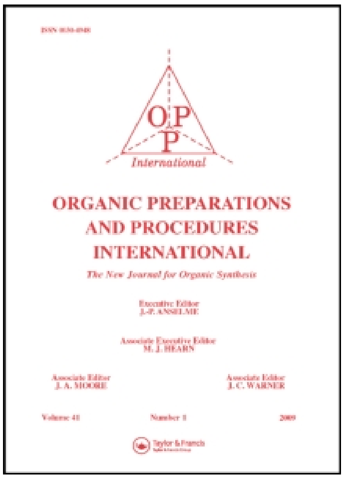

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SYNTHESIS OF 3,4-DIPHENYL-1,2,3,4-TETRAHYDROISOQUINOLINES

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SYNTHESIS OF 3,4-DIPHENYL-1,2,3,4-TETRAHYDROISOQUINOLINES

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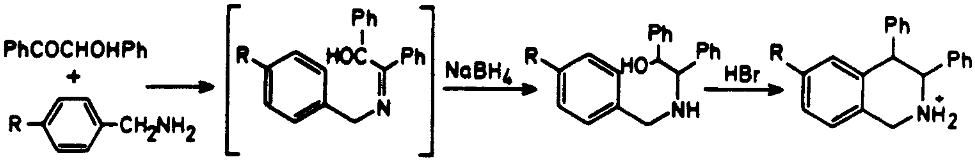
Earlier a convenient synthesis of 1,2,3,4-tetrahydroisoquinolines[1] was developed from ω-bromoalkylamino compounds and aluminium chloride.[2] Still many mono as well as disubstituted tetrahydroisoquinolines are lacking.[3] This note describes a synthesis of 3,4-diphenyl-1,2,3,4-tetrahydroisoquinolines (III) by cyclizationnn of 2-benzylamino-1,2-diphenylethanols (II) in boiling hydrobromic acid which may be obtained from benzoins.[4]' The structure of III is supported by elemental anallysis as well as IR and NMR evidence.



I II III Br⁻

a) R = H b) R = CH₃ c) R = Cl

EXPERIMENTAL SECTION

Melting points are uncorrected. Infrared spectra (KBr pellet) were recorded by using a Perkin-Elmer Model 580 spectrometer. Proton NMR spectra ($CDCl_3$ solvent) were obtained with A-60 A instrument using Me_4Si as internal standard.

2-Benzylamino-1,2-diphenylethanol (II). Typical Procedure.- Benzoin (10.0 g) and freshly distilled benzylamine (10.0 g), were boiled under reflux in methanol (300 ml) for 2 hrs. The solution was cooled and methanol (100 ml) added. A solution of sodium borohydride (15 g) in 1 M sodium hydroxide (100 ml) was added dropwise with stirring, and the temperature was maintained below 20°. Stirring was continued for 1 hr after completion of the addtion and the methanol was distilled. The residue was shaken with cold water (400 ml) and the precipitate obtained was collected and washed with water. Crystallization from methanol gave 11.2 g (78%) of white crystals, mp. 145-146°. IR: 3300(b), 1600(s), 1500(s), 1425(s), 1370(s), 1200(s), 1100(s), 1040(s), 1000(s), 850(s), 750(s), 700(s) cm^{-1}.

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.16; H, 6.93; N, 4.62

Found: C, 82.93; H, 6.71; N, 4.63

The hydrobromide, mp. 230-232° (MeOH/benzene) was obtained by passing dry hydrogen bromide gas into an ice-cold solution of II in methanol.

Anal. Calcd for $C_{21}H_{22}BrNO$: C, 65.64; H, 5.73; Br, 20.81

Found: C, 65.41; H, 5.73; Br, 21.10

Similarly 2-(p-methylbenzylamino) and 2-(p-chlorobenzylamino)-1,2-diphenylethanols gave white crystalline compounds IIb (86%), mp. 157-158° (MeOH) and of IIc (55%), mp. 163-165° (MeOH).

Anal. Calcd for $C_{22}H_{22}NO$: C, 83.54; H, 6.96; N, 4.43

Found: C, 83.41; H, 6.85; N, 4.54

Anal. Calcd for $C_{21}H_{19}ClNO$: C, 74.89; H, 5.64; N, 4.16; Cl, 10.55

Found: C, 74.78; H, 5.55; N, 5.80; Cl, 10.34

3,4-Diphenyl-1,2,3,4-tetrahydroisoquinolines (III). General Procedure.- 2-Benzylamino-1,2-diphenylethanol (10.0 g) and hydrobromic acid (100 ml, 48%) were boiled under reflux for 4 hrs. The solution was chilled in ice and the white crystalline compound collected and recrystallized from methanol to yield 8.5 g. (71%) of colorless solid, mp. 300-302°.

Anal. Calcd for $C_{21}H_{20}BrN$: C, 68.81; H, 5.23; Br, 21.92

Found: C, 68.71; H, 5.22; Br, 21.63

The salt was neutralized with 10% sodium hydroxide and the solution extracted with ether (200 ml), which on concentration gave a product, mp. 120-121° (pet-ether, 60-80°). IR: 3100(b), 1600(s), 1530(s), 1450(s), 1150(s),1050(s), 1000(s), 800(s), 750(s) cm^{-1}. NMR ($CDCl_3$): δ 3.65 (m, 2, CH_2); 4.21(m, 2, CH,CH); 6.63, 7.48 (m, 4 H ArH).

Anal. Calcd for $C_{21}H_{19}N$: C, 88.43; H, 6.71

Found: C, 88.33; H, 6.54

The N-acetyl derivative was obtained by refluxing the free base (1.0 g) with acetic anhydride (20 ml) for 3 hrs, mp. 119-120° (pet-ether, 40-60°).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.43; H, 6.42; N, 4.34

Found: C, 84.60; H, 6.47; N, 4.31

Simmilarly IIIb was obtained in 80% yield as white crystals, mp. 302-305° (EtOH); free base, mp. 138-139° (pet-ether, 60-80°); IR: 3300(s), 3100(s), 1600(s), 1520(s), 1450(s), 1120(s), 860(s), 800(s) and 750(s) cm^{-1}. NMR: δ 1.53(m, 3, CH_3); 2.87(m, 2, CH_2); 3.52(m, 2, CHCH); 6.81, 7.72(m, 3 H ArH).

Anal. Calcd for $C_{22}H_{21}N$: C, 88.29; H, 7.02; N, 4.68

Found: C, 88.34; H, 6.95; N, 4.47

IIIc was obtained in 43% yield, mp. 310-312°; free base, mp. 121-123° (pet-ether, 60-80°), IR: 3300(s), 3100(b), 1600(s), 1510(s), 1420(s), 1100(s), 920(s), 800(s) and 750(s) cm^{-1}. NMR: δ 3.27(m, 2, CH_2); 4.23(m, 2, CHCH); 6.81, 7.72(m, 3 H ArH).

Anal. Calcd for $C_{21}H_{18}ClN$: C, 78.87; H, 5.63; N, 4.38

Found: C, 79.10; H, 5.48; N, 4.36

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A MODIFIED PROCEDURE FOR THE PREPARATION OF 5H, 7H-DIBENZO[c,e]SELENEPIN

Submitted by Daniel J. Williams* and Patrick K. Macy
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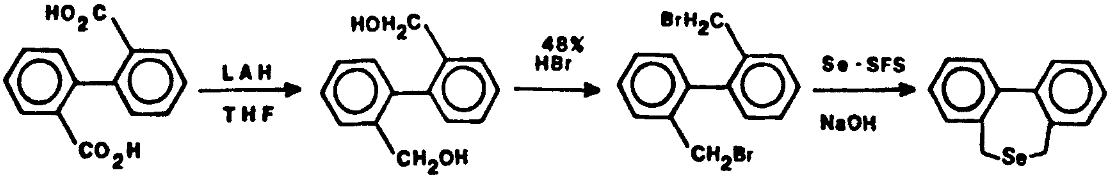
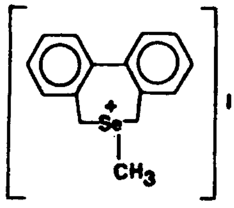
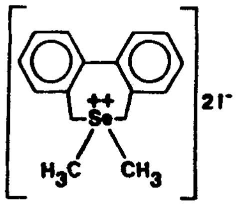
The original procedure of Truce and Emrick[1] describes the preparation of the title compound (IV) by the reaction of H_2Se with 2,2'-bis-(bromomethyl)-biphenyl (III). An alternative route to III was also reported by Hall et al. and incorporated a lithium tetrahydroaluminate (LAH) reduction of either the dimethyl or diethyl ester diphenate to give the diol (II) which in turn was brominated in hot concentrated hydrogen bromide.[2]



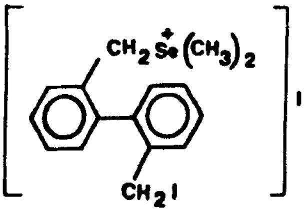
I II III IV



V



VI



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