L-Valyltaurine (5b). To 60 mL of 98% formic acid was added 6 mL of 30% H_2O_2 (60 mmol), and the solution was stirred for 1 h at 0 °C. Crude *N,N'*-bis(*N*-formylvalyl)cystamine (**3b**; X = CHO) (2.1 g, 5.1 mmol), dissolved in 98% formic acid (15 mL), was added at the same temperature and the solution stirred overnight at room temperature. The excess of the oxidant was removed by addition of dimethyl sulfide (3 mL, 41 mmol). The solution was evaporated in vacuo, to give 1.83 g (71%) of L-valyltaurine (**5b**): IR $\nu_{C=O}$ 1670 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.2 (m, 1 H, NCHCO), 3.2 (m, 2 H), 2.8 (t, 2 H), 1.95 (m, 1 H), 0.9 (m, 6 H); MS (FAB) 673 $[(M + H) + 2 M]^+$, 449 $[(M + H) + M]^+$, 225 $[M + H]^+$.

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Registry No. **1a** (X = CBz), 2274-58-0; **1a** (X = BOC), 57133-29-6; **1b** (X = CHO), 4289-97-8; **3a** (X = CBz), 112042-52-1; **3a** (X = BOC), 112042-53-2; **3b** (X = CHO), 112042-54-3; **4a** (X = CBz), 90990-60-6; **5a**, 90970-64-2; **5b**, 53329-38-7; cystamine dihydrochloride, 56-17-7; cystamine, 51-85-4.

New Access to 2-(Arylazo)-, 2-(Arylhydrazo)-, and 2-Aminoindoles, -benzofurans, and -thianaphthenes

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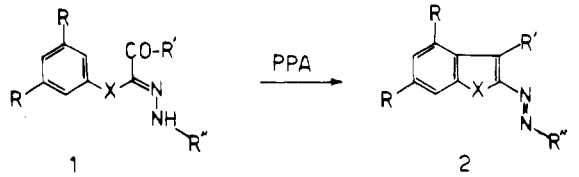
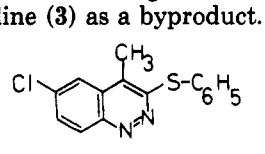
In this paper we describe the reaction of a few α-arylamino, -aryloxy, and -arylthio acyl hydrazones having general structure **1** with polyphosphoric acid (PPA). The reaction affords 2-(arylazo)indoles, -benzofurans, and -thianaphthenes **2**, respectively, in fairly good yields; the reaction is applicable to a rather wide range of substrates.



1 2

	X	R	R'	R''
a	NH	H	CH_3	C_6H_5
b	NH	CH_3	CH_3	C_6H_5
c	NH	H	CH_3	4-Cl-C_6H_4
d	NH	CH_3	C_6H_5	C_6H_5
e	O	H	CH_3	C_6H_5
f	O	CH_3	CH_3	C_6H_5
g	S	CH_3	CH_3	C_6H_5
h	S	H	CH_3	4-Cl-C_6H_4

In the case of **1h**, a concurrent cyclization course was observed affording 6-chloro-4-methyl-3-(phenylthio)-cinnoline (**3**) as a byproduct.



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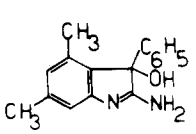

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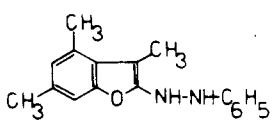

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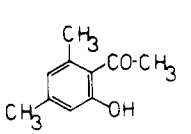


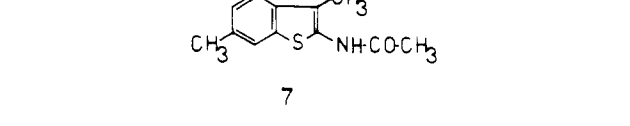
6

The structural assignment to the reaction products **2** was based on the spectral and analytical data as well as on the results of the high-pressure catalytic hydrogenation performed in one case for each class of compounds, namely, **2d**, **2f**, and **2g**.

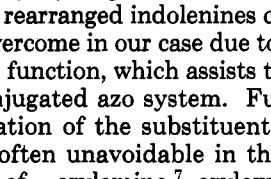
In the case of **2d**, 2-amino-4,6-dimethyl-3-phenyl-3-hydroxyindolenine (**4**) and aniline were formed. This result is in accordance with literature data reporting the easy oxidation in air of 2-aminoindoles.[1]

In the case of **2f**, a more complicated reaction course was observed affording *N*-phenyl-*N'*-[2-(3,4,6-trimethylbenzofuranyl)]hydrazine (**5**), 2,4-dimethyl-6-hydroxyacetophenone (**6**), and aniline. The hydrazo compound **5** could alternatively be prepared in better yields by controlled reduction of **2f** with zinc dust and ammonium chloride in water–acetone solution.

The formation of **6** can be interpreted through a mechanism similar to that producing **4**: the 2-aminobenzofuran derivative initially formed should undergo, like the corresponding indole compound, an easy oxidation by air. Ring opening would give a cyanohydrin as the logical precursor of **6**.



The hydrogenation of **2g** was carried out in the presence of acetic anhydride; 2-acetamido-3,4,6-trimethylthianaphthene (**7**) and acetanilide were the main reaction products.



7

The general reaction scheme leading to **2** from **1** is basically a cyclodehydration,[2] which is a known means for producing benzocondensed five-membered heterocycles from α-arylamino,[3] -aryloxy,[4] and -arylthio ketones.[5] The scope of this synthetic scheme is strongly limited when the carbon atom adjacent to the condensing carbonyl group does not carry any hydrogen atom allowing the water elimination (only rearranged indolenines can be formed[5]): this problem is overcome in our case due to the peculiarity of the hydrazonic function, which assists the loss of water on forming a conjugated azo system. Furthermore, the formal 3–2 migration of the substituent bonded to the carbonyl group, often unavoidable in the course of the cyclodehydration of α-arylamino,[7] -aryloxy,[8] and -arylthio

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ketones,[9] cannot take place in our case.

The formation of the cinnoline derivative **3** represents an alternative reaction course which is expected to be important when R is an electron-withdrawing substituent; the results reported before are however in agreement with the different donor properties of nitrogen, oxygen, and sulfur.

The reaction described above is in any case a facile route to products representative of rather uncommon species in the chemical literature.[10] Furthermore, the hydrazo compounds obtainable by controlled reduction of **2** appear to be very interesting substrates for the study of the rearrangements of the hitherto little known class of hetero hydrazoarenes.

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian EM-390 and Varian XL 300 spectrometers with $CDCl_3$ as a solvent unless otherwise stated and with tetramethylsilane as an internal standard. Chemical shifts are given in δ units and refer to the center of the signal: s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet. IR absorptions are given in cm^{-1}.

1-(Phenylamino)-1-(phenylhydrazono)-2-propanone (1a). A solution of 1-chloro-1-(phenylhydrazono)-2-propanone[11] (5.0 g), aniline (1.8 g), and triethylamine (2.5 mL) in ethanol (150 mL) was refluxed for 16 h, then the solvent was removed under reduced pressure, and the residue was treated with water and ether. The organic layer was washed with 5% hydrochloric acid solution and then with a 5% sodium hydrogen carbonate solution. Evaporation of the solvent left a yellow solid, which was crystallized from *n*-hexane: mp 94 °C (4.7 g); ^1H NMR δ 8.42 (1 H, br s exchanging with D_2O, NHN), 7.2-(8 H, m, aromatic), 6.79 (1 H, s exchanging with D_2O, NH), 6.68 (2 H, m, aromatic in position 2 and 6 of the aniline group), 2.68 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.12 H, 5.97; N, 16.59. Found: C, 70.94; H, 6.04; N, 16.74.

1-[(3,5-Dimethylphenyl)amino]-1-(phenylhydrazono)-2-propanone (1b). A solution of 1-chloro-1-(phenylhydrazono)-2-propanone[11] (10.0 g), 3,5-dimethylaniline (6.2 g), and triethylamine (7.2 g) in ethanol (80 mL) was refluxed for 2 h, and then the solvent was partially removed under reduced pressure. The yellow solid precipitated upon cooling of the solution was washed with water and crystallized from 2-propanol: mp 120 °C (14.1 g); ^1H NMR δ 7.48–6.80 (5 H + 1 H exchanging with D_2O, m, C_6H_5 and NHN), 6.62 (1 H + 1 H exchanging with D_2O, 2 s, aromatic in para position of the xylidine group and NH), 6.27 (2 H, s, aromatic in position 2 and 6 of the xylidine group), 2.65 (3 H, s, $COCH_3$), 2.30 (6 H, s, 2 CH_3). Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.57; H, 6.81; N, 14.93. Found: C, 72.38; H, 6.91; N, 14.70.

1-(Phenylamino)-1-[(4-chlorophenyl)hydrazono]-2-propanone (1c). The reaction between 1-chloro-1-[(4-chlorophenyl)hydrazono]-2-propanone[12] (5.0 g) and aniline (2.0 g) was carried out in ethanol solution (120 mL) in the presence of triethylamine (30 mL) by following the procedure described above for the synthesis of **1a**. The title compound is an orange colored solid with mp 141 °C (2-propanol) (5.1 g): ^1H NMR δ 6.84–7.28 (7 H + 1 H exchanging with D_2O, aromatic and NHN), 6.80 (1 H, s exchanging with D_2O, NH), 6.56 (2 H, d, aromatic in position 2 and 6 of the aniline group), 2.62 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{14}ClN_3O$: C, 62.61; H, 4.90; N, 14.60. Found: C, 62.60; H, 4.53; N, 14.43.

1-Phenyl-2-(phenylhydrazono)-2-[(3,5-dimethylphenyl)-amino]ethanone (1d). A solution of 2-chloro-1-phenyl-2-(phenylhydrazono)ethanone[13] (3 g), 3,5-xylidine (1.4 g), and triethylamine (1.2 g) in ethanol (30 mL) was refluxed for 10 min. The yellow solid precipitated upon cooling of the solution was washed with water and crystallized from 2-propanol: mp 121 °C (2.6 g); ^1H NMR δ 9.04 (1 H, br s exchanging with D_2O), 8.20 (2 H, m, aromatic in position ortho to the carbonyl group), 7.5 (3 H + 1 H exchanging with D_2O, m, aromatic in position meta and para to the carbonyl group and NH), 7.2 (2 H, m, aromatic in meta position of the C_6H_5NH group), 7.0 (3 H, m, aromatic in ortho and para position of the C_6H_5NH group), 6.64 (1 H, s, aromatic in position 4 of the xylidine group), 6.38 (2 H, s, aromatic in position 2 and 6 of the xylidine group), 2.31 (6 H, s, 2 CH_3). Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 76.78; H, 6.21; N, 12.28.

1-Phenoxy-1-(phenylhydrazono)-2-propanone (1e). 1-Chloro-1-(phenylhydrazono)-2-propanone[11] (3.0 g) was added portionwise to a stirred melt of phenol (9 g) and triethylamine (1.7 mL) at 35 °C; the reaction was complete in 10 min. The mixture was poured into a 5% sodium hydroxide solution and exhaustively extracted with ether; removal of the solvent from the combined organic extracts left a residue, which was chromatographed (eluant, carbon tetrachloride); the first fractions eluted gave **1e** as a brown solid, which was crystallized from diisopropyl ether: mp 91 °C (0.9 g); ^1H NMR δ 8.50 (1 H, br s, exchanging with D_2O, NH), 7.42–6.81 (10 H, m, aromatic), 2.55 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 71.02; H, 5.46; N, 11.08.

1-(3,5-Dimethylphenoxy)-1-(phenylhydrazono)-2-propanone (1f). 3,5-Dimethylphenol (5.4 g) was added to a sodium ethoxide solution prepared from sodium (0.9 g) and absolute ethanol (22 mL); solvent was removed under reduced pressure and the solid residue suspended in dry acetonitrile (60 mL). The slurry was added to a stirred solution of 1-chloro-1-(phenylhydrazono)-2-propanone[11] (7.0 g) in acetonitrile (120 mL) under nitrogen. After 15 min of stirring at 25 °C, the mixture was poured into water (200 mL) and exhaustively extracted with chloroform. Removal of the solvent from the combined organic extracts left a residue, which was chromatographed on a silica gel column (eluant, chloroform). The first fractions eluted gave a brown solid, which was crystallized from diisopropyl ether to give the title compound (1.2 g) as a light yellow solid with mp 150 °C: ^1H NMR δ 8.4 (1 H, br s exchanging with D_2O, NH), 7.2–7.5 (5 H, m, C_6H_5), 6.7 (1 H, s, aromatic in position para to the oxygen atom), 6.5 (2 H, s, aromatic in position ortho to the oxygen atom), 2.56 (3 H, s, $COCH_3$), 2.31 (6 H, s, 2 CH_3). Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.25; H, 6.34; N, 9.85.

1-[(3,5-Dimethylphenyl)thio]-1-(phenylhydrazono)-2-propanone (1g). A solution of 1-chloro-1-(phenylhydrazono)-2-propanone[11] (8.8 g), 3,5-dimethylthiophenol[14] (6.2 g), and triethylamine (6.4 mL) in ethanol (100 mL) was refluxed under nitrogen for 2 h. The yellow solid precipitated upon cooling of the solution was filtered, washed with water, and crystallized from ethanol: mp 147 °C (10.7 g); ^1H NMR δ 9.30 (1 H, s exchanging with D_2O, NH), 7.2–7.4 (5 H, m, C_6H_5), 6.87 (3 H, s, C_6H_3), 2.65 (3 H, s, $COCH_3$), 2.30 (6 H, s, 2 CH_3). Anal. Calcd for $C_{17}H_{18}N_2OS$: C, 68.43; H, 6.08; N, 9.39. Found: C, 68.37; H, 6.13; N, 9.21.

1-(Phenylthio)-1-[(4-chlorophenyl)hydrazono]-2-propanone (1h). A solution of 1-chloro-1-[(4-chlorophenyl)-hydrazono]-2-pronanone[12] (3.0 g), thiophenol (1.4 g), and triethylamine (1.8 mL) in ethanol (35 mL) was refluxed under nitrogen for 10 h. The yellow solid precipitated upon cooling of the solution was filtered and crystallized from ethanol: mp 145 °C (3.3 g); ^1H NMR δ 9.20 (1 H, br s exchanging with D_2O, NH), 7.39–6.98 [9 H, m resulting from the superimposition of 2 d at 7.29 and 7.07 (C_6H_4) and a s at 7.26 (C_6H_5)]. Anal. Calcd for

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$C_{15}H_{13}ClN_2OS$: C, 59.11; H, 4.30; N, 9.19. Found: C, 59.11; H, 4.34; N, 9.11.

Reaction of 1a–h with PPA: General Procedure. The powdered substrate was added portionwise to PPA (10-fold in weight) preheated at 80 °C with stirring; when the exothermic phase subsided, the temperature was usually increased to 115 °C to complete the reaction. The dark colored solution was poured into ice–water and the resulting mixture neutralized with 26% ammonium hydroxide solution and then exhaustively extracted with ether. The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness to give a residue, which was either crystallized from *n*-hexane or chromatographed on a silica gel column (eluant, chloroform).

Reaction of 1a with PPA: 3-Methyl-2-(phenylazo)indole (2a). The reaction of **1a** (4 g) with PPA was exothermic, the temperature reaching 110 °C, and was complete in 10 min. Chromatography gave **2a** as orange colored crystals with mp 104 °C (*n*-hexane) (1.4 g): M_r (MS) 235; ^1H NMR δ 8.84 (1 H, br s exchanging with D_2O, NH), 7.9 (2 H, m, aromatic in position ortho to the azo group), 7.65 (1 H, d, aromatic in position 7); 7.55–6.94 (6 H, m, aromatic), 2.79 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.60; H, 5.53; N, 17.80. Found: C, 76.63; H, 5.48; N, 17.66.

Reaction of 1b with PPA: 2-(Phenylazo)-3,4,6-trimethylindole (2b). The reaction of **1b** (9.0 g) with PPA was exothermic, the temperature reaching 95 °C, and was complete in 40 min at this temperature. Chromatography gave **2b** as orange colored crystals with mp 114 °C (3.1 g): ^1H NMR δ 8.74 (1 H, br s exchanging with D_2O, NH), 7.90 (2 H, m, aromatic in position ortho to the azo group), 7.65–7.32 (3 H, m, aromatic of the C_6H_5 group), 6.88 (1 H, s, aromatic in position 7), 6.66 (1 H, s, aromatic in position 5), 2.91, 2.77 and 2.43 (each 3 H, 3 s, 3 CH_3). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.83; H, 6.15; N, 16.02. Found: C, 77.42; H, 6.33; N, 15.77.

Reaction of 1c with PPA: 2-[(4-Chlorophenyl)azo]-3-methylindole (2c). The reaction of **1c** (5.0 g) with PPA was slightly exothermic and was complete in 15 min. Chromatography gave **2c** as a red-orange colored solid with mp 135 °C (*n*-hexane) (2.5 g): ^1H NMR δ 8.83 (1 H, br s exchanging with D_2O, NH), 7.81 (2 H, d, aromatic in position ortho to the azo group), 7.73 (1 H, d, aromatic in position 7), 7.42 (2 H, d, aromatic in position meta to the azo group), 7.40–6.98 (3 H, m, aromatic), 2.80 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{12}ClN_3$: C, 66.79; H, 4.48; N, 15.58. Found: C, 67.01; H, 4.57; N, 15.39.

Reaction of 1d with PPA: 2-(Phenylazo)-3-phenyl-4,6-dimethylindole (2d). The reaction of **1d** (3.0 g) with PPA, carried out at 80 °C, was complete in 30 min. Chromatography gave **2d** (1.4 g) as orange colored crystals with mp 94 °C (*n*-hexane): ^1H NMR δ 9.05 (1 H, br s exchanging with D_2O, NH), 7.75 (2 H, m, aromatic in position ortho to the azo group), 7.6–7.3 (8 H, m, aromatic), 7.01 (1 H, s, aromatic in position 7), 6.71 (1 H, s, aromatic in position 5), 2.49 and 2.30 (each 3 H, 2 s, 2 CH_3). Anal. Calcd for $C_{22}H_{19}N_3$: C, 80.95; H, 6.18; N, 12.87. Found: C, 81.01; H, 6.10; N, 12.88.

Reaction of 1e with PPA: 3-Methyl-2-(phenylazo)benzofuran (2e). The reaction of **1e** (0.7 g) with PPA was complete at 80 °C in 45 min. The crude reaction product was chromatographed (eluant, benzene–ethyl acetate, 9:1) to give **2e** as a red solid with mp 49 °C (*n*-pentane) (0.25 g): ^1H NMR δ 8.0 (2 H, m, aromatic in position ortho to the azo group), 7.72–7.04 (7 H, m, aromatic), 2.74 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.94; H, 5.17; N, 12.01.

Reaction of 1f with PPA: 2-(Phenylazo)-3,4,6-trimethylbenzofuran (2f). The reaction of **1f** (1.1 g), carried out at 80 °C, was complete in 15 min. The crude reaction product was directly crystallized from *n*-hexane to give **2f** as an orange colored solid with mp 120 °C (0.65 g): ^1H NMR δ 8.0 (2 H, m, aromatic in position ortho to the azo group), 7.4 (3 H, m, aromatic of C_6H_5 group), 7.12 (1 H, s, aromatic in position 7), 6.80 (1 H, s, aromatic in position 5), 2.83, 2.68 and 2.45 (each 3 H, 3 s, 3 CH_3). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.17; H, 6.04; N, 10.54.

Reaction of 1g with PPA: 2-(Phenylazo)-3,4,6-trimethylthianaphthene (2g). The reaction of **1g** (10 g) with PPA was exothermic, the temperature reaching 95 °C, and was complete in 10 min. The crude reaction product was chromatographed (eluant, carbon tetrachloride) to give **2g** as orange colored crystals with mp 119 °C (*n*-hexane) (6.5 g): ^1H NMR δ 7.9–7.7 (2 H, m, aromatic in position ortho to the azo group), 7.6–7.4 (3 H, m, aromatic), 7.38 (1 H, s, aromatic in position 7), 6.8 (1 H, s, aromatic in position 5), 3.10, 2.80, 2.41 (each 3 H, 3 s, 3 CH_3). Anal. Calcd for $C_{17}H_{16}N_2S$: C, 72.82; H, 5.75; N, 9.92. Found: C, 73.15; H, 5.45; N, 10.13.

Reaction of 1h with PPA: 2-[(4-Chlorophenyl)azo]-3-methylthianaphthene (2h) and 6-Chloro-4-methyl-3-(phenylthio)cinnoline (3). The reaction of **1h** (3.2 g) with PPA was carried out at 105 °C for 35 min. The crude reaction product was dissolved in ether and some undissolved tarry material (0.2 g) filtered off; removal of the solvent left a residue, which was chromatographed (eluant, chloroform). The first fractions eluted were rechromatographed (eluant, carbon tetrachloride) to give **2h** as an orange colored solid with mp 131 °C (*n*-hexane) (0.32 g): M_r (MS) 286; ^1H NMR δ 8.0–7.7 (4 H, m with a d emerging at 7.85, aromatic in position 4 and 7 and in position ortho to the azo group), 7.58–7.30 (4 H, m with a d emerging at 7.42, aromatic in position 5 and 6 and in position meta to the azo group), 2.92 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{11}ClN_2S$: C, 62.82; H, 3.87; N, 9.77. Found: C, 62.70; H, 3.85; N, 9.65. The final fractions of the first chromatography were rechromatographed (eluant, chloroform) to give **3** as a light brown solid with mp 148 °C (ethanol) (0.1 g): M_r (MS) 286; ^1H NMR δ 8.39 (1 H, d, aromatic in position 8), 7.97 (1 H, d, aromatic in position 5), 7.66 (1 H, dd, aromatic in position 7), 7.61–7.20 (5 H, m, aromatic), 2.80 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{11}ClN_2S$: C, 62.82; H, 3.87; N, 9.77. Found: C, 62.49; H, 3.74; N, 10.02.

Catalytic Hydrogenation of 2d: 2-Amino-4,6-dimethyl-3-hydroxy-3-phenylindolenine (4). A solution of **2d** (1.0 g) in ethanol (30 mL) was hydrogenated in the presence of 10% Pd on charcoal (0.1 g) at 35 atm of hydrogen pressure at room temperature. After 4 h, the catalyst was filtered off and the solvent removed under reduced pressure to give a residue, which was chromatographed on a silica gel column (eluant, chloroform–methanol, 20:1). First aniline, then a white solid, crystallized twice from 2-propanol to give **4** in a pure state (0.2 g), were eluted: mp 220 °C. M_r (MS) 252; ^1H NMR δ 7.32 (5 H, m, C_6H_5), 6.43 (1 H, s, aromatic in position 7), 6.32 (1 H, s, aromatic in position 5), 4.74 (3 H, br s exchanging with D_2O, OH and NH_2), 2.28 and 2.03 (each 3 H, 2 s, 2 CH_3); IR ν_{NH_2} 3480–3460, ν_{OH} 3345, $\nu_{C=N}$ 1635. Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.87; H, 5.99; N, 10.97.

Catalytic Hydrogenation of 2f. The hydrogenation of **2f** (1.5 g) was carried out under the same conditions described above for **2d**. The crude pasty product was treated with diisopropyl ether, and the undissolved solid was crystallized from toluene to give *N*-phenyl-*N'*-[2-(3,4,6-trimethylbenzofuranyl)]hydrazine (**5**): mp 204 °C; M_r (MS) 266; ^1H NMR (DMSO) 8.74 and 6.41 (each 1 H, 2 s exchanging with D_2O, 2 NH), 6.3–7.0 (5 H, m, aromatic), 6.20 (2 H, m, aromatic in ortho position of the C_6H_5 group), 2.22 and 2.10 (each 3 H, 2 s, 2 CH_3 in position 4 and 6), 1.60 (3 H, s, aromatic in position 3). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.23; H, 6.98; N, 10.48. The mother liquors were extracted with a 10% hydrochloric acid solution to remove the aniline, which was then recovered by alkalinization. The organic layer was evaporated to dryness and the residue distilled in vacuo to give 2,4-dimethyl-6-hydroxyacetophenone (**6**) (0.3 g) [bp 140 °C (0.2 mmHg), mp 54 °C] identical with an authentic sample prepared by independent synthesis.[15]

Catalytic Hydrogenation of 2g: 2-Acetamido-3,4,6-trimethylthianaphthene (7). A solution of **2g** (1.0 g) in ethyl acetate (30 mL) was hydrogenated in the presence of 10% Pd on charcoal (0.1 g) and acetic anhydride at 50 atm of hydrogen pressure at room temperature. Catalyst was filtered off and the solvent removed under reduced pressure. The residue was triturated with diisopropyl ether, and the undissolved solid was crystallized from toluene to give **7** (0.15 g) as a white solid with mp 206 °C: M_r (MS) 233; ^1H NMR δ 10.10 (1 H, s exchanging with D_2O, NH), 7.40 (1 H, s, aromatic in position 7), 6.88 (1 H, s, aromatic in position 5), 2.72, 2.52 and 2.34 (each 3 H, 3 s, 3 CH_3), 2.17 (3 H, s, $COCH_3$). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.90; H, 6.43; N, 6.00. Found: C, 66.51; H, 6.65; N, 6.06. Acetanilide could

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be recovered by chromatography from the diisopropyl ether solution.

***N*-Phenyl-*N'*-[2-(3,4,6-trimethylbenzofuranyl)]hydrazine (5).** To a stirred solution of the azo compound **2f** (0.32 g) in acetone (50 mL) were added zinc dust (2.0 g) and a saturated aqueous solution of ammonium chloride (10 mL) portionwise at 0–5 °C; stirring was maintained until the color disappeared. The resulting suspension was filtered and the clear solution diluted with ice-cold water. The pH was adjusted to 8 with concentrated ammonium hydroxide solution, and the separated solid was extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and evaporated to dryness to give a residue, which was treated with diisopropyl ether. The undissolved solid was crystallized from toluene to give the title compound **5** (0.17 g); its analytical and spectral data were identical with those described above for the product obtained from the catalytic hydrogenation of **2f**.

Acknowledgment. We thank Prof. Raffaello Fusco for his helpful advice throughout this research.

Registry No. **1a**, 78241-05-1; **1b**, 112374-86-4; **1c**, 112374-87-5; **1d**, 112374-88-6; **1e**, 112374-89-7; **1f**, 112374-90-0; **1g**, 112374-91-1; **1h**, 112374-92-2; **2a**, 112374-93-3; **2b**, 112374-94-4; **2c**, 112374-95-5; **2d**, 112374-96-6; **2e**, 112374-97-7; **2f**, 112374-98-8; **2g**, 112374-99-9; **2h**, 112375-00-5; **3**, 112375-01-6; **4**, 112375-02-7; **5**, 112375-03-8; **6**, 16108-50-2; **7**, 112375-04-9; AcC(Cl)=NNHPh, 18440-58-9; $PhNH_2$, 62-53-3; 3,5-$(Me)_2C_6H_3NH_2$, 108-69-0; *p*-AcC(Cl)=$NNHC_6H_4Cl$, 18247-78-4; PhCOC(Cl)=NNHPh, 75482-50-7; PhOH, 108-95-2; 3,5-$(Me)_2C_6H_3OH$, 108-68-9; 3,5-$(Me)_2C_6H_3SH$, 38360-81-5; PhSH, 108-98-5.

Regioselective Ring Opening in Annelated Benzocyclopropenes

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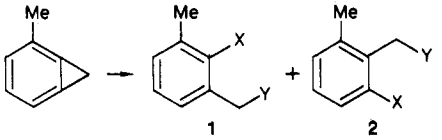
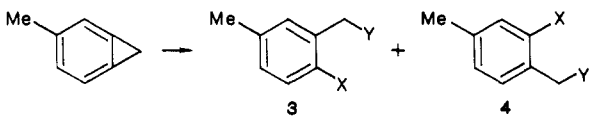
The facile cleavage of the three-membered ring of benzocyclopropenes by electrophiles is of interest with regard to both mechanism and synthesis.[1] Garratt and his coworkers[2] have prepared several asymmetrically substituted benzocyclopropenes and shown that the direction of ring cleavage can be controlled by the selection of electrophile. For example, 2-methylbenzocyclopropene reacts with bromine, iodine, and HCl to give the *m*-xylenes **1a–c** as the major products, whereas it reacts with silver nitrate



1 2

a, X = Y = Br; **b**, X = Y = I; **c**, X = H, Y = Cl; **d**, X = H, Y = OEt; **e**, X = H, Y = NHPh

in the presence of ethanol and aniline to give *o*-xylenes **2d,e** as the major products. Similarly, 3-methylbenzocyclopropene gives mainly *m*-xylenes **3a–c** with the halogens and HCl and gives *p*-xylenes **4d,e** with silver nitrate in ethanol or aniline.



3 4

a, X = Y = Br; **b**, X = Y = I; **c**, X = H, Y = Cl; **d**, X = H, Y = OEt; **e**, X = H, Y = NHPh

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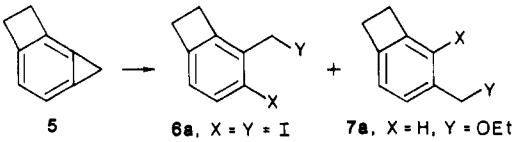
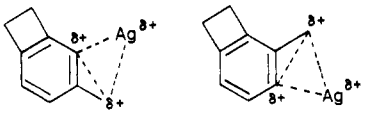
Cyclopropa[3,4]benzocyclobutene (**5**) also gives different products with halogens (**6a,b**) and silver nitrate in ethanol (**7a**), but in this case HCl gives the same type of product (**7b**) as silver ion. These differences in electrophilic be-



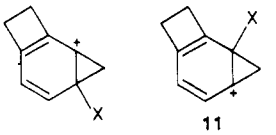
5 **6a**, X = Y = I; **b**, X = Y = Br **7a**, X = H, Y = OEt; **b**, X = H, Y = Cl

havior toward two types of reagents were suggested[2] to arise from attack of the silver ion (and the proton in the case of **5**) on the σ electrons of the cyclopropyl ring. If the reaction of **5** with silver ion proceeds via the σ route, then the observed regiochemistry would require that **8** be preferred to **9**.



8 9

The reaction with halogens presumably proceeds by attack on the π electrons to give the intermediate in which the positive charge is also located at the α position to the four-membered ring, i.e., **10**, in preference to **11**.



10 11

A tendency for benzocycloalkenes with strained rings to react with electrophiles mainly β to the ring junction was reported by Mills and Nixon[3] nearly 60 years ago. Subsequent studies on the electrophilic substitution reactions of benzocyclopropenes and biphenylene also show that the β position of these compounds is more reactive to electrophilic substitution.[4,5] Although a satisfying explanation[6] for these results has not been presented, rehybridization of the framework which occurs in these molecules because of the bond angle requirements of the small ring is most often presented.[7-9]

We report now the synthesis of two new asymmetrically fused benzocyclopropenes **12** and **13**, as well as their linearly fused isomers **14** and **15**, and their reactions with electrophiles. The syntheses were carried out by dehydrohalogenation of the Diels–Alder adducts of 1-bromo-2-chlorocyclopropene[10] and the appropriate diene. The starting materials and yields are presented in Table I.

Studies on the reactions of **12** and **13** with electrophiles showed that **12** follows a path similar to that observed by Garratt for **5**, whereas **13** yields both regioisomers with each electrophile. These results are presented in Table II. The linearly fused benzocyclopropenes **14** and **15** were

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(6) For example, it is not readily apparent why a positive charge located at the α-position (as a **10**) should be preferred.
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