which the oily **15b** (R = cyclohexyl) was isolated by preparative thick-layer chromatography (silica gel; eluent ether–pentane 1:1).

Dimethyl 1-isopropyl-2-methyl-5-phenylpyrrole-3,4-dicarboxylate (15a): ^{1}H NMR ($CDCl_3$) δ 1.36 (6 H, d, J = 7 Hz, Me_2), 2.59 (3 H, s, CH_3), 3.57 (3 H, s, $COOCH_3$), 3.80 (3 H, s, $COOCH_3$), 4.34 (1 H, septet, J = 7 Hz, NCH), 7.36 (5 H, s, Ph); IR (KBr) 1724 and 1700 cm^{-1} ($\nu_{C=O}$); mass spectrum, m/e (relative abundance) 315 (M^+, 12), 283 (18), 282 (30), 242 (12), 241 (18), 181 (12), 58 (48), 43 (100), 40 (36); mp 116 °C. Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.57; H, 6.65; N, 4.65.

Dimethyl 1-cyclohexyl-2-methyl-5-phenylpyrrole-3,4-dicarboxylate (15b): ^{1}H NMR (CCl_4) δ 0.9–2.2 (10 H, m, C_6H_{10}), 2.63 (3 H, s, CH_3), 3.53 (3 H, s, $COOCH_3$), 3.79 (3 H, s, $COOCH_3$), 3.8 (1 H, m, NCH), 7.2–7.5 (5 H, m, Ph); IR (NaCl) 1720–1690 cm^{-1} ($\nu_{C=O}$).

Reaction of *cis*-2-Cyano-1-isopropyl-2-methyl-3-phenylaziridine (3o) with *tert*-Butylamine in Toluene. A solution of 0.01 mol of α-cyanoaziridine **3o** and 0.05 mol of *tert*-butylamine in 20 mL of toluene was refluxed for 16 h, after which toluene and excess amine were evaporated in vacuo. The remaining oil was analyzed by preparative gas chromatography, which revealed the presence of benzylideneisopropylamine (**17a**), benzylidene-*tert*-butylamine (**17b**), and trans α-cyanoaziridine **3o** in a 1:1:2 ratio, respectively. Compounds **17a** and trans **3o** may result from transformation of the cis isomer **3o**. Benzylideneamines **17a,b** were shown to be identical with authentic samples prepared by reaction of benzaldehyde with the corresponding amine.

Benzylideneisopropylamine (17a): ^{1}H NMR (CCl_4) δ 1.14 (6 H, d, J = 6 Hz, Me_2), 3.50 (1 H, septet, J = 6 Hz, NCH), 7.2–7.5 (3 H, m, meta and para protons), 7.5–7.8 (2 H, m, ortho protons), 8.22 (1 H, s, CH=N); IR (NaCl) 1655 cm^{-1} ($\nu_{C=N}$); mass spectrum, m/e (relative abundance) 147 (M^+, 45), 132 (100), 105 (25), 104 (41), 91 (45), 77 (23), 43 (64).

Benzylidene-*tert*-butylamine (17b): ^{1}H NMR (CCl_4) δ 1.26 (9 H, s, *t*-Bu), 7.2–7.5 (3 H, m, meta and para protons), 7.5–7.8 (2 H, m, ortho protons), 7.16 (1 H, s, CH=N); IR (NaCl) 1640 cm^{-1} ($\nu_{C=N}$).

Acknowledgment. We are indebted to the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek (National Fund for Scientific Research) for generous financial support to the laboratory.

Registry No. **1a**, 78827-38-0; **1b**, 81803-16-9; **1c**, 87207-61-2; **1d**, 87207-62-3; **1e**, 87207-63-4; **1f**, 87207-64-5; **1g**, 81815-43-2; **1h**, 84300-49-2; **1i**, 87207-65-6; **1l**, 78827-37-9; **1m**, 78827-36-8; **1o**, 78827-43-7; **1p**, 87207-66-7; **1q**, 87207-67-8; **2a**, 87207-68-9; **2**, 87207-69-0; **2k**, 87207-70-3; **3a**, 81803-21-6; **3b**, 81803-22-7; **3c**, 87207-71-4; **3d**, 87207-72-5; **3e**, 87207-73-6; **3f**, 87207-74-7; *cis*-**3g**, 81803-19-2; *trans*-**3g**, 81803-20-5; *cis*-**3h**, 87207-75-8; *trans*-**3h**, 87207-89-4; **3i**, 87207-76-9; **3j**, 87207-77-0; **3k**, 87207-78-1; *cis*-**3l**, 87207-94-1; *trans*-**3l**, 81803-18-1; *cis*-**3m**, 81803-17-0; *trans*-**3m**, 81803-23-8; *cis*-**3o**, 81803-24-9; *trans*-**3o**, 81803-25-0; *cis*-**3p**, 87207-79-2; *cis*-**3q**, 87207-80-5; **4a**, 81803-26-1; **4b**, 81803-27-2; **4c**, 87207-81-6; **4d**, 87207-82-7; **4e**, 87207-83-8; **4f**, 87207-84-9; **5a**, 87207-85-0; **5c**, 87207-86-1; **5d**, 87207-87-2; **5e**, 87207-88-3; **12a**, 87207-91-8; **15a**, 87207-92-9; **15b**, 87207-93-0; **17a**, 6852-56-8; **17b**, 6852-58-0; *N*-allyl-3,3-dimethoxy-2-butylamine, 84393-18-0; 3-methoxy-3-methyl-2-butanone, 36687-98-6; (2,4-dimethyl-1-penten-3-ylidene)isopropylamine, 87207-90-7.

Supplementary Material Available: Physical and spectrometric data of α-chloro and α-bromo ketimines **1** and **2** (Table I); spectrometric properties of α-cyanoaziridines **3** (Table II); spectrometric data of 1-(*N*-alkyl)aminocyclopropanecarbonitriles **4** (Table III); and ^{13}C NMR data of 1-(*N*-alkyl)aminocyclopropanecarbonitriles **4** (Table IV) (9 pages). Ordering information is given on any current masthead page.

Chemistry of β-Triketones. 1. Structure of Schiff Base Intermediates of 2-Acyl-1,3-indandiones[1]

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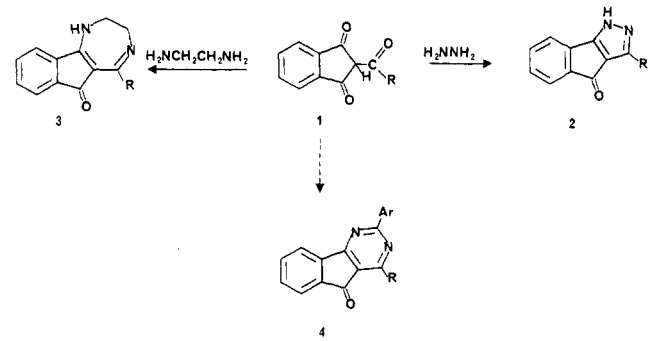
Schiff base formation has been shown to occur preferentially at the exocyclic carbonyl of 2-acyl-1,3-indandiones (**1**). The resulting addition product exists either as an open-chain compound (**10–16**) or as a cyclic hemiketal (**19–27**). The size of the acyl substituent appears to influence the structure of the Schiff bases.

The 2-acyl-1,3-indandiones (**1**) have served as a useful synthon for the preparation of a variety of tricyclic heterocycles. The reaction of **1** with hydrazine results in the formation of indenopyrazoles (**2**),[2-7] while the addition of ethylenediamine and *o*-phenylenediamine gives rise to indenodiazepines (**3**).[8-9] A series of 2-benzylidene-1,3-indandiones were used and condensed with benzamidines, and the indenopyrimidines (**4**) have been prepared.[10]



We have been interested in this area for some time, both for its synthetic utility for the preparation of tricyclic heterocycles and from the theoretical standpoint as to the site of initial addition of the nucleophile. Since most of the reagents previously used have led to symmetrical final

(1) Presented in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982.
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(9) Mosher, W. A.; Piesch, S. *J. Org. Chem.* **1970**, *35*, 2109–2112.
(10) Mosher, W. A.; Brenner, J. L. *J. Org. Chem.* **1971**, *36*, 3382–3385.

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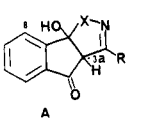
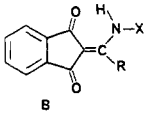
Table I. ^{1}H NMR Chemical Shifts for A and B

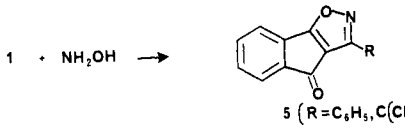

A


B

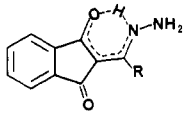
compd	R	X	H_{3a}	H_8		R and/or Ar	exchangeable
10B	CH_3 [a]	OH			2.63	7.58 (s)	
11B	CH_3 [b]	$OCOCH_3$			2.65	7.65 (s), 7.61 (s)	
19A	$(CH_3)_3C$ [b]	O	4.22		1.25	7.3-7.9 (m)	5.63
20A	C_6H_5 [a]	O	4.92			7.4-8.1 (m)	8.52
21A	4-$CH_3OC_6H_4$ [c]	O	4.50			6.9-8.1 (m)	8.2
12B	CH_3 [a]	$NH(C{=}S)NH_2$			2.53	7.7 (s)	11.43 (1 H), 8.1 (2 H)
22A	$(CH_3)_3C$ [b]	$N(C{=}S)NH_2$	4.4	9.03 (d, J = 8 Hz)	1.32	7.27-7.9 (m)	7.27, 7.0, 6.3
23A	C_6H_5 [b]	$N(C{=}S)NH_2$	4.77	9.1 (d, J = 8 Hz)		7.0-8.1 (m)	7.07 (1 H), 6.47 (2 H)
13B	CH_3 [a]	$NHCONH_2$			2.52	7.57 (s)	11.47, 8.7, 6.4
24A	$(CH_3)_3C$ [a]	$NCONH_2$	4.3	8.35 (d, J = 8 Hz)	1.3	7.45-7.95 (m)	7.3 (1 H), 6.3 (2 H)
25A	C_6H_5 [a]	$NCONH_2$	4.87	8.4 (d, J = 8 Hz)		7.35-8.17 (6 H, m) 7.93-8.17 (2 H, m)	3.38 (1 H), 6.6 (2 H)
14B	CH_3 [a]	$NHCOOC_2H_5$			2.53	7.63 (s)	11.37, 9.9
15B	C_6H_5 [a]	$NHCOOC_2H_5$				7.4 (s, 4 H) 7.5-7.7 (m, 5 H)	11.37, 9.6
26A	$(CH_3)_3C$ [b]	$NCOOC_2H_5$	4.28	8.17 (d, J = 8 Hz)	1.37	7.3-7.9 (m)	5.43
27A	C_6H_5 [b]	$NCOOC_2H_5$	4.67	8.19 (d, J = 8 Hz)		7.28-7.8 (6 H, m) 7.88-8.06 (2 H, m)	5.41

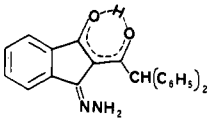
[a] Solvent Me_2SO-d_6. [b] Solvent $CDCl_3$. [c] Solvent $CDCl_3$ + Me_2SO-d_6.

products, the site of nucleophilic addition has remained speculative. One approach to answering the question of initial site of addition has been the use of unsymmetrical nucleophiles, and we have found by the use of hydroxylamine that the preferred site of attack is the exocyclic carbonyl giving rise to the indenoisoxazoles **5**.[11]


5 (R = C_6H_5, $C(CH_3)_3$)

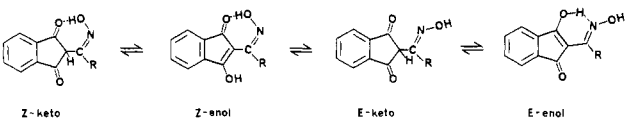
Another means of identifying the initial site of nucleophilic addition would be isolation and identification of the intermediate Schiff base. In many cases these reactions proceed directly to the cyclic products, but in a few cases the Schiff bases have been isolated. In Mosher's first paper in this area he reported the isolation of several hydrazones. The monohydrazones of 2-acetyl-, 2-propionyl-, and 2-phenylacetyl-1,3-indandione were reported to have structure **6** while the 2-diphenylacetyl-1,3-indandione was reported to yield hydrazone **7**.[12] The proof of structure was


6

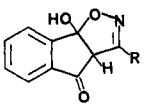

7

based on a positive Tollens test for **6** and a negative Tollens test for **7**. The test was reported to be positive for "hydrazones whenever the carbon atom of the carbonyl group that would be formed in the case of hydrolysis is situated in an open chain". This reference has been quoted in numerous other papers as proof of the location of the Schiff base adduct. We were interested in studying these intermediates with the objective of a more rigorous proof of structure and were also puzzled by the fact that while most condensations proceeded directly to the cyclic products, a few give the intermediate open-chain products, which required more strenuous conditions for cyclization.

Our best method for preparing the indenoisoxazoles **5** consisted of a two-step procedure which involved isolation of the "oxime" intermediates and cyclization of the latter under acidic conditions. While the oxime could be pictured as existing in either the *E* or *Z* configuration as well as


Z-keto Z-enol E-keto E-enol

"enol–keto" structures, Geita and co-workers[13] had proposed that the molecule actually existed in the hemiketal form **8**. Evidence for this assignment was based on in-


8 (R = C_6H_5)

frared spectra. With various Schiff bases in hand, we decided to submit these compounds to a more rigorous analysis using NMR.

Results and Discussion

In most cases, the Schiff bases were readily prepared by heating the 2-acyl-1,3-indandiones with the nucleophile in ethanol. In most cases a single product was obtained (Scheme I). The compounds appeared to fall into two groups, one where the Schiff base was a white or very light colored solid and one where the compounds were a dark yellow or orange solid (**1**, R = CH_3).

The initial ^{1}H NMR spectra of the light colored compounds (**19–27**) was supportive of either the *Z*- or *E*-keto structures or the hemiketal structure A (Table I). The characteristic singlet at δ 4.2–4.9 was assigned to the 2 hydrogen of the keto structure or the 3a hydrogen in the hemiketal structure. While initially not recognized, the multiplet nature of the aromatic protons may be supportive of the unsymmetrical hemiketal structure and rule out the symmetrical keto forms. The more darkly colored Schiff bases (**10–16**) showed the absence of absorption at δ 4–5 which would be compatible with the *Z*- or *E*-enol

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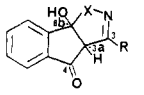
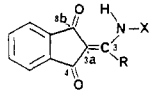
(12) Braun, R. A.; Mosher, W. A. *J. Am. Chem. Soc.* **1958**, *80*, 2749–2751.

Table II. ^{13}C NMR Chemical Shifts for A and B



A

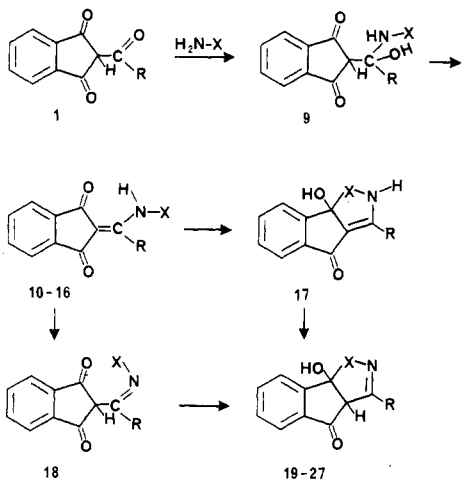


B

compd	R	X	C_3	C_{3a}	C_4	C_{8b}	R and X
10B	CH_3 [a]	OH	163.2	97.9	190.5	190.5	11.5
11B	CH_3 [b]	$OCOCH_3$	166.5	100.6	193.0	190.8	11.8, 161.6, 18.0
19A	$(CH_3)_3C$ [a]	O	161.6	66.1	196.2	112.4	33.7, 28.6
20A	C_6H_5 [a]	O	153.5	64.5	195.1	113.4	
21A	4-$CH_3OC_6H_5$ [a]	O	153.0	64.8	195.2	113.0	55.3
12B	CH_3 [a]	$NH(C{=}S)NH_2$	167.8	101.9	192.3	189.4	12.7, 182.5
22A	$(CH_3)_3C$ [b]	$N(C{=}S)NH_2$	160.7	69.1	194.8	99.0	35.2, 28.4, 175.8
23A	C_6H_5 [b]	$N(C{=}S)NH_2$	149.6	67.5	193.4	99.5	176.0
13B	CH_3 [a]	$NHCONH_2$	167.6	100.9	192.6	189.5	12.8, 157.4
24A	$(CH_3)_3C$ [a]	$NCONH_2$	154.9	69.5	196.6	96.4	34.2, 28.6, 153.7
25A	C_6H_5 [a]	$NCONH_2$	153.6	67.9	195.7	96.8	151.4
14B	CH_3 [a]	$NHCOOC_2H_5$	168.4	101.4	192.6	189.5	12.5, 14.5, 61.6, 155.6
15B	C_6H_5 [a]	$NHCOOC_2H_5$	167.5	102.0	192.9	187.0	155.6
26A	$(CH_3)_3C$ [b]	$NCOOC_2H_5$	159.0	67.8	195.1	97.0	144.4, 62.6, 153.0, 34.8, 28.6
27A	C_6H_5 [b]	$NCOOC_2H_5$	148.8	66.4	193.8	97.4	14.4, 62.9, 153.0
16B	CH_3 [a]	NH_2	165.2	99.4	190.8	190.8	12.5

[a] Solvent Me_2SO-d_6. [b] Solvent $CDCl_3$.

Scheme I



structures as well as structure B. The singlet nature of aromatic absorption (δ 7.4–7.8) would be more explainable with structure B than with either of the unsymmetrical enols.

The ^{13}C NMR spectra was extremely useful in differentiating between the various structures (Table II). The light colored compounds (**19–27**) all exhibited an absorption at 64–70 ppm assignable to the 3a carbon of the hemiketal structure (structure A). The hemiketal carbon 8b was present in all of these compounds at 96–112 ppm and appeared as a singlet in the coupled spectra. The darkly colored Schiff bases (**10–16**) were characterized by the absences of an absorption at 64–70 ppm which was replaced by a vinyl absorption at 98–102 ppm. In addition, it should be noted that in the symmetrical structures B where intramolecular H bonding occurs between the NH proton and one of the carbonyls, the two carbonyls show slightly different chemical shifts (compounds **11–15**). The intramolecular H bonding is supported by the strong deshielding of the exchangeable protons at δ 11.4–11.5 (Table I). Also supportive of structures A and B, and listed in the Experimental Section, are the aromatic carbon absorptions. Compounds existing in structure A show six distinct aromatic carbons, while compounds with structure B show either three aromatic carbons when intramolecular bonding is absent or weak (**10, 16**) and four aromatic carbons (4a and 8a are distinct) in the remaining compounds.

An interesting observation seen in the ^1H NMR spectra is the presence of a deshielded aromatic proton in compounds **22–27**. This proton appears at δ 8.2–9.1 and exists as a doublet with J = 8 Hz (Table I). Molecular models of the hemiketal A, assuming a cis stereochemistry of the proton at C_{3a} and the hydroxyl at C_{8b}, places the thiocarbonyl or carbonyl in close proximity to the C_8 proton. This suggestion is further supported by the greater amount of deshielding in the thiocarbonyl analogues (δ 9.03–9.1) than in the carbonyl analogues (δ 8.2–8.4). A similar deshielding is not seen with the oxime analogues in which X = O.

It is proposed that the condensation of the triketones **1** with a nucleophile occurs at the exocyclic carbonyl to yield intermediate **9**. This compound undergoes dehydration to compounds **10–16** with the exocyclic double bond rather than the expected Schiff base **18**. When R is a small group such as methyl, these intermediates are stable and remain in this form, but with the bulky aryl or tertiary butyl group, these intermediates undergo cyclization to **17** followed by isomerization to **19–27** or isomerization to **18** and cyclization to **19–27**. In one particular case (X = $NHCOOC_2H_5$; R = C_6H_5) the intermediate **15** was isolated and, upon heating, was converted to **27**.

Experimental Section

Melting points were determined on a Thomas-Hoover unimelt apparatus and are uncorrected. All ^1H NMR spectra were recorded on a Varian EM 360 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are quoted in parts per million (s = singlet, d = doublet, m = multiplet). All ^{13}C NMR spectra were recorded on an FT-80A spectrometer system operating in the Fourier transform mode at 20 MHz or on a Varian XL-100-15 spectrometer operating at 25.158 MHz in the Fourier transform mode and equipped with a Nicolet 1180 data system interfaced through a Model 293A' pulse programmer. Chemical shifts are quoted in parts per million downfiled from tetramethylsilane. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA.

Typical Procedure for Preparation of the Schiff Base. A mixture of 0.02 mol of 1 suspended in 25 mL of 95% EtOH was treated with 0.02 mol of the nucleophile dissolved in a minumum amount of 95% EtOH. If the nucleophile is used as its hydrochloride salt, the salt is dissolved in a minimum amount

of H_2O and then treated with 0.02 mol of 10% NaOH. The aqueous layer is added to the triketone. The resulting mixture is heated on a steam bath to give a homogeneous solution and then allowed to stir at 25 °C until the reaction is complete. The Schiff base usually appears as a precipitate and the progress of the reaction can be monitored by TLC on silica gel.

Hydroxylamine of 2-acetyl-1,3-indandione (10): mp 197–197.5 °C (lit.[13] 192–193 °C); recrystallized from EtOAc, 47.4% yield; ^{13}C NMR δ 120.4, 132.7, 138.9.

Thiosemicarbazide of 2-acetyl-1,3-indandione (12): mp 200–201 °C dec; recrystallized from EtOH/H_2O and then from CH_3OH, 73.1% yield; ^{13}C NMR δ 121.1, 133.5, 138.1, 139.7. Anal. Calcd for $C_{12}H_{11}N_3O_2S$: C, 55.12; H, 4.24; N, 16.08; S, 12.27. Found: C, 55.07; H, 4.26; N, 16.05; S, 12.27.

Semicarbazide of 2-acetyl-1,3-indandione (13): mp 233–234 °C dec; recrystallized from 95% EtOH, 94% yield; ^{13}C NMR δ 120.8, 133.3, 138.1, 139.6. Anal. Calcd for $C_{12}H_{11}N_3O_3$: C, 58.77; H, 4.52; N, 17.13. Found: C, 58.52; H, 4.59; N, 17.08.

Ethyl carbazate of 2-acetyl-1,3-indandione (14): mp 205 °C; recrystallized from 95% EtOH, 90% yield; ^{13}C NMR δ 121.0, 133.4, 138.2, 139.7. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.30; H, 5.14, N, 10.21; Found: C, 61.22; H, 5.20; N, 10.18.

Ethyl carbazate of 2-benzoyl-1,3-indandione (15): mp 214–216 °C; recrystallized from 95% EtOH, 73% yield; ^{13}C NMR δ 121.2, 127.6, 128.3, 129.2, 129.9, 133.7, 138.5, 139.5. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.84; H, 4.80; N, 8.33. Found: C, 67.87; H, 4.85; N, 8.29.

Hydrazine of 2-acetyl-1,3-indandione (16): mp 238–239 °C (lit.[14] 238–239 °C); recrystallized from EtOAc, 84% yield; ^{13}C NMR δ 120.3, 132.7, 138.8.

***O*-Acetate of the Hydroxylamine of 2-Acetyl-1,3-indandione (11).** The oxime of 2-acetyl-1,3-indandione (**10**) (1.0 g, 5 mmol) was dissolved in 125 mL of previously distilled THF with heating. The solution was cooled to 15 °C and 0.9 g (8.8 mmol) of acetic anhydride was added. The reaction mixture was stirred at 20 °C for 16 h and then concentrated in vacuo at 15–20 °C. The residue was treated with water and the light yellow solid was collected by filtration. A sample of the product was recrystallized twice from THF–petroleum ether (bp 35–60 °C), mp 135 °C (approximately 60% yield); ^{13}C NMR δ 121.4, 133.2, 138.4, 140.3. Anal. Calcd for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.63; H, 4.56; N, 5.69.

3-*tert*-Butyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]isoxazol-4-one (19): mp 143–145 °C (lit.[11] 143–145 °C); recrystallized from 95% EtOH, 74% yield; ^{13}C NMR δ 123.4, 124.0, 130.4, 136.6, 134.6 (4a), 150.8 (8a).

3-Phenyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]isoxazol-4-one (20): mp 184–186 °C dec (lit.[13] mp 189–190 °C); recrystallized from *c*-C_6H_{12}, 32.3% yield (28% recovery of starting material); ^{13}C NMR δ 123.5, 124.1, 127.5, 128.6, 128.7 (1'), 130.2, 130.7, 134.7 (4a), 136.8, 150.5 (8a).

3-(4-Methoxyphenyl)-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]isoxazol-4-one (21): mp 154–156 °C; recrystallized from C_6H_6, 39% yield (41% recovery of starting material); ^{13}C NMR δ 114.1, 121.2, 123.5, 124.1, 129.23, 130.6, 134.7, 136.8, 150.6, 160.9. Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.11; H, 4.46; N, 4.72.

1-Thiocarbamoyl-3-*tert*-butyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (22): mp 176–178 °C dec; recrystallized from 95% EtOH, 96% yield; ^{13}C NMR δ 123.6, 127.8 130.3, 136.3, 151.2. Anal. Calcd for $C_{15}H_{17}N_3O_2S$: C, 59.38; H, 5.65; N, 13.85; S, 10.57. Found: C, 59.42; H, 5.66; N, 13.84; S, 10.50.

1-Thiocarbamoyl-3-phenyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (23): mp 165–166 °C dec; recrystallized from C_6H_6–*c*-C_6H_{12} and then from 95% EtOH, 62% yield; ^{13}C NMR δ 123.8, 127.9, 128.5, 128.8, 130.4, 131.2, 134.9, 136.4, 151.0. Anal. Calcd for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99; S, 9.92. Found: C, 63.16; H, 4.07; N, 12.95; S, 9.85.

1-Carbamoyl-3-*tert*-butyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (24): mp 157–162 °C; recrystallized from 95% EtOH–H_2O, 82.3% yield; ^{13}C NMR δ 122.8, 128.1, 129.7, 135.3, 135.8, 151.5. Anal. Calcd for $C_{15}H_{17}N_3O_3$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.76; H, 6.40; N, 8.78.

1-Carbamoyl-3-phenyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (25): mp 211–214 °C; recrystallized from 95% EtOH, 49% yield; ^{13}C NMR δ 122.8, 127.6, 128.4, 129.7, 129.9, 130.9, 135.5, 135.8, 144.9. Anal. Calcd for $C_{17}H_{13}N_3O_3 \cdot {}^1/_2C_2H_5OH$: C, 65.44; H, 4.88; N, 12.72; C, 65.37; H, 4.75; N, 12.90.

1-Carbethoxy-3-*tert*-butyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (26): mp 157–162 °C; recrystallized from 95% EtOH–H_2O, 82% yield; ^{13}C NMR δ 123.8, 125.4, 130.0, 135.4, 136.3, 150.8. Anal. Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.26; H, 6.40; N, 8.78.

1-Carbethoxy-3-phenyl-3a,8b-dihydro-8b-hydroxyindeno[1,2-*c*]pyrazol-4-one (27). A mixture of the ethyl carbazate of 2-benzoyl-1,3-indandione (**15**) (0.7 g, 2.1 mmol) in 15 mL of 100% EtOH containing a catalytic amount of Et_3N was heated under reflux for 1 h. TLC eluting with EtOAc/toluene (1:3) indicated the formation of two faster moving compounds. The reaction mixture was concentrated in vacuo and the residue was chromatographed on 80 g of silica gel eluting with EtOAc/toluene (1:4). The first material off of the column consisted of 0.1 g of yellow solid, which was recrystallized from toluene–petroleum ether (bp 35–60 °C), mp 160–162 °C (lit.[3] 163–164 °C), and identified as 1-carbethoxy-3-phenylindeno[1,2-*c*]pyrazol-4(1*H*)-one. The second solid off of the column was **27** (0.12 g), which after recrystallization from toluene–petroleum ether (bp 35–60 °C) had mp 158–160 °C dec. The compound resolidified and exhibited a second melting point, 214–216 °C (isomer **15**), 17% yield. ^{13}C NMR δ 124.1, 125.5, 128.1, 128.3, 129.9, 130.3, 130.4, 135.5, 136.4, 150.6. Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.84; H, 4.79; N, 8.33. Found: C, 67.72; H, 4.83; N, 8.29.

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