slowly. The mixture was allowed to reflux overnight, hydrolyzed, and worked up in the usual manner to yield 2.29 g (0.0042 mol, 85%) of pale yellow crystals: mp 245–248°; ir (CCl_4) 3635 cm^{-1} (OH); nmr (CCl_4) τ 3.10 (m, 30, ArH), 4.50 (s, 1, OH), 7.26 (s, 1, CH).

Anal. Calcd for $C_{41}H_{32}O$: C, 91.07; H, 5.96; mol wt, 540. Found: C, 90.78; H, 6.06; mol wt, 540 (mass spectrum).

1,2,3,4,5,5-Hexaphenyl-1,3-cyclopentadiene[1] (X). A. Using Acetyl Chloride.—Into a 100-ml round-bottomed flask equipped with a condenser was placed 1.00 g (1.8 mmol) of IX and 25 ml of acetyl chloride, and the mixture was refluxed for 24 hr. After cooling to room temperature the mixture was carefully diluted with 100 ml of water and extracted with benzene and the benzene was dried over magnesium sulfate. Removal of the solvent under vacuum afforded a yellow oil which was crystallized from benzene and ethanol to yield 0.88 g (1.68 mmol, 96.5%) of white crystals: mp 175–177° (lit.[1] mp 172°); uv (CH_3CN) 335, 275 (sh), 247 mμ.

Anal. Calcd for $C_{41}H_{30}$: C, 94.21; H, 5.77; mol wt, 522. Found: C, 94.27; H, 5.93; mol wt, 522 (mass spectrum).

B. Using Acetic Anhydride.—Using the same procedure and amounts of reagents as described above but allowing the mixture to reflux for 3 days afforded 90% of product identical with that described above.

Registry No.—III, 2137-74-8; IV, 34759-47-2; VIII, 34759-48-3; IX, 34759-49-4; X, 34759-50-7.

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The Synthesis and Transformations of 2-Nitro-1-phenyl-1-hydroxyindene and Its Isomer

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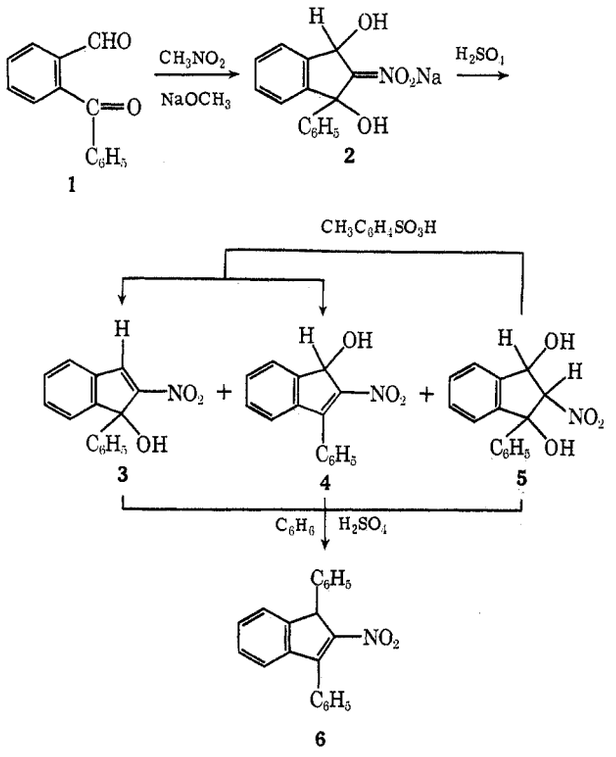
Condensation of 2-benzoylbenzaldehyde (1) with nitromethane in the presence of sodium methoxide gave, after acidification, 2-nitro-1-phenyl-1-hydroxyindene (3), 2-nitro-3-phenyl-1-hydroxyindene (4), and 2-nitro-1-phenyl-1,3-dihydroxyindan (5). The first two compounds were converted to the corresponding acetates 7 and 8, which on treatment with primary or secondary amines gave the nitroenamines 9 and the ammonium salts 11 of the 2-nitro-1-phenyl-3-indanone (12), respectively. Hydrolysis of 9 or 11 afforded 12. Treatment of the acetate 7 with alcohols yielded 2-nitro-3-phenyl-1-alkoxyindene (17). After prolonged reflux the isomeric 2-nitro-1-phenyl-3-alkoxyindene (18) was obtained. A catalytic amount of triethylamine rearranges 17 to 18.

The condensation of 1,4, 1,5, and 1,6 dialdehydes with nitromethane in an alkaline medium followed by acidification is a general method for the synthesis of five-, six-, and seven-membered ring systems.[1] However, little is known about the reactivity of diketones or keto aldehydes toward nitromethane.[1] This led us to study the condensation of *o*-benzoylbenzaldehyde[2] with nitromethane under alkaline conditions.

Treatment of *o*-benzoylbenzaldehyde with nitromethane in the presence of 1 equiv of sodium methoxide in methanol generated within 2 min a white, crystalline precipitate of the 1-phenyl-1,3-dihydroxy-2-acinitroindan sodium salt 2. Acidification of 2 with sulfuric acid in ice yielded two isomeric 2-nitrophenylhydroxyindenes (3 and 4) as well as 2-nitro-1-phenyl-1,3-dihydroxyindan (5). Structures were readily assigned from an interpretation of the nmr spectra for the three compounds. Dehydration of 5 with *p*-toluenesulfonic acid in refluxing benzene gave a mixture consisting mainly of 4 and a small amount of 3. Treatment of either 3, 4, or 5 with sulfuric acid in benzene as dehydrating agent gave 1,3-diphenyl-2-nitroindene (6)[3] (Scheme I).

SCHEME I



Acetylation of 3 was found to be temperature dependent. At −5°, the acetate 7 was obtained usually accompanied by 8. The thermodynamically more stable product 8 was produced either at room temperature from 3, by direct acetylation of 4, or by treatment of 7 with glacial acetic acid at room temperature (Scheme II).

Addition of primary or secondary amines to a solution of 7 resulted in an immediate color change from light yellow to green with the formation of nitroenamines of type 9.[4] Most likely Michael addition with

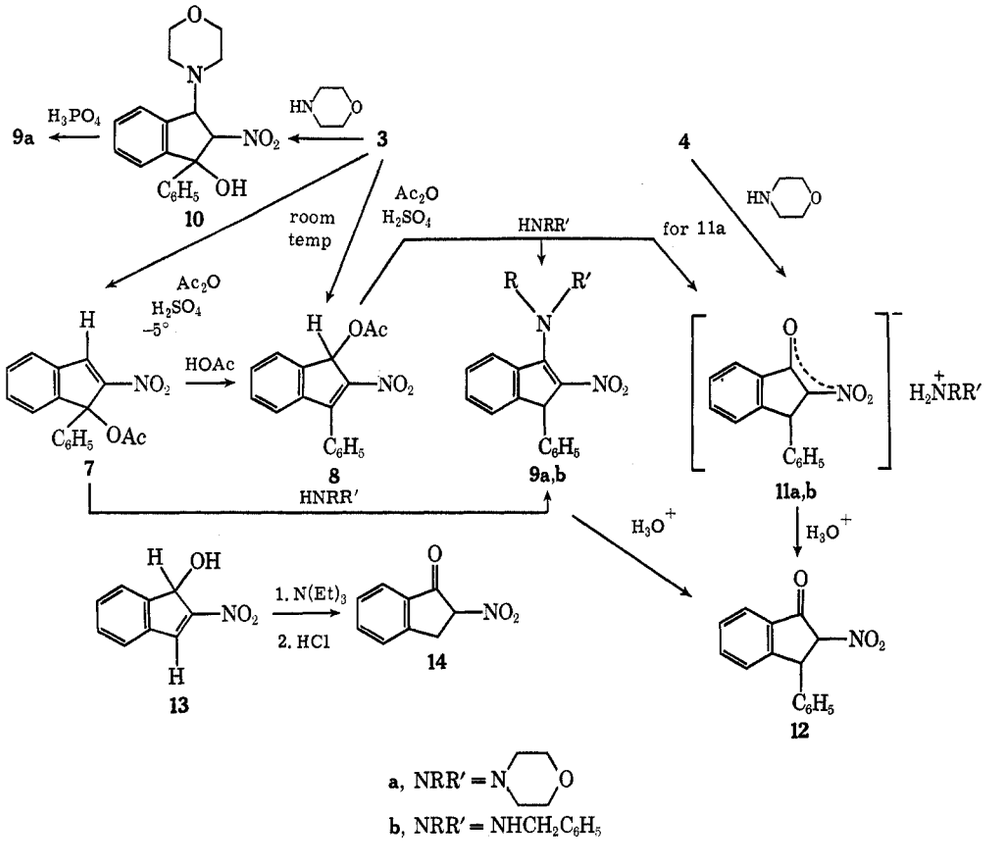
(1) F. W. Lichtenthaler, *Angew. Chem., Int. Ed. Engl.*, **3**, 211 (1964).

(2) W. Metlesics, T. Anton, M. Chaykovsky, V. Toome, and L. H. Sternbach, *J. Org. Chem.*, **33**, 2874 (1968).

(3) C. F. Koelsch, *ibid.*, **26**, 4238 (1961).

(4) See also F. W. Lichtenthaler and N. Majer, *Tetrahedron Lett.*, **411** (1969).

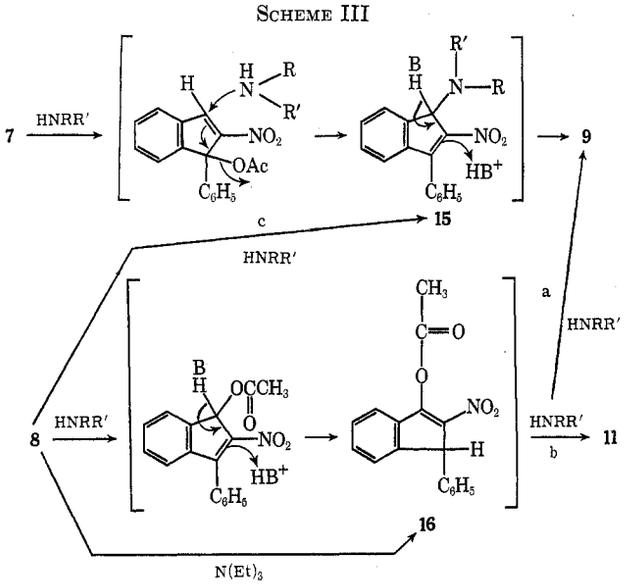
SCHEME II



a, NRR′ = morpholino

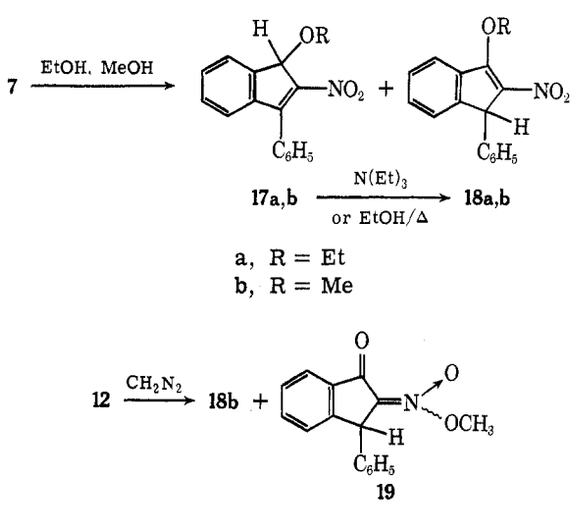
b, NRR′ = $NHCH_2C_6H_5$

SCHEME III



immediate loss of acetic acid leads to an intermediate like **15** (Scheme III) which then rearranges to **9**. If a leaving group less active than acetate is present, *e.g.*, the hydroxyl group in **3**, the reaction sequence stops at the Michael adduct. Thus, treatment of **3** with morpholine leads to compound **10**. However, the reaction will proceed to **9a** if the hydroxyl group is converted into a good leaving group by protonation with phosphoric acid. The transformation of intermediate **15** to compound **9** is facilitated by base[5] as was illustrated by the expeditious rearrangement of **17a** to **18a** in the presence of a catalytic amount of triethylamine (Scheme IV).

SCHEME IV



a, R = Et

b, R = Me

When the isomeric acetate **8** was treated with primary or secondary amines only a small amount of **9** was formed. The major products were the ammonium salts **11** of 2-nitro-1-phenylindanone (**12**). A possible reaction sequence is indicated in Scheme III with the initial formation of the enol acetate **16**, followed by ready cleavage to **9** or **11** by attack of the nucleophile of C_3 (path a) or on the carbonyl function of the acetoxy group (path b), respectively. Direct nucleophilic displacement of the acetoxy group in **8** would also lead to **9** (path c) *via* the intermediate **15**. These mechanisms

(5) A. M. Weidler, *Acta Chem. Scand.*, **17**, 2724 (1963); G. Bergson and A. M. Weidler, *ibid.*, **18**, 1487, 1498 (1964); C. Ohlson, J. Wollmark, and G. Bergson, *ibid.*, **20**, 750 (1966).

were clarified by the isolation of the unstable intermediate **16**, obtained by treatment of **8** with catalytic amounts of triethylamine. Reaction of **16** with morpholine gave exclusively **11a**. No trace of **9** could be detected by tlc, thereby excluding path a. Compound **11** must be derived from **8** as indicated by path c. The formation of the intermediate **16** is analogous to the facile rearrangement of **4** to **11a** with morpholine.

Hydrolysis of **9** or acidification of **11** led to **12**. We found that the unsubstituted 2-nitroindenone (**14**)[6] was also formed in fair yield by treatment of the 1-hydroxy-2-nitroindene (**13**)[7] with 1 equiv of triethylamine followed by immediate acidification.

The ease of formation of nitroenamines from **7** prompted us to investigate the products resulting from the treatment of this compound with alcohols. Two types of compounds were obtained, the adducts **17** and the rearranged compounds **18** (Scheme IV). Prolonged reflux of the reaction mixture led to a high percentage of the rearranged product. This transformation seems to proceed in polar solvents more rapidly than in nonpolar solvents. After 16 hr reflux in ethanol, a pure sample of **17a** was converted to **18a** in 77% yield, whereas reflux in toluene for the same period of time led to only 17% of the rearranged product as estimated by nmr. As mentioned above, this rearrangement was facilitated by the presence of a catalytic amount of triethylamine. The structural assignment for **18** was based on the signal for H_4 at 0.3 ppm downfield of the aromatic region in the nmr spectrum. This would be expected because of the presence of syn axial heteroatoms at C_3. In the case of the nitroenamines **9**, an even stronger deshielding of 0.4 ppm was observed. The structure of **18** was further substantiated by the methylation of **12** with diazomethane to give **18b** and the nitronic ester **19**.[8]

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. The uv spectra were determined on a Cary Model 14 spectrophotometer, nmr spectra with a Varian A-60 instrument, and the ir spectra on a Beckman IR-9 spectrophotometer. All spectra were compared in order to confirm or exclude the expected structural changes.

1,3-Dihydroxy-1-phenyl-2-acinitroindan Sodium Salt (2).—To a solution of 10.5 g (50 mmol) of *o*-benzoylbenzaldehyde and 6.1 g (100 mmol) of nitromethane in 50 ml of methanol was added 50 ml of 1 *N* sodium methoxide solution in methanol. The resulting white precipitate was stirred for 30 min, and after the addition of 100 ml of ether was collected on a funnel and washed with ether, uv max (0.01 *N* KOH) 256 mμ (ε 10,960), 268 (9800), 274.5 (10,200).

2-Nitro-1-phenyl-1-hydroxyindene (3). 2-Nitro-3-phenyl-1-hydroxyindene (4), and 2-Nitro-1-phenyl-1,3-dihydroxyindan (5).—The above prepared salt was suspended in 100 ml of water and, with stirring, 30 g of ice and 10 ml of concentrated sulfuric acid were poured into the reaction mixture. After 30 min of stirring, 100 ml of methylene chloride was added and the organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo* to a viscous oil. On addition of 30 ml of benzene and standing, a white solid appeared which was collected and rinsed with benzene to give 3.91 g (28.8%) of **5** as white rods, nmr ($CDCl_3$) δ 5.32 (s, 2, OH), 5.38, 5.68 (2 d, 2 × 1, CHCH), 7.15 (m, 9, ArH).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.16; H, 4.99; N, 5.13.

The filtrate was evaporated and treated with 15 ml of a mixture of hexane and ethyl acetate (2:1). The product formed yielded, after washing with the above mixture, 3.51 g of **3** as rectangular plates, mp 118.5–120°. Repetition of the above procedure gave an additional 1.44 g of **3**, mp 117–120°, for a combined yield of 4.95 g (39.1%), nmr ($CDCl_3$) δ 3.72 (broad s, 1, OH), 7.60 (m, 9, ArH), 8.01 (s, 1, vinyl H_3).

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.08; H, 4.59; N, 5.69.

Evaporation of the above filtrate yielded an oil, which was extracted several times with 100-ml portions of boiling cyclohexane. The combined cyclohexane solutions were evaporated to a residue and barely dissolved in a small amount of methylene chloride. On addition of a mixture of hexane and ethyl acetate (2:1) and cooling, 390 mg (3.1%) of yellow, clustered prisms of **4** were collected, mp 121–124°, nmr ($CDCl_3$) δ 3.50 (broad s, 1, OH), 3.90 (s, 1, H_1), 7.57 (m, 9, ArH).

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.44; H, 4.50; N, 5.47.

2-Nitro-3-phenyl-1-hydroxyindene (4).—A mixture of 12 g (44.3 mmol) of **5** and 1 g of toluenesulfonic acid was refluxed for 1.5 hr. After evaporation, the obtained residue was recrystallized from methylene chloride–hexane to give a mixture of **3** and **4** as the first crop. Concentration of the mother liquor yielded 5.55 g of **4**. Recrystallization from methylene chloride–hexane afforded 4.84 g (43.2%) of yellow prisms, mp and mmp 121–123.5°.

2-Nitro-1,3-diphenylindene (6).[9]—A solution of 250 mg (0.92 mmol) of **5** in 12 ml of benzene was mixed with 0.6 ml of concentrated sulfuric acid and refluxed for 1.25 hr. The cold solution was extracted three times with 70-ml portions of water, dried over sodium sulfate, filtered, and evaporated. The residue was recrystallized from ether–petroleum ether (bp 30–60°) to give 210 mg (73%) of **6** as yellow prisms, mp 105–107°, nmr ($CDCl_3$) δ 5.36 (1, s, H_1), 7.1–7.6 (m, 14, ArH).

Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.56; H, 5.04; N, 4.43.

2-Nitro-1-phenyl-1-acetoxyindene (7).—A slurry of 40.5 g (160 mmol) of **3** in 100 ml of acetic anhydride was cooled to −5 to −10°, and then 1 ml of concentrated sulfuric acid was added to the vigorously stirred mixture. After 45 min, the temperature was allowed to rise to 0°. The yellow plates formed were collected and washed well with a mixture of hexane and ethyl acetate (2:1) to give 32.0 g (67.7%) of **7**, mp 140–144°. Recrystallization from benzene afforded the analytically pure material, mp 148–150°, nmr ($CDCl_3$) δ 2.17 (s, 3, CH_3), 6.3 (m, 9, ArH), 7.94 (s, 1, vinyl H_3).

Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.42; H, 4.36; N, 4.71.

2-Nitro-3-phenyl-1-acetoxyindene (8). A.—To a solution of 10 g (39.5 mmol) of **3** in 20 ml of acetic anhydride was added 0.1 ml of concentrated sulfuric acid at room temperature. The dark brown solution was stirred for 30 min and then evaporated. The residue was treated with ice and saturated sodium bicarbonate solution. The resulting precipitate was filtered, washed well with water, dissolved in methylene chloride, dried over anhydrous magnesium sulfate, filtered, and evaporated. Addition of ether afforded 8.3 g of **8**, mp 115–120°. Recrystallization from ethanol gave 6.2 g (53.2%) of dark yellow prisms, mp 128–131°, nmr ($CDCl_3$) δ 2.20 (s, 3, CH_3), 7.06 (s, 1, H_1), 7.5 (m, 9, ArH).

Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.10; H, 4.48; N, 4.64.

B.—To a solution of 200 mg (0.79 mmol) of **4** in 2 ml of acetic anhydride was added 1 drop of concentrated sulfuric acid at room temperature. After 20 min of stirring, the mixture was poured into ice and saturated sodium bicarbonate solution. The crystalline, orange precipitate, 210 mg, mp 119–123°, was recrystallized from methylene chloride–hexane to give 100 mg (42.9%) of **8**, mp and mmp 127–131°.

C.—A solution of 100 mg (0.34 mmol) of **7** in 3 ml of acetic acid was stirred overnight at room temperature. On dilution with ice and water, a reddish yellow crystalline solid (70 mg) was obtained, mp 120–126°, which on recrystallization from ethyl acetate and hexane gave **8**, mp and mmp 127–128.5°.

(6) T. Kametani, H. Sugakara, and S. Asagi, *Chem. Pharm. Bull.*, **14**, 1408 (1966); H. H. Baer and S. R. Naik, *J. Org. Chem.*, **35**, 2927 (1970).

(7) J. Thiele and E. Weitz, *Justus Liebigs Ann. Chem.*, **377**, 1 (1910); F. W. Lichtenthaler, *Tetrahedron Lett.*, 775 (1963); H. H. Baer and B. Achmatowicz, *J. Org. Chem.*, **29**, 3180 (1964).

(8) The stereochemistry of this compound has not been established.

(9) The formation of **6** was also observed from **3** and **4** under the same reaction conditions.

2-Nitro-1-phenyl-3-morpholinoindene (9a). A.—A solution of 8 g (27.1 mmol) of **7** in 60 ml of acetone was mixed with 4.7 g (54.5 mmol) of morpholine in 10 ml of acetone. After 45 min of stirring at room temperature, ice and water were added. The precipitate collected was recrystallized from methylene chloride–hexane to give 6.29 g (72.1%) of **9a** as deep yellow prisms, mp 205–206° dec, nmr ($CDCl_3$) δ 3.92 (m, 8, aliphatic H), 5.18 (s, 1, H_1) 7.22 (m, 8, ArH), 7.72 (m, 1, H_4).

Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.92; H, 5.75; N, 8.64.

B.—A mixture of 550 mg (1.62 mmol) of 2-nitro-3-morpholino-1-hydroxy-1-phenylindane (**10**) and 3 g of 85% phosphoric acid was heated on the steam bath for 10 min until a clear brown solution was present. After dilution with water, insoluble solids were filtered off. The filtrate was made basic with concentrated sodium hydroxide solution and then extracted with 75 ml of chloroform. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness to give on addition of methanol 180 mg of yellow prisms, mp and mmp 208–210°. The above insoluble solid was dissolved in chloroform and washed with dilute sodium hydroxide solution. The organic layer was worked up as above to give 100 mg of crude material, mp and mmp 199–205°. A total of 280 mg (53.6%) of **9a** was obtained.

2-Nitro-1-phenyl-3-benzylaminoindene (9b).—This compound was prepared using the same procedure as described for **9a**, method A, in 91% yield as yellow prisms from methylene chloride–ethanol, mp 180–181°, nmr ($CDCl_3$) δ 5.10 (s, 2, CH_2), 5.20 (s, 1, H_1), 7.22, 7.40 (m, 13, ArH), 7.85 (m, 1, H_4), 10.28 (broad s, 1, NH).

Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.18; H, 5.30; N, 8.18. Found: C, 76.88; H, 5.24; N, 8.16.

2-Nitro-3-morpholino-1-hydroxy-1-phenylindan (10).—To a solution of 2.53 g (1 mmol) of **3** in 15 ml of tetrahydrofuran was added a small excess of morpholine in 5 ml of tetrahydrofuran. After 30 min of stirring at room temperature, the mixture was concentrated to *ca.* 1/3rd of the volume and diluted with 25 ml of ether. The product formed was collected to give 2.58 g (76%) of white prisms, mp 172° dec. Recrystallization of a sample from tetrahydrofuran–chloroform afforded the analytically pure product, mp 171–172° dec, nmr (DMSO) δ 2.52, 3.63 (m, 2 × 4, aliphatic H), 5.47 (s, 2, CHCH), 6.56 (s, 1, OH), 7.37 (m, 9, ArH).

Anal. Calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 67.28; H, 5.96; N, 8.23.

Morpholinium 1-Phenyl-3-indanone-2-nitronate (11a). A.—A solution of 20 g (67.8 mmol) of **8** in 150 ml of methylene chloride was added dropwise to a solution of 12 g (138 mmol) of morpholine in 80 ml of methylene chloride. The thick white precipitate which formed was collected after 40 min and washed well with methylene chloride. The filtrate was set aside. The salt obtained (18.7 g) was recrystallized from hot dimethylformamide to give 12.9 g (56%) of **11a** as white needles: mp 204° dec; ir (KBr) 2800–2480 cm^{-1} (amine salt); nmr (DMSO) δ 3.17, 3.83 (m, 2 × 4, aliphatic H), 4.96 (s, 1, H_1), 6.9–7.66 (m, 9, ArH).

Anal. Calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.94; H, 6.00; N, 8.22.

The above filtrate was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was recrystallized from methylene chloride–carbon tetrachloride to give 2.0 g (9%) of **9a** as deep yellow prisms, mp and mmp 208–210° dec.

B.—A solution of 590 mg (2 mmol) of 2-nitro-1-phenyl-3-acetoxyindene (**16**) in a 5 ml of methylene chloride was added dropwise to a solution of 348 mg (4 mmol) of morpholine in 2 ml of methylene chloride. After 10 min, the precipitate was collected to give 622 mg (91.5%) of **11a** as white needles, mp and mmp 196–199° dec.

The methylene chloride filtrate was washed with water and dried over anhydrous sodium sulfate. Tlc of this solution, compared with **9a** using hexane–ethyl acetate (1:1) as eluent showed no trace of **9a**.

C.—To a solution of 100 mg (0.39 mmol) of **4** in a minimum amount of tetrahydrofuran was added 86 mg of morpholine. After the solution had stood for 30 min, the white precipitate formed was filtered off and washed well with ether to give 135 mg (100%) of **11a**, mp and mmp 198–199° dec.

Benzylammonium 1-Phenyl-3-indanone-2-nitronate (11b).—Following procedure A for **11a** this compound was prepared similarly in 52.4% yield as pale yellow needles recrystallized from hot dimethylformamide: mp 200–203° dec; ir (KBr) 2800–2480 cm^{-1} (amine salt); nmr (DMSO) δ 4.10 (s, 2, CH_2), 4.98 (s, 1, H_1), 7.17, 7.38 (m, 14, Ar H), 8.62 (broad s, 3, NH_3).

Anal. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.32; H, 5.61; N, 7.82.

A by-product, **9b**, was obtained in 22.4% yield as yellow needles, mp and mmp 180–183° dec.

2-Nitro-1-phenyl-3-acetoxyindene (16).—To a solution of 2.95 g (10 mmol) of **8** in 10 ml of anhydrous methylene chloride was added 0.05 ml of triethylamine. The solvent was evaporated after 10 min. The residue was treated with ether and petroleum ether to give 2.44 g of a light tan solid. Recrystallization from methylene chloride–ether–petroleum ether afforded 1.35 g (45.8%) of **16** as colorless needles, mp 96–98° dec, nmr ($CDCl_3$) δ 2.37 (s, 3, CH_3), 5.23 (s, 1, H_1), 7.2–7.75 (m, 8, ArH), 7.95 (m, 1, H_4).

Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.34; H, 4.51; N, 5.04.

2-Nitro-1-phenyl-3-indanone (12). A.—A slurry of 500 mg (1.47 mmol) of **11a** in 30 ml of ethanol and 50 ml of 2 *N* hydrochloric acid was warmed on the steam bath for 5 min. The organic solvent was evaporated and the aqueous residue was extracted with methylene chloride. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated. The residue obtained was recrystallized from ether–petroleum ether to give 270 mg (73%) of white rods: mp 93–96°; ir (KBr) 1745 cm^{-1} (CO); nmr ($CDCl_3$) δ 5.26, 5.40 (AB, J = 5 Hz, 2, CHCH), 7.0–8.0 (m, 9, Ar H).

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.15; H, 4.36; N, 5.53.

B.—A solution of 250 mg (0.77 mmol) of **9a** in 50 ml of ethanol was treated with 100 ml of 2 *N* hydrochloric acid on the steam bath until the solution was completely discolored. The reaction was worked up as above to give 85 mg (44%) of crystalline material, mp and mmp 89–93°.

2-Nitro-1-indanone (14).—To a slurry of 3.54 g (20 mmol) of 2-nitro-1-hydroxyindene (**13**) in 13 ml of tetrahydrofuran was added 2.02 g (20 mmol) of triethylamine in 2 ml of tetrahydrofuran. After 4 min, 45 ml of water was added to the green solution and the pH was adjusted to 6 with 2 *N* aqueous hydrochloric acid. This solution was extracted three times with 30 ml of ether. The ethereal layers were discarded. The aqueous layer was cooled in an ice bath and acidified with 2 *N* hydrochloric acid to pH 2.5. A crystalline precipitate appeared and was collected to give 2.25 g, mp 70–75°. The solid was extracted into 1 l. of boiling petroleum ether (bp 60–90°), which was decanted from insoluble material and evaporated. Recrystallization of the residue from isopropyl alcohol–petroleum ether gave 1.05 g (30%) of pale yellow rods, mp 77–80°. A second crop of 300 mg, mp 75–77°, was obtained from the filtrates, nmr ($CDCl_3$) δ 3.78 (m, 2, CH_2), 5.48 (q, 1, H_2), 7.15–7.90 (m, 4, ArH).

Anal. Calcd for $C_9H_7NO_3$: C, 61.01; H, 3.98; N, 7.91. Found: C, 61.05; H, 4.03; N, 7.82.

2-Nitro-3-phenyl-1-ethoxyindene (17a). A.—A solution of 5.9 g (20 mmol) of **7** in 100 ml of ethanol was refluxed for 2 hr and then evaporated. The residue was taken up in 70 ml of ether and washed three times with 100-ml portions of water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated. The product crystallized on addition of ether and petroleum ether. After two recrystallizations from ethanol, 2.6 g (46%) of **17a** was obtained as yellow, clustered needles, mp 81.5–83°. From the filtrates, an additional 830 mg of less pure material, mp 79–81.5°, was isolated, nmr ($CDCl_3$) δ 1.25 (t, 3, CH_3), 3.75 (q, 2, CH_2O), 5.82 (s, 1, H_1), 7.58 (m, 9, ArH).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.82; H, 5.48; N, 4.92.

2-Nitro-3-phenyl-1-methoxyindene (17b).—A solution of 10.6 g (36 mmol) of **7** in 150 ml of methanol was refluxed for 1.5 hr. On concentration and cooling, 7.88 g (82%) of **17b** was collected as yellow rods, mp 113–114°. A second crop (630 mg) of less pure material, mp 112–113°, was obtained from the mother liquor. Recrystallization of a sample from methanol afforded an analytically pure product, mp 113–114.5°, nmr ($CDCl_3$) δ 3.41 (s, 3, CH_3O), 5.74 (s, 1, H_1), 7.49 (m, 9, ArH).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.77; H, 5.01; N, 5.17.

2-Nitro-1-phenyl-3-ethoxyindene (18a). A.—A solution of

295 mg (1 mmol) of **7** in 30 ml of ethanol was refluxed for 23 hr. Evaporation of the solvent and crystallization of the residue from an ether–ethanol mixture gave 154 mg of a crude mixture of **17a** and **18a** (by nmr). Several recrystallizations from ethanol finally afforded a pure sample (29 mg, 10.3%) of **18a** as yellow prisms, mp 88.5–90.5°, nmr ($CDCl_3$) δ 1.52 (t, 3, CH_3), 4.76 (AB of q, 2, CH_2O), 5.18 (s, 1, H_1), 7.29 (m, 8, ArH), 7.73 (m, 1, H_4).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.49; H, 5.38; N, 5.01.

B.—To a solution of 50 mg (0.18 mmol) of **17a** in 5 ml of methylene chloride was added 1 drop of triethylamine. The solvent was evaporated after 5 min and the crystalline residue was treated with ether and petroleum ether to give 35 mg (70%) of **18a** as yellow prisms, mp and mmp 88–90°.

2-Nitro-1-phenyl-3-methoxyindene (18b). A.—**18b** was similarly prepared (see **18a**, procedure A) in 3.8% yield as yellow prisms, mp and mmp 99–102°, after several recrystallizations from ethanol.

B.—A solution of 5 g (19.75 mmol) of **12** in 100 ml of ether was treated with an excess of ethereal diazomethane solution until no more starting material was present as determined by tlc. Evaporation of the solvent gave an off-white, crystalline solid which on recrystallization from ethyl acetate–ether gave 0.85 g of pale yellow prisms, mp 121–122°, which were identified as 1-phenyl-2-methoxyimino-3-indanone *N*-oxide (**19**), ir ($CHCl_3$) 1700 cm^{-1} (CO), nmr ($CDCl_3$) δ 3.88 (s, 3, CH_3O), 5.07 (s, 1, H_1), 7.0–7.65 (m, 8, ArH), 7.90 (m, 1, H_4).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90: H, 4.90; N, 5.24. Found: C, 72.03; H, 5.11; N, 5.25.

The residual mother liquors and filtrates were combined and evaporated and the residue was chromatographed on 400 g of silica gel using hexane–ethyl acetate (2:1) as the eluent. Removal of solvent from the first fractions, gave an additional 390 mg of **19**, for a combined yield of 1.24 g (23.5%), mp and mmp 121–122°. Later fractions gave, after removal of the solvent, 2.2 g (42%) of **18b** as yellow prisms (crystallized from ethyl acetate–ether), mp 91.5–93°, reset mp 101–102°, nmr ($CDCl_3$) δ 4.37 (s, 3, CH_3O), 5.10 (s, 1, H_1), 6.9–7.45 (m, 8, ArH), 7.70 (m, 1, H_4).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.95; H, 4.94; N, 5.28.

Registry No.—**2**, 34764-52-8; **3**, 34764-53-9; **4**, 34764-54-0; **5**, 34764-55-1; **6**, 34764-56-2; **7**, 34764-57-3; **8**, 34789-54-3; **9a**, 34764-58-4; **9b**, 34764-59-5; **10**, 34764-60-8; **11a**, 34764-61-9; **11b**, 34764-62-0; **12**, 34764-63-1; **14**, 13943-70-9; **16**, 34764-65-3; **17a**, 34764-66-4; **17b**, 34764-67-5; **18a**, 34764-68-6; **18b**, 34764-69-7; **19**, 34764-70-0.

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Thermodynamic and Kinetic Analysis of Meisenheimer Complex Formation

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The free-energy change for the reaction of sodium methoxide with 2,4,6-trinitroanisole (**3**) to give the Meisenheimer complex **2** has been measured and combined with the heat of this reaction to give the entropy change in DMSO–methanol mixtures. Using solubility measurements, the activity coefficients of **3** and the complex **2** have been determined. The free energy, enthalpy, and entropy of transfer of **3** and its complex **2** from pure methanol to methanolic dimethyl sulfoxide solutions have been calculated. The solvent effect on the thermodynamics of the reaction between sodium methoxide and **3** has been measured. The degenerate activity coefficients of sodium methoxide in methanol–DMSO mixtures have been obtained using an indirect method.

The chemistry of Meisenheimer or σ complexes, most of which are substituted cyclohexadienylide ions, has recently come under renewed scrutiny[2] and this research area has been quite active. Dipolar aprotic solvents have been found to enhance the stability of Meisenheimer complexes.[3-8] Indeed, this behavior has made possible the isolation of crystalline sodium and potassium cyclohexadienylides.[3-7] We have demonstrated recently that the increase in the equilibrium constant for the formation of sodium 1,1-dimethoxy-2,4-dicyano-6-nitrocyclohexadienylide (**1**) (eq 1) with increasing DMSO concentration in the DMSO–MeOH solvent system is due to an increase in the rate constant for complex formation (k_1) and a decrease in the rate constant for the decomposition of the complex (k_2).[6] These results have been rationalized using the differences in the hydrogen-bonding power of these solvents. Methoxide ions, being strong hydrogen bond acceptors, become considerably less solvated and, therefore, stronger nucleophiles in dipolar aprotic DMSO than in protic methanol[8,9] Since the 2,4,6-trinitroanisole is not effected strongly by this solvent change, k_1 increases with increasing DMSO concentration. The decrease in the rate constant for the decomposition of the complex (k_2) with increasing DMSO concentration is probably caused by the greater solvation of the highly delocalized negative charge of the complex in

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