

## Synthesis of 2-Nitroindanones by Dieckmann Cyclization of 2-(2-Nitroethyl)benzoates<sup>1</sup>

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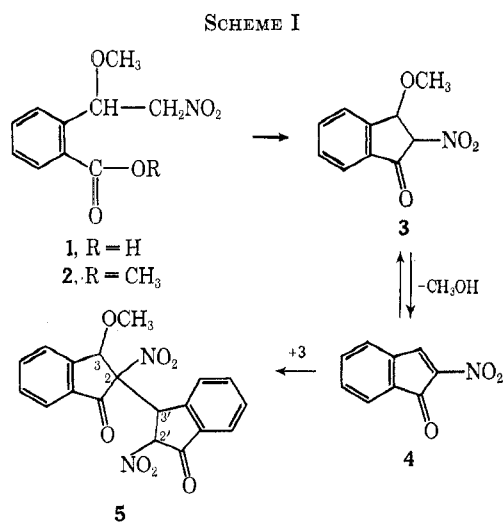
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Methyl 2-(1-methoxy-2-nitroethyl)benzoate (**2**) was prepared from its acid (**1**) with diazomethane and was found to undergo a Dieckmann-type cyclization by the action of sodium methoxide. The reaction is followed by an elimination-addition process that leads to 3-methoxy-2-nitro-2-(2-nitroindanon-3-yl)indanone (**5**). Methyl and phenyl 2-(2-nitroethyl)benzoate (**6** and **8**) are cyclized to 2-nitroindanone (**7**), and methyl 2-(1,3-dinitro-2-propyl)benzoate (**9**) gives 3-nitromethyl-2-nitroindanone (**10**). Trifluoroperoxyacetic acid oxidation of 2-oximino-1-indanone (**11**) provided an alternative route to **7**.

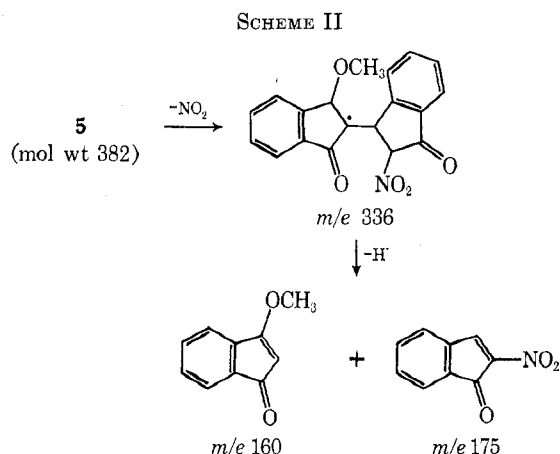
Subsequent to the synthesis<sup>2</sup> of 2-(1-methoxy-2-nitroethyl)benzoic acid (**1**), it was observed that storage of a methanolic solution of **1** (1 day at 25°) followed by addition of sodium methoxide produces a strong ultraviolet peak at 370 nm. This absorption did not correspond to a  $\beta$ -nitrostyrene system (310–320 nm)<sup>2,3</sup> but was reminiscent of the absorptions reported for  $\omega$ -nitroacetophenone (352 nm)<sup>4</sup> and 2-nitrotetralone (370 nm).<sup>5</sup> It seemed possible that part of **1** had become esterified to its methyl ester (**2**) which was then cyclized by the base, in a Dieckmann-type reaction, to give a nitro ketone (Scheme I). This prompted us to

addition is the base-catalyzed formation of 1-methoxy-2,4-dinitro-1,3-diphenylbutane from  $\beta$ -nitrostyrene and methanol.<sup>6</sup>

The structure of **5** was established by analytical and spectral data. Although the mass spectrum did not exhibit a molecular ion peak at  $m/e$  382, it showed a strong peak at  $m/e$  336 resulting from loss of  $\text{NO}_2$  and two further, intense peaks ( $m/e$  175 and 160) that may have arisen by fragmentation with loss of a hydrogen atom as depicted in Scheme II. The nmr spectrum in



examine whether such a reaction might provide a preparative avenue to the 2-nitroindanone system. When crystalline methyl 2-(1-methoxy-2-nitroethyl)benzoate (**2**), prepared from **1** and diazomethane, was treated with methanolic sodium methoxide it was indeed converted, within a few minutes, into a product possessing  $\lambda_{\text{max}}$  370 nm. The isolated product, however, proved to be 3-methoxy-2-nitro-(2-nitroindanon-3-yl)indanone (**5**) rather than 3-methoxy-2-nitroindanone (**3**). This is explained by a (reversible)  $\beta$  elimination of methanol from part of the cyclization product **3** to give the intermediate nitroalkene **4** which is then removed from the equilibrium by Michael addition of surviving **3** (Scheme I). A closely related precedent for such a Michael



$\text{CDCl}_3$  showed an intensity ratio of 8:3 in the signals attributable to the aromatic protons (multiplet at  $\tau$  2.28) and the methoxyl protons (singlet at  $\tau$  6.69). A one-proton singlet ( $\tau$  4.52) was assigned to H-3; H-2' and H-3' fortuitously had identical chemical shifts ( $\tau$  4.43) and gave a two-proton singlet.

Cyclization of methyl 2-(2-nitroethyl)benzoate (**6**) and of the corresponding phenyl ester (**8**) gave 2-nitroindanone (**7**), and methyl 2-(1,3-dinitro-2-propyl)benzoate (**9**) afforded 3-nitromethyl-2-nitroindanone (**10**) (Scheme III). The yields in these reactions were 43–62%. Proof of structure was provided for **7** and **10** by spectral data and, for **7**, by an independent synthesis recorded in a later paragraph. The mass spectra of **7** and **10** exhibited molecular ion peaks at  $m/e$  177 and 236, respectively. The nmr spectrum of **7** (in  $\text{CDCl}_3$ ) showed a 4:2 intensity ratio for the aromatic protons (multiplet at  $\tau$  2.32) and benzylic protons (two overlapping quartets near  $\tau$  6.20). A quartet attributable to H-2 ( $\tau$  4.49) had an intensity 25% less than that calculated for one proton, and this may be explained by

(1) Taken from the Ph.D. Thesis of S. R. Naik, University of Ottawa, 1967.

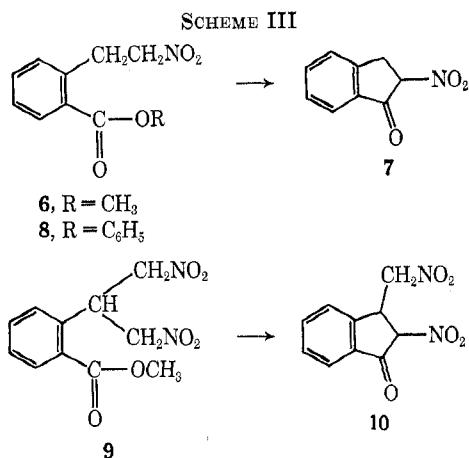
(2) H. H. Baer and F. Kienzle, *Can. J. Chem.*, **43**, 190 (1965).

(3) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1105 (1947); R. Stuart and L. G. Walker, *Can. J. Chem.*, **35**, 1561 (1957).

(4) R. D. Campbell and C. L. Pitzer, *J. Org. Chem.*, **24**, 1531 (1959).

(5) H. Feuer and P. M. Pivawer, *ibid.*, **31**, 3152 (1966).

(6) J. Meisenheimer and F. Heim, *Ber.*, **38**, 467 (1905); *Justus Liebigs Ann. Chem.*, **355**, 260 (1907).



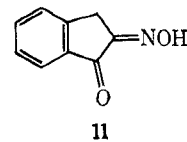
partial enolization as has been previously observed<sup>5</sup> in other cyclic  $\alpha$ -nitro ketones. In agreement herewith, the signal disappeared upon deuterium exchange with D<sub>2</sub>O. In the spectrum of **10** (in DMSO-*d*<sub>6</sub>) the corresponding H-2 signal was a doublet ( $\tau$  3.9,  $J$  = 4 Hz) that showed a similarly reduced intensity. An intensity ratio of 4:3 was seen for the aryl protons (multiplet at  $\tau$  2.19) and a group of poorly resolved resonances ( $\tau$  4.3–5.3) assignable to the benzylic and nitromethyl protons.

In attempts to prepare 2-nitropentanone by cyclization of methyl 5-nitropentanoate<sup>7</sup> an absorption maximum at 345 nm was generated. This may be taken as evidence<sup>5</sup> for the formation of the desired ketone nitronate. However, on deionization and work-up, no product other than the starting ester was detected. Feuer and coworkers<sup>5,8</sup> in their studies on the alkyl nitrate nitration of ketones also were unable to isolate 2-nitrocyclopentanone, and they as well as other workers commented upon the fact that certain  $\alpha$ -nitro ketones are extremely prone to cleavage under basic<sup>5,9</sup> and acidic<sup>10</sup> conditions.

As far as we are aware, ester condensations utilizing a reactive nitromethylene group as the nucleophilic reaction partner are not common in the literature. One analogous reaction is the condensation of nitroalkanes with the ethoxymethylene derivatives of various  $\beta$ -dicarbonyl compounds;<sup>11</sup> the latter were viewed as vinylogous esters; and the similarity of the reaction to the Claisen ester condensation was pointed out. Another reaction, more closely akin to ours, involved condensation of ethyl acetonedicarboxylate with 1-dimethylamino-2-nitroethylene, which led to an aromatic product by way of cyclization of an intermediate  $\omega$ -nitro ester.<sup>12</sup>

In order to confirm the structure of the cyclization product obtained from **6** or **8**, the then unknown 2-nitroindanone (**7**)<sup>13</sup> was synthesized by an independent

route. It was obtained in 18% yield by oxidation of 2-oximino-1-indanone (**11**) with trifluoroacetic acid<sup>14</sup>



in acetonitrile solution at room temperature.<sup>15</sup> We were unable to prepare **7** from 2-bromoindanone and sodium nitrite, or by nitration of indanone with acetyl nitrate<sup>16</sup> or alkyl nitrates.<sup>5,17</sup>

### Experimental Section<sup>18</sup>

**Methyl 2-(1-Methoxy-2-nitroethyl)benzoate (2).**—To a solution of 2-(1-methoxy-2-nitroethyl)benzoic acid<sup>2</sup> (**1**) (0.80 g) in ether (75 ml) was added a distilled, ethereal solution of diazomethane in slight excess. The solution was kept at 4° for 1 hr and then evaporated to give **2** which crystallized from methanol as colorless plates (0.60 g, 71%): mp 98°;  $\nu_{\max}$  1720 (C=O) and 1560 cm<sup>-1</sup> (NO<sub>2</sub>); nmr spectrum (CDCl<sub>3</sub>)  $\tau$  2.22 (4 H, aromatic), 4.26 (q, H-1'), 5.30 and 5.42 (two quartets due to the magnetically nonequivalent nitromethyl protons), 6.67 and 6.72 (s, OCH<sub>3</sub>).

*Anal.* Calcd for C<sub>11</sub>H<sub>13</sub>NO<sub>5</sub> (239.2): C, 55.24; H, 5.48; N, 5.85. Found: C, 55.31; H, 5.46; N, 5.98.

**3-Methoxy-2-nitro-2-(2-nitroindanon-3-yl)indanone (5).**—A solution of sodium methoxide (444 mg) in methanol (10 ml) was added (over a period of 30 min) to a solution of the ester **2** (1.195 g) in methanol (100 ml). After standing at room temperature for 8 hr the solution was deionized with cation-exchange resin, Rexyn-50 (H<sup>+</sup>), and evaporated to give a solid which, on recrystallization from methanol, afforded **5** as colorless prisms (475 mg): mp 164°;  $\nu_{\max}$  1750 (C=O) and 1550 cm<sup>-1</sup> (NO<sub>2</sub>);  $\lambda_{\max}$  372 nm ( $\epsilon$  8300, in methanol). For nmr data see the discussion.

*Anal.* Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>7</sub> (382.3): C, 59.69; H, 3.66; N, 7.35; OCH<sub>3</sub>, 8.15. Found: C, 59.56; H, 3.97; N, 7.50; OCH<sub>3</sub>, 9.20; mol wt, 380 (by osmometry in acetone solution).

**2-Nitroindanone (7).** **A. By Cyclization of the Methyl Ester 6.**—A solution of sodium methoxide (13 mg) in methanol (1 ml) was added to a solution of methyl 2-(2-nitroethyl)benzoate<sup>19</sup> (**6**) (50 mg) in methanol (5 ml). A yellow precipitate was formed after a few minutes. The mixture was stirred at room temperature for 6 hr and then cooled to 0°, neutralized with cold 1 N hydrochloric acid, and evaporated to dryness. The residue was extracted with boiling petroleum ether (bp 60–80°), and evaporation of the extract gave a white solid that was recrystallized from petroleum ether to yield **7** (26 mg) as colorless plates: mp 80–81°;  $\nu_{\max}$  1730 (C=O) and 1550 cm<sup>-1</sup> (NO<sub>2</sub>);  $\lambda_{\max}$  in methanol 256 nm ( $\epsilon$  11,000) and 372 (8600). For nmr data see the discussion. Kametani, *et al.*, described **7** as "pale yellowish brown scales, mp 80–81.5°."

*Anal.* Calcd for C<sub>9</sub>H<sub>7</sub>NO<sub>3</sub> (177.1): C, 61.01; H, 3.95; N, 7.91. Found: C, 61.15; H, 3.99; N, 7.81.

**B. By Cyclization of the Phenyl Ester 8.**—The phenyl ester<sup>19</sup> (**8**) (about 45 mg) was cyclized as described for **6**, except for a

(1963), and H. H. Baer and B. Achmatowicz, *J. Org. Chem.*, **29**, 3180 (1964). A synthesis of **7** departing from indene nitrosite has since been reported by T. Kametani, H. Sugahara, and S. Asagi, *Chem. Pharm. Bull.*, **14**, 1408 (1966).

(14) W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, **77**, 4557 (1955).

(15) An earlier attempt<sup>4</sup> to perform the same reaction at reflux temperature had been unsuccessful.

(16) F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2323, 3049 (1962); **28**, 1765 (1963). A. A. Griswold and P. S. Starcher, *ibid.*, **31**, 357 (1966).

(17) W. Wislicenus and M. Waldmueller, *Ber.*, **41**, 3334 (1908); H. Feuer, J. W. Shepherd, and C. Savides, *J. Amer. Chem. Soc.*, **78**, 4364 (1956).

(18) Melting points were taken in capillaries in an electric aluminum block apparatus. Evaporations were performed *in vacuo* at a bath temperature of 35–40°. Infrared spectra were taken from Nujol mulls on a Perkin-Elmer infracord instrument. Ultraviolet spectra were recorded with a Perkin-Elmer spectrometer, Model 202. Nmr spectra (60 MHz) were obtained from a Varian HA-60 instrument using tetramethylsilane as internal standard.

(19) H. H. Baer and S. R. Naik, *J. Org. Chem.*, **35**, 3161 (1970).

(7) This nitro ester was prepared from the corresponding bromo ester by displacement with sodium nitrite according to N. Kornblum, *Org. React.*, **12**, 101 (1962), but was obtained in an impure state only.

(8) H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, *J. Org. Chem.*, **33**, 3622 (1968).

(9) A. S. Matlack and D. S. Breslow, *ibid.*, **32**, 1995 (1967), and references cited therein.

(10) H. Feuer and P. M. Pivawer, *ibid.*, **34**, 2917 (1969), and references cited therein.

(11) A. Dornow and S. Lüpfer, *Justus Liebig's Ann. Chem.*, **606**, 56 (1957).

(12) T. Severin, B. Brueck, and P. Adhikary, *Ber.*, **99**, 3097 (1966).

(13) A compound previously described as **7** [J. Thiele and E. Weitz, *Justus Liebig's Ann. Chem.*, **377**, 1 (1910)], had been shown to be, in fact, 1-hydroxy-2-nitroindene: see F. W. Lichtenthaler, *Tetrahedron Lett.*, 775

reaction time of 1 hr. The product (13 mg) was identical in all respects with 7 as prepared from 6.

C. **By Oxidation of the Oxime 11.**—Trifluoroacetic anhydride (504 mg) was added with stirring to an ice-cooled solution of 98% hydrogen peroxide (68 mg) in acetonitrile (5 ml). The solution was allowed to reach room temperature and was then added dropwise (over a period of 1 hr) to a stirred solution of 2-oximino-1-indanone<sup>20</sup> (11) (161 mg) and urea (150 mg) in acetonitrile (15 ml). After 8 hr the reaction mixture was poured onto crushed ice. The product was extracted by ether which was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to leave a brown residue. This residue was extracted with boiling petroleum ether (bp 60–80°). Evaporation of the extract gave a pale yellow solid (71 mg) that was recrystallized from petroleum ether to furnish 7 (32 mg) as colorless plates, mp 81°. The product was identical with 7 from the cyclization (see A and B), according to ir and uv spectra.

**3-Nitromethyl-2-nitroindanone (10).**—To an ice-cooled solution of methyl 2-(1,3-dinitro-2-propyl)benzoate<sup>19</sup> (9) (380 mg) in methanol (35 ml) was added a solution of sodium methoxide (160 mg) in methanol (3 ml) over a period of 15 min. The mixture was stirred at 0° for 1 hr and was then neutralized with cold 1 N hydrochloric acid and evaporated to dryness. The residue was extracted with chloroform, and the extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated to a small volume, and cooled in a refrigerator. Yellow crystals (135 mg) melting at 116–117° were deposited; recrystallization from chloroform raised the melting point to 118–119°; for nmr data see the discussion:  $\nu_{\max}$  1725 (C=O) and 1550 cm<sup>-1</sup> (NO<sub>2</sub>);  $\lambda_{\max}$  370 nm ( $\epsilon$  8400, in methanol).

(20) H. O. House, W. F. Gannon, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, **82**, 1463 (1960).

*Anal.* Calcd for C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>O<sub>6</sub> (236.2): C, 50.84; H, 3.41; N, 11.85. Found: C, 50.90; H, 3.60; N, 11.98.

**Attempted Preparation of 2-Nitrocyclopentanone.**—Commercial methyl 5-bromopentanoate (4.2 g), sodium nitrite (2.8 g), and phloroglucinol (1.75 g) were stirred in a mixture of methyl sulfoxide (28 ml) and N,N-dimethylformamide (7 ml) for 5 hr at room temperature. The mixture was then poured into a large volume of ice water which was extracted with ether. The extract was washed twice with water and dried (Na<sub>2</sub>SO<sub>4</sub>), and the ether was evaporated leaving a brown liquid which was distilled *in vacuo*. The distillate (1.5 g) collected at 100–102° (0.8 Torr) was colorless and exhibited infrared bands at 1730 (C=O) and 1550 cm<sup>-1</sup> (NO<sub>2</sub>). It was presumed to contain methyl 5-nitropentanoate although the elemental analysis was unsatisfactory (Calcd: C, 44.75; H, 7.32; N, 8.68. Found: C, 47.77; H, 7.59; N, 7.92). The high carbon and low nitrogen content possibly indicated contamination by methyl 4-pentenoate that may have arisen by partial dehydrobromination of the starting ester. Attempts at purification were unsuccessful. A part (0.1 g) of the product was mixed with methanol (2.5 ml) containing sodium methoxide (35 mg). A uv maximum at 345 nm developed. After standing at room temperature for 8 hr the solution was deionized with Rexyn-101 (H<sup>+</sup>), the solvent was removed under reduced pressure, and a liquid remained which showed no absorption in the 300–390-nm region and gave an infrared spectrum completely identical with that obtained prior to the methoxide treatment.

**Registry No.**—2, 25116-44-3; 5, 25116-45-4; 7, 13943-70-9; 10, 25116-47-6.

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## The Acid-Catalyzed Disproportionation of Indan

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The hydrogen fluoride–boron trifluoride catalyzed disproportionation of indan was investigated over a range of temperatures, contact times, and boron trifluoride concentrations. At 30° phenylpropylindans were the major products while at 70° *as*-hydrindacene was the principal tricyclic product formed. The isomerization of *s*-hydrindacene and *as*-hydrindacene was also investigated at 30, 50, and 70°. An explanation is offered for the formation of *as*-hydrindacene.

The acid-catalyzed disproportionation of alkyl aromatic compounds has been given considerable attention in the literature.<sup>1–4</sup> By comparison, little has been published on the acid-catalyzed disproportionation of alicyclic systems. Schroeter,<sup>5</sup> some time ago, investigated the action of aluminum chloride on 1,2,3,4-tetrahydronaphthalene (tetralin). Several products were obtained, the major ones being benzene, 1,2,3,4,5,6,7,8-octahydroanthracene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, and 6-(4-phenylbutyl)-1,2,3,4-tetrahydronaphthalene. All were produced in very low yield. More recently we reexamined this reaction<sup>6</sup> and found hydrogen fluoride–boron trifluoride to be superior to any other catalyst for the formation of 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,5,6,7,8-octahydrophenanthrene or 6-(4-phenylbutyl)-1,2,3,4-tetrahydronaphthalene. The type of products that

was obtained was very much dependent upon the reaction conditions employed.

The disproportionation of other alicyclic systems such as indan has likewise received little attention. A report by Turova-Pollak and Podolskaya<sup>7</sup> described the use of aluminum chloride at 170–230° for 10 hr to give a mixture of "hexamethylene hydrocarbons, pentamethylene hydrocarbons, and some saturated aliphatic hydrocarbons."

We wish to report our results for the hydrogen fluoride–boron trifluoride catalyzed disproportionation of indan. The effect of changes of reaction parameters on the products formed will be presented and discussed, and certain comparisons will be made with the results of our previous work on tetralin disproportionation.<sup>6</sup>

### Experimental Section

**Materials.**—The anhydrous hydrogen fluoride and boron trifluoride were commercial grade of 99.9 and 99.0% purity, respectively, obtained from the Matheson Company. They were used without further purification. The indan was purchased

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(6) R. D. Bushick, *Ind. Eng. Chem., Prod. Res. Develop.*, **6**, 172 (1967).

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