occurring at the third atom from the benzene ring does not seem to be involved in this δ value.

In the present correlations, the steric effect of o-NO_2 group is fit best with the E_s value for its maximum dimension. In the sterically critical step of hydrolysis reactions, the o-NO_2 group seems to remain coplanar with the benzene ring. The conjugation of the o-NO_2 group is not inhibited, while the intergroup through-resonance between o-NO_2 and acyloxy groups is not significant.

Substituent effects on the hydrolytic reaction course of phenyl acetates and dimethylcarbamates are very similar to each other including ortho-substituted derivatives as far as the ordinary polar and steric effects are concerned. However, the proximity polar effect of ortho substituents significantly differs between these two series. A distinct proximity effect appears to be involved for the ortho-substituted phenyl acetates (set 1, cor 1 and 3) while not significant for the ortho-substituted dimethylcarbamates (set 2, cor 1 and 3). As suggested in our recent analyses, the magnitude of f may be subject not only to the distance between reaction site and the benzene ring but also to the side chain structure to some extent.[9] Even though the geometrical location of the rate-limiting reaction site is similar to the above cases, the negative f value (-0.29 ± 0.05) has been found for three phenylacetyl transfer reactions.[9]

The large f value (3.0) for set 4 should come mostly from a high susceptibility of the rate-determining phenoxide formation step to the electron-withdrawing proximity polar effect of ortho substituents, which can be compared with that for the dissociation of phenols, 2.4 in eq 7 and 9. The difference may be attributed to the effect of ortho substituents on the preequilibrium deprotonation step. The f value, 0.90 ± 0.04, for set 3 is larger than that for set 1 of phenyl acetates. It may be mostly attributed to the step of addition intermediate formation, containing in part a component due to the phenoxide splitting.

The above work indicates that the ortho effect on the alkaline hydrolysis of phenyl esters can be analyzed quantitatively by means of δ and f terms of component effects overlapping on the ordinary polar effect of ortho substituents. The component effects participate in the total effect of ortho substituents generally to varying degrees according to reaction systems. We must be careful in discussing mechanism of reactions of these classes of compounds including ortho derivatives with enzyme systems so as to select reference reaction systems and conditions as close as possible to those of the enzymatic reactions.

Acknowledgment. We are grateful to Messrs. Izumi Kumita and Masahide Nohta for a part of measurements. Calculations were performed on a FACOM 230/75 computer at the Data Processing Center of this University.

References and Notes

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3-Cycloalkenylindoles

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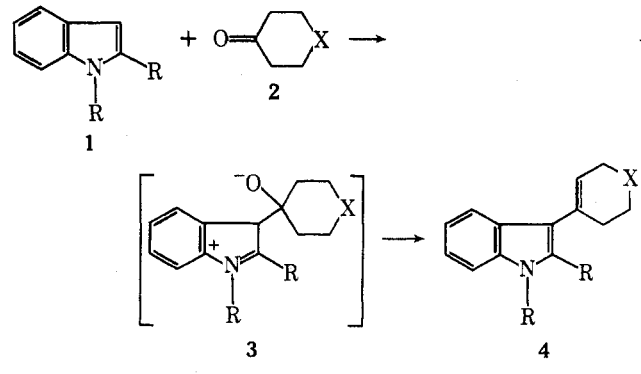
A simple method for the preparation of the title compounds 4 is described and demonstrated on a variety of indoles (1) and ketones (2). Some reactions of these new derivatives are discussed.

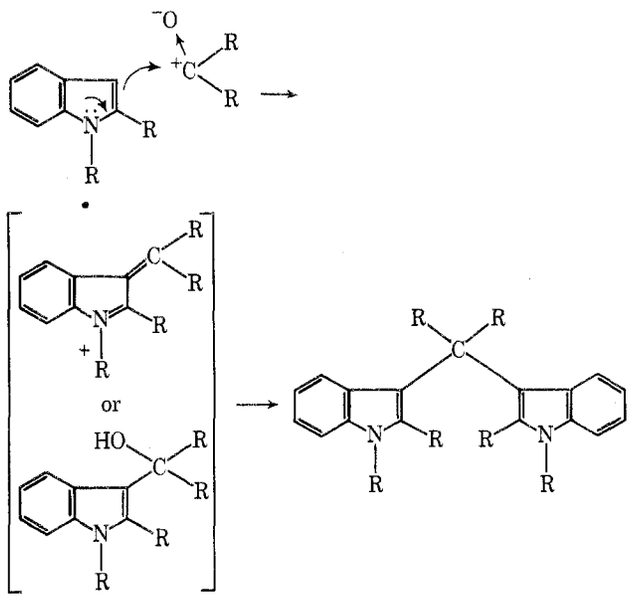
Reactions of indoles with ketones under acidic conditions are well documented.[1] The general course is electrophilic attack by the carbonyl carbon at the indole 3 position, leading via 3-methyleneindolenines or indolyl-3-carbinols to diindolylmethanes (Scheme I).

We found that cyclic ketones (2), contrary to this general observation, give 1:1 reaction products with 3-unsubstituted indoles (1). This reaction proceeds with a wide variety of cyclic ketones in excellent yields, affording indole derivatives of the general formula 4, hitherto little known[2,3] and accessible only via tedious de novo syntheses. Obviously, the intermediates 3 stabilize by water elimination.

The scope of this reaction was investigated using 1,2-



Scheme I



dimethylindole and a number of cyclic ketones (Table I) and secondly by combining *N*-methyl-4-piperidone with a number of indoles (Table II).

The variety of ketones leading to cycloalkenylindoles can be seen from Table I. The reaction did not proceed with the following cyclic ketones: tetrahydrofuranone, cyclopentanone, and adamantanone.

Some ketones were selected with the expectation to find biologically interesting compounds; e.g. **6** and **7** (**4o**) and their hydrogenation product **8** are cyclic tryptamines.

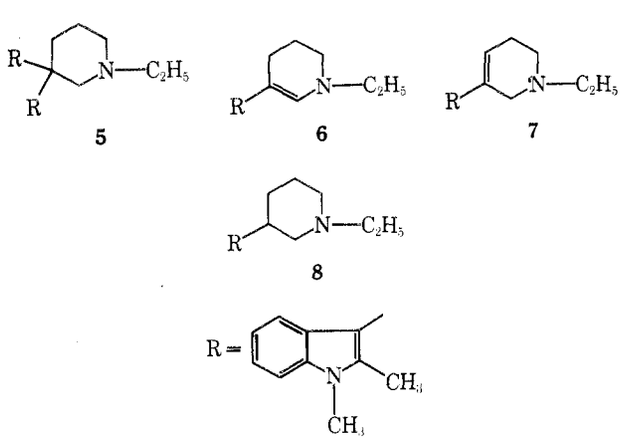
The same concept governed our choice of indoles in Table II, giving some preference to 5-substituted indoles.

Some reactions with unsymmetrically substituted ketones produced the expected mixture of isomers.

The product **4d**, obtained from 1,2-dimethylindole and ethyl cyclohexanone-2-carboxylate and subsequent saponification, is a mixture of the 1- and 2-unsaturated isomers, as shown by their NMR spectrum.

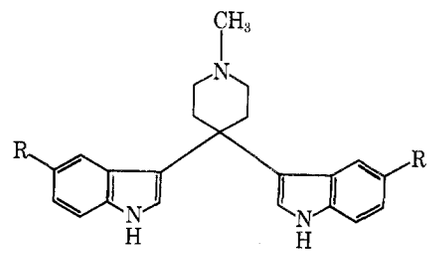
A similar mixture was detected by TLC in the case of **4m**. A small part of the α,β-unsaturated ester could be separated by column chromatography. The remaining mixture crystallized as hydrochlorides and showed an NMR spectrum indicative for a ratio of α,β:β,γ-unsaturated esters of 3:1.

The reaction of *N*-ethyl-3-piperidone with 1,2-dimethylindole resulted in three compounds which could be separated on silica: the dimer (**5**), the 2,3-piperideine (**6**), and the 3,4-piperideine (**7**).



Hydrogenation of either **6** or **7** gave the indolylpiperidine **8**.

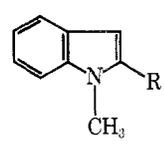
The 1,2,3-unsubstituted indoles gave under these conditions a considerable amount of the bisindolylcycloalkanes, **9** and **10**, in addition to the main products **4q** and **4r**.



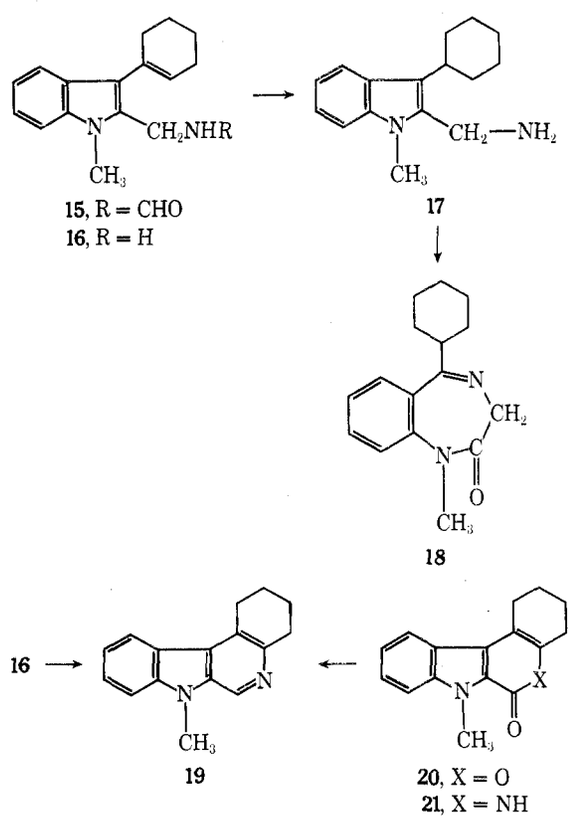
9, R = H
10, R = OCH_3

Ethyl 1-methylindole-2-carboxylate (**11**), 1-methylindole-2-carboxamide (**12**), and 1-methyl-2-aminomethylindole (**13**) failed to react with cyclohexanone and *N*-methyl-4-piperidone. We were especially interested in this reaction and succeeded finally with 1-methyl-2-formylaminomethylindole (**14**) and cyclohexanone (Scheme II). The resulting

Scheme II

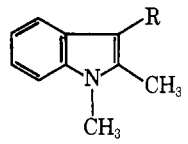


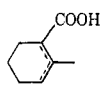
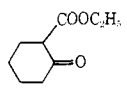
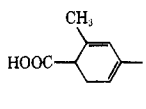
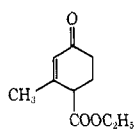
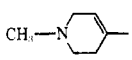
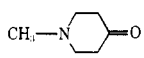
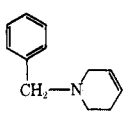
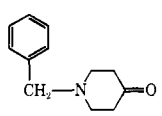
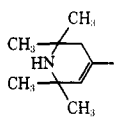
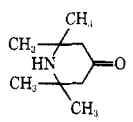
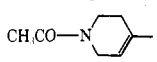
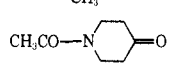
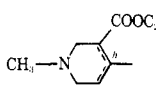
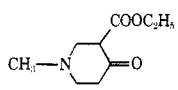
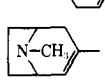
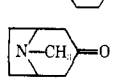
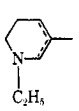
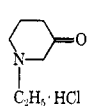
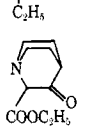
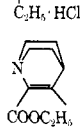
11, R = $COOC_2H_5$
12, R = $CONH_2$
13, R = CH_2NH_2
14, R = CH_2NH-CHO



product (**15**), after hydrolysis and hydrogenation, smoothly underwent the chromium trioxide oxidation–rearrangement of Yamamoto et al.[4] to the benzodiazepine **18**. Under

Table I[a]



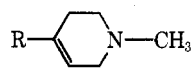
4	R	Ketone 2	Reaction time	Temp, °C	Yield, %	Mp, °C	Empirical formula	Calcd / Found	C, %	H, %	N, %
a			40 min	60–70	89	109	$C_{16}H_{19}N$	Calcd	85.28	8.50	6.22
								Found	85.54	8.35	6.30
b			4 hr	90	75	161[b]					
c			4 hr	60	85	165–168	$C_{16}H_{17}NO$	Calcd	80.30	7.16	5.85
								Found	80.10	7.34	5.87
d			1 hr	75	69[d]	153–155	$C_{17}H_{19}NO_2$	Calcd	75.81	7.11	5.20
								Found	75.76	7.05	5.28
e			90 min	75	30[e]	168–171	$C_{18}H_{19}NO_2$	Calcd	76.84	6.81	4.98
								Found	76.82	6.89	5.08
f			6 hr	70	97	118	$C_{15}H_{17}NS$	Calcd	74.05	7.04	5.76
								Found	73.99	6.89	5.82
g			30 min	60	95	79 270–275[f]	$C_{16}H_{20}N_2 \cdot HCl$	Calcd	69.40	7.66	10.11
								Found	69.07	7.55	9.89
h			2 hr	60	85	246[f]	$C_{22}H_{24}N_2 \cdot HCl$	Calcd	74.87	7.14	7.93
								Found	74.67	7.67	7.93
i			60 min	60	87	76 255–265[f]	$C_{15}H_{18}N_2 \cdot HCl$	Calcd	68.56	7.29	10.66
								Found	68.64	7.45	10.57
k			90 min	80	82	112	$C_{19}H_{26}N_2$	Calcd	80.80	9.28	9.92
								Found	80.45	9.31	9.97
l			3 hr	20	95	199	$C_{17}H_{20}N_2O$	Calcd	76.08	7.51	10.43
								Found	76.02	7.52	10.37
m			7 hr	110	67[h]	197[i]	$C_{19}H_{24}N_2O_2 \cdot HCl$	Calcd	65.41	7.22	8.03
								Found	65.66	6.94	8.10
n			23 hr	60	85	118 260[f]	$C_{18}H_{22}N_2 \cdot HCl$	Calcd	71.38	7.65	9.25
								Found	71.26	7.51	9.14
o			90 min	75	*k*						
p			13 hr	80	40	148	$C_{20}H_{24}N_2O_2$	Calcd	74.04	7.46	8.64
								Found	73.98	7.58	8.68

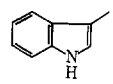
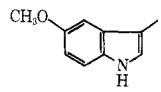
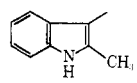
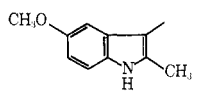
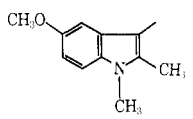
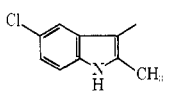
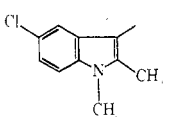
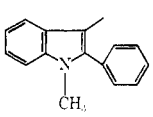
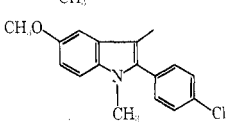
[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in this table. [b] See also literature.[5] [c] Or from 3-ethoxy-2-cyclohexen-1-one. [d] The crude ester was saponified with KOH–ethanol to give this yield of crystalline acid, a mixture of two isomers. See text. [e] The crude ester was saponified, overall yield. [f] Hydrochloride. [g] 4-Piperidone monohydrate hydrochloride. [h] Mixture of both isomers. [i] 1,2-Dimethyl-3-[4-(1-methyl-3-ethoxycarbonyl-1,2,5,6-tetrahydropyridyl)]indole hydrochloride. [k] See text.

the same conditions, the unsaturated intermediate **16** cyclized and dehydrogenated to the carboline **19**, which we synthesized independently from the indolocoumarin **20**[5] via **21** as indicated in Scheme II.

The structures of **4** were verified by elemental analyses, spectral evidence (all show the characteristic vinyl proton at δ 5.8), and subsequent reactions. Hydrogenation, wherever attempted, yielded smoothly the cycloalkylindoles, as shown for **8**. Dehydrogenation of **4e** under the usual conditions afforded the expected substituted phenylindole **22**.

Table II[a]



4	R	Reaction time, hr	Temp, °C	Yield, %	Mp, °C	Empirical formula	Calcd / Found	C, %	H, %	N, %	Registry no.
q		4	90	45 + 30% **9**	210–220[b] dec						120-72-9
r		2	reflux	50 + 35% **10**	235 dec	$C_{15}H_{18}N_2O$	Calcd	74.34	7.48	11.56	1006-94-6
							Found	74.24	7.63	11.60	
s		2	70	91	139–141	$C_{15}H_{18}N_2$	Calcd	79.60	8.02	12.38	95-20-5
							Found	79.53	7.89	12.48	
t		1	70	88	137	$C_{16}H_{20}N_2O$	Calcd	74.96	7.86	10.93	1076-74-0
							Found	74.87	7.72	11.03	
u		1	60	80	104	$C_{17}H_{22}N_2O$	Calcd	75.52	8.20	10.36	17591-06-9
							Found	75.49	8.00	10.04	
v		2	60	85	155	$C_{15}H_{17}ClN_2$	Calcd	69.08	6.57	10.74	1075-35-0
							Found	68.89	6.65	10.69	
w		1	60	63	95	$C_{16}H_{19}ClN_2$	Calcd	69.93	6.96	10.19	55556-49-5
							Found	69.84	7.02	10.07	
x		8	80	60	103	$C_{21}H_{22}N_2$	Calcd	83.40	7.33	9.26	3558-24-5
							Found	83.76	7.42	9.15	
y		6	80	50	251[c]	$C_{22}H_{23}ClN_2O \cdot HCl$	Calcd	65.50	5.99	6.94	55556-50-8
							Found	66.09	6.34	6.89	

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compunds listed in this table. [b] See literature.[3] [c] Hydrochloride.

Experimental Section[9]

General Procedure for the Preparation of 3-Cycloalkenylindoles (4). The appropriate indole derivative (20 g) was dissolved in 400 ml of glacial acetic acid. When the temperature stated in Table I or II was reached, 100 ml of 2 *N* phosphoric acid and an 1.5–3 molar excess of the appropriate ketone was added. The mixture was stirred at this temperature for the time indicated. In some cases the end product was collected by filtration after cooling; in many cases the mixture was poured on ice–ammonia and the reaction products were extracted, mainly with ethyl acetate and worked up as usual. A typical[7] uv spectrum (**4g**): λ_{max} 230 nm (ϵ 24,000), 285 (6200).

3-(1,2-Dimethyl-3-indolyl)-*N*-ethyltetrahydropyridines (6 and 7). 1,2-Dimethylindole (10 g, 69 mmol) and 1-ethyl-3-piperidone hydrochloride (15 g, 91 mmol) were allowed to react as shown in the general procedure for **4o**. The resulting oil was separated on silica [20 cm column, 8 cm diameter, eluent chloroform–methanol (97:3)].

The first (**6**) of the three main reaction products (TLC) was an oil, 4.7 g, which gave a crystalline hydrochloride from ethanol–ether: mp 95–100°; 3.3 g (17%); NMR (D_2O) δ 8.4 (s, 1), 7.5–7.1 (m, 4), 4.2–3.8 (m, 4), 3.7 (s, 3), 2.5 (s, 3), 2.5–1.9 (m, 4), 1.6 (t, 3, J = 7 Hz).

Anal. Calcd for $C_{17}H_{22}N_2 \cdot HCl$: C, 70.18; H, 7.98; N, 9.63. Found: C, 70.34; H, 7.76; N, 9.32.

The second fraction crystallized from ethanol and appeared to be 3,3-bis(1,2-dimethyl-3-indolyl)-1-ethylpiperidine (**5**): yield 2.2 g (16%); mp 182°; NMR ($CDCl_3$) δ 8.4–8.2 (m, 1), 8.3–7.8 (m, 1), 7.2–6.9 (m, 6), 4.0–1.5 (m, 10), 3.25 (s, 3), 3.20 (s, 3), 1.35 (s, 3), 1.30 (s, 3), 0.9 (t, 3, J = 7 Hz).

Anal. Calcd for $C_{27}H_{33}N_3$: C, 81.15; H, 8.32; N, 10.51. Found: C, 80.91; H, 8.45; N, 10.31.

The major component eluted last from the column (**7**) yielding 9.8 g (56%) of a clear oil. It crystallized as the picrate from ethanol: mp 172°; NMR (DMSO-d_6) δ 9.6 (s, 1), 8.6 (s, 2), 7.6–6.9 (m, 4), 5.8 (s, broad, 1), 4.0 (s, 2), 3.7 (s, 3), 3.7–2.3 (m, 6), 2.4 (s, 3), 1.3 (t, 3, J = 7 Hz).

Anal. Calcd for $C_{17}H_{22}N_2 \cdot C_6H_3N_3O_7$: C, 57.13; H, 5.21; N, 14.49. Found: C, 57.44; H, 5.24; N, 14.75.

3-(1,2-Dimethyl-3-indolyl)-*N*-ethylpiperidine Hydrochloride (8). Hydrogenation of either **6** or **7** in ethanol at room temperature and 50 psi over palladium on charcoal and subsequent treatment with hydrochloric acid afforded the title compound in almost quantitative yield: mp 250°; NMR ($CDCl_3$) δ 12.1 (s, 1), 7.8–6.9 (m, 4), 4.2–1.7 (m, 11), 3.6 (s, 3), 2.4 (s, 3), 1.4 (t, 3, J = 7 Hz).

Anal. Calcd for $C_{17}H_{24}N_2 \cdot HCl$: C, 69.69; H, 8.60; N, 9.56. Found: C, 69.80; H, 8.71; N, 9.68.

4,4-Di(3-indolyl)-1-methylpiperidine (9). The reaction mixture from indole and a twofold excess of 1-methyl-4-piperidone (see general procedure for **4q**) was chromatographed on silica with chloroform–methanol–ammonia (70:29:1). The main fraction leaving the column first was compound **4q** (see Table II). The second fraction (30%) crystallized from methanol: mp 295–300°; NMR (DMSO-d_6) δ 10.8 (s, 2), 7.6–6.5 (m, 10), 2.8–2.3 (m, 8), 2.2 (s, 3).

Anal. Calcd for $C_{22}H_{23}N_3$: C, 80.20; H, 7.03; N, 12.75. Found: C, 80.14; H, 7.12; N, 12.67.

4,4-Bis(5-methoxy-3-indolyl)-1-methylpiperidine (10). This

compound was obtained analogously to **9**, as a by-product in the preparation of **4r**: mp 275–280° dec from ethyl acetate; yield 35%; NMR (DMSO-d_6) δ 10.6 (s, 2), 7.5–6.5 (m, 8), 3.6 (s, 6), 2.7–2.4 (m, 8), 2.2 (s, 3).

Anal. Calcd for $C_{24}H_{27}N_3O_2$: C, 74.00; H, 6.98; N, 10.78. Found: C, 73.86; H, 7.15; N, 10.75.

1-Methyl-2-formylaminomethylindole (14). 1-Methyl-2-aminomethylindole (13[6] 1.8 g, 11 mmol) was heated to reflux for 6 hr in 20 ml of ethyl formate. The residue after evaporation was recrystallized from ethyl acetate–petroleum ether: yield 1.6 g (75%); mp 110–112°; NMR ($CDCl_3$) δ 8.0 (s, 1), 7.6–6.9 (m, 4), 6.3 (s, 2), 4.4 (d, 2, J = 6 Hz), 3.5 (s, 3).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.61; H, 6.65; N, 15.28.

1-Methyl-2-formylaminomethyl-3-cyclohexen(1)ylindole (15). A mixture of 14 (10 g, 50 mmol), cyclohexanone (20 ml, 190 mmol), glacial acetic acid (200 ml), and 4 N phosphoric acid (100 ml) was heated under stirring at 70° for 7 hr. After cooling to room temperature, water (40 ml) was added and the mixture was kept at 5° overnight. The crystalline reaction product was collected, washed with water, and recrystallized from ethanol: yield 5.9 g (42%); mp 178°; NMR ($CDCl_3$) δ 8.1 (s, 1), 7.7–6.9 (m, 4), 5.9 (s, 1), 5.6 (s, 1), 4.6 (d, 2, J = 6 Hz), 3.6 (s, 3), 2.5–2.0 (m, 4), 2.0–1.6 (m, 4).

Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.44. Found: C, 76.54; H, 7.31; N, 10.73.

1-Methyl-2-aminomethyl-3-cyclohexen(1)ylindole (16). A solution of the above formyl compound (**15**, 17.3 g, 65 mmol) in 300 ml of ethanol and 15 ml of 30% sodium hydroxide was heated to reflux for 5 hr. The solution was filtered, concentrated in vacuo, and extracted with ether. The ether extracts were washed, dried, and evaporated. The solid residue (15.2 g, 97%) was used as such for the next step. A sample was crystallized from petroleum ether: mp 56°; NMR ($CDCl_3$) δ 7.6–6.8 (m, 4), 5.6 (s, 1), 3.9 (s, 2), 3.6 (s, 3), 2.5–2.0 (m, 4), 1.9–1.4 (m, 4), 1.2 (s, 2, NH_2).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.28; H, 8.50; N, 11.70.

1-Methyl-2-aminomethyl-3-cyclohexylindole (17). The above described unsaturated compound **16** (5.8 g, 24 mmol) was dissolved in 200 ml of ethanol and shaken with 0.5 g of palladium on charcoal (10%) at room temperature and about 40 psi hydrogen pressure for 3 days. The residue after filtration and evaporation was a light oil (5.8 g, 100%). Aside from the NMR spectrum, no attempt was made to characterize it. The spectrum was essentially unchanged from the one of the starting material; only the vinyl proton signal at δ 5.6 was missing and the cyclohexyl portion was more complex.

2-Oxo-1-methyl-5-cyclohexyl-2,3-dihydro-1*H*-1,4-benzodiazepine (18). The crude cyclohexylindole **17** (5.5 g, 23 mmol) was dissolved in 30 ml of glacial acetic acid and cooled to 15°. A solution of chromium trioxide (5 g) in 5 ml of water was added under stirring in such a way that the temperature remained between 15 and 18°. When the addition was completed, the mixture was allowed to stand at room temperature for 2 hr. It was poured on ice–ammonium hydroxide and the reaction products were extracted with ethyl acetate. The residue after washing, drying, and evaporation (3.8 g) was chromatographed on silica with chloroform–methanol (97:3).

The main fraction (R_f 0.7 on TLC) was dissolved in ether; a hydrochloride was precipitated with dry HCl, which was recrystallized from ethanol–ether. From this, the free base was liberated with sodium carbonate, which crystallized from ether: yield 0.9 g (16%); mp 98–100°; NMR ($CDCl_3$) δ 7.7–7.0 (m, 4), 4.5 (d, 1, J = 11 Hz), 3.5 (d, 1, J = 11 Hz),[8] 3.3 (s, 3), 3.0–0.6 (m, 11).

Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.96; H, 7.86; N, 10.93. Found: C, 74.53; H, 7.94; N, 10.45.

7-Methyl-6-oxo-1,2,3,4,5,6-hexahydroindolo[2,3-*c*]quinoline (21). 7-Methyl-1,2,3,4-tetrahydroindolo[2,3-*c*]coumarin (**20**, 4 g, 16 mmol)[5] was heated in 50 ml of ethanol, saturated with ammonia, for 7 days at 180° in a steel pressure vessel. The residue after evaporation was crystallized from ethanol by extraction from a Soxhlet apparatus: yield 3 g (75%); mp 280° dec; NMR (CF_3COOD) δ 8.2–7.3 (m, 4), 4.1 (s, 3), 3.3–2.7 (m, 4), 2.2–1.9 (m, 4).

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.29; H, 6.34; N, 11.03.

7-Methyl-1,2,3,4-tetrahydroindolo[2,3-*c*]quinoline (19). A. From 21. A mixture of the above compound **21** (3 g, 12 mmol), $LiAlH_4$ (2 g, 53 mmol), and 100 ml of anhydrous toluene was heated to reflux for 7 hours. The residue after the usual work-up was chromatographed on silica [chloroform–methanol (97:3)]. The main fraction (R_f 0.5) was the title compound. It crystallized as hydrochloride from ethanol–ether: yield 1.6 g (49%); mp 320–323°; NMR ($CDCl_3$) of the free base δ 8.4 (s, 1), 8.1–6.9 (m, 4), 3.6 (s, 3), 3.3–2.8 (m, 4), 2.1–1.7 (m, 4).

Anal. Calcd for $C_{16}H_{16}N_2$·HCl: C, 70.45; H, 6.28; N, 10.27; Cl, 13.00. Found: C, 69.98; H, 6.35; N, 10.34; Cl, 12.70.

B. From 16. 1-Methyl-2-aminomethyl-3-cyclohexen(1)ylindole (**16**, 7 g, 29 mmol) was dissolved in glacial acetic acid (100 ml). The solution was cooled to 15° and chromium trioxide (6 g) in water (7 ml) was added slowly with stirring. The mixture was worked up after 2 hr as described under **18**. The main fraction from column chromatography [silica, chloroform–methanol (97:3)] (2 g, 28%) was converted to the hydrochloride and was found identical with the above preparation.

4-(1,2-Dimethyl-3-indolyl)-2-methylbenzoic Acid (22). The cyclohexadiene derivative **4e** (0.4 g, 14 mmol) was heated to reflux in mesitylene (25 ml) under CO_2 with 0.3 g of palladium on charcoal (5%) for 2 hr. The residue after filtration and evaporation was recrystallized from ethanol: yield 0.2 g (50%); mp 205–207°; NMR (DMSO-d_6) δ 8.2–7.0 (m, 7), 3.8 (s, 3), 2.7 (s, 3), 2.5 (s, 3).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.46; H, 6.22; N, 5.02.

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Registry No.—1 (R = Me), 875-79-6; **2a**, 108-94-1; **2b**, 533-60-8; **2c**, 504-02-9; **2d**, 1655-07-8; **2e**, 487-51-4; **2f**, 1072-72-6; **2g**, 1445-73-4; **2h**, 3612-20-2; **2i**, 41661-47-6; **2k**, 826-36-8; **2l**, 32161-06-1; **2m**, 25012-72-0; **2n**, 532-24-1; **2o**, 41361-28-8; **2p**, 34286-16-3; **4a**, 55556-25-7; **4b**, 32544-46-0; **4c**, 55556-26-8; **4d** isomer 1, 55556-27-9; **4d** isomer 2, 55556-28-0; **4e**, 55556-29-1; **4f**, 55556-30-4; **4g**, 55556-31-5; **4h**, 55556-32-6; **4i**, 55556-33-7; **4k**, 55556-34-8; **4l**, 55556-35-9; **4m** isomer 1, 55556-36-0; **4m** isomer 2, 55556-37-1; **4n**, 55556-38-2; **4o** isomer 1, 55556-39-3; **4o** isomer 2, 55556-40-6; **4p**, 55606-54-7; **4q**, 17403-03-1; **4r**, 55556-41-7; **4s**, 55556-42-8; **4t**, 55556-43-9; **4u**, 55556-44-0; **4v**, 55556-45-1; **4w**, 55556-46-2; **4x**, 55556-47-3; **4y**, 55556-48-4; **5**, 55556-51-9; **6**, 55556-52-0; **7**, 55556-53-1; **8**, 55556-54-2; **9**, 55556-55-3; **10**, 55556-56-4; **13**, 55556-57-5; **14**, 55556-58-6; **15**, 55556-59-7; **16**, 55556-60-0; **17**, 55556-61-1; **18**, 31269-24-6; **19**, 55556-62-2; **20**, 32500-45-1; **21**, 55556-63-3; **22**, 55556-64-4; ethyl formate, 109-94-4.

References and Notes

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(9) Melting points were determined on a Fisher-Johns block and are uncorrected. Microanalyses were performed by Dr. A. B. Gygli, Toronto. The NMR spectra were taken on a Varian T-60 instrument.