Acetyl Nitrate Addition to Cyclic Olefins. The Isomeric 9-Acetoxy-10-nitro-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrenes[1]

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Addition of acetyl nitrate to 1,2,3,4,4a,10a-(*trans*-4a,10a)-hexahydrophenanthrene produced a mixture of nitro acetates and olefinic nitro compounds. The four isomeric 9-acetoxy-10-nitro-octahydrophenanthrene addition products were separated and characterized based on nmr spectral data and X-ray diffraction techniques.

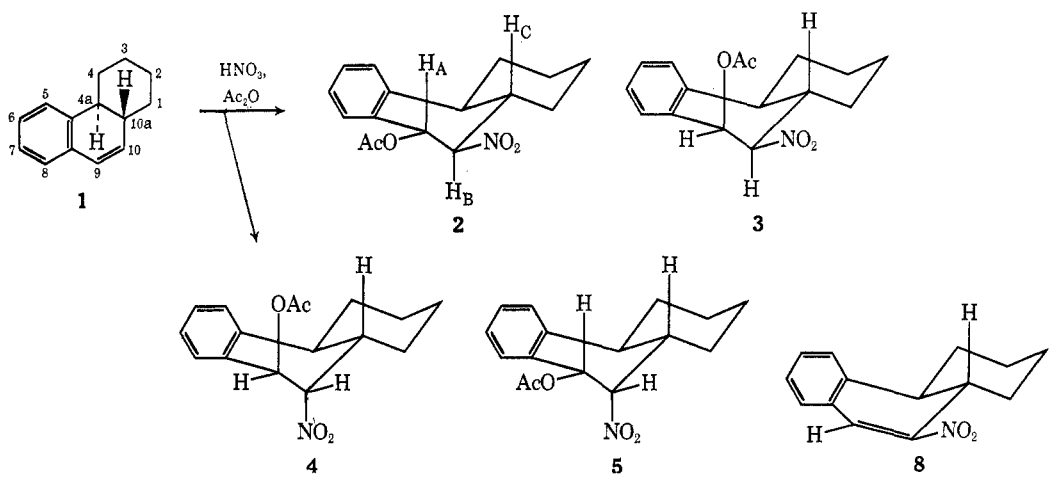
Addition of acetyl nitrate to various olefins has been reported to be a useful method of preparation of β-nitro acetates, the stereochemistry of which is somewhat dependent on the nature of the starting olefin. This fact, coupled with our interests in obtaining some substituted 2-amino-1-phenylethanol derivatives prompted us to explore this addition to a polycyclic styrene, 1,2,3,4,4a,10a-(*trans*-4a,10a)-hexahydrophenanthrene (**1**).[3]

Earlier workers have reported products of cis and trans addition depending on the structure of the olefinic starting material.[4,5] Net cis addition has been reported to *cis*- and *trans*-2-butene,[4a] and in many styryl systems, such as *trans*-1-phenylpropene,[4b,5a] *cis*-2-phenyl-2-butene,[4b] *cis*-3-phenyl-2-pentene,[4b] and in *trans*-stilbene.[4c,5b] However trans addition is preferred to some similar olefins, *e.g.*, *cis*-1-phenylpropene,[4b] *trans*-2-phenyl-2-butene,[4b] and to *trans*-3-phenyl-2-pentene.[4b] Addition to styryl systems which are partially incorporated into a cyclic structure, such as 1-phenylcyclohexene, affords mixtures of products with trans addition predominating.[4d,e] From 1-phenylcyclopentene only the product of trans addition was isolated.[4e]

In view of the variability of the steric course of the addition of this electrophilic reagent, we considered that this process might lead to some or all of the four isomeric 9-acetoxy-10-nitro compounds, **2**, **3**, **4**, and **5**, at the same time offering the opportunity for investigation of conformational aspects of this addition process.

Olefin **1** was prepared by borohydride reduction of 1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydro-9-oxophenanthrene (**6**)[6] followed by acid-catalyzed elimination of water using β-naphthalenesulfonic acid as catalyst.[7]

Addition of acetyl nitrate to the olefin afforded a complex mixture of products. Careful column chromatography afforded, in addition to a small amount of starting material, *ca.* 50% nitration products and nitroalkenes from which was isolated a mixture of nitro acetates and nitrostyrene **8** in about 10% yield. β-Nitrostyrene **8** accounted for about half of this amount.



The four nitro acetates were separated by column chromatography and tedious fractional crystallization.

Structure assignment to the two compounds with equatorial nitro groups, **2** and **3**, proved reasonably facile.[8] The nmr spectra of these compounds show large J_{BC} coupling constants (Table I) since proton H_B is axially disposed adjacent to C-10a leaving axial proton H_C. The nmr spectra showed J_{BC} = 11 Hz in **2** and 10 Hz in **3**, both consistent with an axial proton at C-10. Differences were noted in J_{AB} consistent with

(1) A preliminary account of this work was presented at the 24th Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 1969, Abstract 199.

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(3) All materials are racemic although only a single isomer is drawn.

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(5) (a) G. Drefahl, H. Crahmer, and W. Thomas, *Chem. Ber.*, **91**, 282 (1958); (b) G. Drefahl and H. Crahmer, *ibid.*, **91**, 754 (1958).

(6) C. D. Gutsche and W. S. Johnson, *J. Amer. Chem. Soc.*, **68**, 2239 (1946).

(7) (a) W. L. Nelson and D. D. Miller, *J. Med. Chem.*, **13**, 807 (1970); (b) D. D. Miller, Ph.D. Thesis, University of Washington, July 1969.

(8) (a) The central ring is arbitrarily assigned the half-chair conformation where the equatorial (e) and axial (a) substituents at C-9 are in fact pseudoequatorial and pseudoaxial, respectively. (b) Consistently throughout the nmr discussion of the 9,10-disubstituted compounds, the proton at C-9 is designated A, the proton at C-10, B, and the C-10a axial proton, C.

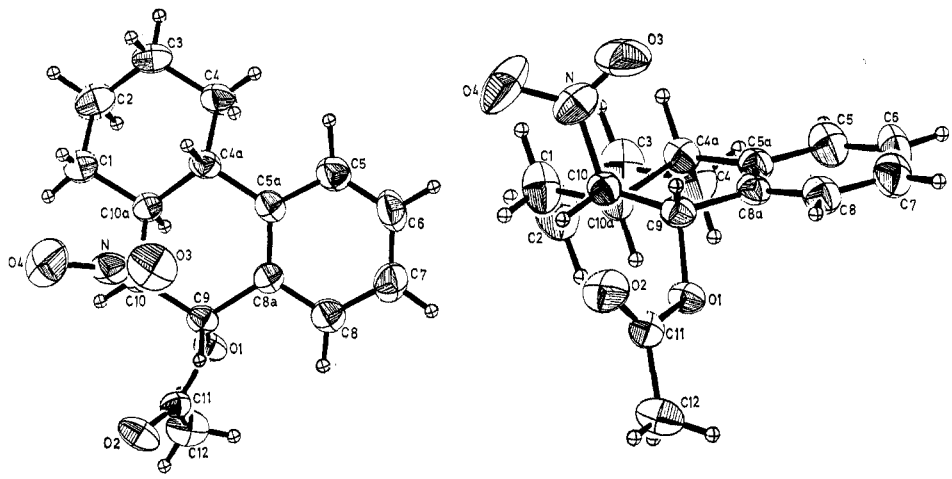

Figure 1.—Top and side views of nitro acetate **4**. The thermal ellipsoids enclose a probability density of 0.50 of the nonhydrogen atoms, plotted according to the program of C. K. Johnson, ORTEP, U. S. Atomic Energy Commission Report, ORNL-3794, 1965. Coincidentally, the absolute configuration of molecules in this figure is the same as used for structural formulas in this paper, but are viewed from the opposite side of the molecule.

assignment of the 9(e)-acetoxyl group to **3** and 9(a)-acetoxyl to **2**. Benzylic proton H_A showed a doublet, J_{AB} = 9 Hz in **2**, and J_{AB} = 4 Hz in **3**, consistent with an axial–axial coupling in the former compound and an equatorial–apial coupling in the latter.[9]

TABLE I

60-MHz NMR DATA ON THE ISOMERIC NITRO ACETATES[a]

Compd	Isolated yield, %	H_A (δ)	J_{AB} (Hz)	H_B (δ)	J_{BC} (Hz)
2	0.3	6.72	9	4.75	11
3	3.8	6.43	4	4.79	10
4	0.9	6.34	2.5	4.83	4
5	1.1	6.07	2	5.20	2 ~ 3

[a] Recorded in $CDCl_3$ solution relative to tetramethylsilane as internal standard.

Assignment of the relative stereochemistry of **4** and **5** proved to be much more difficult. The nmr spectra of these nitro acetates showed only small differences in chemical shifts for protons H_A and H_B, and no great differences in coupling constants.

Attempts to compare and correlate nmr spectral data of these two compounds with analogous amino alcohols and azido alcohols in this system[7] and with 6α,7α- and 6β,7α-dichloroestrone[10] were only partly successful. However, some similarities were noted: *e.g.*, consistent differences of similar magnitude between chemical shifts of benzylic protons when comparing pseudoaxial and pseudoequatorial isomeric pairs. Considering the differences in anisotropy of the azido, acetamido, and chloro substituents, especially when compared with the nitro group, no definitive assignments could be made.

An attempt to analyze the effect of the nitro group, known to be axial in the nitro acetates in question, on adjacent protons was made by comparison with reported nmr spectra of *cis*- and *trans*-4-*t*-butylnitrocyclohexane.[11] The 2,6-equatorial protons are further downfield than the 2,6-axial protons in both of these rigid nitrocyclohexanes, and are further downfield in the cis compound (axial nitro group) than in the trans compound (equatorial nitro group), indicating a large deshielding effect of the axial nitro group on the adjacent equatorial protons. If this model can be validly applied to the nitro acetates, then the compound with the more deshielded H_A proton must have the equatorial H_A and the 9(a)-acetoxy group, and structure **4**. A large difference in chemical shifts of the H_A proton is noted in **4** and **5**, *ca.* δ 0.27, consistent with the nitrocyclohexane model. Also a difference in chemical shifts of protons H_B of δ 0.37 was noted with H_B being upfield in **4**, in agreement with a possible shielding effect of the axial acetoxyl group on the adjacent equatorial proton.[12] However, these analogies suffer from the disadvantage of comparing cyclohexane with cyclohexene systems and cannot take into account effects of the benzene ring, other carbon–carbon or carbon–hydrogen bonds, or combinations of effects of one functional group in the presence of another.

Attempts to generate chemical evidence to differentiate between these structures failed. Base-catalyzed isomerization of the nitro group to the equatorial position, which would have provided compounds of known configuration, **2** and **3**, failed. Insufficient material was available for reduction to amino alcohols of known configuration.[7]

Single-crystal X-ray analysis of one of the compounds allowed structure assignment. Analysis of **4** showed unequivocally that both the acetoxy and nitro substituents are in the axial position, thus allowing for assignment of the 9(e)-acetoxy group to **5**. The structure of **4** is shown in Figure 1 from the top and side of the molecule. The dihedral angle between the nitro and acetoxy groups is 159.5°, and the angle between H_A and H_B is 78.2°. These results are consistent with expected angles, Dreiding models, and the nmr spectral analysis made in terms of the rigid nitrocyclohexane models.

Because of the low total yield of nitro acetates obtained from this olefin, no worthwhile speculation can

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(10) Y. Osawa and M. Neeman, *J. Amer. Chem. Soc.*, **85**, 2856 (1963).

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be made concerning the stereoselectivity of this addition process. It is noteworthy that all four of the possible nitro acetates are produced, in contrast to additions to some noncyclic olefins from which a single addition product is found.[4,5] The nitro acetate obtained in greatest yield is cis adduct **3**, resulting from addition on the same side of the molecule as the axial proton at C-10a, and the sum of products resulting from addition to this side is greater than from the opposite side, which seems slightly less hindered in Dreiding models. This may be only a coincidence because of the propensity of **3** isolated. These results are in contrast to the trans addition of iodine isocyanate and hypobromous acid to this olefin, but similar to the direction of epoxidation with peracid.[7]

Experimental Section[13]

9(ξ)-Hydroxy-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (7).—At room temperature 2.28 g (0.053 mol) of sodium borohydride (Alfa Inorganics, Inc.) in 20 ml of water was added slowly over a 20-min period to 20 g (0.10 mol) of ketone **6**[6] in 1 l. of 95% ethanol. The mixture was stirred 19 hr. After the addition of 10 ml of 1 *N* sodium hydroxide, the ethanol was removed *in vacuo*. The oily residue was dissolved in ether and washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to give 19.5 g (92%) of white solid material, mp 102°. An analytical sample was prepared by recrystallization from petroleum ether (bp 30–60°): mp 102°; ir (KBr) 3.05 (broad peak, O–H stretching), 3.40 and 3.48 (aliphatic C–H stretching), 6.75, 6.93, 9.38, 9.54, 9.95 and 13.3 μ (broad); nmr ($CDCl_3$) δ 7.90–7.55 (m, 1, C-8 aromatic proton), 7.50–7.18 (m, 3, aromatic protons), 5.13–4.65 (m, 1, benzylic proton), and 3.8–0.7 (m, 12, methylene–methine envelope).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.08; H, 8.79.

A *p*-nitrobenzoate derivative was prepared, mp 130–131°; the nmr ($CDCl_3$) multiplet of the benzylic proton between δ 5.13 and 4.65 was replaced by a triplet at δ 6.40 (J = 8.5 Hz).

1,2,3,4,4a,10a-(*trans*-4a,10a)-Hexahydrophenanthrene (1). A mixture of 24.0 g (0.12 mol) of alcohol **7** and 500 mg (2.4 mmol) of 2-naphthalenesulfonic acid (Eastman Organic Chemicals) in 1 l. of benzene was refluxed with an attached Dean–Stark trap for 48 hr. The mixture was evaporated *in vacuo* and the remaining residue was dissolved in ether and washed with several portions of an aqueous saturated sodium bicarbonate solution and water. The ether layer was dried (Na_2SO_4) and then evaporated *in vacuo* to give 25 g of a yellow oil. Column chromatography on 900 g of silica gel (Brinkmann), Brockmann activity III, using hexane as eluent afforded 20.6 g of colorless alkene (93%) in first 750 ml of hexane collected: uv max (95% C_2H_5OH) 262 (ε 8200); ir (neat) 3.27 (vinyl C–H stretching), 3.39 and 3.49 (aliphatic C–H stretching), 6.72, 6.90, 12.23, 13.50, 13.70, and 14.4 μ; nmr ($CDCl_3$) δ 7.26 (m, 4, aromatic protons), 6.55 (q, 1, J_{AB} = 10 Hz, J_{AC} = 2 Hz, C-9 proton, H_A), 5.85 (d, 1, J_{BC} = 0–1 Hz, C-10 proton, H_B), 3.0–1.0 (m, 10, broad methylene–methine envelope); mass spectrum (70 eV) *m/e* 184.

Addition of Acetyl Nitrate to 1,2,3,4,4a,10a-(*trans*-4a,10a)-hexahydrophenanthrene (1).—The nitration reagent was prepared using the method of Bordwell and Biranowski[4b] by adding 7.3 g (81 mmol) of 70% nitric acid to 52 ml of acetic anhydride at 25°, and the resulting mixture was cooled with stirring to −20° and then 5.0 g of the alkene **1** in 16 ml of acetic anhydride was added. The temperature was allowed to warm to 0°, and the solution was then cooled again to −20° and maintained at this temperature for 5 min. The resulting solution was then poured into 200 ml of water and this mixture was stirred until the excess acetic anhydride was hydrolyzed. The mixture was then extracted with several portions of ether, and the ether layers were combined, dried (Na_2SO_4), and then evaporated *in vacuo* to give 7.3 g of light yellow oil. The oil was placed on 360 g of silica gel (Brinkmann), Brockmann activity I, and eluted with 2400 ml of hexane, 1650 ml of 5% ether in hexane, 1050 ml of 10% ether in hexane, 900 ml of 15% ether in hexane, 450 ml of 20% ether in hexane, 750 ml of 50% ether in hexane, 500 ml of chloroform, and 600 ml of methanol. First collected in the hexane eluent was 362 mg of unreacted alkene followed by 2.18 g of a yellow oil that could be aromatic ring substitution products plus some conjugated nitroalkene. Next was collected a 700-mg mixture of nitrostyrene **8** plus *cis*-β-nitro acetate **5**. The solid material was dissolved in a combination of ether–hexane and two types of crystals formed which were separated using magnifying glass and forceps. The clear plate crystals were dissolved in ether–hexane and 74 mg of square crystals were isolated, mp 115–116°, assigned 9(e)-acetoxy-10(a)-nitro-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**5**): ir (KBr) 3.40 and 3.48 (aliphatic C—H stretching), 5.80 (C=O stretching), 7.15, 7.30 (N=O stretching), 7.38, 8.25, 9.85, 10.30, 10.90, 11.25, 11.78 (broad), 12.75, 13.30, 13.75, 14.50, and 15.75 μ; nmr ($CDCl_3$) δ 7.30 (s, 4, aromatic protons), 6.07 (d, 1, J_{AB} = 2 Hz benzylic proton H_A), 5.20 (m, 1, J_{BC} ≈ 3 Hz, C-10 proton H_B), 2.05 (s, 3, methyl protons), and 2.9–0.8 (m, 10, methylene–methine envelope).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.15; H, 6.98; N, 4.87.

The yellow needles that were separated were recrystallized from ether–hexane to give 111 mg of light yellow needles of the nitrostyrene **8**: mp 102–103°; ir (KBr) 3.25, 3.39, and 3.49 (aliphatic C–H stretching), 6.12, 6.69, 6.92, 7.50, 8.18, 13.11, 13.28, and 14.95 μ; uv max (95% C_2H_5OH) 239 mμ (ε 5400), 331 (5800); nmr ($CDCl_3$) δ 7.45–7.05 (m, 5, aromatic and C-9 proton), 2.8–0.8 (m, 10, methylene–methine envelope).

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.58; H, 6.62; N, 6.05.

This was followed by another fraction which contained two nitro acetates. Upon crystallization of the solid material from ether–hexane, 267 mg of clear square plate-like crystals of 9(a)-acetoxy-10(e)-nitro-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**3**) were formed: mp 139°; ir (KBr) 3.38 and 3.48 (aliphatic C—H stretching), 5.80 (C=O stretching), 6.50 (N=O stretching), 6.70, 6.92, 7.32 8.20 (broad), 8.75, 9.78, 10.48, 13.18, 13.31, and 13.85 μ; nmr ($CDCl_3$) δ 7.30 (broadened s, 4, aromatic protons), 6.43 (d, 1, J_{AB} = 4 Hz, benzylic proton, H_A), 4.79 (q, 1, J_{BC} = 10 Hz, C-10 proton, H_B), 2.13 (s, 3, methyl protons), and 2.8–0.7 (m, 0, methylene–methine envelope).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.58; H, 6.75; N, 5.00.

When the mother liquor from the above fraction was concentrated, two types of crystals formed which were separated using magnifying glass and forceps. The square plate-like crystals had mp 139° and were identical with those of β-nitro acetate **3**. The light yellow needlelike crystals separated from the mixture were recrystallized from hexane ether to give 22 mg of clear needle-like crystals of 9(e)-acetoxy-10(e)-nitro-1,2,3,4,4a,9,10,-10a-(*trans*-4a,10a)-octahydrophenanthrene (**2**): mp 136–137°; ir (KBr) 3.38 and 3.48 (aliphatic C—H stetching), 5.73 (C=O stretching), 6.48 (N=O stretching), 7.32 (N=O stretching), 8.2 (broad), 9.8, 13.23, and 13.52 μ; nmr ($CDCl_3$) δ 7.31 (m, 4, aromatic protons), 6.72 (d, 1, J_{AB} = 9 Hz, benzylic proton, H_A), 4.75 (q, 1, J_{BC} = 11 Hz, C-10 proton, H_B), 2.13 (s, 3, methyl protons), 2.9–0.8 (m, 10, methylene–methine envelope).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.65; H, 6.67; N, 4.95.

In the next fraction 110 mg of a light yellow solid was isolated. The material was recrystallized from ether–hexane to give 60 mg of clear long needle crystals of 9(a)-acetoxy-10(a)-nitro-1,2,3,4,-4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**4**): mp 137°; ir (KBr) 3.40 (broad) and 3.50 (aliphatic C—H stretching), 5.80 (broad, C=O stretching), 6.15, 6.55, 6.95, 8.25, 9.40, 10.35, 11.52, 13.02, 13.35, and 13.80 μ; nmr ($CDCl_3$) δ 7.31 (m, 4, aromatic protons), 6.34 (d, 1, J_{AB} = 2.5 Hz, benzylic proton, H_A), 4.83 (q, 1, J_{BC} = 4 Hz, C-10 proton, H_B), 2.10 (s, 3, methyl protons), 2.9–0.7 (m, 10, methylene–methine envelope).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.43; H, 6.64; N, 4.74.

X-Ray Analysis of 4.—The following crystallographic data were obtained from a prism of nitro acetate **4**: a = 9.878

(13) Melting points were obtained on a calibrated Thomas–Hoover Unimelt and are corrected. Infrared data were recorded on Beckman IR-5A, IR-8, and IR-20 spectrophotometers. Nmr spectra were determined with Varian A-60 and Varian T-60 spectrometers using tetramethylsilane as internal standard. In nmr descriptions, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were recorded on AEI MS-9. Microanalyses were conducted by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(±0.002) Å, b = 17.509 (±0.002) Å, c = 8.833 (±0.001) Å, β = 102.78 (±0.03)°, space group, $P2_1/c$, molecules/unit cell, 4, density (calcd) = 1.289 g/cm³, and density (measured by flotation) = 1.32 g/cm³.

Intensity data were collected by the stationary counter-stationary crystal technique using balanced filters for Cu Kα radiation.[14] The intensities (maximum *two* θ = 100°) were converted to structure factor amplitudes by applying appropriate corrections for absorption, α_1–α_2 splitting, and Lorentz-polarization effects. These data were scaled by Wilson statistics[15] and converted to their respective normalized structure factors.

The phases of the 159 largest normalized structure factors were derived by the application of the Sayre relationships.[16] Electron density and least squares calculations using all the data enabled the atomic coordinates of atoms and the thermal parameters (hydrogens isotropically and others anisotropically) to be refined. The final R index for the observed data was 0.038. A table of the positional and thermal parameters for the molecule, as well as the F tables, the bond distances, and angles, can be obtained from the authors.

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Registry No.—**1**, 16804-85-6; **2**, 25662-67-3; **3**, 25716-06-7; **4**, 25662-64-0; **5**, 25743-82-2; **8**, 25662-76-4; 9(ξ)-hydroxy-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene, 25662-65-1; 9(ξ)-hydroxy-1,2,-3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene *p*-nitrobenzoate, 25662-66-2.

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Halogenation with Copper(II) Halides. The Synthesis of Aryl Iodides

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Aryl iodides have been synthesized by a simple, single-step reaction of aromatic compounds with copper salts and an iodide donor. The reaction is capable of application to substituted and unsubstituted aromatic substrates. Iodination fails to occur only with ring systems bearing strongly deactivating substituents or possessing functional groups that deactivate the copper salt through complexation. Iodine may be supplied to the reaction by molecular iodine or by any group I–VIII metallic or nonmetallic iodide. Certain metal iodides exhibit greater reactivity than iodine itself; aluminum and ferrous iodides, in particular, have been found to be potent catalysts for this iodination reaction. The new synthetic method affords several advantages with regard to classical iodination procedures.

Halogenation by molecular halogen is one of the classical reactions of aromatic compounds and has been thoroughly investigated for both its theoretical and synthetic value.[1] The reactions of chlorine, bromine, and iodine with aromatic structures have generated a wealth of physical–organic data that define the structure-reactivity relationships and the steric and electronic factors that control these systems. The general reaction is agreed to involve the electrophilic attack of polarized halogen, or suitable halogen donor, on the aromatic and to proceed through a sequence of π and σ complexes to aryl halide product. The reaction is markedly sensitive to the presence of a catalyst whose principal function is to polarize the halogen source.

In contrast to chlorination and bromination which occur in the absence of catalysts, iodination demands the use of a catalytic agent. The failure of noncatalyzed iodination to occur was originally believed to be indicative of the reduction of aryl iodide product by hydrogen iodide.[2] Rather, the fact is that the role of the catalyst is to convert molecular iodine to a more reactive species, notably the iodonium (I^+) ion. Historically, this has *not* been accomplished through the use of conventional Lewis acid metal salts, for the coordination of iodine with these salts is reportedly weak owing to steric inhibition of orbital overlap.[1] Consequently, the synthesis of aryl iodides has required specialized conditions. These traditional procedures include (1) iodination of active aromatics with iodine in water;[3,4] (2) iodination of benzene and its alkyl homologs in the presence of strong mineral acids,[4–6] oxidizing agents,[4,6] or silver and mercury salts;[4,6,7] (3) decomposition of diazonium salts or arylthallium ditrifluoroacetates[8] with potassium iodide; (4) reaction of iodine with certain arylmercury chlorides.[4]

All of these procedures suffer from one or more deficiencies. The most serious of these are substrate limitations due to reaction conditions and the loss of iodine from the reaction as hydrogen iodide or metallic iodide.

The reaction of olefins with copper halides in various solvent media has been a topic of investigation in these laboratories.[9] During these studies it had been found that olefins react readily with copper(II) chloride and iodine in an inert hydrocarbon diluent to give high yields of chloroiodoalkanes.[10] When this reaction was performed in high-boiling aromatic solvents, the forma-

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