mg (13%) of unreacted **30**. Both the ester **30** and the photoproducts **32** and **33**, appeared to decompose during chromatography.

The mixture of photoproducts **17**, **32**, and **33** from fractions 14–15 had nmr (CCl_4, TMS) δ 7.12 (broad s), 6.17 (d of d), 5.88 (s), 5.83 (s), 2.90 (s), 2.87 (s); ir (CCl_4) 3.22 (sh): 3.25 (m); 3.28, 3.37, 3.40 (s); 3.48 (m); 5.78 (w); 6.27 (m); 6.70, 6.90, 7.95, 8.03, 8.72, 9.30, 9.73, 9.90, 11.63, 14.40 μ (s). Mass spectra (70 eV) of the products were obtained with the gc/mass spectral interface. **33** had *m/e* (rel intensity) 162 (23), 81 (100), 53 (22); **32**, 172 (25), 91 (31), 81 (100), 65 (9), 53 (12); **17**, 182 (19), 91 (100), 65 (13).

Photolysis of α-Naphthylmethyl Phenylacetate (31).—As above, the irradiation of the ester was monitored by use of a limewater bubbler; 336 mg (1.22 mmol) of **31** in 15 ml of dioxane was degassed and irradiated (2537 Å). After 2900 min, vpc analysis (as above) showed three products (relative areas 1:10:1) in *ca.* 40% yield; limewater test was positive. Removal of the solvent and chromatography of the residue (327 mg) on a 1.5 × 52 cm column of Davison Grade 950 silica gel, slurry packed with hexane, gave (75 ml fractions) 1–6, hexane eluent, 3 mg residue; 7–10, 1% ether–hexane, 2 mg residue; 11–13, 2% ether–hexane, nil; 14–16, 2% ether–hexane, 114 mg (40%) of a mixture of dibenzyl (**17**), 5%, and 1-α-naphthyl-2-phenylethane (**34**), 95%; 17–18, 2% ether–hexane, 3 mg of residue; 19–22, 4% ether–hexane, nil; 23–27, 10% ether–hexane, 130 mg (39%) of unchanged **31**. The di-α-naphthylethane was present in only trace quantities. However, it was shown to be present by coinjection with a sample obtained from the RPR 3000 Å irradiation (*vide infra*).

The viscous oil from fractions 14–16 had nmr ($CDCl_3$, TMS) δ 7.22 (s) superimposed on 8.20–7.13 (m, 12 H), 3.18 (AA'BB', 4 H); ir ($CHCl_3$) 3.25, 3.31, 3.39 (s); 3.48 (m); 5.15, 5.37, 5.55 (w); 6.26, 6.70, 6.90, 7.20 (m); 8.60 (w); 9.30, 9.72, 9.85 (m); 10.38, 11.68 (w); 14.45 μ (s); mass spectra (70 eV, gc/mass spectral interface) **17**, *m/e* (rel intensity) 182 (12), 92 (9), 91 (100), 65 (15) (identical with authentic mass spectrum of dibenzyl); **34**, 232 (19), 142 (12), 141 (100), 115 (16), 91 (6).

Photolysis of **31** with the RPR-3000 Å lamps (568 mg **31**, 2.06 mmol, in 15 ml dioxane) led to a positive limewater test. Vpc analysis showed 54% conversion after 2850 min, with three products formed in a 1:13:1 ratio. The major product was identical with 1-α-naphthyl-2-phenylethane (**34**) by vpc coinjection. Dibenzyl (**17**) was also observed as a minor product. Removal of the solvent and addition of ether resulted in formation of white crystals of 1,2-di-α-naphthylethane (**35**), mp 161–163° (lit.[40] mp 161–162°).

Solvent Effects on the Photostationary State of *cis*- and *trans*-1,2-Diphenylcyclopropane.—Samples of synthetic *cis*- and *trans*-1,2-diphenylcyclopropane (**13** and **14**) were dissolved in 15 ml of solvent, degassed, and irradiated in the merry-go-round at 2537 Å. Aliquots were withdrawn at intervals for vpc analysis (column 200°). For each solvent, the photostationary state was reached from *ca.* 5% excess cis or from 5% excess trans. The results are summarized in Tables III and IV.

Quantum Yield Determinations. General Procedure.—A solution of the lactone or ester in 15 ml of solvent in a quartz tube was degassed, placed in the merry-go-round, and irradiated with the RPR-2537 Å lamps. Light output was monitored by potassium ferrioxalate actinometry by the method of Hatchard and Parker.[41] Samples were withdrawn at intervals and analyzed directly by vpc.

Quantum yields for carbon dioxide evolution were measured by passing oxygen-free dry nitrogen through the photolysis mixture. The effluent gas from the photolysis vessel was then passed through a tared Ascarite–Anhydrone (magnesium perchlorate) trap.

Registry No.—**4**, 1008-76-0; **8**, 33574-07-1; **9**, 5279-82-3; **10**, 5590-14-7; **11**, 20272-24-6; **12**, 20272-26-8; **16**, 102-16-9; **18**, 36707-18-3; **19**, 33574-08-2; **20**, 538-39-6; **21**, 16557-55-2; **22**, 33574-09-3; **23**, 36707-23-0; **24**, 36707-24-1; **25**, 36707-25-2; **26**, 4960-53-6; **28**, 36707-27-4; **30**, 36707-28-5; **31**, 36707-29-6; **32**, 36707-30-9; **33**, 36707-31-0; **34**, 36707-32-1.

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Kinetic Control in the Formation of Dienamines. Cross-Conjugated Dienamines of $\Delta^{3(9)}$-4-Hydrindenones

FEIGA WEISBUCH,* CHISAKO YAMAGAMI, AND GILBERT DANA

Laboratoire de Chimie Organique Structurale, Université de Paris VI, Paris 5e, France

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A series of $\Delta^{3(9)}$-4-hydrindenones gives, with pyrrolidine, pure cross-conjugated dienamines. Systematic attempts to demonstrate the presence or to prepare the isomeric linearly conjugated dienamines having the amine group at the terminus of the diene were unsuccessful. Since the stereoisomeric 2,3-dimethyl-$\Delta^{3(9)}$-4-hydrindenones (**11**) give the corresponding cross-conjugated dienamines without any interconversion, this is regarded as a direct evidence for kinetic control in the formation of these bicyclic dienamines as a group. This generalization is supported by synthesis of the dienamines with N-deuterated pyrrolidine. The high regiospecificity of the reaction is explained in terms of steric hindrance in the concerned bicyclic system.

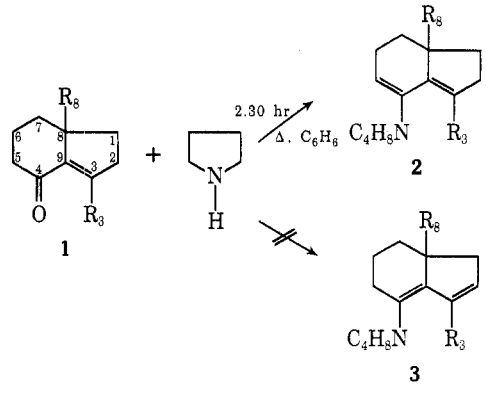
The enamines of 2-methylcyclohexanone and related unsymetrical ketones are known to be generally formed by thermodynamic control process. The less-substituted olefin is formed by a fast equilibrium, with steric effect control.[1,2]

The formation of the dienamines of α,β-unsaturated ketones also seems to be thermodynamically controlled, but products generally appear as mixtures of several dienamines, among which linear forms are predominant or exclusive. The yields in cross-conjugated forms are dependent on the structure of the reacting ketone and, for each ketone, on the structure of the antagonist secondary amine.[3,4] The determining factors for the ratio between linear and cross-conjugated dienamines are steric effects.[5] However,

(1) G. Stork, A. Brizzilara, H. Landesman, J. Smuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(2) S. K. Malhotra and F. Johnson, *Tetrahedron Lett.*, 4027 (1965).
(3) G. Stork and G. Birnbaum, *ibid.*, 313 (1961).
(4) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc. B*, 293 (1969).
(5) (a) F. Johnson, *Chem. Rev.*, **68**, 375 (1968); (b) P. W. Hickmott, B. J. Hopkins and C. T. Yoxall, *J. Chem. Soc., B*, 205 (1971).

as for other unsaturated systems,[6] a linear conjugation is probably better than a cross conjugation, and electronic effects also account for the observed equilibrium.

The behavior of cisoid unsaturated cyclohexanones is different. These ketones (2-alkylidenecyclohexanones or Δ^8-1-octalone) give mixtures of dienamines with a predominant cross-conjugated form.[8] The limit case is that of $\Delta^{3(9)}$-4-hydrindenones **1**, which afford with good yields pure cross-conjugated dienamines **2**.[7]



a, R_3 = H; R_8 = CH_3
b, R_3 = CH_3; R_8 = H
c, R_3 = R_8 = CH_3

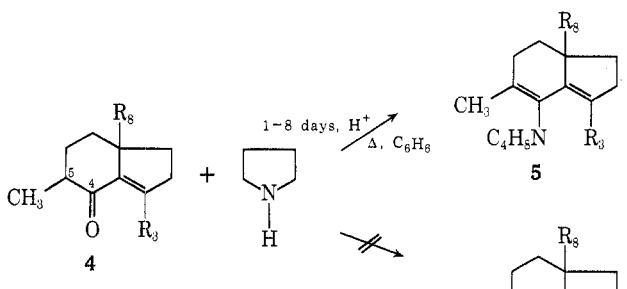
In the case of pulegone, we had observed an obvious kinetic control process followed by a slow equilibrium[8] since the ratio of different forms was time dependent.

In the present work we look over the control process in the formation of the pure cross-conjugated dienamines of $\Delta^{3(9)}$-4-hydrindenones **1**.

Results

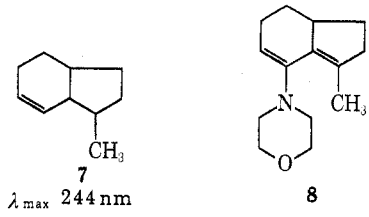
All the attempts to demonstrate the existence of an equilibrium between the cross-conjugated dienamines **2** and an uncertain linear form **3** lead to negative results.

I. Attempts of the Displacement of the Equilibrium toward the Linear Form.—The formation of pure cross-conjugated dienamines **2** formally appears similar to that of the less-substituted enamine from α-substituted cyclohexanone. Then we expected that the ketones **4** having a substituent on C_5 position could give a certain amount of linear dienamines **6**. In fact, in the three cases investigated, we have obtained pure cross-conjugated dienamines **5**. The reaction is more difficult than in the case of hydrindenones **1** and gives yields of only about 30–60% instead of 80–90% for **1**.



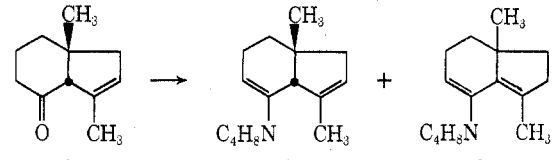
a, R_3 = H; R_8 = CH_3
b, R_3 = CH_3; R_8 = H
c, R_3 = R_8 = CH_3

On the other hand, it is known that the change of amine may modify the observed equilibrium between the dienamines.[4] Nevertheless, the 3-methyl-$\Delta^{3(9)}$-4-hydrindenone **1b** gives slowly (12-hr reflux in toluene with TsOH), with morpholine, a pure cross-conjugated dienamine **8**.



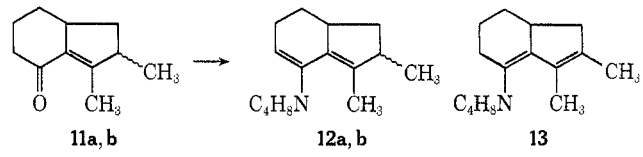
II. An Attempt of Direct Synthesis of the Linear Dienamine.—If the equilibrium between the cross-conjugated form and the expected linear form is slow, the direct synthesis of the linear dienamine could allow the study of the equilibrium.

The synthesis starts from the 3,8-dimethyl-Δ^2-4-hydrindenone **9**. This ketone is an α-substituted cyclohexanone and should give the dienamine with the less-substituted double bond (**10**), but the equilibrium



must be displaced, at least partially, by the presence of the C_2–C_3 double bond, since there is an important conjugation in the linear form **3c**, counteracting the steric effects. Then it would be possible to detect the formation of the dienamine **3c**. In fact, the reaction product of the ketone with pyrrolidine in excess (reflux in benzene with TsOH as a catalyst and distillation) is a mixture of the unconjugated dienamine **10** and the cross-conjugated dienamine **2c**, the latter being formed in small amounts. If this mixture is heated in benzene with TsOH, it evolves towards the pure cross-conjugated dienamine **2c**.

III. Direct Evidence of the Kinetic Control and Absence of the Equilibrium.—The two stereoisomeric hydrindenones **11a** and **11b** have two different stereoisomeric cross-conjugated dienamines **12a** and **12b**, but they have a common hypothetic linear dienamine **13**.



We have then investigated the case of the two separated pure ketones **11a** and **11b**. The experimental result is as follows. Each ketone gives a pure cross-conjugated dienamine by refluxing with pyrrolidine

(6) N. F. Phelan and M. Orchin, *J. Chem. Educ.*, **45**, 633 (1968).
(7) G. Dana and F. Weisbuch, *C. R. Acad. Sci., Ser. C*, **267**, 1154 (1968).
(8) C. Yamagami, F. Weisbuch, and G. Dana, *Tetrahedron*, **27**, 2967 (1971).

in benzene (without TsOH). The nmr data show that these two dienamines are different species. After distillation, these products are submitted to equilibrating conditions by a reflux for 24–48 hr in benzene with TsOH as a catalyst (10 mol % with respect to the dienamine). The dienamines remain pure and unchanged. They are then hydrolyzed, and each regenerated ketone is identical with the starting one (identification by nmr and vpc).

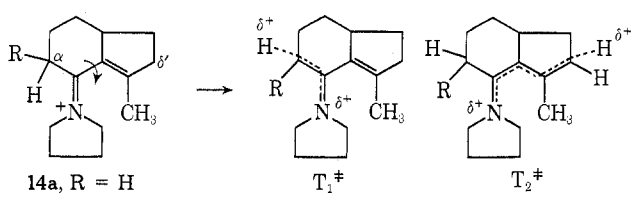
This result shows unambiguously that the two cross-conjugated dienamines **12a** and **12b** are not in equilibrium with each other, and that the linear dienamine **13** is not formed as an intermediate neither during the preparation of dienamines, nor during their acidic equilibration, even as an imperceptible trace. Then the reaction occurs under kinetic control, and the formation of the kinetic product is not followed by a thermodynamical equilibrium. This behavior is definitely different from that of the unsaturated transoid ketones (thermodynamic control process with fast equilibrium),[5] and from that of some less-strained cisoid ketones (kinetic control process followed by a slow equilibrium), as pulegone.[8]

The generalization of this result to the cases of the other hydrindenones **1** (or **4**) is supported by the synthesis or by the equilibration of the dienamines with deuteriopyrrolidine and a trace of deuterio-*p*-toluenesulfonic acid. If there was an equilibrating process involving the linear dienamines **3** (or **6**), we would have obtained di- and trideuterated dienamines **2** (or mono- and dideuterated dienamines **5**).

The experiments have been carried out in the case of hydrindenones **1c** and **4c** with pyrrolidine (50% d_1). The following results have been obtained: (a) synthesis of **2c**, 67.5% d_0 + 30% d_1 + 2.5% d_2; (b) equilibration of **2c** (3 hr in boiling benzene), 71% d_0 + 25% d_1 + 4% d_2; (c) equilibration of **5c** (1 hr in boiling benzene), 98% d_0 + 2% d_1; (d) synthesis of **12**, 68% d_0 + 29% d_1 + 3% d_2.

We observed that the precision of our measurements of isotopic abundance was about 2–4.5% (error relative to the theoretical values in natural samples, or error of reproducibility of the results with the same samples). As the dienamine **12** is formed with kinetic control, the small excess deuteration appears as insignificant (or arising from some slow unknown reaction), and we can say that the entire series reacts with kinetic control and does not involve the linear dienamine form with a noticeable rate.

This exclusive exchange of protons in the α position may be attributed to a hindered coplanarity of the double bonds of the intermediate immonium cations **14**.



14a, R = H
b, R = CH_3

Indeed these cations have been obtained as perchlorate salts of the corresponding dienamines, and their uv absorption spectra show a low conjugation between the two double bonds ($\epsilon \sim 6000$).

This lack of coplanarity would prevent the transmission of the positive charge from the N atom to the $C_{\gamma'}$ position[9] in the transition state ($T_2^{\pm}$).

Conclusion

The dramatic behavior observed in the formation of the cross-conjugated dienamines of $\Delta^{3(9)}$-4-hydrindenones results from a kinetic control process of the reaction caused by the hindered coplanarity of the intermediate immonium salt. This lack of coplanarity seems specific to this bicyclic system and is related to its particular strain.

This rigorous regiospecific reaction gives interesting synthetic intermediates, with good yields, allowing new possibilities of steroidal skeleton synthesis.[10]

Experimental Section[11]

The $\Delta^{3(9)}$-4-hydrindenones **1** are synthetized by the reduction of a mixture of cyclohex-2-en-1-one (or 3-methylcyclohex-2-en-1-one) with an α,β-unsaturated aliphatic aldehyde or ketone.[12]

The methyl-5 derivatives (ketones **4**) are obtained by normal reaction of methyl iodide with the dienamines **2**. (The yields are better than by the direct alkylation of the ketone by action of NaH or NH_2Na.) We obtained good elemental analyses after elimination of the residual starting ketone by a new reaction with pyrrolidine. (The residual starting ketone is not easily discernible either by vpc or by nmr.)

The structure and purity of the dienamines is demonstrated by mass spectral molecular weight determination and by nmr and ir spectroscopy (Table I).

4-Pyrrolidino-8-methyl-$\Delta^{3(9),4}$-hydrindane (2a).—A mixture of 22 mmol (3.3 g) of 8-methyl-$\Delta^{3(9)}$-4-hydrindenone **1a** and 75 mmol (5.4 g) of pyrrolidine is refluxed for 2.30 hr with 100 ml of benzene in a Dean–Stark separatory funnel; then benzene is evaporated under reduced pressure. The residue is then distilled and gives **2a**, bp 75° (0.05 mm), 4.35 g (yield 73%). The same result is obtained with TsOH as a catalyst (reflux 45 min only). *Anal.* Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.58; H, 10.39; N, 6.79.

Alkylation of the Dienamine 2a. Formation of the 5,8-Dimethyl-$\Delta^{3(9)}$-4-hydrindenone 4a.—A mixture of 15 mmol (3 g) of the dienamine **2a** and 20 mmol of methyl iodide (2.9 g) dissolved in 30 ml of dioxane is refluxed for 18 hr. The solution is hydrolyzed with acetic acid–sodium acetate–methanol buffer[13] (205 ml), neutralized with 35 g of NaOH in 120 ml of water, and diluted with 210 ml of water saturated with NaCl. The extraction with benzene yields **4a**, bp 100° (16 mm), 1.15 g (yield 50%). Nmr spectra show the presence of two geometrical isomers giving two triplets (J = 2.5 Hz) for the olefinic proton, δ_H (CCl_4) 6.15 (65%) and 6.32 ppm (35%). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.36; H, 9.71.

4-Pyrrolidino-5,8-dimethyl-$\Delta^{3(9),4}$-hydrindane (5a).—A mixture of 3.6 mmol (600 mg) of the preceding ketone **4a** and 14 mmol (1 g) of pyrrolidine is refluxed with 12 ml of benzene and 15 mg of TsOH for 18 hr. The product is distilled, bp 75° (0.01 mm), but appears with an important residual ketone. This product is evaporated *in vacuo* at 30° for 4 hr and gives the pure dienamine **5a**. *Anal.* Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.78; H, 10.49; N, 6.41.

4-Pyrrolidino-3-methyl-$\Delta^{3(9),4}$-hydrindane (2b).—A mixture of 174 mmol (26 g) of 3-methyl-$\Delta^{3(9)}$-4-hydrindenone (**1b**) and 520 mmol (37 g) of pyrrolidine is refluxed with 370 ml of benzene containing 40 mg of TsOH for 2.30 hr. Distillation of the product gives **2b**, bp 78° (0.01 mm), 33 g (yield 93%). *Anal.* Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.61; H, 10.42; N, 6.96.

The perchlorate of **2b** has mp 132.5–133° (crystallized from

(9) N. A. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 716 (1970).
(10) F. Weisbuch and G. Dana, *Tetrahedron Lett.*, 1511 (1969).
(11) With contribution of H. Guiguen.
(12) F. Weisbuch, *C. R. Acad. Sci., Ser. C*, **263**, 1234 (1966); Thesis, Paris, 1966.
(13) F. W. Heyl and M. E. Herr, *J. Amer. Chem. Soc.*, **75**, 1918 (1953).

TABLE I

SPECTROSCOPIC DESCRIPTION OF THE CROSS-CONJUGATED DIENAMINES

Compd	Mol wt m/e[a] at 8 eV	Ir,[b] cm^{-1}	Uv,[c] nm (ε)	Nmr,[d] δ, ppm
2a	203	1598	230 (11,800)	H(5) 4.57 (t, J = 4 Hz)
			271 (5500)	H(3) 5.53 (t, J = 2.2 Hz)
			Δλ +27	CH_3(8) 0.97 (s)
2b	203	1601		H(5) 4.60 (t, J = 3.8 Hz)
				CH_3(3) 1.87
2c	217	1605	231 (17,000)	H(5) 4.58 (t, J = 3.9 Hz)
			260 (infl)	CH_3(3) 1.88
				CH_3(8) 0.98 (s)
5a	217	1605	242 (12,000)	H(3) 5.22
			283 (1700)	CH_3(5) 1.72
			Δλ +34	CH_3(8) 0.92 (s)
5b	217	1606	244 (15,500)	CH_3(5) 1.60
			285 (3100)	CH_3(3) 1.80
			Δλ +31	
5c	231	1608	246 (15,100)	CH_3(5) 1.60
			285 (2600)	CH_3(3) 1.77
			Δλ +31	CH_3(8) 0.89 (s)
8			235 (15,100)	H(5) 4.77 (t, J = 4 Hz)
			250 (infl)	

[a] Mass spectra; the molecular weights have been determined with a spectrometer Hitachi-Perkin-Elmer RMU 6E MS. [b] Ir spectra are registered as films of pure material (polystyrene as reference) (Perkin-Elmer 137G). [c] Uv spectra are taken in dry cyclohexane solution (Spectralux double-beam spectrograph, SAFAS, Monaco). The Δλ increment of pyrrolidine group on the conjugation band is calculated from the λ_{max} observed for 3-methyl-$\Delta^{3(9),4}$-hydrindane **7**, as reference. [d] Nmr spectra are taken in dry CCl_4 solution at 60 MHz (Varian A 60); δ in ppm from internal TMS; s, singlet; t, triplet.

methanol and ether); ir 1636 and 1090 cm^{-1}; uv $\lambda_{max}^{CHCl_3}$ 288 nm (ε 5500); nmr ($CDCl_3$) δ_{CH_3} 2.87 ppm.

Alkylation of the Dienamine 2b. Formation of the 3,5-Dimethyl-$\Delta^{3(9)}$-4-hydrindenone 4b.—A mixture of 61 mmol (12.4 g) of the dienamine **2b** and 73 mmol (11 g) of methyl iodide, dissolved in 124 ml of dried dioxane, is refluxed for 17 hr. After being cooled, the solution gives a white solid mass which is hydrolyzed in the buffered solution[13] (820 ml) for 20 hr, diluted with 800 ml of water saturated with NaCl, neutralized with 150 g of NaOH in 450 ml of water, extracted with ether, and dried over Na_2SO_4. Distillation gives **4b**: bp 118–122° (20 mm); 9.4 g (yield 97%); ir $\nu_{C=O}$ 1680 cm^{-1}, $\nu_{C=C}$ 1629 cm^{-1}. The nmr spectrum of **4b** in solution in C_6H_6 shows two isomers characterized by their methyl doublets at 1.03 (J = 7.2 Hz, 40–45%) and 1.15 ppm (J = 6.2 Hz, 55–60%). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.40; H, 9.92.

4-Pyrrolidino-3,5-dimethyl-$\Delta^{3(9),4}$-hydrindane (5b).—A mixture of 37 mmol (6 g) of the hydrindenone **4b**, with a great excess of pyrrolidine (280 mmol) in 50 ml of benzene containing TsOH, is refluxed under a condenser containing molecular sieves (4 Å) for 48 hr. Distillation (0.05 mm) gives pure unreacted starting ketone, bp 40°, 3 g; intermediate, bp 40–78°, 1 g; and dienamine **5b**, bp 78–80°, 3 g. *Anal.* Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.96; H, 10.65; N, 6.51.

The perchlorate of **5b** has mp 137–166° (mixture of the two isomers which appear in the nmr spectrum); δ_{CH_3} ($CDCl_3$, TMS internal reference) 1.15 (29%) and 1.29 ppm (71%) (doublets); uv $\lambda_{max}^{CHCl_3}$ 289 nm (ε 6000); $\lambda_{max}^{CH_3OH}$ 288 nm (ε 6200).

4-Pyrrolidino-3,8-dimethyl-$\Delta^{3(9)4}$-hydrindane (2c).—The previous procedure gives with the 3,8-dimethyl-$\Delta^{3(9)}$-4-hydrindenone **1c** the dienamine **2c**, bp 82° (0.01 mm), yield 75%. *Anal.* Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.83; H, 10.69; N, 6.37.

4-Pyrrolidino-3,8-dimethyl-$\Delta^{2,4}$-hydrindane (10).—The same ketone **1c** contains 5–10% unconjugated form **9**, 3,8-dimethyl-Δ^2-4-hydrindenone,[12] which is separated as a pure isomer, by vpc on silicone SE-30 at 160°.

A mixture of 463 mg of the unconjugated ketone **9** and 800 mg of pyrrolidine is heated in 10 ml of benzene with TsOH for 4.15 hr in a Dean–Stark separatory funnel. The raw product, examined by nmr after distillation, shows (1) the unreacted ketone, about 22%, characterized by its olefinic proton (5.40 ppm) and angular methyl group (1.17 ppm); (2) the unconjugated dienamine **10**, about 55%, characterized by the two olefinic protons (4.37 ppm, triplet, J = 4 Hz, and 5.23 ppm, massive $\nu_{1/2}$ = 5 Hz) and the angular methyl (1.09 ppm); (3) the cross-conjugated dienamine **2c**, about 24%, characterized by its olefinic proton (4.59 ppm, triplet, J = 3.9 Hz) and the angular methyl (0.98 ppm). The residual ketone is evaporated *in vacuo*, and the dienamine mixture is dissolved in 10 ml of benzene with TsOH and refluxed for 12 hr. The nmr spectrum shows the cross-conjugated dienamine **2c** (about 85%) and the residual unconjugated dienamine **10** (15%).

The perchlorate of **10** has mp 218–219° (insoluble in $CHCl_3$); nmr (CD_3COCD_3, TMS internal reference) $\delta_{H(2)}$ 5.75 ppm (m), $\delta_{H(3)}$ 2.96 ppm (sharp singlet), $\delta_{CH_3(8)}$ 1.30 ppm (sharp singlet), $\delta_{CH_3(3)}$ 1.72 ppm.

Alkylation of the Dienamine 2c to Give 3,5,8-Trimethyl-$\Delta^{3(9)}$-4-hydrindenone 4c.—The procedure, used for **4b**, gives, with the dienamine **2c** the ketone **4c**: bp 110–113° (15 mm); yield 52%; ir $\nu_{C=O}$ 1680 cm^{-1}, $\nu_{C=C}$ 1627 cm^{-1}. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18; Found: C, 81.00; H, 10.28. The nmr spectrum in C_6H_6 shows the formation of two isomers: (a) $\delta_{CH_3(8)}$ 0.85 ppm (s) and $\delta_{CH_3(5)}$ 1.17 ppm (d, J = 5.1 Hz), about 55%; (b) $\delta_{CH_3(8)}$ 0.91 ppm (s) and $\delta_{CH_3(5)}$ 1.06 ppm (d, J = 6.2 Hz), about 45%.

4-Pyrrolidino-3,5,8-trimethyl-$\Delta^{3(9),4}$-hydrindane (5c).—A 9.7-g sample of the pure ketone **4c** and 30 g of pyrrolidine are refluxed with molecular sieves in the condenser (as for **5b**) for 8 days in 120 ml of benzene with TsOH. Distillation gives 5.9 g of the unreacted ketone **4c** (high purity), bp 40° (0.01 mm), and 4.2 g of the dienamine **5c**, bp 76° (0.01 mm). *Anal.* Calcd for $C_{16}H_{25}N$: C, 83.11; H, 10.82; N, 6.06. Found: C, 83.03; H, 10.92; N, 6.18.

4-Pyrrolidino-2,3-dimethyl-$\Delta^{3(9),4}$-hydrindanes (12a and b).—The two starting stereoisomeric ketones **11a** and **b**, easily discernible by nmr spectroscopy owing to the doublets of the 2-methyl group, are separated by vpc on Apiezon N at 160° (length of the column 4 m, 30 μl for each injection) and obtained rigorously free from one another by a second fractionation.

The two dienamines, prepared as indicated, are characterized by the triplets of the olefinic proton in CCl_4: δ_H 4.57 ppm for the dienamine of the first predominant ketone and δ_H 4.68 ppm for the second one.

The experiments have been carried out with 280 mg of hydrindenone **11a**, the first isomer, and 110 mg of hydrindenone **11b**, the second isomer.

Anal. Calcd for $C_{15}H_{23}N$ (mixture of the two isomers)[7]: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.80; H, 10.72; N, 6.52.

Registry No.—**2a**, 22508-86-7; **2b**, 22508-83-4; **2c**, 22508-84-5; **4a**, 36803-70-0; **4b**, 36803-71-1; **4c**, 36803-72-2; **5a**, 36803-73-3; **5b**, 36803-74-4; **5b** perchlorate, 36803-75-5; **5c**, 36803-76-6; **10** perchlorate, 36807-50-8; **12**, 36803-77-7.