triazin-5-yl]amino]benzoate (20). A solution of **19** (150 mg) and ethyl *p*-aminobenzoate (155 mg) in dioxane (20 ml) was refluxed for 72 hr and evaporated to dryness in vacuo. The residue was triturated with Et_2O, and the resulting solid was reprecipitated from a DMSO solution by the addition of H_2O, yield 46 mg (22%), mp 157° dec taken rapidly. A sample was dried in vacuo over P_2O_5 at 78° for analysis. The ^1H NMR spectrum indicated that this sample was contaminated with a trace amount of an unidentified material.

7-Amino-3-(azidomethyl)-5-(benzylthio)pyrimido[5,4-*e*]-*as*-triazine (22). A mixture of **19** (100 mg), NaN_3 (25 mg), and KI (55 mg) in DMAC (2 ml) was stirred at room temperature for 18 hr and diluted with H_2O (10 ml), and the resulting precipitate was collected by filtration and recrystallized from C_6H_6: yield, 42 mg (60.5%); mp 210° dec; M^+ *m/e* 325. The ^1H NMR spectrum of this sample showed the presence of C_6H_6.

***N*-[*p*-[[[7-Amino-5-(benzylthio)pyrimido[5,4-*e*]-*as*-triazin-3-yl]methyl]amino]benzoyl]-L-glutamic Acid (23).** A mixture of **19** (500 mg, 1.57 mmol), *p*-aminobenzoyl-L-glutamic acid (425 mg, 1.59 mmol), and KI (250 mg) in DMAC (10 ml) was stirred at room temperature for 40 hr and diluted with H_2O (100 ml). The resulting precipitate was collected by filtration, washed with H_2O and Et_2O, and dried in vacuo over P_2O_5, yield 648 mg. This material appeared to decompose at 203°. A solution of this product in ethanolic HCl showed several spots on TLC (9:1 $CHCl_3$–MeOH), one of which was identical with that of the diethyl ester of **23**.[5]

When a portion of this sample was treated with 0.1 *N* HCl to obtain the free acid, elemental analyses indicated partial loss of the benzylthio group in the recovered material.

7-Azafolic Acid (24).[5] A mixture of **23** (50 mg) in oxygen-free 0.1 *N* NaOH (10 ml) was stirred at room temperature for 18 hr, neutralized with 1 *N* HCl, and centrifuged. The resulting residue was washed with Et_2O and identified as **24** by TLC [BuOH (5)–HOAc (2)–H_2O (3)] and by its uv and ir spectra, yield 19 mg.

Also, this compound was prepared by treatment of a solution of **23** (50 mg) in DMSO (2 ml) containing $KHCO_3$ (100 mg) and H_2O (1 ml) at 90° for 18 hr, yield 10 mg.

***N*-[*p*-[[(5,7-Diaminopyrimido[5,4-*e*]-*as*-triazin-3-yl)methyl]amino]benzoyl]-L-glutamic Acid (7-Azaaminopterin 25).** A mixture of **23** (200 mg) and NaN_3 (100 mg) in DMSO (2 ml) was heated with stirring at 90° for 4 hr and diluted with H_2O (20 ml), and the resulting solution was adjusted to pH 2 (paper) with 1 *N* HCl and centrifuged. The residue was washed successively with 0.1 *N* HCl, Et_2O, 10% aqueous DMAC, and H_2O and dried in vacuo over P_2O_5, yield 95 mg, mp >270°. A solution of this product in ethanolic HCl was shown to contain the diethyl ester of **25**[5] by TLC (EtOH). Another spot in the TLC of this solution was identified as the diethyl ester of **24**, presumably formed via acidic hydrolysis of the 5-amino group of **25** or its diethyl ester.

Acknowledgments. The authors are indebted to Dr. W. C. Coburn, Jr., and members of the Molecular Spectroscopy Section of Southern Research Institute, who performed most of the microanalytical and spectral determinations reported.

Registry No.—**1**, 30855-45-9; **3**, 55428-87-0; **6**, 30855-48-2; **7**, 55428-88-1; **9**, 55428-89-2; **11**, 55428-90-5; **12**, 55428-91-6; **13**, 31736-47-7; **14**, 55428-92-7; **16**, 55428-93-8; **16** HCl, 55428-94-9; **17** HCl, 55428-95-0; **18**, 55428-96-1; **19**, 55428-97-2; **20**, 55428-98-3; **22**, 55428-99-4; **23** K salt, 55429-00-0; **24**, 51043-68-6; **25**, 55429-01-1; ethyl *p*-aminobenzoate, 94-09-7; *p*-aminobenzoyl-L-glutamic acid, 4271-30-1; ethyl ortho(ethoxycarbonyl)acetate, 32650-62-7.

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(17) Melting points were determined on a Kofler-Heizbank apparatus.

Synthesis of 3,3a-Dihydro-8*H*-pyrazolo[5,1-*a*]isoindol-8-ones and 8*H*-Pyrazolo[5,1-*a*]isoindol-8-ones

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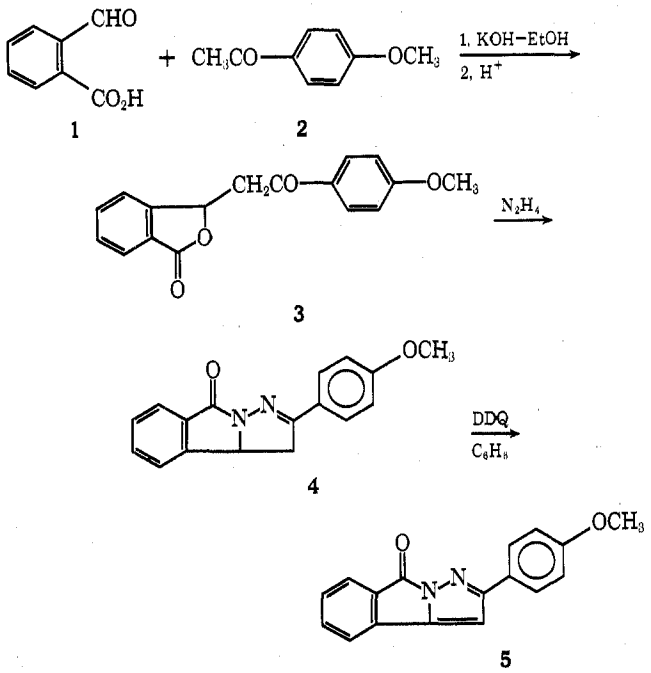
3-(4-Methoxyphenacyl)phthalide (**3**) arises from the base-catalyzed condensation of phthalaldehydic acid (**1**) with 4-methoxyacetophenone (**2**), and readily undergoes cyclization with hydrazine to form 2-(4-methoxyphenyl)-3,3a-dihydro-8*H*-pyrazolo[5,1-*a*]isoindol-8-one (**4**). Dehydrogenation of **4** produces 2-(4-methoxyphenyl)-8*H*-pyrazolo[5,1-*a*]isoindol-8-one (**5**). This synthetic sequence is completely general, and may be used to prepare numerous analogs of structures **3–5**.

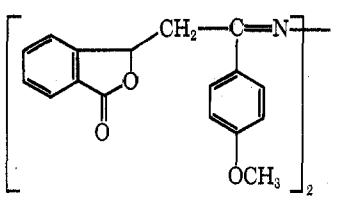
The condensation of 3,4-dimethoxyphthalaldehydic acid (opianic acid) with acetone and acetophenone under Claisen conditions to give 1:1 and 1:2 products was described in 1891 by Goldschmiedt,[1] elaborated by Hemmelmayr[2,3] shortly thereafter, and extended to phthalaldehydic acid (**1**) by Hamburger[4] in 1898. We have found their structural assignments of these reaction products as ketonic phthalide derivatives to be essentially correct,[5] and have investigated their further reaction products with hydrazine.[6,7] Hamburger[4] described the reaction products of 3-phenacylphthalide with hydroxylamine and phenylhydrazine, but his structural conclusions were uncertain, and the present work establishes the reaction course of carbonyl reagents with these interesting compounds.

Our exploratory work was done with the condensation product of **1** and 4-methoxyacetophenone (**2**) (Scheme I).

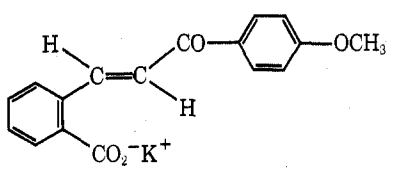
Scheme I



The product of this reaction, 3-(4-methoxyphenacyl)-phthalide (**3**), reacts normally at the ketonic carbonyl with hydroxylamine and semicarbazide, but undergoes a further cyclization with hydrazine to form pale yellow 2-(4-methoxyphenyl)-3,3a-dihydro-8*H*-pyrazolo[5,1-*a*]isoindol-8-one (**4**). Simple hydrazones of structure **3** have not been isolated, but small amounts of the azine **6** accompany **4**.



6

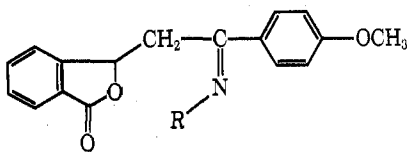


7

Dehydrogenation of **4** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gives 2-(4-methoxyphenyl)-8*H*-pyrazolo-[5,1-*a*]isoindol-8-one (**5**) as a bright yellow, crystalline solid. Our interest in structures **3–5** arises from their plant growth regulatory activity.[6-13] The synthetic procedures illustrated by the preparation of structures **3–5** are quite general, and some representative examples of their analogs (**8–10**) are listed in Table I.

Discussion

The initial condensation product of **1** and **2** in aqueous ethanolic KOH is the potassium salt **7**, which precipitates from the basic reaction mixture. The *trans*-chalcone structure is evident from its spectra [ν_{max} (Nujol) 1650, 1610, 1580 cm^{-1}; NMR (DMSO-d_6) two doublets (J = 16 Hz) at δ 8.70 and 7.57]; an intermediate ketol has not been seen in this reaction. In preparing the analogs **8** (Table I), the intermediate potassium salt does not always precipitate, but in all cases acidification precipitates the cyclized 3-phenacylphthalide derivative. The reaction of **3** with hydrazine or hydrazine salts in the presence of a tertiary base gives **4** as the major product; the yield of the minor product **6** may be enhanced by reducing the molar proportion of hydrazine used, but the ratio of **4**:**6** is always much larger than unity, indicating that cyclization is the strongly preferred pathway.[14] No simple hydrazone (**11**) of phthalide **3** has been isolated, but substitution of hydroxylamine for hydrazine gives the simple oxime (**12**), which was further characterized as its carbamate (**13**); similar substitution of semicarbazide for hydrazine gives the simple semicarbazone (**14**). Azine, oxime, and semicarbazone formation suggest that hydrazine also attacks first at the ketonic carbonyl, and the NH_2 group of the transient intermediate hydrazone **11** then attacks the lactone under the existing basic conditions to form **4**. This is supported by the observation that **3** does not react with hydrazine salts unless 1 equiv of tertiary base is present. Competition of a second molecule of **3** for the free NH_2 terminus of **11** (formation of **6**) is hindered both sterically and by the lower intrinsic reactivity of this moiety; the lactone ring is suitably placed for further nucleophilic attack, followed by ring opening, dehydration, and recyclization to **4**. No cyclic eight-membered intermediate has been isolated from this reaction, and this is not surprising in view of attempts to prepare analogous 1,4-diaza systems,[15,16] and the known propensity for intramolecular reactions to occur in eight-membered rings. Structure **4** and its analogs **9** are readily dehydrogenated to **5** and its analogs **10** in refluxing benzene with DDQ.



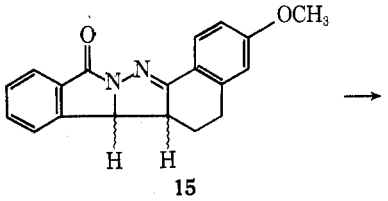
11, R = NH_2
12, R = OH
13, R = $OCONHCH_3$
14, R = $NHCONH_2$

The brief note published by Leclerc[17] concerning the preparation of the parent phenyl compound (**10**, entry 25, Table I) contains two serious errors in the spectral identification of this compound. The fused γ-lactam structure **5** is characterized by a weak band at 1780–1790 cm^{-1} and a strong band at 1760 cm^{-1} in the infrared, and by a pair of intense maxima at 346 nm (ϵ 12,100) and 331 (22,300) in the ultraviolet in an *unreactive solvent* such as THF. Corresponding values for **10** (R = C_6H_5) are λ_{max} (THF) 337 nm (ϵ 10,960) and 323 (10,880). Leclerc quotes ν_{max} 1790 and 1555 cm^{-1}, and λ_{max} (EtOH) 335 nm (ϵ 1480); the 1555-cm^{-1} value is an obvious misprint, but the low value of the extinction coefficient in the uv recorded by him is due to reaction with the solvent, a phenomenon which we shall discuss in a subsequent paper.

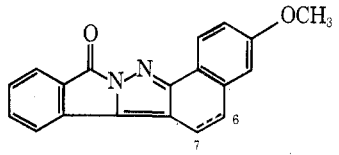
Two special examples which illustrate the ease of pyrazole formation are shown in the sequence **15–17** (Scheme II), in which the heterocyclic ring of **4** and **5** has been connected to the 2 substituent by a two-carbon bridge to restrict the rotation of the system. The mixture of geometric isomers (**15**) undergoes stepwise dehydrogenation to **16** and **17**. The use of 1 molar equiv of DDQ produces **16** exclusively; **16** can then be converted to **17** with a further 1 molar equiv of DDQ.

Spectra. The structures of **3–5** and their analogs are clearly assignable from their spectra. In the infrared, the phenacylphthalide **3** shows its lactone absorption at 1765 cm^{-1} and its ketone absorption at 1680 cm^{-1}; the fused γ-

Scheme II



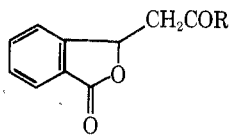
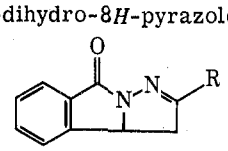
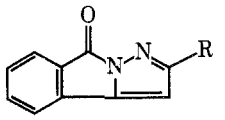
15



16, 6,7 single bond
17, 6,7 double bond

lactam carbonyl of 4 at 1700 cm^{-1} shifts to a weak band at 1780 cm^{-1} and a strong band at 1760 cm^{-1} on dehydrogenation to **5**. In the ultraviolet, colorless phthalide **3** has λ_{max} (CH_2Cl_2) 282 nm (ϵ 20,800) and 276 (20,200); pale yellow fused γ-lactam **4** has λ_{max} (CH_2Cl_2) 323 nm (ϵ 18,080), 277 (9080), and 268 (9150), while bright yellow **5** has λ_{max} (THF) 346 nm (ϵ 12,100), 331 (22,300), 285 (22,300), 260 (33,600), and 240 (32,000). In the NMR the $-CH_2CH-$ protons of **3** and **4** show a distinct ABX pattern; in **3** the tertiary proton (X) is centered at δ 6.13 ppm and the CH_2 protons (AB) at δ 3.75 ppm, while in **4** where the system is part of a five-membered ring, the X part is at δ 5.40 ppm, and the AB part is at δ 3.22 ppm. The coupling constants in the ABX pattern of **4**, obtained by decoupling its 100-MHz spectrum, are $J_{3a}J_{3\text{-trans}}$ = 10.64 Hz, $J_{3a}J_{3\text{-cis}}$ = 10.95 Hz, and $J_{3\text{-cis}3\text{-trans}}$ = −16.46 Hz. The pyrazole proton of **5** is

Table I
Synthesis of 8H-Pyrazolo[5,1-*a*]isoindol-8-ones[a]

Entry	R	Yield, %	Mp, °C	Recrystn solvent	Registry no.
	A. 3-Substituted Phthalides				
					
	8				
1	4-$CH_3OC_6H_4$ (3)	79	119.5–120	MeOH	
2	4-$C_2H_5OC_6H_4$	72.5	136.5–137.5	MeOH	55222-52-1
3	2,4-$(CH_3)_2C_6H_3$	68	112.5–113	EtOH	55222-53-2
4	2,4,6-$(CH_3)_3C_6H_2$	82	150–152	EtOH–$CHCl_3$	55222-54-3
5	3-$CH_3C_6H_4$	71	96–98	C_6H_6–C_6H_{12}	55222-55-4
6	4-$CF_3C_6H_4$	66	150–153	EtOH	55222-56-5
7	3-BrC_6H_4	73	124–127	CH_3CN	55222-57-6
8	3,4-$Cl_2C_6H_3$	98	184–186	CH_3CN	55222-58-7
9	4-FC_6H_4	62	130–133	C_6H_6	55222-59-8
10	$(CH_3)_3C$	8	72–73	MeOH	55222-60-1
	B. 2-Substituted 3,3a-dihydro-8*H*-pyrazolo[5,1-*a*]isoindol-8-ones				
					
	9				
11	4-$CH_3OC_6H_4$ (4)	88.5	177–178.5	MeOH	
12	4-$C_2H_5OC_6H_4$	58	157.8–159	MeOH	55222-61-2
13	2,4-$(CH_3)_2C_6H_3$	91	150.5–151.5	MeOH	55222-62-3
14	2,4,6-$(CH_3)_3C_6H_2$	38	129–131	MeOH	55222-63-4
15	3-$CH_3C_6H_4$	85	156–158	CH_3CN	55222-64-5
16	4-$CF_3C_6H_4$	82	239–241	CH_3CN	55222-65-6
17	3-BrC_6H_4	65	220–223	CH_3CN	55222-66-7
18	3,4-$Cl_2C_6H_3$	95	226–228	Dioxane	55222-67-8
19	4-FC_6H_4	75	171–173	MeOH	21138-14-7
20	$(CH_3)_3C$	7	118–119	C_6H_{12}	55222-68-9
	C. 2-Substituted 8*H*-pyrazolo[5,1-*a*]isoindol-8-ones				
					
	10				
21	4-$CH_3OC_6H_4$ (5)	83	186–187	Acetone	
22	4-$C_2H_5OC_6H_4$	70	171–172	Acetone	37564-19-5
23	2,4-$(CH_3)_2C_6H_3$	63	183–184	Acetone	37564-18-4
24	2,4,6-$(CH_3)_3C_6H_2$	20	153 dec	Acetone	55222-69-0
25	C_6H_5	29	146–147	Acetone	35564-20-8

[a] Satisfactory analyses (±0.3% for C, H) were reported for the compounds in part A of Table; analyses for C, H, N (±0.3%) were reported for compounds in parts B and C. Ed.

distinct from the benzenoid protons (δ 7.95–6.88 ppm) as a sharp singlet at δ 6.63 ppm. The spectra of analogs **8–10** follow the above patterns.

Experimental Section[18]

The general procedures described in detail for **3–5** were used to prepare the analogs listed in Table I.

3-(4-Methoxyphenacyl)phthalide (3). A solution of 85% KOH (66 g, 1.0 mol) in 50% EtOH (200 ml) was added dropwise to a vigorously stirred solution of phthalaldehydic acid (**1**, 75 g, 0.50 mol), 4-methoxyacetophenone (**2**, 75 g, 0.50 mol), and EtOH (300 ml) maintained at 25–30°. The mixture solidified after 75% of the KOH had been added, and it was necessary to add a further 600 ml of EtOH and continue the stirring for 30 min to complete the reaction. The potassium salt **7** was filtered, rinsed with EtOH, and air dried. This salt contained an indefinite amount of water and did not give satisfactory analysis, but its structure is clear from its spectra (see text). The crude salt **7** was dissolved in H_2O (500 ml), acidified with HCl, cooled, and filtered to give phthalide **3** (82 g). Concentration and acidification of the reaction mother liquors gave a further 29.8 g of **3**, total crude yield 111.8 g (0.396 mol, 79%), of material which was sufficiently pure for condensation with hydrazine. Recrystallization of a small sample (MeOH) gave pure 3-(4-methoxyphenacyl)phthalide as colorless crystals, mp 119.5–120°.

2-(4-Methoxyphenyl)-3,3a-dihydro-8*H*-pyrazolo[5,1-*a*]-isoindol-8-one (4). A stirred solution of phthalide **3** (14.0 g, 0.05 mol) in EtOH (400 ml) was heated to reflux and treated consecutively with a solution of hydrazine dihydrochloride (10.0 g, 0.10 mol) in H_2O (50 ml), and with triethylamine (20 g, 0.20 mol). The heating was continued for 2–3 hr, then the solution was cooled, acidified with HCl, concentrated to one-third its volume, diluted to turbidity with H_2O, and allowed to stand. The pale yellow, crystalline product **4** was filtered, yield 12.3 g (88.5%), mp 170–171°. Recrystallization (MeOH) gave 2-(4-methoxyphenyl)-3,3a-dihydro-8*H*-pyrazolo[5,1-*a*]isoindol-8-one, mp 177–178.5°. The use of hydrazine hydrate in place of the hydrochloride was equally satisfactory, either in the presence of Et_3N or with an extra 1 molar equiv of hydrazine hydrate.

3-(4-Methoxyphenacyl)phthalide azine (6) was obtained as a yellow, insoluble solid by filtering hot some of the reaction mixtures used to prepare **4**. Azine **6** has mp 185–185.5°; ν_{max} (Nujol) 1775, 1615, 1565 cm^{-1}; λ_{max} (CH_2Cl_2) 338 nm (ε 29,200), 282 (12,380), 275 (11,640); ^1H NMR ($CDCl_3$) δ 8.0–6.95 (m, 16 H, aromatic), 6.0 (X part, 2 H, tertiary protons), 3.75 (AB part, 4 H, CH_2), 3.95 ppm (s, 3 H, OCH_3). Anal. Calcd for $C_{34}H_{28}N_2O_6$: C, 72.84; H, 5.03; N, 5.00. Found: C, 72.90; H, 5.12; N, 4.98.

2-(4-Methoxyphenyl)-8*H*-pyrazolo[5,1-*a*]isoindol-8-one (5). A mixture of **4** (23.34 g, 0.084 mol), DDQ (9.95 g, 0.044 mol), and C_6H_6 (350 ml) was stirred at reflux for 2 hr and treated with another 9.95 g of DDQ, and the heating was continued for 3 hr longer. The insoluble dihydro-DDQ was filtered and rinsed with C_6H_6, and the filtrate was evaporated to leave an orange solid which was stirred at 25° for 1 hr with 1% KOH (500 ml) to remove residual quinone and by-products. The residue was rinsed with 5% $NaHCO_3$ and H_2O and air dried to a yellow powder which was recrystallized from acetone (1250 ml), yield 19.32 g (0.07 mol, 83%) of yellow needles of **5**, mp 180–181°. Further recrystallization raised the melting point to 186–187°. Anal. Calcd for $C_{17}H_{12}O_2N_2$: *m/e* 276.0899. Found: *m/e* 276.0878.

3-(4-Methoxyphenacyl)phthalide Oxime (12), Its Carbamate (13), and Semicarbazone (14). A mixture of **3** (2.82 g, 10 mmol), EtOH (170 ml), hydroxylamine hydrochloride (1.0 g, 14 mmol), and pyridine (2 ml) was stirred at reflux for 4 hr, then evaporated to dryness. The residue was extracted with H_2O and recrystallized from 90% MeOH (45 ml), yield 2.30 g (7.74 mmol, 77%) of oxime **12**, mp 116–117°. Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.53; H, 5.00; N, 4.62.

Treatment of oxime **12** (5.94 g, 20 mmol) with CH_3NCO (3 ml) in warm CH_3CN (200 ml) for 3 hr, followed by evaporation, gave a residue which was recrystallized from 60% MeOH (40 ml), yield 5.5 g (15.52 mmol, 78%) of carbamate **13**, mp 132–134°. Anal. Calcd for $C_{19}H_{18}N_2O_5$: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.24; H, 5.23; N, 7.52.

Analogous treatment of **3** with semicarbazide hydrochloride gave semicarbazone **14** (24% yield), colorless crystals, mp 179–180° after recrystallization from *i*-PrOH. Anal. Calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found: C, 63.39; H, 5.03; N, 12.65.

4-Methoxy-6,7,7a,13a-tetrahydronaphtho[2,3-*a*]-12*H*-pyrazolo[5,1-*a*]isoindol-8-one (15) was prepared in 33% yield by reaction of hydrazine with the condensation product of **1** and 6-methoxy-1-tetralone. It was recrystallized from CF_3CO_2H as a colorless solid: mp 256–259° dec; ν_{max} 1700 cm^{-1}; λ_{max} (CF_3CO_2H) 357 nm (ε 30,000), 298 (3950); ^1H NMR (CF_3CO_2H) δ 7.93–7.09 (m, 7 H, aromatic), 6.02 (d, J = 11 Hz) and 5.59 (d, J = 10 Hz) (2 H tertiary protons), 4.04 (s) and 3.97 (s) (3 H, OCH_3), 3.20–2.67 ppm (m, 4 H CH_2); the isomer ratio 3:2 was estimated from the OCH_3 peak integrals. Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.86; H, 5.36; N, 9.09.

4-Methoxy-6,7-dihydronaphtho[2,3-*a*]-12*H*-pyrazolo[5,1-*a*]-isoindol-12-one (16). A mixture of **15** (1.0 g, 3.29 mmol), C_6H_6 (50 ml), and DDQ (0.755 g, 3.29 mmol) was stirred at reflux for 6 hr and evaporated. The combined solids were washed with 0.5% KOH and with 5% $NaHCO_3$ to leave 0.96 g (3.18 mmol, 95%) of crude **14** as a yellow powder which was recrystallized from acetone (200 ml). Pure **15** has mp 239–242°; ν_{max} (KBr) 1790, 1740 cm^{-1}; λ_{max} (EtOH) 362 nm (ε 16,400), 348 (15,700), 288 (15,300), 268 (24,700), 258 (24,400), 241 (33,400); ^1H NMR (CF_3CO_2H) δ 7.90–7.20 (m, 7 H, aromatic), 4.05 (s, 3 H, OCH_3), 3.27 ppm (s, 4 H, CH_2). Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.35; H, 4.74; N, 9.26.

4-Methoxynaphtho[2,3-*a*]-12*H*-pyrazolo[5,1-*a*]isoindol-12-one (17). A. From 15. The above experiment was repeated using a 1:2 molar ratio of **15** to DDQ to give **17** as a red, crystalline solid (42% yield) after recrystallization from acetone. Pure **17** has mp 223–226°; ν_{max} (KBr) 1790, 1750 cm^{-1}; λ_{max} (EtOH) 395 nm (ε 5600), 365 (6250), 336 (4900), 311 (14,100), 298 (16,300), 254 (39,300). The only suitable NMR solvent, D_2SO_4, caused decomposition. Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 76.01; H, 4.26; N, 9.40.

B. From 16. Experiment A was repeated using a 1:1 molar ratio of **16** to DDQ to give **17** in 80% yield after recrystallization from acetone.

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Registry No.—**1**, 119-67-5; **2**, 100-06-1; **3**, 55222-45-2; **4**, 21138-13-6; **5**, 37564-17-3; **6**, 55222-46-3; **7**, 55222-47-4; **12**, 55254-61-0; **13**, 55222-48-5; **14**, 55222-49-6; *cis*-**15**, 55222-50-9; *trans*-**15**, 55222-51-0; **16**, 39785-30-3; **17**, 39785-31-4; hydrazine dihydrochloride, 5341-61-7; hydroxylamine hydrochloride, 5470-11-1; isocyanatomethane, 624-83-9; semicarbazide hydrochloride, 57-56-7; 6-methoxy-1-tetralone, 1078-19-9.

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