mass spectrum *m/e* (rel intensity) 263 (M^+, 20), 232 (27), 231 (73), 217 (27), 216 (94), 204 (27), 203 (100), 189 (13), 188 (73), 175 (20), 147 (10).

Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 64.05; H, 6.45; N, 5.21.

Registry No.—**1**, 1830-54-2; **2a**, 504-02-9; **2b**, 126-81-8; **8**, 141-97-9; **9a**, 61062-44-0; **10c**, 61104-46-9; **11a**, 61062-45-1; **11b**, 61062-46-2; **12b**, 61062-47-3.

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Alkylations of 1-(4-Chlorophenyl)-3-ethoxy-1*H*-isoindole

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Abstraction of the benzylic proton from 1-(4-chlorophenyl)-3-ethoxy-1*H*-isoindole (**1a**) with sodium hydride gave the corresponding carbanion which was alkylated with a variety of alkyl halides to give the imino esters **1d–i**, **5** while oxidation yielded **1b**. Hydrolysis led to the lactams **2d–i**, **6** and 2-(4-chlorobenzoyl)benzoic acid ethyl ester, respectively. The tetrazolo compounds **4e–l** were prepared via the intermediates **3e–i**. Heating of **6** resulted in the formation of **7a** which could be reduced to the amine **7b**. From the imino ester **5** the triazole **9** was prepared.

Recently we have described the preparation of 1-(4-chlorophenyl)-3-ethoxy-1*H*-isoindole (**1a**) and its conversion to 1-amino-4-(4-chlorophenyl)phthalazine[1] via reaction with hydrazine. As a continuation of our efforts to explore the synthetic usefulness of **1a** we have prepared[2] a variety of 3-alkylated derivatives and converted them to the novel tricyclic systems.

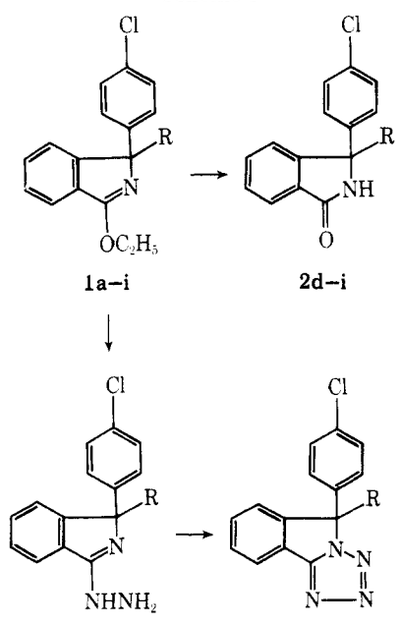
The proton of the benzylic position of **1a** was abstracted by sodium hydride in an aprotic solvent (DMF) to generate the corresponding carbanion of **1a**. Treatment of the carbanion with oxygen led to the crystalline hydroxy imino ester **1b** in 43% yield. For structure proof, **1b** was hydrolyzed to the known 2-(4-chlorophenyl)benzoic acid ethyl ester.[3] Spectral data indicated that **1b** exists in the cyclic form; no absorption for the open benzophenone tautomer was observed in the IR spectrum of **1b** (Nujol) in the region between 1650 and 1700 cm^{-1}. Furthermore, the UV spectrum of **1b** closely resembles that of the known methoxy homologue **1c**.[4]

The carbanion of **1a** on treatment with alkyl halides, e.g., methyl iodide, propargyl bromide, allyl bromide, isopropyl iodide, and benzyl chloride, gave the alkylated analogues **1e–i** (Tables II–IV). Reaction with methylene chloride led in good yield to **1d**, which was found to be inert in the presence of excess of carbanion.

The substituted 1-alkyl-1-(4-chlorophenyl)-3-ethoxy-1*H*-isoindoles **1d–i** on treatment with hydrochloric acid in ethanol were hydrolyzed to the corresponding 1-alkyl-1-(4-chlorophenyl)phthalimidines **2d–i**.[5a,b]

While the reaction of 1-(4-chlorophenyl)-3-ethoxy-1*H*-

Scheme I



1a–i **2d–i**

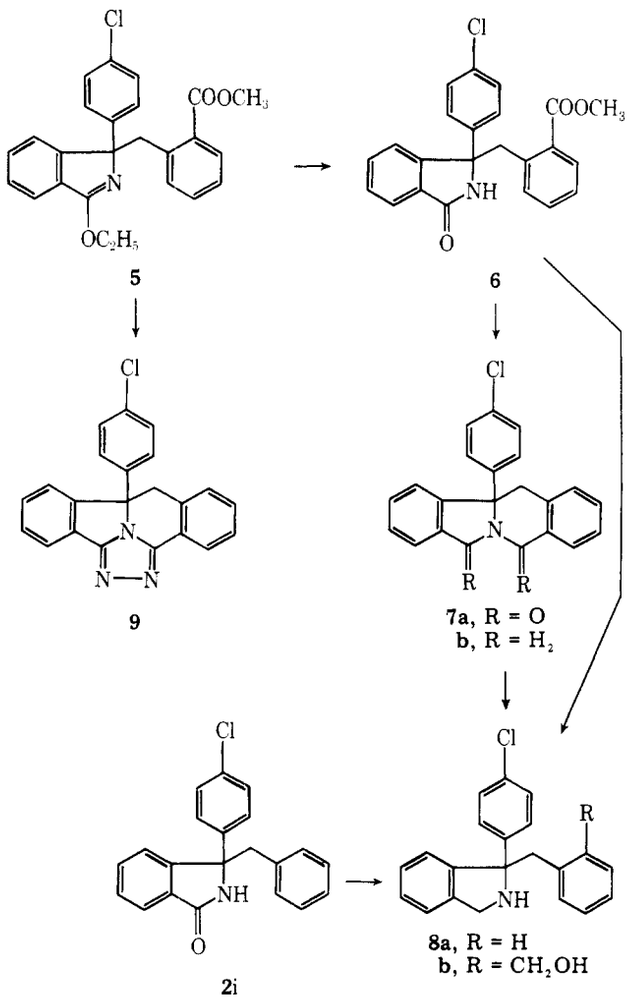
3e–i **4e–i**

a, R = H
b, R = OH
c, R = OCH_3
d, R = CH_2Cl
e, R = CH_3
f, R = $CH_2C{\equiv}CH$
g, R = $CH_2CH{=}CH_2$
h, R = i-C_3H_7
i, R = $CH_2C_6H_5$

isoindole (**1a**) with hydrazine led to 1-amino-4-(4-chlorophenyl)phthalazine,[1] the alkylated imino esters **1e–i** gave with hydrazine the 3-hydrazinoisoindoles **3e–i**. To ascertain that these reactions proceeded without rearrangement the hydrazinoisoindoles **3e–i** were cyclized[6] to the corresponding tetrazolo[5,1-*a*]isoindoles **4e–i**. Analytical and spectral data agreed with the proposed structures.

Treatment of the carbanion of **1a** with α-bromo-*o*-toluic acid methyl ester[12] gave the imino ester **5** as a liquid which was characterized by NMR and IR spectral data. After hydrolysis of **5** under acidic conditions the crystalline phthalimidine **6** was obtained in 46% overall yield. Pyrolysis of this ester lactam at 240 °C led to the tetracyclic imide **7a**, which was readily reduced to the tertiary amine **7b** in the presence of diborane. However, attempts to reduce the imide **7a** in the presence of lithium aluminum hydride gave the amino alcohol **8b**. The

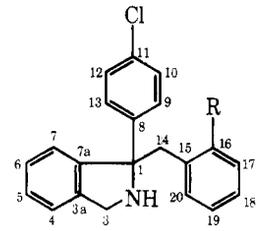
Scheme II



structure was assigned based on a comparative study of the ^{13}C NMR spectrum of **8b** with that of **8a**, a compound obtained from the reduction of **2i**. The chemical shifts of **8a** were assigned based on data available from the literature.[8a–c] The chemical shifts for the fully substituted aromatic carbons and all aliphatic carbons of **8a** are listed (see Table I) in juxtaposition to the corresponding values observed for the amino alcohol **8b**. The deviations are ≤0.4 ppm for the carbons 1–13, for which no changes are anticipated. The carbons 14–21 show the expected shifts due to the introduction of the hydroxymethyl group on C-16. The chemical shifts for the remaining aromatic carbons have been tentatively assigned as well.

For additional support of the assigned structure **8b**, we have reduced **6** in the presence of lithium aluminum hydride first at room temperature and then at elevated temperature. The reduction product was found to be identical with **8b** in every respect.

Table I. ^{13}C NMR Spectra of Compounds 8a and 8b



8a, R = H
b, R = CH_2OH (21)

8a			8b		
Absorption obsd, ppm	Rel intensity	Assignment	Absorption obsd, ppm	Rel intensity	Assignment
147.6	24	C-8	147.5	26	C-8
145.8	31	C-7a	146.1	35	C-7a
142.3	20	C-3a	142.1	35	C-3a
			141.6	38	C-16
137.6	50	C-15	135.7	52	C-15
131.3	21	C-11	131.4	20	C-11
130.7	219	C-16, 20	130.7	98	C-20
			129.0	100	C-17
128.7	170	C-10, 12	128.7	217	C-10, 12
128.0	166	C-9, 13	128.2	210	C-9, 13
127.9	189	C-17, 19			
127.2	112	C-6	127.4	126	C-6
			127.0	134	C-19
126.8	99	C-18			
126.4	89	C-5	126.5	158	C-5, 18
123.3	77	C-7	123.7	134	C-7
122.6	104	C-4	122.5	104	C-4
72.3	23	C-1	72.3	41	C-1
			61.7	150	C-21
50.5	110	C-3	50.6	125	C-3
46.9	103	C-14	43.0	135	C-14

The dual functionality of **5** prompted us to investigate the feasibility of a synthesis of the pentacyclic triazole **9**. We were successful in isolating the desired compound from **5** in the presence of hydrazine, albeit in low yield (10%). The product was obtained as a colorless solid and was fully characterized by spectral and analytical data.

Discussion

The NMR spectra of the compounds described in this paper exhibited the expected patterns[9,10] for the protons of the newly introduced side chains. Since spectral data for 2-benzyl-3-phenylphthalimide had been published,[9a] a direct comparison seemed of interest. For the *N*-benzyl case a difference in chemical shift of 1.75 ppm was observed for the two diastereotopic protons. In the case of our 3-benzyl-3-(4-chlorophenyl)phthalimidine (**2i**) a difference of only 7.5 Hz (0.125 ppm) was recorded and this despite the fact that the benzylic protons are located closer to the center of chirality than in the case of the *N*-benzyl compound. In accordance with the model[9a] both benzylic protons of **2i** are deshielded by the phenyl group in position 3 of the phthalimidine. It may therefore be concluded that in the lowest energy conformation the 1,2-diphenylethane portion of **2i** lies in a plane in an antiperiplanar arrangement with the chlorophenyl ring in and the phenyl ring perpendicular to the plane.

Compound **6** may be cited to illustrate this point further. The additional carbomethoxy group would preclude the presence of a "plane of symmetry" as defined above. That this is indeed the case may be concluded from the observation of

a quartet in the NMR spectrum of **6** centered at δ 4.04 ppm with a separation of the two doublets by 27.6 Hz (0.46 ppm).

A similar deshielding effect was observed for the chloromethyl compound **2d**. In this case a quartet centered at δ 4.19 ppm was observed, the two doublets being separated[11] by ($\Delta\nu$) 25.75 Hz (0.43 ppm).

Diastereotopic methyl groups[10] were observed in the NMR spectra of **2h**, **3h**, and **4h**. The largest degree of separation for the methyl groups in this series of compounds was recorded for the tetrazolo compound **4h**.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are not corrected. NMR spectra were measured on either a Varian A-60 and/or T-60 spectrometer and are recorded in δ (ppm) values from Me_4Si as internal standard. ^{13}C NMR spectra were measured on a Varian XL-100 spectrometer and are recorded in parts per million values from Me_4Si as internal standard. UV absorption spectra were measured in ethanol on a Cary spectrometer, Model 14. IR spectra were taken on a Perkin-Elmer Model 257 or 457. Gas–liquid chromatography was carried out on a Hewlett-Packard 5750 chromatograph. Mass spectra were taken on a LKB 9000 mass spectrometer.

3-Ethoxy-1-hydroxyl-1-(4-chlorophenyl)-1*H*-isoindole (1b). To the solution of 1.5 g (0.005 mol) of imino ester **1a** in 40 ml of absolute DMF there was added a catalytic amount (25 mg) of NaH to give a dark brown solution. The mixture was stirred at room temperature and treated with a stream of dry air during 2 h. The solvent was evaporated under reduced pressure and the residue was treated with water and extracted with methylene chloride. The solvent was evaporated to give 0.85 g of crude **1b** which was recrystallized from ethanol: yield 0.7 g (43%); mp 189–191 °C; *m/e* 287 (M^+); NMR ($CDCl_3$ + Me_2SO) δ 1.47 (t, 3, J = 7 Hz, CH_3) 4.6 (q, 2, J = 7 Hz, OCH_2), 6.7 (s, 1, exchangeable with D_2O, OH), 7.2–7.7 (m, 8, 2 C_6H_4); IR (Nujol) 3100 (OH), 1623 (C=N), 1580 cm^{-1}; UV 217 nm (ϵ 12 500), 325 (3500).

Anal. Calcd for $C_{16}H_{14}ClNO_2$ (287.8): C, 66.8; H, 4.9; N, 4.9; Cl, 12.3. Found: C, 66.8; H, 5.1; N, 4.8; Cl, 12.3.

Hydrolysis of 1b to 2-(4-Chlorobenzoyl)benzoic Acid Ethyl Ester. A mixture of 1.0 g (0.003 mol) of the imino ester **1b** and 1.0 ml of 1 N HCl solution in 30 ml of ethanol was heated to reflux for 3 h. The solid that precipitated from the cold solution was filtered off and recrystallized from ethanol to give 0.7 g (70%) of the benzoylbenzoic acid ethyl ester: mp 85–86 °C (lit.[4] mp 88 °C); *m/e* 288 (M^+); NMR ($CDCl_3$ + Me_2SO) δ 1.13 (t, 3, J = 7 Hz, CH_3), 4.16 (q, 2, J = 7 Hz, CH_2), 7.3–7.9 (m, 7, aromatic), 8.0–8.4 (m, 1, C_6H_1); IR (CH_2Cl_2) 1712 (COOEt), 1672 cm^{-1} (C=O).

1-Chloromethyl-1-(4-chlorophenyl)-3-ethoxy-1*H*-isoindole (1d). To the stirred suspension of 3.4 g (0.08 mol) of sodium hydride in 50 ml of absolute DMF a solution of 21.0 g (0.08 mol) of **1a** in 250 ml of DMF was added dropwise. The dark solution was kept at room temperature under an atmosphere of nitrogen for 2 h. Then 10.2 g (0.12 mol) of methylene chloride was added to the mixture and stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure, and the residue dissolved in methylene chloride and worked up in the usual way. The crude product (26 g) was chromatographed on silica gel to give 18.8 g (73%) of the product **1d** as a liquid: NMR ($CDCl_3$) δ 1.47 (t, 3, J = 7 Hz, CH_3), 4.06 (q, 2, J = 11 Hz, $\Delta\nu$ = 10.2 Hz, CH_2Cl), 4.56 (q, 2, J = 7 Hz, OCH_2), 7.1–7.8 (m, 8, 2 C_6H_4); IR (CH_2Cl_2) 1622 cm^{-1} (C=N).

3-Chloromethyl-3-(4-chlorophenyl)phthalimidine (2d). A mixture of 4.0 g (0.01 mol) of the imino ester **1d**, 75 ml of ethanol, and 4 ml of 2 N HCl was heated on the water bath during 3 h. From the cold solution 3.0 g (80%) of **2d** precipitated, mp 160–163 °C. A sample was recrystallized from methylene chloride/hexane: mp 165–167 °C; *m/e* 291 (M^+), 242 (M^+ – CH_2Cl); NMR ($CDCl_3$) δ 4.19 (q, 2, J = 11 Hz, $\Delta\nu$ = 24.7 Hz, CH_2Cl), 7.1–7.7 (m, 7, C_6H_4 + C_6H_3), 7.7–8.0 (m, 1, C_6H_1), 8.25 (broad, 1, NH); IR (CH_2Cl_2) 3420 (NH), 1705 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{11}Cl_2NO$ (292.2): C, 61.7; H, 3.8; N, 4.8; Cl, 24.3. Found: C, 61.8; H, 3.8; N, 4.8; Cl, 24.6.

1-(4-Chlorophenyl)-3-ethoxy-1-[2-(methoxycarbonyl)benzyl]-1*H*-isoindole (5). To the stirred suspension of 2.64 g (0.11 mol) of sodium hydride in absolute DMF there was added dropwise a solution of 21.6 g (0.08 mol) of **1a** in 250 ml of absolute DMF. After 2 h at room temperature and under an atmosphere of nitrogen 26.0 g (0.11 mol) of methyl α-bromo-*o*-toluate[7] was added and the mixture was stirred overnight. The solvent was evaporated under reduced pressure. The residual liquid was dissolved in methylene chloride and washed with water. After evaporation of the solvent the residue was filtered through silica gel with benzene as eluent: yield 31 g (92%); NMR ($CDCl_3$) δ 1.38 (t, 3, J = 7 Hz, CH_2CH_3), 3.76 (s, 3, OCH_3), 4.15 (s, 2, $C_6H_4CH_2$), 4.49 (q, 2, J = 7 Hz, OCH_2), 6.9–7.8 (m, 8, aromatic); IR (CH_2Cl_2) 1720 (C=O), 1624 (C=N), 1600 cm^{-1}.

3-(4-Chlorophenyl)-3-[2-methoxycarbonyl)benzyl]phthalimidine (6). A mixture of 28.0 g (0.067 mol) of the liquid **5**, 150 ml of ethanol, and 40 ml of 1 N HCl solution was stirred at room temperature for 12 h. The resultant solid was filtered off to give 12.5 g (46% for two steps) of crude **6**, mp 165–170 °C. After recrystallization from ethanol 10.0 g of **6** was obtained: mp 182–184 °C; *m/e* 391 (M^+); NMR ($CDCl_3$) δ 3.84 (s, 3, OCH_3), 4.04 (q, 2, J = 13 Hz, $\Delta\nu$ = 27.6 Hz, CH_2), 6.3–6.6 (m, 1, aromatic H), 6.7–7.7 (m, 11, 1 exchangeable with D_2O, 10 aromatic H + NH), 7.7–8.0 (m, 1, 1 aromatic H); IR (CH_2Cl_2) 3400 (NH), 1690–1720 (C=O), 1595 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}ClNO_3$ (391.9): C, 70.5; H, 4.6; Cl, 9.0. Found: C, 70.8; H, 4.6; Cl, 9.2.

12a-(4-Chlorophenyl)-12,12a-dihydro-5*H*-7*H*-isoindolo-[2,1-*b*]isoquinoline-5,7-dione (7a). Heating of 8.0 g (0.02 mol) of **6** to 240 °C resulted in the formation of 7.2 g (92%) of **7a** after recrystallization from methylene chloride/hexane: mp 307–308 °C; *m/e* 359 (M^+); NMR (CF_3COOH) δ 4.0 (q, 2, J = 16.5 Hz, $\Delta\nu$ = 39.7 Hz, CH_2), 7.0–8.0 (m, 10, aromatic H), 8.0–8.5 (m, 2, aromatic H); IR (Nujol) 1745 (C=O), 1672 (C=O), 1604 cm^{-1}; UV 263 nm (ϵ 18 900).

Anal. Calcd for $C_{22}H_{14}ClNO_2$ (359.8): C, 73.4; H, 3.9; N, 3.9; Cl, 9.9. Found: C, 73.8; H, 3.8; N, 4.1; Cl, 10.3.

12a-(4-Chlorophenyl)-12,12a-dihydro-5*H*,7*H*-isoindolo-[2,1-*b*]isoquinoline (7b). A suspension of 10.0 g (0.028 mol) of **7a** in 800 ml of dry THF was treated with 100 ml (0.1 mol) of 1 M diborane solution and kept at room temperature for 2 h under an atmosphere of nitrogen. The solvent was evaporated under reduced pressure and the residue was dissolved with methylene chloride and washed with water. After evaporation of the solvent 10.5 g of crude **7b** was obtained which was crystallized twice from ethanol to give 6.1 g (66%) of pure **7b**: mp 99–101 °C; *m/e* 331 (M^+); NMR ($CDCl_3$) δ 3.27 (q, 2, J = 16 Hz, $\Delta\nu$ = 9.3 Hz, CH_2), 3.94 (s, 2, CH_2), 4.23 (q, 2, J = 12 Hz, $\Delta\nu$ = 21.9 Hz, CH_2), 6.8–7.5 (m, 12, aromatic H); IR (CH_2Cl_2) 1585 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}ClN$ (331.9): C, 79.6; H, 5.5; N, 4.2; Cl, 10.7. Found: C, 79.5; H, 5.4; N, 3.9; Cl, 10.7.

1-Benzyl-1-(4-chlorophenyl)isoindoline (8a). The mixture of 1.5 g (0.004 mol) of **2i** and 1.0 g (0.03 mol) of $LiAlH_4$ in 50 ml of THF was heated to reflux overnight under an atmosphere of nitrogen. After the usual workup the product was treated with maleic acid to give 0.4 g of **8a**: mp after recrystallization from methanol/ether 176–177 °C; ^{13}C NMR, see Table I; NMR ($CDCl_3$) δ 3.82 (s, 2, CH_2N), 4.39 (q, 2, J = 15 Hz, $\Delta\nu$ = 16 Hz, $C_6H_5CH_2$), 6.05 (s, 2, maleic acid), 6.7–8.7 (m, 13, aromatic), 11.6–13.0 (broad, 3, NH); IR (Nujol) 2400–3400 (NH, acid), 1620 cm^{-1} (aromatic).

Anal. Calcd for $C_{21}H_{18}NCl{\cdot}C_4H_4O_4$ (438.9): C, 68.9; H, 5.1; N, 3.2; Cl, 8.1. Found: C, 69.1; H, 5.2, N, 3.6; Cl, 8.3.

The base was prepared from the salt in the usual way.

1-(4-Chlorophenyl)-1-[2-(hydroxymethyl)benzyl]isoindoline (8b). The mixture of 2.0 g (0.0055 mol) of **7a** and 2.0 g (0.053 mol) of $LiAlH_4$ in 110 ml of THF was kept at room temperature for 2 h and then heated to reflux overnight under an atmosphere of nitrogen. Following the usual workup there was isolated 1.7 g of crude material from which 0.3 g (16%) of **8b** was obtained: mp 163–165 °C; recrystallized from methanol/water mp 164–166 °C; *m/e* 349 (M^+); ^{13}C NMR, see Table I; NMR ($CDCl_3$) δ 2.5–3.3 (m, 2, CH_2), 3.7–4.1 (m, 2, CH_2), 4.65 (q, J = 11 Hz, $\Delta\delta$ = 9.5 Hz, CH_2OH), 5.9–6.2 (m, 1, aromatic), 6.6–7.6 (m, 11, aromatic), 4.2–5.6 (broad, 2, exchangeable with D_2O, NH, OH); IR (CH_2Cl_2) 3100 (NH, OH), 1590 cm^{-1} (weak).

Anal. Calcd for $C_{22}H_{20}NOCl$ (349.9): C, 75.5; H, 5.8; N, 4.0; Cl, 10.1. Found: C, 75.2; H, 5.4; N, 3.9; Cl, 10.1.

The same compound was obtained starting with **6** under conditions equivalent to those employed above.

6b-(4-Chlorophenyl)dibenzo[*af*]-*s*-triazolo[3,4,5-*cd*]indolizine (9). A mixture of 2.0 g (0.005 mol) of the imino ester **5** and 10.0 g (0.31 mol) of hydrazine was heated to reflux for 3 h. The excess of hydrazine was evaporated under reduced pressure and the residue was dissolved in methylene chloride to give 0.2 g (11%) of **9** as a white solid: mp 275–277 °C; *m/e* 355 (M^+); NMR ($CDCl_3$) δ 3.6 (q, 2, J = 15 Hz, $\Delta\nu$ = 34.9 Hz, CH_2), 7.0–7.7 (m, 10, aromatic H), 7.8–8.2 (m, 2, aromatic H); IR (CH_2Cl_2) 1612 cm^{-1} (weak); UV 219 nm (ϵ 36 900), 255 (9400), 285 (11 800).

Anal. Calcd for $C_{22}H_{14}ClN_3$ (355.8): C, 74.3; H, 4.0; N, 11.8; Cl, 10.0. Found: C, 74.1; H, 4.4; N, 12.1; Cl, 10.0.

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Registry No.—**1a,** 26859-66-5; **1b,** 61139-60-4; **1c,** 41581-41-3; **1d,** 61139-61-5; **1e,** 28006-50-0; **1f,** 36033-98-4; **1g,** 36033-95-1; **1h,** 36037-78-2; **1i,** 36033-91-7; **2d,** 61139-62-6; **2e,** 61139-55-7; **2f,** 61139-56-8; **2g,** 61139-57-9; **2h,** 61139-58-0; **2i,** 61139-59-1; **3e,** 36033-89-3; **3f,** 36033-99-5; **3g,** 36033-96-2; **3h,** 36037-79-3; **3i,** 36033-92-8; **4e,** 28006-52-2; **4f,** 36033-97-3; **4g,** 36033-94-0; **4h,** 36037-71-1; **4i,** 36033-90-6; **5,** 61139-63-7; **6,** 61139-64-8; **7a,** 61139-65-9; **7b,** 61139-66-0; **8a,** 61139-53-5; **8b,** 61139-54-6; **9,** 61139-67-1; 2-(4-chlorobenzoyl)benzoic acid ethyl ester, 51476-10-9; methyl α-bromo-*o*-toluate, 2417-73-4.

Supplementary Material Available. Additional experimental and spectral and analytical information (Tables II–IV) (4 pages). Ordering information is given on any current masthead page.

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Furazans and Furazan Oxides. 7.[1] Interconversions of Anthranils, Benzofurazan Oxides, and Indazoles

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7-Nitroanthranil (1, R = R′ = H) and 4-formylbenzofurazan oxide (2, R = R′ = H) equilibrate on heating. The latter condenses with primary amines and the resulting imines rearrange to 7-nitroindazoles (8). The corresponding 6-methoxy and 6-chloro derivatives of 1 behave similarly. Neither 5- nor 6-nitroanthranil forms an indazole on heating with aniline or other primary amines.

An example of a general heterocyclic rearrangement which was first described some years ago[2] is the interconversion of 7-nitroanthranils with 4-acylbenzofurazan oxides (1 ⇌ 2). In the earliest case to be investigated[2,3] (1, R = Me; R′ = H) the reaction was found to proceed in the direction 2 → 1, to provide 1 exclusively. Later,[4] an example was discovered (1 ⇌ 2, R = H; R′ = Cl) in which at normal temperatures the furazan oxide isomer 2 was thermodynamically the more stable compound, and it was suggested that steric inhibition of resonance of the nitro group with the ring system of 1 led to its destabilization, with consequent preference for structure 2. We now find that, in the simplest example of this system (1 ⇌ 2, R = R′ = H) the equilibrium balance is finely poised, with only a moderate preference (K = [1]/[2] = ca. 2) for 1.

7-Nitroanthranil (1, R = R′ = H) was prepared as follows. 3-Nitrosalicylaldehyde (3) was warmed with tosyl chloride in dry pyridine. Initially, a small amount of the tosylate 4 separated: this redissolved, and the pyridinium salt[5a] 5 crystallized out. The salt 5 was dissolved in aqueous sodium azide solution, giving the azide 6, which was decomposed in hot toluene.

Condensation of the acyl group of 2 with a primary amine, followed by rearrangement, leads to the formation of 2-substituted indazoles (7 → 8).[2,3] Consistent with this, we find that reflux of the nitroanthranil (1, R = R′ = H) with aniline produces 7-nitro-2-phenylindazole (8, R′ = H; R″ = Ph), through condensation of the intermediate 4-formylbenzofurazan oxide (2, R = R′ = H) with the aniline. An attempt to extend this reaction to the preparation of 2-methyl-7-nitroindazole (8, R′ = H; R″ = Me), by heating 1 (R = R′ = H) with methylamine in ethanol, led to the formation of ethyl 3-nitroanthranilate (9), and the corresponding methylamide (10). It appears that the alkylamine is sufficiently strong a base to