Rearrangements and Ring Expansions during the Deoxygenation of β,β-Disubstituted *o*-Nitrostyrenes[1]

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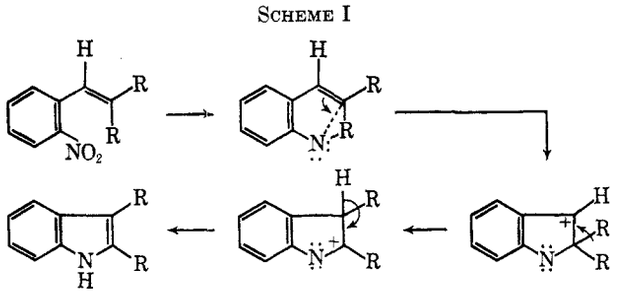
The deoxygenation of four representative β,β-disubstituted *o*-nitrostyrenes by triethyl phosphite has been investigated. Each nitrostyrene gave a rearranged indole as a product. In the case of α-methyl-2′-nitrostilbene, where phenyl migration is possible, high yields of rearranged products were isolated. In the other cases examined, competing reactions leading to 2,2-disubstituted 3-indolinones and biindolines occur.

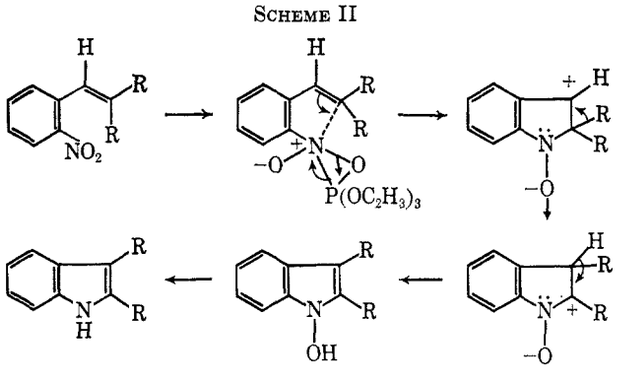
Heating aromatic nitro compounds with triethyl phosphite results in the deoxygenation of the nitro group and the formation of triethyl phosphate.[2,3] When the nitro compound carries a saturated *ortho* substituent the subsequent transformations of the deoxygenated fragment strongly suggest that the intermediate is an aryl nitrene.[3,4] The deoxygenation of aromatic nitro compounds containing adjacent unsaturated side chains usually leads to the formation of heterocyclic nitrogen compounds.[2,5,6] For example, deoxygenation of *trans*-1-(*o*-nitrophenyl)propene gives 2-methylindole,[5] whereas reduction of the same nitrostyrene with iron–acetic acid gives *trans*-*o*-propenylaniline as the main product.[3] Cadogan and coworkers[2,6] have demonstrated that the deoxygenation reaction is adaptable to the synthesis of a wide variety of heterocyclic compounds of nitrogen. The successful cyclizations reported to date involve substrates which can give fully conjugated cyclic products by loss of a proton after cyclization.[2,5,6] The formation of these heterocyclic products can be rationalized in terms of a nitrene intermediate, but there is evidence, at least in the case of the conversion of *o*-nitrostilbene into 2-phenylindole,[5] that some ring closure occurs prior to total deoxygenation of the nitro group. We report here on the deoxygenation by triethyl phosphite of four β,β-disubstituted *o*-nitrostyrenes. This study was carried out to extend the scope of this reductive cyclization and in the hope of providing additional insight into the mechanism of the reaction.

Either a nitrene mechanism (Scheme I) or a process analogous to that proposed for the deoxygenation of *o*-nitrostilbene[5] (Scheme II) suggests that a β,β-disubstituted *o*-nitrostyrene might give rise to rearranged deoxygenation products.

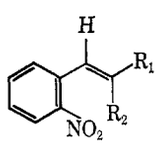
SCHEME I



SCHEME II



Compounds **1–4** were chosen for study. Nitrostyrenes **1–3** are new compounds. Each was synthesized from diethyl *o*-nitrobenzylphosphonate and the appropriate ketone, using the phosphonate modification of the Wittig reaction.[5,7,8] α-Methyl-2′-nitrostilbene



1, R_1, R_2 = $(CH_2)_5$
2, R_1, R_2 = $(CH_2)_4$
3, R_1 = R_2 = CH_3
4, R_1 = C_6H_5; R_2 = CH_3

(**4**) was prepared by a known procedure.[9] The structures of **1–3** were confirmed by analytical data and by nmr and infrared spectral data (see the Experimental Section for details).

Each of the nitrostyrenes gave the expected rearranged indole as a product when subjected to deoxygenation in triethyl phosphite. Yields varied for the different nitrostyrenes, as did the nature of accompanying by-products. Each deoxygenation is therefore considered in turn below.

The deoxygenation of **1** was effected by refluxing a solution of the nitrostyrene in excess triethyl phosphite for 6 hr. Chromatography of the crude product gave 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5**) in 35% yield in a typical run.

The product was identified by melting point and the identity of the infrared spectrum with that of an authentic sample. Two other products were isolated by chromatography. One was a high-melting, white solid, $C_{26}H_{32}N_2$ (elemental analysis, molecular weight), which

(1) Abstracted in part from the M.S. thesis of T. Y., July 1966.
(2) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965).
(3) R. J. Sundberg, *J. Am. Chem. Soc.*, **88**, 3781 (1966).
(4) G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **31**, 3882 (1966).
(5) R. J. Sundberg, *ibid.*, **30**, 3604 (1965).
(6) J. I. G. Cadogan, R. K. Mackie, and M. J. Todd, *Chem. Commun.*, 491 (1966).
(7) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).
(8) D. H. Wadsworth, O. E. Schupp, III, E. J. Seus, and J. A. Ford, Jr., *J. Org. Chem.*, **30**, 680 (1965).
(9) A. V. Dombrovskii, Ya. G. Bal'on, and K. G. Tashchuk, *J. Gen. Chem. USSR* (Engl. Transl.), **32**, 592 (1962).

had ultraviolet absorption characteristic of an indoline. The yield in a typical run was 24%. The infrared spectrum shows an absorption at 3350 cm^{-1}, and there is a signal at δ 4.0 in the nmr spectrum which is readily exchanged by deuterium oxide. These features suggest the presence of an N–H group. The nmr spectrum also shows signals expected for an aromatic ring and a cyclohexane ring. The only other signal in the nmr spectrum is a sharp singlet at δ 3.13 which is unaffected by deuterium oxide. On the basis of these data the high-melting solid must be 3′,3‴-bispiro-[cyclohexane-1,2′-indoline] (**6**). The third identifiable product of the deoxygenation of **1** was a yellow solid ($C_{13}H_{15}NO$, 8% yield) which showed both NH and C=O (1680 cm^{-1}) absorption in the infrared spectrum. The ultraviolet spectrum corresponds to that of a known 2,2-disubstituted 3-indolinone[10] (see Table I),

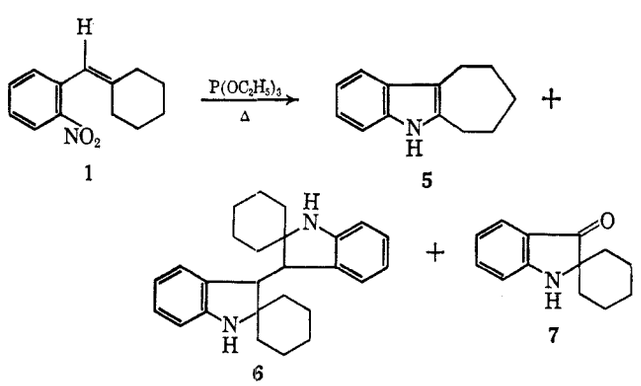
TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	λ_{max}, mμ (log ε), in ethanol		
Spiro[cyclohexane-1,2′-indolin-3′-one] (**7**)	230 (4.34)	252 (3.79)	391 (3.58)
Spiro[cyclopentane-1,2′-indolin-3′-one][a]	231 (4.3)	258 (3.7)	398 (3.6)
2,2-Dimethyl-3-indolinone (**10**)	230 (4.33)	253 (3.79)	391 (3.60)

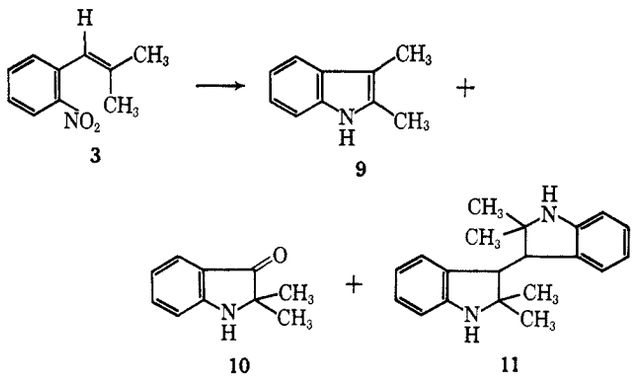
[a] Reference 10.

and on this basis the yellow compound was identified as spiro[cyclohexane-1,2′-indolin-3′-one] (**7**). To further confirm this structural assignment **7** was reduced with sodium borohydride. The spectral properties (see the Experimental Section) of the resulting alcohol, spiro[cyclohexane-1,2′-indolin-3′-ol], fully support the structural assignment.

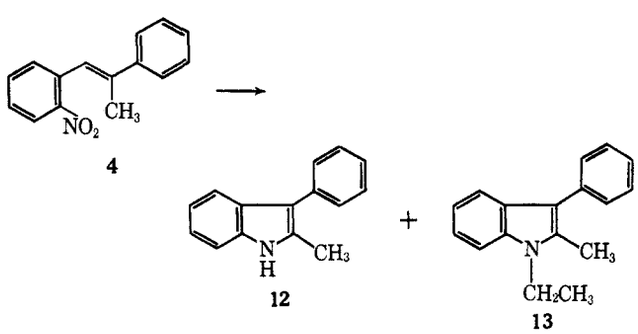


Cyclopentylidene(*o*-nitrophenyl)methane (**2**) gave a mixture of products on deoxygenation also, but less success in resolving the mixture was achieved than in the case of **1**. The only product obtained in pure form was 1,2,3,4-tetrahydrocarbazole (**8**), the expected rearranged indole. This product was isolated 15% yield and identified by infrared spectral comparison with an authentic sample. A particular effort was made to find the indolinone corresponding to **7**, since this compound has been reported in the literature,[10] but none was isolated.

Deoxygenation of β,β-dimethyl-*o*-nitrostyrene (**3**) gave a modest yield (~33%) of the rearranged product 2,3-dimethylindole (**9**) which was identified by spectral comparison with an authetic sample. In addition 2,2-dimethyl-3-indolinone (**10**) was isolated in 11% yield. The indolinone was identified on the basis of its nmr and infrared spectra and by the ultraviolet spectrum which is very similar to that of **7**. A dimeric indoline (**11**) analogous to **6** was also isolated in very low yield. The structural assignment rests on analytical and infrared spectral data. Thin layer chromatography of the crude reaction mixture suggests that the yield of this product may be substantially higher than the isolated yield.



α-Methyl-2′-nitrostilbene (**4**) underwent deoxygenation with rearrangement in high yield. Chromatography of the product gave 1-ethyl-2-methyl-3-phenylindole (**13**, 21%), and 2-methyl-3-phenylindole (**12**, 77%). The 1-ethyl derivative is presumed to have arisen from **12** by alkylation with triethyl phosphate.[11] Compound **13** was isolated as a liquid and identified by spectral comparison with a sample prepared by alkylation of **12** with ethyl iodide and sodium amide in liquid ammonia. The high yield of 3-phenyl-substituted indoles demonstrates that phenyl migration has greatly predominated over methyl migration. This is the expected course for migration to a cationic center,[12] but the preference for phenyl migration may also be determined by the stereochemical configuration of the nitrostilbene. The fact that the deoxygenation of **4** leads to a substantially higher proportion of migration than does the deoxygenation of **1**, **2**, and **3** indicates that the effectiveness of the phenyl group as a migrating group favors the reaction path which involves rearrangement. In the case of **1**, **2**, and **3**, where only alkyl groups are available for migration, other reaction paths compete more successfully with the rearrangement–aromatization that is the predominant reaction path for the deoxygenation of **4**.



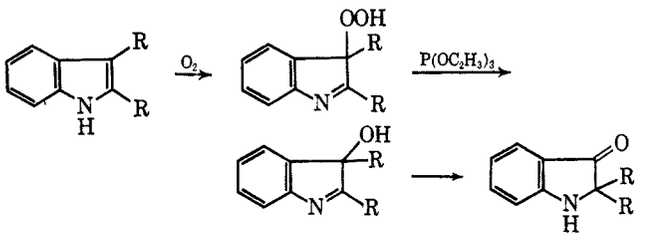
(10) B. Witkop, *J. Am. Chem. Soc.*, **72**, 614 (1950).

(11) See ref 2, 5, and 6 for earlier examples of alkylation as a secondary reaction during similar deoxygenations.

(12) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960).

The indolines **7** and **10** were unexpected products, and their origin is of interest. The possibility that they are oxidative products derived from the indoles **5** and **9** has been considered. Several facts argue against this possibility. The decomposition products of 2,3-dimethyl-3H-indol-3-yl hydroperoxide would be the expected autoxidation products of 2,3-dimethylindole These are known to be 3-methylindole-2-carboxaldehyde[13] and *o*-acetaminoacetophenone[14] and not the indolinone **10** found in this work. Similarly the autoxidation of cyclooct[*b*]indole leads to a 2-acylindole, 8,-9,10,11-tetrahydro-5H-cyclooct[*b*]indol-6(7H)-one and not to an indolinone.[15] Another route which might explain the formation of **7** and **10** is shown in Scheme III.

SCHEME III



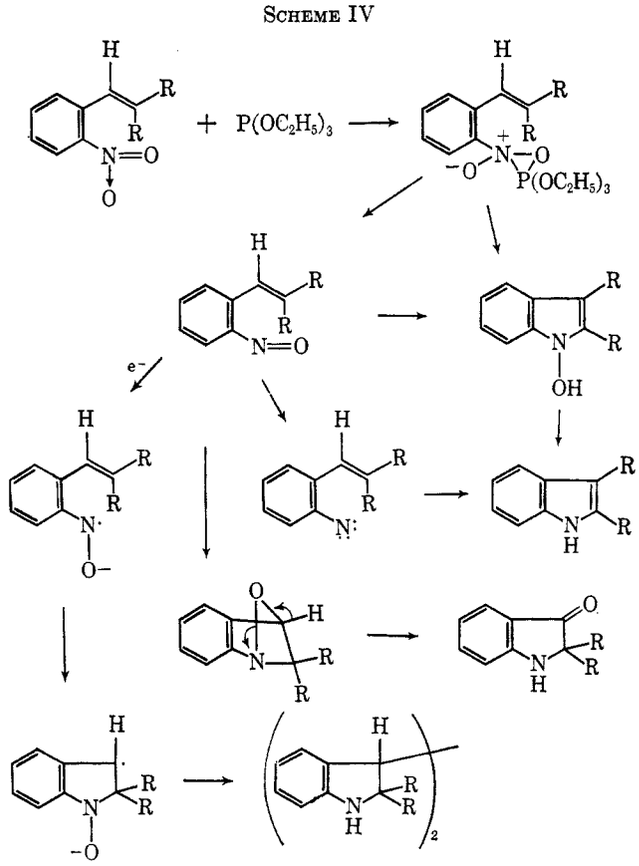
Hydroperoxides are known to be reduced to alcohols by triethyl phosphite.[16] If a hydroperoxide were formed in the presence of triethyl phosphite a 3H-indol-3-ol would presumably result. There are several examples in the literature of rearrangement of 3H-indol-3-ols to 3-indolinones.[17] In order to investigate this possibility, a stream of air was passed through an ether solution of **5** and triethyl phosphite for 24 hr. The only product which could be isolated was unchanged indole **5** (>99% recovery). No **7** was detected. The reaction sequence depicted in Scheme III, therefore, cannot account for the formation of the indolinones **7** and **10**. We conclude that **7** and **10** are authentic products of the deoxygenation reaction. This conclusion is supported by the observation of the characteristic yellow spot of **10** in a thin layer chromatogram of the crude deoxygenation product prior to chromatography. The over-all pattern of the conversion of **1** to **7** and **3** to **10** is reminiscent of several reactions which result in the cyclization of *ortho*-substituted nitroaromatics accompanied by transfer of an oxygen atom to the adjacent substituent,[18] and the present transformation may be mechanistically related. The reaction sequence leading to **7** and **10** must be initiated by deoxygenation, since nitrostyrene has been shown to be stable at 160° in the absence of triethyl phosphite.

(13) W. I. Taylor, *Proc. Chem. Soc.*, 247 (1962).
(14) E. Leete, *J. Am. Chem. Soc.*, **83**, 3645 (1961).
(15) B. Witkop, J. B. Patrick. and M. Rosenblum, *ibid.*, **73**, 2641 (1951).
(16) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).
(17) For example (a) ref 10; (b) R. J. S. Beer, T. Donavanik, and A. Robertson, *J. Chem. Soc.*, 4139 (1954); (c) C. Niemann and J. W. Kessel, *J. Org. Chem.*, **31**, 2265 (1966); (d) D. F. Dickel, C. L. Holden, R. C. Maxfield, L. E. Paszek, and W. I. Taylor, *J. Am. Chem. Soc.*, **80**, 123 (1958).
(18) For example: photochemical conversion of substituted *o*-nitrostilbenes into 2-arylisatogens [J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955)]; photochemical conversion of *o*-nitrocinnamic acid into 3-hydroxy-3H-indole-2-carboxylic acid 1-oxide [I. Tanasesca, *Bull. Soc. Chim. France*, [4] **41**, 1074 (1927)]; thermal or photochemical conversion of *o*-nitrotolane into 2-phenylisatogen [P. Pfeiffer, *Ann. Chem.*, **411**, 72 (1916)]; thermal conversion, under basic conditions, of pyridinium salts derived from *o*-nitrostilbene into 2-phenylisatogen [F. Krökhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951)].

Reference to Schemes I and II shows that the "nitrene" and "N-hydroxyindole" mechanisms involve alternative timing of the deoxygenation and rearrangement steps. As written, Scheme II suggests that rearranged N-hydroxyindoles would be intermediates in these deoxygenations. The deoxygenation of **4** was therefore interrupted at 0.5, 1.0, and 2.0 hr in an attempt to isolate 1-hydroxy-2-methyl-3-phenylindole by a procedure similar to that used to isolate 1-hydroxy-2-phenylindole during the deoxygenation of *o*-nitrostilbene,[5] but none was found. The products observed in the interrupted deoxygenations were unreacted **4** and the totally deoxygenated and rearranged indoles **12** and **13**. This result permits no distinction between the mechanisms depicted in Schemes I and II. No N-hydroxyindole intermediate may be involved (Scheme I) or the relative rates of deoxygenation of the nitro compound and the hydroxyindole may be such that no detectable concentration of hydroxyindole can form (Scheme II).

In summary, this work further attests to the strong tendency toward cyclization that is exhibited by deoxygenation reactions in triethyl phosphite. The rearranged products are best accounted for by a mechanism which involves cyclization by electrophilic attack at the double bond followed or accompanied by a 1,2 shift of a substituent from the 2 carbon of the indole ring system. At present only tentative suggestions as to the mechanism of formation of the indolinones and biindolines are possible. In Scheme IV we present a

SCHEME IV



rationale for the formation of the various products involving the corresponding nitroso compounds as important intermediates.

As discussed earlier, at least two routes to rearranged indoles are possible. The intramolecular cycloaddition leading to the hypothetical benzo[*b*]-5,1-oxazabicyclo-[2.1.1]hexane system in Scheme IV has analogy in a similar cycloaddition to a C=N double bond invoked by Taylor, Furth, and Pfau to explain the formation of 6-cyanophenanthridine from *o*-(cyanoanilinomethyl)-*o'*-nitrobiphenyl on irradiation or treatment with base.[19] The isolation of the dimeric indolines **6** and **11** from deoxygenation of **1** and **3** suggests that free-radical reaction paths may be competitive with the ionic reaction leading to the rearrangement.[20] Aromatic nitroso compounds are known to act as electron acceptors to give radical anions.[21] The N-hydroxyindole intermediates which are, in a sense, substituted hydroxylamines, are reasonable candidates for the role of electron donor,[21] if indeed they are formed. Experiments designed to test validity of the ideas envisaged in Scheme IV are planned.

Experimental Section[22]

Cyclohexylidene(*o*-nitrophenyl)methane (1).—A mixture of *o*-nitrobenzyl bromide[23] (21.6 g, 0.100 mole) and triethyl phosphite (16.6 g, 0.100 mole) was heated at 90 ± 2° for 1 hr under nitrogen. The resulting solution was then evacuated for several hours at room temperature using a rotary evaporator and a water aspirator. To the residue there was carefully added, with cooling, a suspension of sodium methoxide (6.7 g, 0.12 mole) in dry dimethylformamide (30 ml). Cyclohexanone (9.8 g, 0.10) was added to the purple reaction mixture, and the resulting solution was stirred at 0° for 1 hr and then at room temperature for 90 min. The color of the solution turned to brown during this period. Water (250 ml) was added, and the resulting mixture was extracted with five 100-ml portions of hexane. The extract was dried over magnesium sulfate and concentrated. Distillation of the residue gave **1**: 14.4 g; 0.066 mole; 66%; bp 97–98° (0.07 mm); ν_{NO_2} 1525, 1350 cm^{-1}; nmr peaks (CCl_4) at δ 1.6 (multiplet, 5.4 H), 2.2 (multiplet, 4.6 H), 6.4 (singlet, 1 H), and 7.1–8.1 (multiplet, 4.6 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96. Found: C, 71.95; H, 7.02.

Cyclopentylidene(*o*-nitrophenyl)methane (2).—A procedure similar to that described above gave **2** in 37% yield from cyclopentanone: bp 105–110° (0.26 mm); ν_{NO_2} 1520, 1350 cm^{-1}; nmr peaks (CCl_4) at δ 1.6–1.9 (multiplet, 4 H), 2.2–2.8 (multiplet, 4 H), 6.60 (apparent triplet, J = 2.5 cps, 1 H), and 7.1–8.0 (multiplet, 4 H).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45. Found: C, 70.82; H, 6.45.

β,β-Dimethyl-*o*-nitrostyrene (3).—A procedure similar to that described above gave **3** in 45% yield from acetone: bp 115–117° (3 mm); ν_{NO_2} 1525, 1350 cm^{-1}; nmr peaks (CCl_4) at δ 1.7 (singlet, 3 H), 1.9 (singlet, 3 H), 6.45 (broad singlet, 1 H), and 7.1–8.0 (multiplet, 4 H).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.76; H, 6.27. Found: C, 67.59; H, 6.49.

***trans*-α-Methyl-2'-nitrostilbene (4).**—The compound was prepared by the method of Dombrovskii:[9] mp 70–71° (lit.[9] mp 70–71°).

Thermal Stability of β,β-Dimethyl-*o*-nitrostyrene.—A solution of **3** (1.15 g, 6.5 mmoles) in triethyl phosphate (7.1 g, 39 mmoles) was maintained at 163–165° for 6 hr. The triethyl phosphate was distilled, bp 45° (0.35 mm), and the residue was dissolved in ether, washed with water, dried, and concentrated. Analysis by thin layer chromatography and infrared spectroscopy showed the residue to be unchanged **3**.

Deoxygenation of Cyclohexylidene(*o*-nitrophenyl)methane (1).—A solution of **1** (8.45 g, 38.9 mmoles) in triethyl phosphite (38.8 g, 234 mmoles) was kept at 163 ± 2° for 6 hr in an electrically heated oil bath (nitrogen atmosphere). The reaction mixture was then cooled, and the triethyl phosphite and most of the triethyl phosphate [bp 54–56° (0.6–0.8 mm)] were removed by distillation. The residue was dissolved in ether and washed twice with water. The ether solution was dried over magnesium sulfate and concentrated on a rotary evaporator. The residue was dissolved in benzene and chromatographed. Benzene–hexane (1:1) eluted 5,6,7,8,9,10-hexahydrocyclohept[*b*]indole (**5**, 2.56 g, 13.9 mmoles, 35%), mp 146–147° (lit. mp 142–144°,[24] 144–145°[25]). The infrared spectrum was identical with that of an authentic sample prepared from cycloheptanone by the method of Rogers and Corson.[26]

Benzene–hexane (7:3) eluted 3',3''-bispiro[cyclohexane-1,2'-indoline] (**6**): 1.72 g; 4.6 mmoles; 24%; mp 246°; ν_{NH} 3350 cm^{-1}; λ_{max} (ethanol) 244 mμ (log ε 4.15), 295 mμ (log ε 3.68); mol wt 352 (by osmometry), calcd 372; nmr peaks at δ 1.7 (very broad singlet, 20 H), 3.1 (singlet, 2 H), 4.0 (broad singlet, 2 H, exchanged by D_2O), and 6.3–7.4 (multiplet, 8 H).

Anal. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.86. Found: C, 83.60; H, 8.69.

Benzene–ether (19:1) eluted spiro[cyclohexane 1,2'-indolin-3'-one] (**7**): mp 136°; ν_{NH} 3320 cm^{-1}; $\nu_{C=O}$ 1680 cm^{-1}; $\lambda\lambda_{max}$ (ethanol) 230 mμ (log ε 4.34), 252 (3.79), and 391 (3.58); nmr peaks at δ 1.2–2.2 (very broad singlet, 10 H) 5.3 (broad singlet, 1 H, exchanged by D_2O), and 6.4–7.8 (multiplet 4 H).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.59; H, 7.51; N, 6.97. Found: C, 77.62; H, 7.41; N, 7.33.

Spiro[cyclohexane-1,2'-indolin-3'-ol].—Compound **7** (96 mg, 0.48 mmole) was dissolved in methanol (5 ml) and treated with excess sodium borohydride. The reaction mixture was refluxed for 3.5 hr and then diluted with water (100 ml). The product was extracted with ether and recrystallized from benzene, giving the product as white needles: 53 mg; 0.26 mmole; 54%; mp 138–140°; $\nu_{NH,OH}$ 3200 cm^{-1}; $\lambda\lambda_{max}$ (ethanol) 247, 299 mμ; nmr peaks at δ 1.5 (broad singlet, 10 H), 2.8 (broad singlet, 2 H, exchanged by D_2O), 4.66 (sharp singlet, 1 H), and 6.5–7.4 (multiplet, 4 H).

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.97; H, 8.35.

Deoxygenation of Cyclopentylidene(*o*-nitrophenyl)methane (2).—The deoxygenation of **2** (2.0 g, 10 mmoles) in triethyl phosphite (16.4 g, 100 mmoles) was carried out as described for **1**. Benzene–hexane (1:1) eluted 1,2,3,4-tetrahydrocarbazole (259 mg, 1.51 mmoles, 15%), mp 120° (lit. mp 120–121°,[27] 118–119°[28]). The infrared spectrum was identical with that of an authentic sample of 1,2,3,4-tetrahydrocarbazole.[29] No other pure products were obtained.

Deoxygenation of β,β-Dimethyl-*o*-nitrostyrene (3).—A solution of **3** (3.8 g, 22 mmoles) in triethyl phosphite (21.6 g, 130 mmoles) was maintained at 163 ± 2° for 6 hr. The triethyl phosphite and triethyl phosphate were distilled off at reduced pressure. The residue was dissolved in ether and washed with water. The ether was dried and evaporated, and the residue was chromatographed on Florisil. Benzene–hexane (1:4) eluted 2,3-dimethylindole (1.15 g, >90% pure, 7.1 mmoles, ~32% yield) contaminated (tlc) by a small amount of a less polar oil (probably 1-ethyl-2,3-

(19) E. C. Taylor, B. Furth, and M. Pfau, *J. Am. Chem. Soc.*, **87**, 1400 (1965).

(20) A referee has suggested that the dimeric indolines might also arise *via* an ionic sequence of reactions initated by alkylation of unreacted *o*-nitrostyrene by the cyclized but unrearranged carbonium ions shown in Schemes I and II.

(21) G. A. Russell and E. J. Geels, *ibid.*, **87**, 122 (1965).

(22) Commercial samples of triethyl phosphite (Mobil Chemical Co.) were distilled through a short Vigreux column at reduced pressure. Melting points were taken using a calibrated Fisher-Johns apparatus. Thin layer chromatograms were obtained using silica gel H (Brinkmann Instruments). Spots were developed by iodine vapor. Column chromatography was carried out using Mallinckrodt silicic acid (100 mesh). Unless otherwise stated, infrared spectra of solids were run as KBr pellets and oils as thin films using a Perkin-Elmer Model 337 instrument. Ultraviolet spectra were determined in ethanol (U.S.P., Publicker Industries, Inc.) with a Beckman DK-2 spectrophotometer, and nmr spectra were obtained with a Varian Model A-60 instrument. Microanalyses were by Galbraith Laboratories Inc., Knoxville, Tenn.

(23) N. Kornblum and D. C. Iffland, *ibid.*, **71**, 2137 (1949); G. H. Daub and R. C. Castle, *J. Org. Chem.*, **19**, 1571 (1954).

(24) C. W. Muth, D. O. Steiniger, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 1006 (1955).

(25) V. F. Martynov, *Zh. Obshch. Khim.*, **23**, 2006 (1953); *Chem. Abstr.*, **49**, 3124*e* (1955).

(26) C. V. Rogers and B. B. Corson, *J. Am. Chem. Soc.*, **69**, 2910 (1947).

(27) J. E. Brennen, *ibid.*, **26**, 22 (1961).

(28) H. Dressler and M. E. Baum, *ibid.*, **26**, 102 (1961).

(29) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 852.

dimethylindole). Recrystallization of this material proved troublesome, but rechromatography of the product gave a sample having an infrared spectrum identical with that of a commercial sample, mp 104° (lit.[30] mp 104–104.5°).

Benzene–ether (9:1) eluted a mixture (0.8 g) which was mainly 2,2-dimethylindolin-3-one but contained two other components. Rechromatography on alumina gave pure (tlc) **10** (0.40 g, 2.5 mmoles, 11%) as an oil. Crystallization from cyclohexane–hexane gave yellow needles: mp 87–88° (lit. mp 88°,[31] 89°[32]); ν_{NH} 3340 cm^{-1}; $\nu_{C=O}$ 1675 cm^{-1}; $\lambda\lambda_{max}$ 230 mμ (log ε 4.33), 253 (3.79), 391 (3.60); nmr peaks ($CDCl_3$) at δ 1.32 (singlet, 6 H), 4.78 (broad singlet, 1 H), and 6.6–7.75 (multiplet, 4 H).

The fractions containing the two contaminants were combined and chromatographed on alumina. Poor separation resulted, but recrystallization of the residue from the concentrated fractions gave 2,2,2′,2′-tetramethyl-3,3′-biindoline (**11**) as white crystals: mp 172–174°, ν_{NH} 3315 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27. Found: C, 82.19; H, 8.43.

Deoxygenation of α-Methyl-2′-nitrostilbene (4).—A solution of **4** (3.1 g, 13 mmoles) in triethyl phosphite (12.9 g, 78 mmoles) was heated at 163 ± 2° for 6 hr and then subjected to the usual work-up. Chromatography on silicic acid gave 1-ethyl-2-methyl-3-phenylindole (0.658 g, 2.8 mmoles, 21%), a liquid eluted by hexane–benzene (9:1). The nmr and infrared spectra of this material were identical with those of an authentic sample described below.

Benzene–hexane (1:1) eluted 2-methyl-3-phenylindole (2.07 g, 10 mmoles, 77%), mp 60–61° (lit.[33] mp 58–60°) after recrystallization from benzene–hexane: ν_{NH} 3375 cm^{-1}; $\lambda\lambda_{max}$ (ethanol) 225 mμ (log ε 4.72), 275 mμ (log ε 4.29); nmr peaks at δ 2.37 (singlet, 3 H), and 6.9–7.8 (multiplet, 10 H). The infrared spectrum of the sample was identical with that of an authentic sample prepared as described by Ockenden and Schofield.[33]

1-Ethyl-2-methyl-3-phenylindole (13).—Sodium amide (0.39 g, 10 mmoles) was placed in a three-neck flask equipped with a Dry Ice–acetone condenser. Liquid ammonia (20 ml) was added, followed by dropwise addition of an ether solution of 2-methyl-3-phenylindole (1.35 g, 6.5 mmoles). After 5 min ethyl iodide (1.0 g, 6.5 mmoles) in ether (5 ml) was added. The reaction mixture was stirred for 30 min, and the ammonia was then allowed to evaporate. Water (100 ml) was added to the residue, and the mixture was extracted with ether. Chromatography of the crude product on silicic acid gave **13** (0.563 g, 2.3 mmoles, 47%) as well as unreacted **12** (0.327 g). An analytical sample was prepared by short-path distillation: bp 145–147° (0.36 mm); nmr peaks at δ 1.3 (triplet, 3 H), 2.4 (singlet, 3 H), 4.1 (quartet, 2 H), and 6.9–7.7 (multiplet, 4 H).

Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28. Found: C, 86.60; H, 7.52.

Interrupted Deoxygenations of 4.—The usual temperature and reactant ratios were used, but in separate runs the reaction was stopped 0.5, 1, and 2 hr after heating began. The crude reaction product obtained after distillation of triethyl phosphite and triethyl phosphate was dissolved in ether and extracted with base to isolate any N-hydroxyindole. None was found. The neutral products from the 1- and 2-hr runs were subsequently chromatographed, giving unreacted **4** as well as **12** and **13**.

Attempted Oxidation of 5,6,7,8,9,10-Hexahydrocyclohept[*b*]-indole in the Presence of Triethyl Phosphite.—Air was passed for 24 hr through a solution of **5** (9.25 g, 50 mmoles) and triethyl phosphite (49.8 g, 300 mmoles) in ether (150 ml). The ether was evaporated, and the residue was filtered, giving unchanged **5** (7.1 g). The filtrate was diluted with hexane and refrigerated, giving additional **5** (1.7 g). The mother liquor was distilled, giving triethyl phosphate (1.1 g), and additional unreacted **5** (0.4 g) remained as the residue. Total recovery was 9.2 g, >99%. The recovered indole was homogeneous to thin layer chromatography.

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Reversal of the Hudson Rules of Rotation. Effect of Solvent and Temperature on the Rotations of the Anomeric 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranoses[1]

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The specific rotations of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranose (**1**) and its β-D anomer (**2**) have been determined over the temperature range 20–60° in the solvents chloroform, benzene, pyridine, acetone, and methanol, and ORD spectra of **1** and **2** in chloroform have been measured over the wavelength range 300–500 mμ. In all cases the β-D anomer **2** is more dextrorotatory than the α-D anomer **1**, contrary to expectations based on Hudson's rule. The rotatory anomaly is related to the nitro group at the *ortho* position of the aryl moiety.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranose (**1**) and its β-D anomer (**2**) have been synthesized[1,4] by several definitive routes, and their anomeric configurations have also been verified by nmr.[1] This pair of anomers is unusual in that β-D anomer **2** is considerably more dextrorotatory than α-D anomer **1**, for rotations measured in chloroform solution at room temperature. This constitutes a complete reversal of the Hudson rule[5] that α-D anomers should be more dextrorotatory than the corresponding β-D anomers, and is the first recorded example of such a reversal for a pair of anomers having a simple aglycon. In the present work it is shown that this reversal of the normal rotatory relationships by the anomeric pair **1** and **2** is observed with a variety of different solvents, at various temperatures; in most cases the rotations show marked changes as the temperature is varied.

The specific rotations of **1** and **2**, measured at various temperatures between 20 and 60° for the solvents chloroform, benzene, pyridine, acetone, and methanol,

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