THE JOURNAL OF Organic Chemistry®

VOLUME 35, NUMBER 7

JULY 1970

Reactions of 2-Acyl-1,3-indandiones with *o*-Phenylenediamines

WILLIAM A. MOSHER AND STEFFEN PIESCH

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received October 24, 1969

The condensation of 2-acyl-1,3-indandiones with various *o*-phenylenediamines gave benz[*b*]indeno[1,2-*e*][1,4]-diazepin-12(5H)-ones (**2a–s**) in good yields. In some cases, depending upon the reaction conditions, the intermediate noncyclic 1:1 adducts, 2-[1-(*o*-aminophenylimino)alkyl]-1,3-indandiones (**1a–d**), or the 1:2 adduct, 2,2′-[*o*-phenylenebis(nitrilomethylidyne)]di-1,3-indandione (**3**), were obtained. The reactions of the carbonyl group of several benzindenodiazepinones **2** with hydroxylamine and with various hydrazines were investigated.

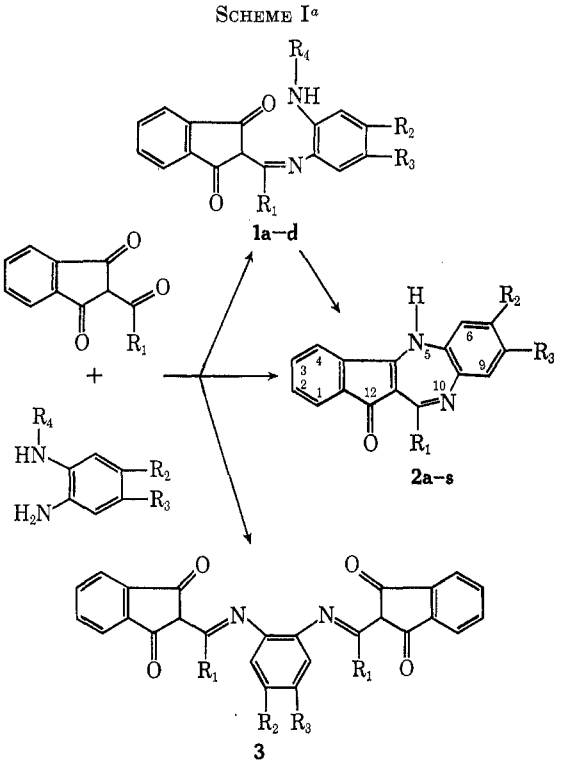
In a previous paper[1] in this field, we described the reactions of 2-acyl-1,3-indandiones with aliphatic diamines. Now we report the reactions of 2-acyl-1,3-indandiones with a variety of *o*-phenylenediamines with the emphasis on a new class of compounds, the benz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ones (**2a–s**, Scheme I).

The cyclization of open-chain β-diketones with *o*-phenylenediamine to give 2,4-disubstituted 1,5-benzodiazepines has been studied extensively,[2–4] but prior to our work there has been no report on the cyclization of 2-acyl-1,3-indandiones with *o*-phenylenediamine. Two somewhat related reactions are described in the literature, namely, the condensation of 1-chloroindene-2-carboxaldehyde and of 1-oxo-2-indanglyoxylic acid with *o*-phenylenediamine to give respectively 5,12-dihydrobenz[*b*]indeno[1,2-*e*][1,4]diazepine[5] and the corresponding 11-carboxylic acid.[6]

In our study we found that addition of 2-acyl-1,3-indandiones to refluxing ethanolic solutions of *o*-phenylenediamines, in the presence of an acidic catalyst, usually formic acid, gave benz[*b*]indeno[1,2-*e*]-[1,4]diazepin-12(5H)-ones (**2a–s**) in very good yields.

Only in four cases, the intermediate noncyclic 1:1 adducts, 2-[1-(*o*-aminophenylimino)alkyl]-1,3-indandiones (**1a–d**), were isolated. The indandiones **1a** ($R_1 = R_2 = R_3 = R_4 = H$) and **1b** ($R_1 = CH_3$; $R_2 = R_3 = R_4 = H$) were obtained by adding the appropriate 2-acyl-1,3-indandione to *o*-phenylenediamine at or below room temperature. The indandiones **1c** ($R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = C_6H_5$) and **1d** ($R_1 = C_6H_5$; $R_2 = R_3 = H$; $R_4 = C_6H_5$) were formed when

SCHEME I[a]



[a] For R_1, R_2, R_3, and R_4 see Tables I–III and Experimental Section.

N-phenyl-*o*-phenylenediamine was used in refluxing ethanol. When **1a** and **1b** were heated to reflux in dry ethanol or were treated with hydrochloric or perchloric acid in the cold, the corresponding ring-closed compounds **2a** ($R_1 = R_2 = R_3 = H$) and **2b** ($R_1 = CH_3$; $R_2 = R_3 = H$) were obtained. With the above acids the salts of **2a** and **2b** were formed. Several attempts to ring-close **1c** and **1d** were unsuccessful, even when concentrated sulfuric acid or polyphosphoric acid was used.

(1) W. A. Mosher and S. Piesch, *J. Org. Chem.*, **35**, 1026 (1970).
(2) J. Thiele and G. Steimming, *Chem. Ber.*, **40**, 955 (1907).
(3) C. A. Haley and P. Maitland, *J. Chem. Soc.*, 3159 (1951).
(4) J. A. Barltrop, C. G. Richards, D. M. Russel, and G. Ryback, *J. Chem. Soc.*, 1132 (1959).
(5) M. Weissenfels, H. Schurig, and G. Hühsam, *Chem. Ber.*, **100**, 584 (1967).
(6) J. N. Chatterjea and K. Prasad, *J. Indian Chem. Soc.*, **34**, 377 (1957).

TABLE I

11-SUBSTITUTED BENZ[*b*]INDENO[1,2-*e*][1,4]DIAZEPIN-12(5H)-ONES (**2**, $R_2 = R_3 = H$)

Compd	R_1	Method	Reaction time	Yield, %	Mp, °C	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2b	CH_3[a]	A	5 hr	86	299–300[b]	$C_{17}H_{12}N_2O$	78.44	4.65	10.76	78.03	4.82	10.73
2c	C_2H_5	B	20 hr	60	244[b]	$C_{18}H_{14}N_2O$	78.81	5.15	10.21	78.69	5.27	10.06
2d	$CH(CH_3)_2$	B	20 hr	75	202–203[c]	$C_{19}H_{16}N_2O$	79.16	5.55	9.64	79.30	5.68	9.64
2e	$CH_2CH(CH_3)_2$[d]	B	48 hr	60	204–205	$C_{20}H_{18}N_2O$	79.44	6.00	9.27	79.32	5.80	9.13
2f	$CH(C_6H_5)_2$	B	9 days	55	190–192[c]	$C_{29}H_{20}N_2O$	84.44	4.89	6.79	84.42	4.98	6.79
2g	C_6H_5	A	20 hr	65	>300[e]	$C_{22}H_{14}N_2O$	82.00	4.36	8.69	81.85	4.45	8.64
2h	C_6H_4-*p*-Cl	A	15 hr	35	>300[e]	$C_{22}H_{13}ClN_2O$	74.05	3.66	7.85	74.20	3.81	7.74

[a] Perchlorate, mp 300° dec. [b] Recrystn solvent: dioxane. [c] Recrystn solvent: ethanol. [d] Perchlorate, mp 279° dec. [e] Recrystn solvent: ethanol–dimethylformamide.

TABLE II

7 (or 8),11-DISUBSTITUTED BENZ[*b*]INDENO[1,2-*e*][1,4]DIAZEPIN-12(5H)-ONES (**2**)

Compd	R_1	R_2 or R_3	Method	Reaction time	Yield, %	Mp, °C	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2i	CH_3	CH_3[a]	A	10 hr	75	285 dec[b]	$C_{18}H_{14}N_2O$	78.81	5.15	10.21	78.93	5.31	9.96
2j	C_6H_5	CH_3[a]	A	10 hr	65	276–286[b]	$C_{23}H_{16}N_2O$	82.12	4.80	8.33	82.00	4.85	8.39
2k	CH_3	Cl[c,d]	A	12 hr	80	298–300 dec[b]	$C_{17}H_{11}ClN_2O$	69.27	3.78	9.51	69.55	3.99	9.32
2l	$CH_2CH(CH_3)_2$	Cl[c]	B	36 hr	75	200[e]	$C_{20}H_{17}ClN_2O$	69.01	6.06	7.32	68.95	6.24	7.51
2m	$CH(C_6H_5)_2$	NO_2[c]	B	10 days	45	>300[b]	$C_{29}H_{19}N_3O_3$	76.20	4.16	9.17	76.44	4.16	9.11
2n	C_6H_5	Cl[c]	A	36 hr	70	298–300 dec[b]	$C_{22}H_{13}ClN_2O$	74.05	3.66	9.94	74.02	3.82	9.88
2o	C_6H_5	NO_2[c]	B	24 hr	60	>300[b]	$C_{22}H_{13}N_3O_3$	72.33	3.59	11.50	72.11	3.74	11.69

[a] A mixture of 7 and 8 isomers is probably formed. [b] Recrystn solvent: ethanol–dimethylformamide. [c] A single isomer (7 or 8) is formed. [d] Perchlorate, mp 300. [e] Recrystn solvent: ethanol.

TABLE III

7,8,11-TRISUBSTITUTED BENZ[*b*]INDENO[1,2-*e*][1,4]DIAZEPIN-12(5H)-ONES (**2**)

Compd	R_1	$R_2 = R_3$	Method	Reaction time	Yield, %	Mp, °C	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
2p	CH_3	CH_3	A	10 hr	75	284–286 dec[a]	$C_{19}H_{16}N_2O$	79.16	5.55	9.64	79.00	5.74	9.63
2q	C_6H_5	CH_3	A	10 hr	75	>300[b]	$C_{24}H_{18}N_2O$	82.26	5.18	8.00	82.48	5.16	8.41
2r	CH_3	Cl	A	10 hr	70	>300[b]	$C_{17}H_{10}Cl_2N_2O$	62.02	3.06	8.54	61.99	3.40	8.34
2s	$CH(C_6H_5)_2$	Cl	B	3 days	70	260–261[b]	$C_{29}H_{18}Cl_2N_2O$	72.35	3.77	5.82	72.24	4.13	5.71

[a] Recrystn solvent: dimethylformamide. [b] Recrystn solvent: ethanol–dimethylformamide.

Reverse addition of the reactants, *o*-phenylenediamine to 2-formyl-1,3-indandione, gave the 1:2 adduct, 2,2′-[*o*-phenylenebis(nitrilomethylidyne)]di-1,3-indandione (**3**, $R_1 = R_2 = R_3 = H$). Attempts to ring-close **3** failed.

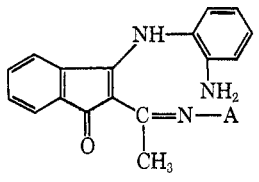
The structures of these compounds are based upon the elemental analyses and are consistent with the infrared spectra. The benzindenodiazepinones (**2a–s**) are red crystalline compounds. Their melting points and elemental analyses are summarized in Tables I–III. In neutral alcoholic solution these compounds show absorption bands between 300 mμ (ε 14,000–35,000) and 430 mμ (ε 3500–6000). In acidic solution the absorption bands are shifted bathochromically [325 mμ (ε 20,000–35,000) and 640–675 mμ (ε 400–750)]. The infrared spectra show absorption peaks at *ca.* 3300, at 1675–1640, and at *ca.* 1600 cm^{-1}.

Treatment of compounds **2a–s** with concentrated hydrochloric or perchloric acid gave the corresponding salts, which have a characteristic intense blue color and a metallic luster. Anhydrous hydrazine reacted with **2b** (Scheme II) in ethanolic solution, splitting off *o*-phenylenediamine and yielding the known hydrazone of the 3-methylindeno[1,2-*c*]pyrazol-4(1H)-one[7] (**4**).

Treatment of **2b** and **2g** with 1,1-dimethylhydrazine in dioxane gave respectively the 11-methyl- and 11-phenyl-12-(2,2-dimethylhydrazino)benz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ols (**5a** and **5b**). When phenylhydrazine was used in place of 1,1-dimethylhydrazine in the reaction with **2b**, 11-methyl-12-(2-phenylhydrazino)benz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ol (**5c**) was formed.[8] Treatment of **2b**, **2e**, and **2g** with hydroxylamine in dimethylformamide yielded respectively the 11-methyl-, 11-isobutyl- and 11-phenyl-12-hydroxyaminobenz[*b*]indeno[1,2-*e*][1,4]diazepin-12-(5H)-ols (**6a–c**).[8] All attempts to dehydrate compounds **5** or **6** to the corresponding hydrazones or oximes failed. Reaction of **5** or **6** with ethanolic hydrochloric acid gave the characteristic blue salts **7**. Treatment of these salts with aqueous ammonia yielded the benzindenodiazepinones **2**. These benzindenodiazepinones were also obtained when compounds **5** and **6** were heated for several minutes in refluxing 95% ethanol.

(7) R. A. Braun and W. A. Mosher, *J. Amer. Chem. Soc.*, **80**, 4919 (1958).

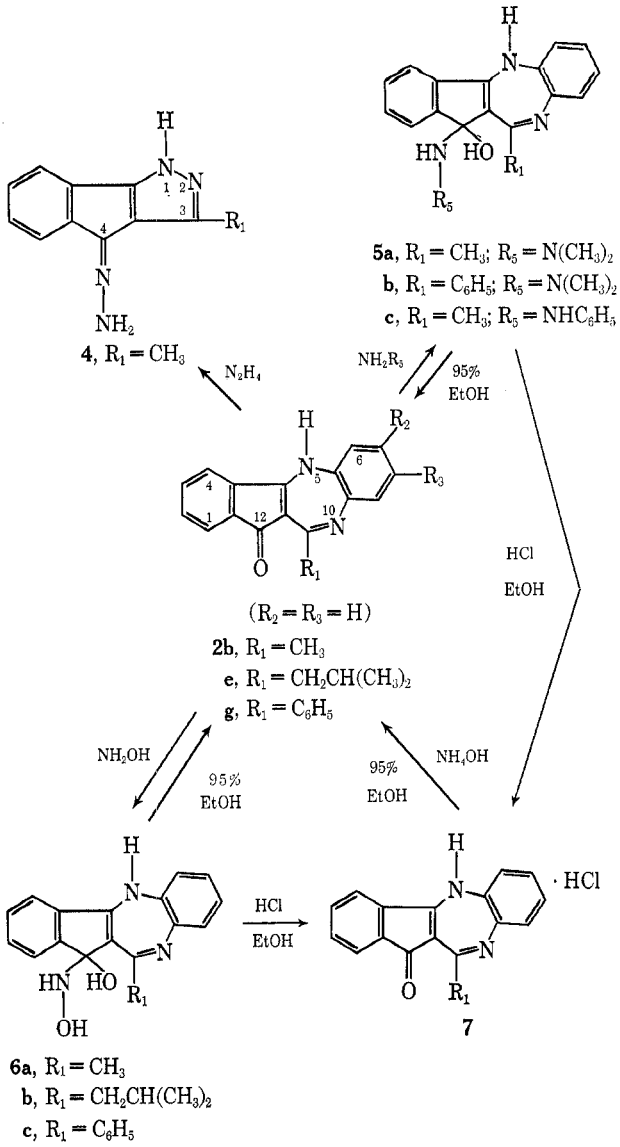
(8) Referee II has suggested that the diazepine ring of compounds **2** may open in the reaction with substituted hydrazines and with hydroxylamine to give the isomeric structure.



A = NHR, NR_2, or OH

The mass spectral fragmentation patterns of products **5c** and **6a** are very similar to that of the starting material **2b**, after the loss of the phenylhydrazine and of hydroxylamine, respectively. These results support the structures given to compounds **5** and **6**.

SCHEME II



Experimental Section[9]

2-Acyl-1,3-indandiones.—2-Formyl-1,3-indandione was prepared as described in ref 1 from triethyl orthoformate, acetic anhydride, and 1,3-indandione. All the other 2-acyl-1,3-indandiones were prepared according to known methods[10,11] from dimethyl phthalate and the appropriate methyl ketones in the presence of sodium amide[12] instead of sodium methoxide. It was found that sodium amide generally gives better yields than sodium methoxide. For example, in the preparation of 2-(*p*-chlorobenzoyl)-1,3-indandione, 70% yields were obtained using sodium amide (the reported[11] yield using sodium methoxide is only 5%).

2-[(*o*-Aminophenylimino)methyl]-1,3-indandione (1a, R_1 = R_2 = R_3 = R_4 = H).—A solution of 2-formyl-1,3-indandione (5 g) in ethanol (100 ml) was added dropwise over a period of 5 min to a stirred, cold solution of an excess of *o*-phenylenediamine (3 g) in acetic acid (2 ml) and ethanol (50 ml). The yellow precipitate was collected by filtration and washed with cold ethanol to give an 80% yield of **1a**, as fine yellow needles of mp 197° dec.

Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.58; N, 10.60. Found: C, 72.85; H, 4.63; N, 10.43.

A solution of **1a** in dry ethanol, refluxed for 10 min, yielded **2a**, as red needles. Treatment of **1a** with cold perchloric acid gave the characteristic blue salt of the ring-closed compound **2a**.

2-[1-(*o*-Aminophenylimino)ethyl]-1,3-indandione (1b, R_1 = CH_3; R_2 = R_3 = R_4 = H).—2-Acetyl-1,3-indandione was allowed to react with *o*-phenylenediamine as described above for **1a** (reaction time 20 min) to give fine yellow needles of **1b**, contaminated with a small amount of the ring-closed compound **2b**.

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07. Found: C, 73.73; H, 5.38.

The perchlorate of the ring-closed compound **2b** was obtained as blue crystals by treatment of **1b** with cold perchloric acid. Upon refluxing **1b** in dry ethanol **2b** was formed as red needles.

2-[1-(*o*-Anilinophenylimino)ethyl]1,3-indandione (1c, R_1 = CH_3; R_2 = R_3 = H; R_4 = C_6H_5).—2-Acetyl-1,3-indandione was allowed to react with N-phenyl-*o*-phenylenediamine as described in method A (reaction time 7 hr) to give an 80% yield of **1c**, as deep yellow needles of mp 218° (dioxane or 1-propanol).

Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.94; H, 5.12, O, 9.03. Found: C, 78.21; H, 5.29; O, 9.20.

2-[(*o*-Anilinophenylimino)benzyl]-1,3-indandione (1d, R_1 = C_6H_5; R_2 = R_3 = H; R_4 = C_6H_5) was prepared from 2-benzoyl-1,3-indandione and N-phenyl-*o*-phenylenediamine as described in method B (reaction time 24 hr). A 60% yield of **1d**, as brownish yellow needles of mp 185° (1-propanol), was obtained. The 1-propanol solution fluoresces deep red under ultraviolet light.

Anal. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.77; H, 4.84; O, 7.66. Found: C, 80.83; H, 5.13; O, 8.73.

Compounds **1c** and **1d** failed to give the perchlorates of the corresponding ring-closed compounds by treatment with perchloric acid.

Benz[*b*]indeno[1,2-*e*][1,4]-diazepin-12(5H)-one (2a, R_1 = R_2 = R_3 = H).—A solution of 2-formyl-1,3-indandione (10 g, 57 mmol) in ethanol (200 ml) was added dropwise over a 3-hr period to a refluxing solution of formic acid (2 ml) and *o*-phenylenediamine (10 g, 100 mmol) in ethanol (200 ml). The mixture was refluxed for 1 additional hr and then filtered rapidly through a sintered-glass funnel. The insoluble yellow material was shown to be compound **3** (R_1 = R_2 = R_3 = H), formed as a by-product. The deep red filtrate was concentrated to 100 ml by distillation and the residue allowed to stand at room temperature. The dark red solid was collected and recrystallized from dioxane or ethanol to give a 60% yield of **2a**, as deep red needles of mp 287° dec: λ_{max}, mμ (ε), in neutral alcoholic solution 300 (14,000), 328 (12,000), 342 (10,000), 413 (7500), and 435 (6000); in acidic solution, 325 (20,000), 350 (11,000), 570 (1000), 618 (1000), 675 (650); ir 3300, 1675–1650, 1600–1525 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}N_2O$: C, 78.03; H, 4.09; N, 11.38. Found: C, 77.83; H, 4.20; N, 11.41.

Treatment of the mother liquor of **2a** with concentrated hydrochloric acid gave the corresponding hydrochloride as blue crystals of mp 268°.

Anal. Calcd for $C_{16}H_{10}N_2O \cdot HCl$: C, 67.97; H, 3.92; N, 9.91; Cl, 12.54. Found: C, 68.06; H, 3.93; N, 9.82; Cl, 12.39.

Mono-, Di-, and Trisubstituted Benz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ones (2b–s). Method A.—A solution of the appropriate 2-acyl-1,3-indandione (90 mmol) in ethanol (200 ml, or more if necessary to obtain a solution) was added dropwise over a 2-hr period to a refluxing and stirred solution of the appropriate *o*-phenylenediamine (90 mmol) in a mixture of formic acid (2.5 ml) and ethanol (1000 ml). The mixture was refluxed for the time indicated in Tables I–III. The product was then collected by filtration at room temperature, washed with cold methanol, and recrystallized from suitable solvents (see Tables I–III) to give red needles (except **2p**, red plates, and **2r**, violet-red prisms). Compound **2h**: λ_{max}, mμ (ε), in neutral alcoholic solution, 325 (25,000), 340 (18,000), 390 (5000), 410 (3500); in acidic solution, 335 (35,000), 540 (1100), 640 (500); ir 3400, 1640, and 1600 cm^{-1}. Compound **2r**: λ_{max}, mμ (ε), in neutral alcoholic solution, 310 (35,000), 340 (12,000), 390 (5500), and 410 (4000); in acidic solution, 325 (30,000), 540 (850), 585 (850), and 640 (750); ir 3300, 1650, and 1590–1550 cm^{-1}.

An additional amount of product (about 5% of the yield given in Tables I–III) was obtained, as the hydrochlorides or perchlorates, by adding 20 ml of the appropriate concentrated acid

(9) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. The infrared spectra were recorded with a Perkin-Elmer Infracord Model 137 (Nujol), and the electron spectra were recorded with a Perkin-Elmer 202 instrument. Mass spectra were taken with a CEC 21/110B mass spectrometer. Elemental analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max Planck Institut für Kohlenforschung, Mülheim (Ruhr), West Germany.

(10) L. B. Kilgore, J. H. Ford, and C. W. Wolfe, *Ind. Eng. Chem.*, **34**, 494 (1942).

(11) R. L. Horton and K. C. Murdock, *J. Org. Chem.*, **25**, 938 (1960).

(12) L. Gattermann, "Die Praxis des Organischen Chemikers," 38th ed, Walter de Gruyter and Co., Berlin, 1958, p 220.

to the mother liquors and precipitating the blue salts by addition of ether.

Method B.—The appropriate 2-acyl-1,3-indandione and the appropriate *o*-phenylenediamine were condensed as described in method A except that, after the reaction time indicated in Tables I–III, the mixture was concentrated to 150 ml and allowed to stand for 2 days. The solid was collected by filtration, washed twice with methanol (25 ml), and recrystallized from a suitable solvent (see Tables I–III) to give red needles (except **2f**, red plates). Compound **2c**: λ_{max}, mμ (ϵ), in neutral alcoholic solution, 400 (6000); in acidic solution, 550 (680), 590 (630), and 650 (400); ir 3300, 1645, and 1580–1550 cm^{-1}. Treatment of the mother liquor with concentrated hydrochloric or perchloric acid gave an additional amount of product, as the corresponding salt of intense blue color.

2,2′-[*o*-Phenylenebis(nitrilomethylidyne)]di-1,3-indandione (3, $R_1 = R_2 = R_3 = H$).—A solution of *o*-phenylenediamine (2.5 g) and formic acid (0.5 ml) in ethanol (50 ml) was added dropwise over a period of 15 min to a refluxing solution of 2-formyl-1,3-indandione (5 g) in ethanol (100 ml). The mixture was then cooled to room temperature and the precipitate was collected by filtration. A 90% yield of **3**, as bright yellow plates of mp >300° (dimethylformamide), was obtained.

Anal. Calcd for $C_{26}H_{16}N_2O_4$: C, 74.28; H, 3.84; N, 6.66. Found: C, 74.27; H, 3.73; N, 6.75.

Compound **3** failed to cyclize by treatment with perchloric, sulfuric, or polyphosphoric acid.

Reactions of 2b and 2g with Hydrazines.—The general procedure used was as follows. The appropriate anhydrous substituted hydrazine (75 mmol) was added to a stirred, cold solution or suspension of the appropriate benzindenodiazepinone **2** (50 mmol) in anhydrous dioxane (100 ml), followed by the addition of anhydrous formic acid (0.5 ml). Agitation was continued for about 5 hr. Then the reaction mixture was evaporated to dryness under reduced pressure at room temperature and the residue was recrystallized from a suitable solvent.

12-(2,2-Dimethylhydrazino)-11-methylbenz[*b*]indeno[1,2-*e*]-[1,4]diazepin-12(5H)-ol (5a) was obtained in 60% yield, as yellow-red plates of mp 172° (anhydrous ethanol or dioxane–hexane) by reaction of **2b** with 1,1-dimethylhydrazine.

Anal. Calcd for $C_{19}H_{20}N_4O$: C, 71.23; H, 6.25; N, 17.49. Found: C, 71.22; H, 6.33; N, 17.31.

12-(2,2-Dimethylhydrazino)-11-phenylbenz[*b*]indeno[1,2-*e*]-[1,4]diazepin-12(5H)-ol (5b) was obtained in 40% yield as yellow needles of mp 210–212° (dioxane–hexane) by reaction of **2g** with 1,1-dimethylhydrazine.

Anal. Calcd for $C_{24}H_{22}N_4O$: C, 75.37; H, 5.80; N, 14.65. Found: C, 75.05; H, 5.90; N, 14.19.

11-Methyl-12-(2-phenylhydrazino)benz[*b*]indeno[1,2-*e*][1,4]-diazepin-12(5H)-ol (5c) was obtained in 40% yield as yellow plates of mp 165–168° (ethanol) by reaction of **2b** with phenylhydrazine. In the mass spectrum of **5c**, there was molecular ion peak at *m/e* 368 with abundant fragment peaks at *m/e* 353, 260, 245, 231, 219, 190, 132, 115, 108, 92, and 77. The mass spectrum of the starting material **2b** revealed a molecular ion peak at *m/e* 260 with abundant fragment peaks at *m/e* 245, 231, 219, 190, 130, 115, 108, 102, and 77.

Anal. Calcd for $C_{23}H_{20}N_4O$: C, 75.18; H, 5.21; N, 15.25. Found: C, 75.27; H, 5.53; N, 14.72.

3-Methylindeno[1,2-*c*]pyrazol-4(1H)-one 4-Hydrazone (4).—When anhydrous hydrazine in ethanol was used, in place of the above substituted hydrazine in dioxane, in the reaction with **2b**, yellow crystals of mp 250–255° were obtained. The identity of this compound with an authentic sample of 3-methylindeno-[1,2-*c*]pyrazol-4(1H)-one 4-hydrazone, obtained from 2-acetyl-1,3-indandione and hydrazine,[7] was established by mixture melting point determinations and by comparison of the ir spectra.

Reactions of 2b, 2e, and 2g with Hydroxylamine.—The following general procedure was used. A mixture of hydroxylamine hydrochloride (55 mmol) and sodium acetate (55 mmol) was added in one portion to a stirred, cold solution of the appropriate benzindenodiazepinone **2** (50 mmol) in dimethylformamide (100 ml). The agitation was continued until the solution turned dull yellow. Then the reaction mixture was poured into 600 ml of vigorously stirred ice–water. (The reverse procedure, *i.e.*, addition of water to the reaction mixture, caused decomposition of the product giving the starting material.) The yellow precipitate was collected by filtration, washed with ice–water, dried over P_2O_5, and recrystallized from anhydrous solvents.

12-Hydroxyamino-11-methylbenz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ol (6a) was obtained in 90% yield as yellow plates of mp 205° dec (dioxane–hexane or ethanol) by reaction of **2b** with hydroxylamine for 5 hr. The mass spectrum of **6a** revealed a molecular ion peak at *m/e* 293 with abundant fragment peaks at *m/e* 278, 260, 245, 231, 219, 190, 160, 133, 130, 115, 108, 102, 92, and 77. The mass spectrum of the starting material **2b** is reported above (see compound **5c**).

Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.62; H, 5.16; N, 14.33. Found: C, 69.28; H, 5.40; N, 14.43.

12-Hydroxyamino-11-isobutylbenz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ol (6b) was obtained in 75% yield as brownish yellow plates of mp 215° dec (ethanol) by treating **2e** with hydroxylamine for 10 hr.

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.62; H, 6.31; N, 12.53. Found: C, 71.75; H, 6.23; N, 12.46.

12-Hydroxyamino-11-phenylbenz[*b*]indeno[1,2-*e*][1,4]diazepin-12(5H)-ol (6c) was obtained in 55% yield as deep yellow crystals of mp 223° (ethanol or dioxane–hexane) by reaction of **2g** with hydroxylamine for 10 hr.

Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.12; H, 4.96; N, 12.37.

Miscellaneous Reactions of Compounds 5 and 6.—These compounds reduced silver nitrate solution in the cold. When refluxed for a few minutes in 95% ethanol they gave the corresponding benzindenodiazepinones **2** and when treated with hydrochloric acid in ethanol solution produced the blue hydrochlorides **7**. Treatment of these salts with aqueous alcoholic solutions of ammonia gave the corresponding bases **2**.

Registry No.—**1a**, 24472-20-6; **1b**, 24515-43-3; **1c**, 24472-21-7; **1d**, 24472-22-8; **2a**, 24472-23-9; **2a** (HCl), 24472-24-0; **2b**, 24472-25-1; **2b** ($HClO_4$), 24467-34-3; **2c**, 24472-26-2; **2d**, 24472-27-3; **2e**, 24472-28-4; **2e** ($HClO_4$), 24523-21-5; **2f**, 24472-29-5; **2g**, 24472-30-8; **2b**, 24472-31-9; **2i** (7 isomer), 24472-32-0; **2i** (8 isomer), 24472-49-9; **2j** (7 isomer), 24472-34-2; **2j** (8 isomer), 24472-50-2; **2p**, 24472-35-3; **2q**, 24472-36-4; **2r**, 24472-37-5; **2s**, 24472-38-6; **3a**, 24472-39-7; **4**, 24472-40-0; **5a**, 24472-41-1; **5b**, 24472-42-2; **5c**, 24472-43-3; **6a**, 24472-46-6; **6b**, 24472-47-7; **6c**, 24472-48-8.

Acknowledgment.—We gratefully acknowledge the valuable assistance of Dr. Mario F. Sartori in connection with this research.