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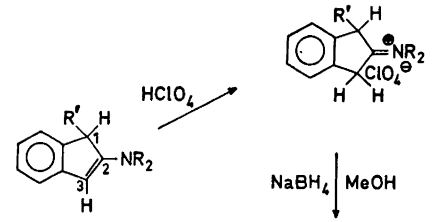
Preparation of Some *N*-Substituted 2-Aminoindanes

ULF EDLUND

Department of Organic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

In connection with the studies of enamines of 2-indanones [1,2] we want to report a versatile method for the preparation of some *N*-substituted 2-aminoindanes. Some of these compounds have been synthesized previously by catalytic reduction of the corresponding enamines at high pressure.[3] Structurally these indanamines form an interesting group of compounds since the presence of a phenethylamine skeleton relates them to the pharmacologically and physiologically well-known phenylisopropylamines. Thus these compounds are indane analogs corresponding to amphetamine. The pharmacological effect upon *N*-alkylation of 2-aminoindanes has earlier been reported.[4,5]

2-Indanone and 1-methyl-2-indanone are most conveniently prepared by oxidation of the corresponding indenes with performic acid.[1,6] The syntheses of the enamines are then easily achieved by mixing the ketone and the desired secondary amine in methanol at room temperature.[1,7] Since the reduction of enamines by hydride depends on the prior generation of an immonium salt,[8] we have prepared the stable perchlorate salts of our enamines.

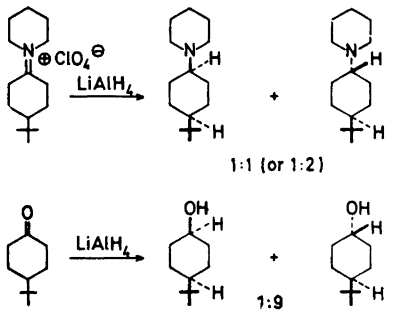


R_2	R′	Enamine
$(CH_2)_4$	H	Ia
$(CH_2)_5$	H	Ib
$(CH_2)_6$	H	Ic
$(CH_3)_2$	H	Id
$(CH_2)_5$	CH_3	Ie

Scheme 1.

Treatment of these salts with sodium borohydride in methanolic solution affords, after usual workup, the saturated tertiary amines in almost quantitative yields. A series of *N*-substituted 2-aminoindanes has been prepared in this way (Scheme 1).

Previous studies of the stereochemical course of lithium aluminium hydride reductions of an immonium salt [9] (Scheme 2) have shown that the two possible



Scheme 2.

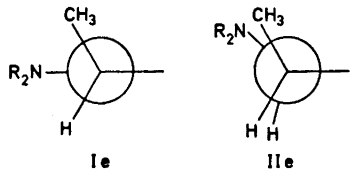
isomers are formed in almost equal proportions. This is in contrast to the reduction of the analogous ketone where the thermodynamically stable isomer predominates. In our 2-indanone system we have a more planar conformation and this framework is in good agreement with the open-chain model chosen to illustrate Cram's rule of steric control of asymmetric induction. In view of these considerations and the greater effective size of the borohydride we should therefore, in the case of reduction of the 1-methyl-2-(*N*-piperidyl)indene (I e) salt, expect the *cis* isomer to be equally favoured or possibly more favoured compared with the product formed by "*product development control*". The isomer distribution we observed shows that one isomer predominates as determined by the ^{1}H NMR spectrum. A small doublet downfield the dominant methyl signal is ascribed to the other isomer. This contamination (< 5 %) could not be eliminated by careful distillation. However, the recrystallization of the hydrochloride afforded pure product. In a ^{13}C NMR study where steric compression effects are more significant an upfield shift of about 3 ppm (Table 1) was observed compared with the methyl peak from (I e). Even if interpretations of small shielding

Table 1. Carbon-13 shieldings of some 2-(*N*-piperidyl)indenes and their saturated analogs.[a,b]

Compound	C_1	C_2	C_3	R′
I b	37.4	157.9	98.9	
II b	37.3	67.6	37.3	
I e	42.1	163.1	99.3	18.0
II e	41.3	70.2	34.7	15.1

[a] δ ppm from TMS; 1 M solution in chloroform-D. [b] wide-band (noise) decoupled; pulse width 8 μs (π/4); repetition rate 1 sec.

changes must be approached with caution in ^{13}C NMR, it is invariably found that steric crowding produces an upfield shift of a carbon with a nucleus other than hydrogen in the γ position.[10] Thus this shift difference implies increased steric



Ie IIe

Scheme 3.

hindrance and confirms our proposal that the main isomer is the kinetically formed *cis* isomer (II e) (Scheme 3).

Experimental. All ^{1}H NMR- and ^{13}C NMR-work was performed on a JEOL JNM PFT-60 NMR spectrometer. The computer system (EC-100; 20 K core) allowed acquisition of 16 K spectral data points. The mass spectra were obtained with a LKB 9000 mass spectrometer.

2-(N-Cycloamino)indenes (I a–c). The enamines (I a–c) were prepared in good yields according to a method published by Schroth and Fischer [7] by simply mixing 2-indanone [6] and the cyclic secondary amine in methanol.

2-(N-Dimethylamino)indene (I d). To an ice-cooled solution of 2.64 g (0.020 mol) 2-indanone in 75 ml methanol *p.a.* were added 2.0 g (0.044 mol) dimethylamine (99 % GLC) in one portion. After a few minutes the crystalline product separated, m.p. 79.5–80.0°C.

Yield; 2.50 g (79 %) $M^{+\cdot}=159$. (Found: C 82.8; H 8.1; N 8.6. Calc. for $C_{11}H_{13}N$ (159): C 83.0; H 8.2; N 8.8). ^1H NMR in chloroform-D (TMS) of (I d); 2.73 (6 H singlet), 3.23 (2 H singlet), 5.20 (1 H singlet), 6.50–7.17 (4 H complex) (δ ppm).

1-Methyl-2-(N-piperidyl)indene (I e). The contaminated (I e) (4 % of the 3-isomer) was synthesized as we have earlier described from 4.38 g (0.030 mol) 1-methyl-2-indanone.[1] Yield: 62 %.

The perchlorate salts of (I a–e). According to a method described by Blomquist and Moriconi[11] a solution of 25 ml 70 % perchloric acid and 25 ml abs. ethanol was added to a solution of (I a–e) in ether until pH<3 (Congo Red paper). Yields were almost quantitative.

General procedure for the preparation of (II a–e). To an ice-cooled stirred slurry of 0.014 mol of the perchlorate salt in methanol *p.a.*, 1.0 g (0.026 mol) sodium borohydride was added cautiously in small portions. The temperature was not allowed to exceed 5°C. After addition of the hydride the stirring was continued for another 15 min. The solution was then concentrated to a small volume. 50 ml 5 % sodium hydroxide was added and the mixture was extracted with ether. The combined ether layers were then dried over anhydrous sodium sulphate. Removal of solvent gave pure *N*-substituted 2-aminoindane (II a–e) in quantitative yield. Distillation under reduced pressure did not affect physical data or spectral characteristics.

2-(N-Pyrrolidyl)indane (II a). Colourless crystals, m.p. 44.5–46.0°C. Hydrochloride (ethanol-ether); m.p. 234–236°C (lit.[3] 191–193°C). $M^{+\cdot}=187$. (Found: C 83.3; H 9.2; N 7.3. Calc. for $C_{13}H_{17}N$ (187): C 83.4; H 9.2; N 7.5). ^1H NMR in chloroform-D (TMS) of (II a); 1.50–1.90 (4 H complex), 2.25–2.65 (4 H complex), 2.86 (5 H complex), 6.93 (4 H singlet) (δ ppm).

2-(N-Piperidyl)indane (II b). Colourless crystals, m.p. 59.0–60.0°C. Hydrochloride (ethanol–ether); m.p. 256–259°C (lit.[3] 252–253°C). $M^{+\cdot}=201$. (Found: C 83.7; H 9.5; N 6.8. Calc. for $C_{14}H_{19}N$ (201); C 83.5; H 9.5; N 7.0). ^1H NMR in chloroform-D (TMS) of (II b); 1.20–1.83 (6 H complex) 2.10–2.60 (4 H complex), 2.60–3.33 (5 H complex), 6.93 (4 H singlet) (δ ppm).

2-(N-Hexamethyleneimino)indane (II c). Colourless oil, b.p. 164–166°C (10 mm). Hydrochloride (ethanol–ether); m.p. 194–196°C (lit.[3] 232°C). $M^{+\cdot}=215$. (Found: C 83.6; H 9.8; N 6.5. Calc. for $C_{15}H_{21}N$ (215); C 83.7; H 9.8; N 6.5). ^1H NMR in chloroform-D (TMS) of (II c); 1.30–1.83 (8 H complex) 2.30–3.70 (9 H complex) 6.93 (4 H complex) (δ ppm).

2-(N-Dimethylamino)indane (II d). Fairly hygroscopic colourless oil, b.p. 99–101°C (10 mm). Hydrochloride (ethanol–ether); m.p. 205–207°C. $M^{+\cdot}=161$. (Found: C 66.8; H 8.2; N 6.9; Cl 17.9. Calc. for $C_{11}H_{16}NCl$ (197.5); C 66.8; H 8.2; N 7.1; Cl 17.9). ^1H NMR in chloroform-D (TMS) of (II d); 2.23 (6 H singlet), 2.90 (5 H complex), 7.00 (4 H singlet) (δ ppm).

cis-*1-Methyl-2-(N-piperidyl)indane (II e).* The residue after evaporation consists mainly of (II e) as determined by ^1H NMR and ^{13}C NMR spectra. A small doublet in the ^1H NMR spectrum at 1.27 ppm downfield TMS is ascribed to the other isomer. One recrystallization of the hydrochloride (ethanol–ether) followed by generation of the free amine affords pure (II e), b.p. 152–154°C (10 mm). Hydrochloride (ethanol–ether); m.p. 218–221°C. $M^{+\cdot}=215$. (Found: C 83.3; H 9.9; N 6.5. Calc. for $C_{15}H_{21}N$ (215): C 83.7; H 9.8; N 6.5). ^1H NMR in chloroform-D (TMS) of (II e): 1.05 (3 H doublet), 1.20–1.80 (6 H complex) 2.10–2.60 (4 H complex) 2.67–3.27 (4 H complex) 6.96 (4 H singlet) (δ ppm).

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