = 7.2 c.p.s., proton *ortho* to the nitro group), a complex multiplet (3.1) from 7.84 to 7.27 with the strongest peak at 7.59 (remaining three aromatic protons), and a hyperfinely split doublet (1.9) centered at 4.15 ($J = \sim 0.5$ c.p.s., methylene group).

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(15) On several occasions yellow crystals of sulfur (0.5–0.7 g.), m.p. 116–117°, separated from the oil at this point, and were removed by suction filtration.

(16) A Kontes Glass Co. Bantamware short-path distillation head, no. K-28710, was used.

Some Studies of 1,3,5-Hexatriene Systems

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The preparation of pure substituted 1,3,5-hexatrienes has been accomplished recently[2,3] by utilization of a procedure[4] in which the triene is generated by means of a Hofmann elimination. Previous preparations of substituted 1,3,5-hexatrienes involved, in general, either a vapor phase catalytic dehydration over alumina or an acid-catalyzed dehydration of an appropriately substituted hexadienol. The corresponding cyclohexadiene inevitably forms as a by-product in the former procedure and can assume major proportion. The formation of these cyclohexadienes has been described by Woods and co-workers.[5,6] Woods and Viola[6] chose to look upon this reaction as an internal Diels–Alder reaction of the intermediate triene. In most cases, a temperature range can be found in which the triene is the major product of the dehydration.

Woods and Fleischacker[5] attempted the preparation of the three possible methyl-1,3,5-hexatrienes by dehydration of an appropriately substituted hexadienol by either of two procedures: (1) catalytic reaction over alumina, or (2) reaction with phosphorus pentoxide. Only the 1-methyltriene was obtained in a relatively pure state. The 2-methyl- and 3-methyl-1,3,5-hexatrienes apparently were contaminated with appreciable quantities of methylcyclohexadienes. They also found that dehydration of methylhexadienols over alumina at 500° or passage of methyl-1,3,5-hexatriene over the catalyst under the same conditions yielded methylcyclohexadienes.

We decided to reinvestigate the above system in order to elucidate the structures of the methylcyclohexadienes obtained from the pure methyl-1,3,5-hexatrienes prepared by the Hwa procedure. 1-Methyl- and 3-methyl-1,3,5-hexatriene were passed over alumina at 410–420°. The products were trapped in a Dry Ice–acetone bath and subsequently distilled. The purified products were analyzed by g.l.p.c., which indicated that the crude products were mixtures containing, in both cases, at least eight compounds. A minimum of 80% of each crude product was represented by one peak in the chromatogram. In both cases, this substance was isolated by successive collections of the appropriate peak by trapping in a Dry Ice–acetone bath. Both products were analyzed and identified as toluene by refractive index, ultraviolet spectrum, and retention time compared with an authentic sample. No appreciable quantity of methylcyclohexadiene could be found in either product. The formation of toluene as the major product can be rationalized only the basis of cyclization followed by dehydrogenation over alumina, or under the conditions in the chromatograph. This latter explanation does not seem reasonable, since cyclohexadiene does not form benzene under identical chromatographic conditions, as demonstrated with known calibrated solutions. The formation of toluene and lack of significant quantities of methylcyclohexadiene in the product differs markedly from the results reported by Woods and Fleischacker.[5]

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