(KCl) 3190, 2920, 2860, 1440, 1360 cm$^{-1}$; $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 0.77 (3 H, d, $J$ = 6 Hz), 0.88 (3 H, s), 1.28 (3 H, s), 3.67 (1 H, br s).

**Monoacetate of 10.** Acetylation of **10** (7 mg) with acetic anhydride–pyridine at room temperature overnight afforded the monoacetate (4 mg); $^1$H NMR ($CDCl_3$, 80 MHz) $\delta$ 0.76 (3 H, d, $J$ = 6 Hz), 0.90 (3 H, s), 2.17 (3 H, s), 5.18 (1 H, s).

**Keto Alcohol 9 from 10.** Jones oxidation of **10** (2 mg) gave the keto alcohol **9**: mass spectrum, $m/e$ 236 ($M^+$), 208, 193, 190, 175, 165, 150, 123, 109; IR $\nu_{max}$ (Nujol) 3400–3280 (br), 2920, 2860, 1730, 1455, 1380 cm$^{-1}$.

**Acid Isomerization of Ishwarane (3).** A solution of **3** (100 mg) in dry ether (5 mL) was saturated with dry HCl gas and kept at room temperature for 2 days. The product was a mixture from which **7** (one of the two major components) was separated (28% yield) by chromatography over $SiO_2$–$AgNO_3$: mass spectrum, $m/e$ 204 ($M^+$), 189, 176, 161, 133, 120, 106; IR (neat) $\nu_{max}$ 2900, 1660, 1440, 1380, 1050 cm$^{-1}$; $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 0.70 (3 H, d, $J$ = 6 Hz), 0.87 (3 H, s), 1.70 (3 H, d, $J$ = 2 Hz), 5.62 (1 H, s).

The minor acid-isomerization product, which was found to be identical with **8**, was obtained from the same chromatography in 1% yield.

**Diol 5b from endo-Isoishwarane (7).** Treatment with $OsO_4$, as above, of **7** gave (43%) a crystalline diol: mp 172–174 °C; $[\alpha]^{25}_D$ −140.9° ($c$ 0.44); mass spectrum, $m/e$ 238 ($M^+$), 223, 220, 208, 205, 202, 189, 177, 162, 147, 135; IR $\nu_{max}$(KCl) 3230, 2940, 2860, 1450, 1380, 1320, 1065 cm$^{-1}$; $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 0.78 (3 H, d, $J$ = 6 Hz), 0.93 (3 H, s), 1.28 (3 H, s), 2.4–2.6 (2 H, br s), 3.75 (1 H, s).

**Keto Alcohol from *endo*-Isoishwarane (7)-Diol.** Jones oxidation of the diol, mp 172–174 °C, afforded in 50% yield the keto alcohol: mass spectrum, $m/e$ 236 ($M^+$), 218, 208, 190, 175, 165, 136, 123, 109; IR $\nu_{max}$ (Nujol) 3340, 2925, 2860, 1715, 1460, 1375 cm$^{-1}$.

**Epoxidation of 11 to 12.** Treatment of a $CHCl_3$ solution of **11** (20 mg) with a $CHCl_3$ solution of perbenzoic acid at 0 °C for 1 h followed by usual workup and chromatography over neutral alumina yielded **12** (12 mg); IR (neat) $\nu_{max}$ 2930, 2860, 1450, 1385 cm$^{-1}$.

**Reduction of 12 to 1.** The epoxide (12 mg) was reduced with an excess of $LiAlH_4$ in ether (10 mL) at room temperature for 27 h. Usual workup followed by chromatographic purification afforded the predominant product (6 mg) which was found to be identical (melting point, mixture melting point, TLC, $[\alpha]_D$, IR) with **1**.

**Epoxidation of 8 to 13.** Treatment of **8** (40 mg) with a $CHCl_3$ solution (5 mL) of perbenzoic acid at 0 °C for 1 h, usual workup, and subsequent chromatography over neutral alumina yielded **13** (22 mg): mp 46–48 °C; mass spectrum, $m/e$ 220 ($M^+$), 205, 191, 177, 163, 151, 135, 121, 109, 107, 95, 93, 91, 81, 71; IR (neat) $\nu_{max}$ 1070, 1020, 900, 845 cm$^{-1}$; $^1$H NMR ($CCl_4$, 60 MHz) $\delta$ 0.77 (3 H, d, $J$ = 6 Hz), 0.85 (3 H, s), 1.35 (3 H, s), 3.17 (1 H, s).

**Isomerization of 13 to 14.** A drop (0.02 mL) of freshly distilled $BF_3$·$Et_2O$ was added to **13** (20 mg) in dry benzene (2 mL) and left at 20 °C for 15 min. Usual workup and chromatography yielded **14** (15 mg): mass spectrum, $m/e$ 220 ($M^+$), 202, 192, 191, 177, 163, 162, 147, 135, 123, 109, 107, 95, 93, 91, 81, 79; IR (neat) $\nu_{max}$ 1710, 1440, 1327, 1103, 1083, 910 cm$^{-1}$; CD (MeOH) $\lambda_{max}$ 291 nm ($\Delta\epsilon$ = +3.56).

**Conversion of 7 to 14.** An ether solution (3 mL) of monoperphthalic acid was added to 69 mg of **7** and the mixture was left at 0 °C for 5 h and worked up in the usual manner. Chromatographic purification yielded **14** (25 mg), identified from TLC and IR.

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**Registry No.** **1**, 74912-09-7; **1** acetate, 74912-10-0; **2**, 577-27-5; **3**, 26620-70-2; **5b**, 74912-17-7; **5b** keto alcohol, 74912-18-8; **7**, 22471-63-2; **8**, 74929-66-1; **9**, 74912-11-1; **10**, 74912-12-2; **10** monoacetate, 74958-41-1; **11**, 74912-13-3; **12**, 74912-14-4; **13**, 74912-15-5; **14**, 74912-16-6.

## Thermochemical Behavior of *o*-Azidocinnamonitriles

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Ring-closed products have been reported from heat treatment of aryl azides that have unsaturated ortho substituents.[1-6] We wished to study the thermal reactions of *o*-azidocinnamonitriles to determine whether the azido group, or its intermediate nitrene, would attack the C=C unsaturation or the CN group. In addition, this system offered the opportunity to determine the effect of the two different geometrical arrangements around the double bond on the course of the cyclization. Accordingly, we have synthesized compounds **2a–c** and **6a–c** and have examined their thermal reactions.

### Results and Discussion

The aryl azides were obtained as analytically pure, crystalline compounds from the corresponding anilines by diazotization and treatment with sodium azide (see Table I). Preparation of the intemediate *o*-aminocinnamonitriles **1** and **5** and the assignment of their configurations are described below.

Reaction of *o*-nitrobenzaldehyde with diethyl cyanomethylphosphonate[7] gave principally (*Z*)-*o*-nitrocinnamonitrile, with a small amount of the *E* isomer, from which it was separated by chromatography. Hydrogenation of the *Z* isomer gave **1a** (see Chart I) contaminated with a little 3-(2-aminophenyl)propionitrile. This mixture was used in the subsequent diazotization reaction, from which **2a** was isolated by chromatography. The facile conversion of **1a** to **4a** has interfered with previous attempts to obtain it.[8] The methyl analogue **1c** was also made by hydrogenation of the corresponding nitrocinnamonitrile, while **1b** was prepared by thermal decomposition of 7-chloro-5-phenyl-1*H*-1,2-benzodiazepine-3-carboxylic acid.[9] Compounds **5a–c** were made by reaction of the corresponding *o*-aminoaryl carbonyl compounds with diethyl cyanomethylphosphonate.[7]

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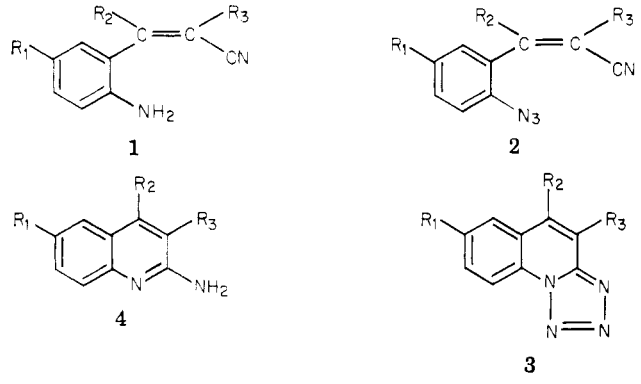
Table I. Preparation of Azides 2 and 6[a]

| compd | yield, % | mp, °C | IR (Nujol), cm$^{-1}$ | NMR, δ |
|---|---|---|---|---|
| 2a | 28 | 49-50 | 2225, 2140 | 5.46 (1 H, d, $J$ = 12 Hz), 7.1-7.6 (4 H, m), 8.1-8.3 (1 H, m) |
| 2b | 78 | 102-103 | 2225, 2140 | 6.02 (1 H, s), 7.0-7.6 (8 H, m) |
| 2c | 85 | 38-39 | 2220, 2140 | 2.11 (3 H, d, $J$ = 1.8 Hz), 7.0-7.5 (4 H, m), 7.8-8.0 (1 H, m) |
| 6a | 85 | 52-53 | 2230, 2140 | 5.90 (1 H, d, $J$ = 16 Hz), 6.9-7.6 (5 H, m) |
| 6b | 75 | 97-98 | 2230, 2140 | 5.65 (1 H, s), 7.0-7.6 (8 H, m) |
| 6c | 72 | 47-49 | 2225, 2140 | 2.41 (3 H, d, $J$ = 1.2 Hz), 5.41 (1 H, q, $J$ = 1.2 Hz), 7.0-7.5 (4 H, m) |

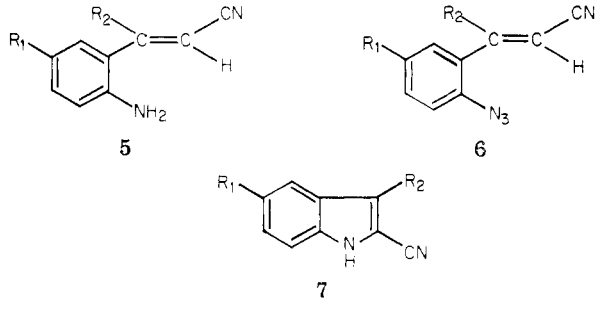
[a] All compounds listed gave satisfactory elemental analyses (±0.3 for C, H, and N).

Chart I[a]




[a] a, $R_1 = R_2 = R_3 = H$; b, $R_1$ = Cl, $R_2$ = Ph, $R_3$ = H; c, $R_1 = R_2 = H$, $R_3$ = Me.

Chart II[a]




[a] a, $R_1 = R_2 = H$; b, $R_1$ = Cl, $R_2$ = Ph; c, $R_1$ = H, $R_2$ = Me.

The $Z$ structures of **1a** and its azido analogue **2a** are established by the coupling constants of the olefinic protons ($J$ = 12 Hz). The $Z$ structures of **1b** and **1c** were assigned on the basis of their facile conversion to the quinolines **4b** and **4c** by boiling in ethanol. Conversely, the isomers **5b** and **5c** (see Chart II) were unchanged in boiling ethanol, indicating $E$ structures, although **5b**, like **5a**,[10] could be converted to the quinoline by treatment with sodium ethoxide in boiling ethanol.

The thermal reactions of azides **2** and **6** followed different courses. Treatment of **2** in boiling toluene converted them rapidly (<30 min) to tetrazolo[1,5-*a*]quinolines (**3**) in high yields (see Table II). Compounds **6** were stable under these conditions; they did change in boiling xylene, but rather slowly, particularly in the case of **6c**, which was largely unchanged after 3 days. However, when heated at 140 °C in dimethyl sulfoxide solution, compounds **6** decomposed within 2 h to tarry mixtures, from which 2-cyanoindoles **7** were obtained as the only characterizable products, in modest yields (see Table II).

Table II. Thermal Reaction of Azides 2 and 6

| compd | solvent (temp) | time, h | product | yield, % | mp (lit. mp), °C |
|---|---|---|---|---|---|
| 2a | toluene (reflux) | 0.5 | 3a[11] | 75 | 155 (157) |
| 2b | toluene (reflux) | 0.5 | 3b[12] | 81 | 201-202 (206-209) |
| 2c | toluene (reflux) | 0.5 | 3c[a] | 83 | 187 |
| 6a | $Me_2SO$ (140 °C) | 1 | 7a[13] | 34 | 99 (101) |
| 6b | $Me_2SO$ (140 °C) | 2 | 7b[14] | 31 | 208 (200-202.5) |
| 6c | $Me_2SO$ (140 °C) | 1 | 7c[15] | 60 | 103-104 (104-106) |

[a] NMR δ 2.76 (3 H, d, $J$ = 2 Hz), 7.5-8.0 (4 H, m), 8.4-8.6 (1 H, m).

The different reactions of azides **2** and **6** can be rationalized as follows. The formation of the fused-ring tetrazoles **3** clearly involves a 1,3-dipolar cycloaddition of the azido group onto the neighboring C≡N bond. Although this type of intramolecular reaction has been observed with 2-azido-2′-cyanobiphenyl[16] and 2-(2-azidophenoxy)acetonitrile,[3] it could not be foreseen with certainty with compounds **2** since nitriles are generally poor dipolarophiles,[17] and aryl azides have been shown to add exclusively to the C=C bond of cinnamonitriles.[18] Our results show that intramolecular cycloaddition of azides to nitriles can occur readily if the two groups are in the proper spatial relationship.

Azides **6**, whose geometry precludes the intramolecular 1,3-cycloaddition, have greater thermal stability than azides **2** but react under more severe conditions to form 2-cyanoindoles **7**. This reaction may involve loss of nitrogen from the azido group and subsequent addition of the resulting nitrene to the C=C group. On the other hand, studies of the thermal reactions of 2-nitrophenyl,[19] 2-acylphenyl,[19] and 2-(2-pyridyl)phenyl[20] azides indicate a concerted mechanism without formation of intermediate nitrenes, and a similar mechanism may be involved in the cyclizations of **6a-c**. Evidence for such a concerted

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mechanism is provided by the apparent absence of reaction products derived from dimethyl sulfoxide, which is known to react with nitrenes.[21] A concerted mechanism should involve some degree of charge separation in the transition state, which is consistent with the observed increase in rate on changing from xylene to dimethyl sulfoxide.

## Experimental Section

Melting points were taken on a Büchi apparatus and are uncorrected. NMR and infrared spectra were recorded, respectively, on a Varian HA-100 instrument and on a Perkin-Elmer 377 spectrophotometer. Chemical shifts are given in parts per million from internal $Me_4Si$ and refer to deuteriochloroform solutions.

Compounds **5a**[10] and **1b**[9] were prepared according to known methods.

**(*Z*)-*o*-Nitrocinnamonitrile.** Sodium hydride (1.2 g, 0.05 mol) was added in portions to a solution of diethyl cyanomethylphosphonate[22] (8.85 g, 0.05 mol) in anhydrous dimethylformamide (100 mL) under stirring and ice cooling. A solution of *o*-nitrobenzaldehyde (7.55 g 0.05 mol) in dimethylformamide (20 mL) was then added dropwise during 10 min. After being stirred for 5 min, the reaction mixture was poured in ice water, neutralized with ammonium chloride, and extracted with ether. The organic solution was dried over sodium sulfate and evaporated. The residue was chromatographed on a silica gel column with hexane–diethyl ether (1:1) as eluent to give the title compound:[23] 1.6 g; mp 87 °C (from diisopropyl ether); NMR $\delta$ 5.73 (1 H, d, $J$ = 12 Hz), 7.5–8.4 (5 H, m); IR (Nujol) 2220 $cm^{-1}$. Subsequent fractions gave a mixture (2.3 g) of the title compound and its *E* isomer in the approximate ratio of 3:2.

**Amine 1a.** A solution of (*Z*)-*o*-nitrocinnamonitrile (1.2 g) in methyl acetate (100 mL) was hydrogenated in the presence of 10% palladium/charcoal (0.25 g). After 500 mL of hydrogen was absorbed, the catalyst was filtered off, and the solvent was removed in vacuo at room temperature. The oily residue (0.90 g) was a mixture of **1a** (80%) and 3-(2-aminophenyl)propionitrile[3] (20%): NMR $\delta$ 3.8 (br s), 5.26 (d, $J$ = 12 Hz), 6.5–7.9 (m); IR (Nujol) 2220 $cm^{-1}$.

**Amine 1c.** *o*-Nitro-$\alpha$-methylcinnamonitrile[24] (5.0 g) was hydrogenated according to the above procedure. The crude product was dissolved in anhydrous ether and treated with ethereal hydrogen chloride to give the hydrochloride of **1c**: 2.2 g; mp 240–242 °C; NMR ($D_2O$) $\delta$ 2.20 (3 H, d, $J$ = 1.8 Hz), 7.3–7.9 (5 H, m); IR (Nujol) 2225 $cm^{-1}$.

A sample of **1c** (0.10 g) in ethanol (20 mL) was refluxed for 30 min. Evaporation of the solvent and recrystallization of the residue from methanol gave **4c**: 0.075 g; mp 228–230 °C; NMR ($CD_3SOCD_3$) $\delta$ 2.38 (3 H, s), 7.0–7.8 (4 H, m), 8.3–8.5 (1 H, m).

**Amine 5b.** Sodium hydride (0.65 g) was added in portions to a solution of diethyl cyanomethylphosphonate (5.94 g) in anhdrous dimethylformamide (60 mL) under stirring and ice cooling. A solution of 2-amino-5-chlorobenzophenone (5.2 g) in dimethylformamide (15 mL) was added dropwise, and the mixture was stirred for 16 h at room temperature. The solvent was partly removed in vacuo, and the residue was pured in ice–water, neutralized with ammonium chloride, and extracted with ether. The organic solution was dried over sodium sulfate and evaporated.

Chromatography of the residue on a silica gel column with hexane–diethyl ether (1:1) as eluent gave **5b**: 4.3 g; mp 92–93 °C (from diisopropyl ether); NMR $\delta$ 3.5 (2 H, br s), 5.58 (1H, s), 6.4–7.6 (8 H, m); IR (Nujol) 2220 $cm^{-1}$. A sample of **5b** was recovered unchanged after 24 h of refluxing in ethanol.

**Amine 5c.** This compound[9] was prepared from *o*-aminoacetophenone according to the procedure described for **5b** (3 h; 54% yield). A sample of **5c** was recovered unchanged after 24 h of refluxing in ethanol.

**Cyclization of 1b.** A solution of **1b** (0.20 g) in ethanol (30 mL) was refluxed for 7 h. Evaporation of the solvent and recrystallization of the residue from methanol gave **4b** (0.12 g).[25]

**Preparation of Azides 2 and 6. General Procedure.** Sodium nitrite (5 mmol) in water (5 mL) was added to a solution of amine **1** or **5** (5 mmol) in 1 N aqueous hydrochloric acid (20 mL) under stirring and ice cooling. The solution was adjusted to pH 5 with sodium acetate; sodium azide (5 mmol) was then added in portions with vigorous stirring. After 30 min, the mixture was extracted with ether, and the organic layer was dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave practically pure azide **2** or **6**, with the exception of **2a** which was isolated by chromatography on a silica gel column (diethyl ether as eluent). Samples of analytical purity were obtained upon recrystallization from pentane–diisopropyl ether (see Table I).

**Thermal Reaction of Azides 2. General Procedure.** A solution of **2** (3 mmol) in anhydrous toluene (150 mL) was refluxed for 30 min. Evaporation of the solvent and recrystallization of the residue from methanol gave **3** (see Table II).

**Thermal Reaction of Azides 6. General Procedure.** A solution of **6** (5 mmol) in anhydrous dimethyl sulfoxide (250 mL) was heated at 140 °C for the time indicated in Table II. After the solvent was partly removed under reduced pressure, the mixture was treated with water and extracted with chloroform. The organic layer was dried over sodium sulfate and evaporated. The residue was chromatographed on a silica gel column with hexane–diethyl ether (1:1) as eluent to give **6** (see Table II).

**Registry No. 1a**, 72119-96-1; **1c**, 74844-95-4; **2a**, 74844-96-5; **2b**, 74844-97-6; **2c**, 74844-98-7; **3a**, 235-25-6; **3b**, 27537-94-6; **3c**, 72716-16-6; **4b**, 51478-40-1; **4c**, 74844-99-8; **5b**, 74868-71-6; **5c**, 74845-00-4; **6a**, 74845-01-5; **6b**, 74845-02-6; **6c**, 74845-03-7; **7a**, 36193-65-4; **7b**, 24139-17-1; **7c**, 13006-59-2; (*Z*)-*o*-nitrocinnamonitrile, 74845-04-8; *o*-nitro-$\alpha$-methylcinnamonitrile, 74845-05-9; diethyl cyanomethylphosphonate, 2537-48-6; *o*-nitrobenzaldehyde, 552-89-6; 3-(2-aminophenyl)propionitrile, 55000-16-3; 2-amino-5-chlorobenzophenone, 719-59-5; *o*-aminoacetophenone, 551-93-9; **5a**, 58106-57-3.

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# Regioselective Acid-Catalyzed Cyclodimerization of 1,2-Dihydronaphthalene. Mechanism of Formation and Single-Crystal X-ray Analysis of Two Octahydrobenzo[*j*]fluoranthenes

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Treatment of 1,2-dihydronaphthalene (**1a**) with sulfuric acid gives a $C_{20}H_{20}$ hydrocarbon,[2] mp 92–93 °C, whereas with $P_2O_2$ in the presence of tetralin a diastereomer,[3] mp 151–153 °C, is formed. Both were readily dehydrogenated to benzo[*j*]fluoroanthene which established their gross structure.[3] Earlier $^1H$ NMR studies and use of Dreiding models suggested (±)-*cis,anti*- and (±)-*cis,syn*-4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthenes, **5a** and

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