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Formation of a Non-planar Dienamine from 1-(2-Indanylidene)-indan-2-one and Pyrrolidine

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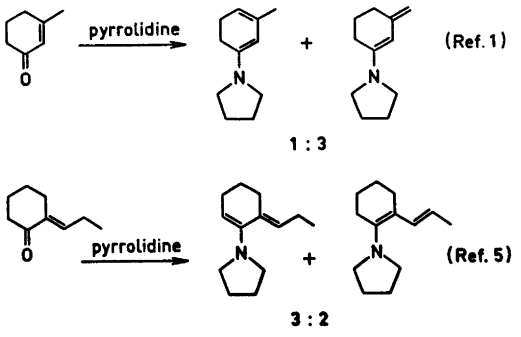
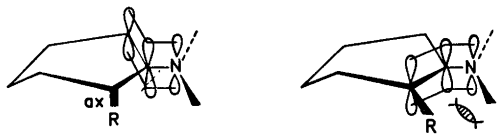
1-(2-Indanylidene)indan-2-one (I) may be converted into a mixture of the linear dienamine, 3-(2-indenyl)-2-(*N*-pyrrolidyl)-indene (II), and isomeric enamine, 1-(2-indenyl)-2-(*N*-pyrrolidyl)indene (III). In the main product (II), isolated by recrystallization, the indenyl substituent is proposed to be more or less twisted out of conjugation as shown by protium-deuterium exchange and PMR data. Factors affecting the formation and the relative stability of the isomeric forms are briefly discussed.

Several investigations concerning the preparation and the structure of dienamines from cyclic and acyclic ketones have been published.[1-4] In the case of ketones with an endocyclic double bond the products generally appear as mixtures of dienamines among which linear forms seem to be predominant, or exclusive. A different behaviour has been reported for cisoid, unsaturated cyclohexanones where the cross-conjugated isomer is the major component in the dienamine mixture[5,6] (Scheme 1). In the case of enamines derived from 2-substituted ketones the isomeric distribution is controlled

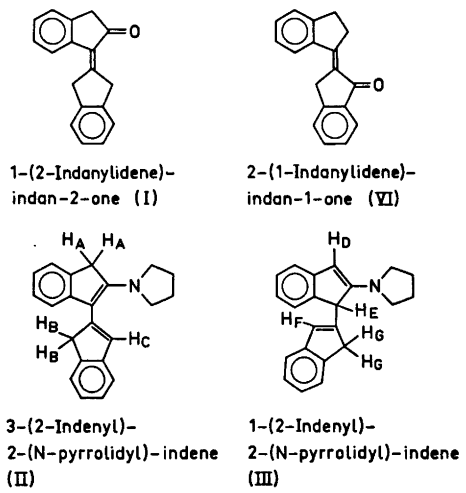


Scheme 1.



Scheme 2.

by various steric and electronic factors which affect the overlap between the nitrogen lone pair and the double bond of the enamine. Gurowitz and Joseph[7] have proposed that, within a given series, the greater the overlap the greater is the amount of the less substituted enamine (Scheme 2). In connection with the study of enamines from 1-methylindan-2-one we observed an isomeric ratio which deviated



Scheme 3.

from the general formulation mentioned above.[8] In the pyrrolidine enamine case, where overlap between the nitrogen lone pair and the double bond is strongest, the proportion of the most substituted enamine was greater than in the cases with other amine components. Since the controlling factors may or may not act in the same direction or will be differently weighted in our system, we have tried to obtain more information by studying the condensation between the reactive, secondary amine, pyrrolidine, and the planar, cisoid ketone 1-(2-indanylidene)indan-2-one (I)[9] (Scheme 3).

RESULTS AND DISCUSSION

Treatment of (I) with pyrrolidine in chloroform affords at room temperature two isomeric amines, (II) and (III), roughly in the ratio 9:1. Crystallization of the crude mixture from tetrachloroethylene gave only the pure isomer (II). The isomer (III) could not be obtained in a pure state. The ease of formation and the stability against hydrolysis are the same properties as ascribed to enamines of simpler 2-indanones.[8,10] In a comparative study, a similar compound, 2-(1-indanylidene)indan-1-one, ((VI),

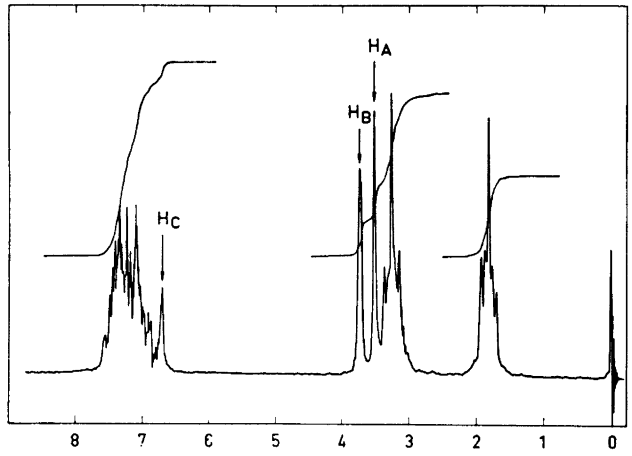


Fig. 1. PMR-spectrum of the pure isomer (II) (Concentration: 0.5 M) in chloroform-D. A small amount of 1,8-(*N*,*N*,*N'*,*N'*-tetramethyl)diaminonaphthalene is added to avoid equilibration due to acidic impurities in the solvent.

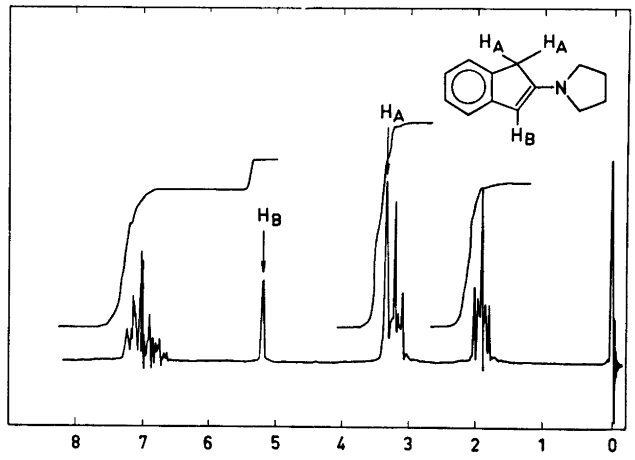


Fig. 2. PMR-spectrum of 2-(*N*-pyrrolidyl)indene (Concentration: 0.5 M) in chloroform-D.

Scheme 3) prepared according to Kipping,[11] was shown to be completely unreactive against condensation with pyrrolidine even after a prolonged reaction period. This demonstrates that the unusual reactivity observed for the simpler 2-indanones seems to be valid also in this unsaturated case (I). The PMR spectrum of the pure dienamine (II) is given in Fig. 1. This spectrum could be obtained only if the solvent chloroform-D had been carefully dried and with a trace of 1,8-(*N*,*N*,*N'*,*N'*-tetramethyl)diaminonaphthalene added in order to inhibit acid-catalyzed isomerization. The signals at $\delta \approx 1.6-2.0$ (ppm) and $\delta \approx 3.0-3.4$ (ppm) are ascribed to the protons of the pyrrolidine ring and the singlet at $\delta = 3.5$ (ppm) to the protons at the 1-position (H_A) in the enamine part. This assumption is based on the similarities with the spectrum of 2-(*N*-pyrrolidyl)indene shown in Fig. 2. The peaks from the protons at the 1- and 3-position in the indenyl part appear at $\delta = 6.7$ (ppm) (H_C) and $\delta = 3.7$ (ppm) (H_B), respectively, and the complex signals at $\delta \approx 6.7-7.7$ (ppm) are assigned to the eight aromatic protons. If the solution of (II) contains traces of acidic impurities, the PMR spectrum rapidly changes to that given in Fig. 3. In this spectrum the peaks at $\delta = 4.6$ and 5.3 (ppm) are interpreted as resulting from the protons H_E and H_D, respectively, in the isomeric form (III). The signals from the remaining protons in (III) are as expected overlapped by the signals from (II). As no changes in the spectrum (Fig. 3) was observed after addition of *p*-toluenesulphonic acid, the equilibrium ratio between (II) and (III), found to be 9:1, could be determined by integration. The area under the peak at $\delta = 3.7$ (ppm) due to H_B in (II) and H_G in (III) was compared with the area of the H_D and H_E peaks in (III) using the pyrrolidine proton signals at $\delta \approx 1.6-2.0$ (ppm) as internal standard. The equilibrium ratio is equal to that reported for pyrrolidyl enamines of 1-phenylindan-2-one.[12]

An interesting observation from this spectrum of (II) is the lowfield signal assigned to the terminal vinylic proton (H_C) with a shift value ($\delta = 6.7$ (ppm)) close to that ascribed to the olefinic proton in the 3-position of indenes ($\delta \approx 6.4-6.7$ (ppm)).[13,16,17] This fact cannot be in accordance with any significant increase in electron density at the carbon atom bearing the vinylic proton in our dienamine. This proposal is based on earlier reports [1,3] which clearly show that an increased conjugation caused a marked upfield shift of the signal from the terminal vinylic proton of the dienamine. Thus the PMR spectrum shows much greater likeness to a superposition of an enamine and an indene than a dienamine. This together with above-mentioned isomeric ratio and the non-coplanarity proposed for enamines of 1-phenylindan-2-one [12] suggests that the indene systems are twisted out of conjugation.

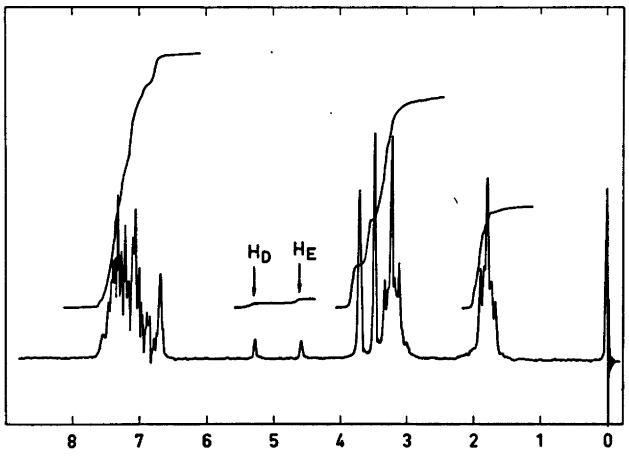
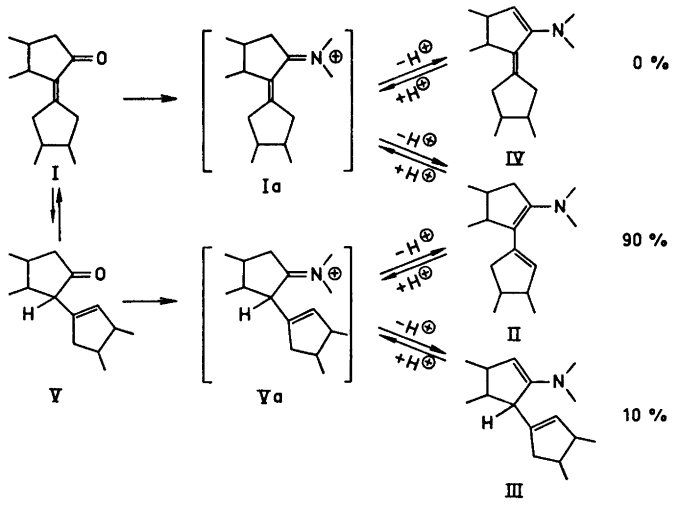


Fig. 3. PMR-spectrum of a mixture of (II) and (III) (9:1) (Concentration: 0.5 M) in chloroform-D. A catalytic amount of *p*-toluenesulphonic acid is added to confirm the equilibrium proportions (II/III = 9:1).



Scheme 4.

In order to confirm the assumption that the enamine part remains isolated from the indenyl substituent we have studied isotopic exchange between the equilibrium mixture (II + III) and methanol-OD, since deuterium incorporation rates have been shown to correlate well with estimated electron densities at different sites.[14] These results are summarized in Table 1, which shows that there is a fast exchange in the enamine part as compared to the indenyl part when chloroform was used as solvent. The decreased rate observed in pyridine could possibly be explained by hydrogen bonding between methanol-OD and pyridine. Even a small but significant deuterium content is observed in the indenyl substituent. This could be caused by involvement of an enimmonium structure like (I a, Scheme 4) but it can more likely be explained in terms of a simple base-catalyzed isotopic exchange as earlier reported.[15] To summarize, these results strongly indicate a decreased coplanarity and a decreased orbital interaction between the nitrogen lone pair and the indenyl substituent in agreement with our proposal.

Table 1. Protium-deuterium exchange between 3-(2-indenyl)-2-(*N*-pyrrolidyl)-indene (II) and 1-(2-indenyl)-2-(*N*-pyrrolidyl)indene (III) and methanol-OD at 27°C. Molar ratio: Amines: methanol-OD (1:4) Concentration of amines: 0.32 M.

Solvent	Time (h)	Percentage deuterium [a] in the enamine part (A,D,E)	Percentage deuterium [a] in the indenyl part (B,C,G,F)
Chloroform	0.5	18	0
	1.0	30	0
	2.0	50	0
	4.5	63	0
Pyridine	4.0	10	0
	27.0	33	5
	45.0	48	10
	64.0	50	13

[a] Estimated error ±4 %.

Consideration of the route of formation of the isomeric mixture (II + III) indicates that at least two different pathways are plausible (Scheme 4). One possibility is a direct formation of the highly sterically strained enimmonium structure (I a) followed by proton abstraction theoretically yielding two different structures (II + IV). The linear form (II) is thermodynamically much more stable than (IV). The observed equilibrium between (II) and (III) is then established through structure (V a) in accordance with the above-mentioned results from hydrogen-deuterium exchange. Another plausible pathway is a base-catalyzed inter-

conversion of the cisoid unsaturated ketone (I) to an indenyl-substituted 2-indanone (V). Subsequent reaction with pyrrolidine, in analogy with the preparation of alkyl-substituted enamines of 2-indanones, gives a less sterically restricted intermediate (V a) compared with (I a). Whether one or both of these mechanisms is operative cannot be clarified. No trace of formation of the isomer (IV) could be detected during the course of the reaction. This fact can be explained either by assuming that the mechanism proceeding *via* (I a) does not operate, or that (IV) possibly formed too rapidly isomerizes to structure (II) in order to be detected. Referring to the very high reactivity of 2-indanone and the alkylsubstituted 2-indanones it seems plausible to exclude the path *via* (I a).

The ratio between the obtained isomeric compounds (II + III) is quite different from that expected from earlier investigations of cisoid unsaturated ketones. In these studies the cross-conjugated isomer was, as mentioned, the predominating product. The factors, which affect the isomeric proportions in our case, seem to be the same as in the case of enamines of substituted 2-indanones. The unusually large proportion of the most substituted isomer, that was obtained when pyrrolidine was used as amine component, could possibly be caused by differently weighted steric effects in our enamine systems compared to the conditions in enamines of other substituted ketones. An extension of conjugation by the aromatic part and an increased difference in hyperconjugative stabilization between the 1-substituted and 3-substituted forms in our systems are factors that also could be responsible for this unexpected effect. However, these differences in isomeric proportions from those expected, on the basis of the now widely accepted rule of Gurowitz and Joseph,[7] correspond to very small differences in free energy of the different structures. This means, that any closer treatment of these factors is very difficult.

EXPERIMENTAL

A JEOL C-60 HL instrument was used to obtain the PMR spectra. The mass spectrum was recorded on a LKB 9000 mass spectrometer, and the IR spectrum was determined on a Perkin-Elmer 257 Spectrophotometer. Melting points are uncorrected.

1-(2-Indanylidene)indan-2-one (I) was prepared from 2-indanone according to a method published by Treibs and Schroth.[9] m.p. 176.5 – 178°C (lit.[9] 178°).

3-(2-Indenyl)-2-(N-pyrrolidyl)indene (II). A mixture of 2.0 g 1-(2-indanylidene)indan-2-one (0.007 mol) and 1.07 g pyrrolidine *p.a.* (0.015 mol) dissolved in 20 ml chloroform was allowed to stand for two days at room temperature over anhydrous calcium sulphate. Evaporation in vacuum affords a crude mixture mainly consisting of (II) and (III) approximately in a ratio 9:1. Recrystallization from tetrachloroethylene yields pure (II). The yield was 1.28 g. (52 %) m.p. 140 – 142°C. (Found: C 88.2; H 7.0; N 4.7. Calc. for $C_{22}H_{21}N$ (299): C 88.3; H 7.1; N 4.7.) $M^{+\cdot}$ (*m/e*): 299. $\nu_{C=C}$ (KBr): 1600, 1580 sh, 1550 (cm^{-1}).

PMR spectrum (Fig. 1, Fig. 3). Isomer (II): 1.6 – 2.0 (4 H complex), 3.0 – 3.4 (4 H complex), 3.5 (2 H_A singlet), 3.7 (2 H_B singlet), 5.7 (1 H_C singlet), 6.7 – 7.7 (8 H complex).

Isomer (III): 4.6 (1 H_E singlet), 5.3 (1 H_D singlet), (δ (ppm) in chloroform-D (TMS). Conc. 0.5 M).

Protium-deuterium exchange. Pyridine p.a. (Mallinckrodt) was freshly distilled and dried over calcium hydride. Chloroform *p.a.* was purified from alcohol. Methanol-OD (CIBA) was > 99 % D. The isotopic incorporation was followed by PMR-integration with sealed NMR tubes. Further data is given in Table 1.

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