DIMERISATION OF CINNAMALANILINE WITH POTASSIUM CYANIDE: A NOVEL SYNTHESIS OF 4,5-TRANS-DIPHENYL-1-PHENYL-2-PHENYLIMINO-2,3,4,5-TETRAHYDRO-1H-AZEPINE+

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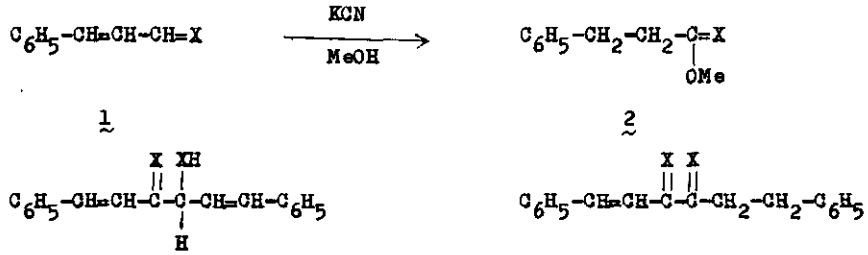
Abstract - Reaction of cinnamalaniline 1b with potassium cyanide in dimethylsulfoxide or dimethylformamide gave rise to 4,5-trans-diphenyl-1-phenyl-2-phenylimino-2,3,4,5-tetrahydro-1H-azepine 5 in 15% yield. The structure was established from spectroscopic data and degradation study.

In continuation of our studies directed to the establishment of correct mechanism involved in the cyanide ion catalysed conversion of cinnamaldehyde 1a and cinnamalaniline 1b in methanol to methyl β-phenylpropionate 2a and N-(1-methoxy-3-phenyl)-propylideneaniline 2b[2,3], it was considered necessary to attempt the reaction of 1b with cyanide ion in aprotic solvent, such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) in the hope of isolating the dimeric dianil 4, itself obtained by the initial dimerisation of 1b to the anilino-anil 3[4] (benzoin-type condensation), followed by a 1,3-prototropic shift. Subsequent cleavage by methanol-cyanide ion could result in the formation of 2b[5], and this would then be considered as an evidence in favour of the benzoin dimerisation mechanism, as postulated for the analogous reaction of 1a[3].

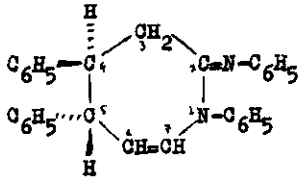


a, X = O; b, X = N-C_6H_5

Thus, the reaction of 1b dissolved in anhydrous DMSO or DMF with powdered

+Dedicated to Professor Herbert C Brown on the occasion of his 70th birthday

potassium cyanide at room temperature gave after purification through column chromatography over neutral alumina, followed by crystallisation, a highly crystalline bright yellow solid, mp 172°, in 15% yield. Elemental analysis and mass spectral evidence (M^+ 414) fixed the composition to $C_{30}H_{26}N_2$ for this product, indicating that dimerisation had indeed taken place during the reaction. The spectral data [IR (liquid film), 1665 cm^{-1} (C=N), PMR δ (CCl_4), 2.8-3.70 (m, 3H), 4.21 (dd, 1H, J = 9.0 Hz, 2.0 Hz), 6.80-7.60 (m, 22H, Aromatic)] coupled with the observation that the compound was recovered unchanged on treatment with cyanide ion in *refluxing methanol* and no iminoether 2b was formed, ruled out the open-chain dianil formulation 4b. Therefore, it was considered that an initial dimerisation had been followed by internal cyclisation. On the basis of the spectral characteristics, the amidine structure 5 has been suggested for the 172° dimer.



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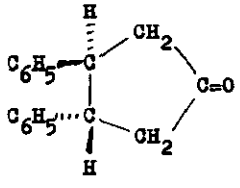

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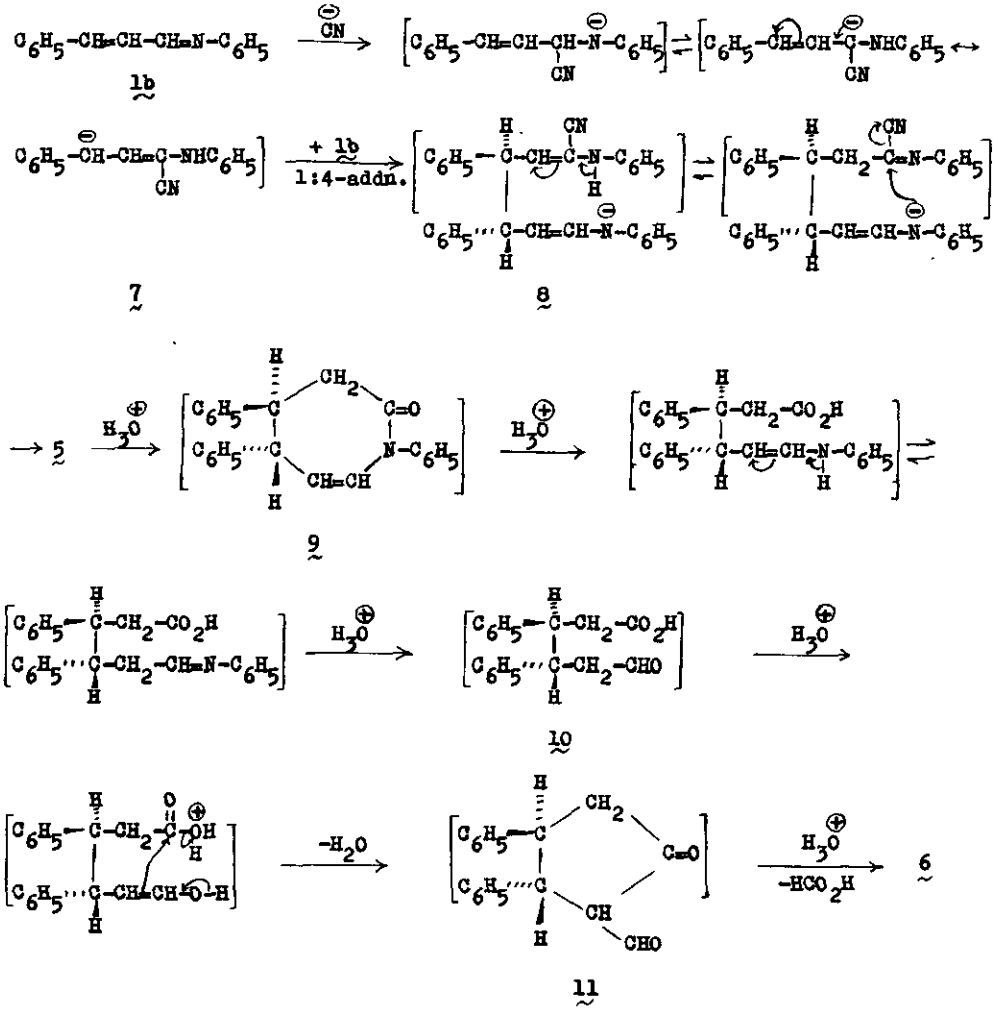
In the PMR, the double doublet at δ 4.21 (J = 9.0 Hz, 2.0 Hz) is assigned to 5-C<u>H</u>. This order of coupling could arise with the 7-membered ring of 5 in a chair conformation with 4,5-<u>trans</u> *stereochemistry* (4-C$\underline{H}_{ax}$, 5-C$\underline{H}_{ax}$, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 2.0 Hz) or in a boat conformation with 4,5-<u>trans</u> stereochemistry (4-C$\underline{H}_{ax}$, 5-C$\underline{H}_{eq}$, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 9.0 Hz). An inspection of the Dreiding model for 5 revealed that the chair conformation where the two phenyl groups are disposed in diequitorial fashion would be the preferred conformation because of least steric interaction. Further evidence in favour of amidine structure 5 is forthcoming from the degradation of the above dimer. As an amidine, the dimer was found to be somewhat soluble in hydrochloric acid and was recovered unchanged at room temperature for several days. However, when a solution of the dimer in dioxane or methanol was refluxed with concentrated hydrochloric acid, it was possible to effect the hydrolytic changes, even though a considerable portion of the dimer is recovered unchanged. Column chromatography of the reaction mixture followed by crystallisation provided a white crystalline material, mp 178°, corresponding to the composition $C_{17}H_{16}O$ in 45% yield. The IR spectrum displayed

a strong absorption band at 1750 cm^{-1} indicating the presence of a five-membered ketone. In the PMR spectrum, it showed two sets of multiplet in the aliphatic region, one corresponding to four protons at δ 2.50-3.00 and the other corresponding to two protons at δ 3.30-3.80. The ten aromatic protons appeared at δ 7.20-7.55 as multiplet. We assigned the formulation of trans-3,4-diphenylcyclopentanone 6 to this product (lit.[6] mp 177°) by direct comparison (IR, PMR, mmp, TLC) with an authentic sample prepared by following a literature procedure[6]. The formation of 5 from 1b and its degradation to 6 can be interpreted by the route shown in Scheme 1.



Scheme 1

1:4-Addition of 7 to 1b would furnish 8 which then undergoes a prototropic shift followed by internal cyclisation to yield 5. Hydrolysis of 5 with acid would provide the aldehydo-acid 10 via the amide 9. Acid-catalysed aldol type condensation[7] of 10 to the β-ketoaldehyde 11 and subsequent loss of a formyl group would give rise to 6.

REFERENCES AND NOTES

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