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BENZOYLATION OF 2,3,4,5-TETRAMETHYLPYRROLE

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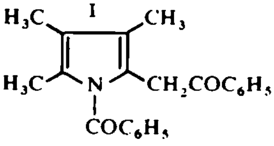
Abstract—Further evidence is presented to show that benzoylation of 2.3.4.5-tetramethypyrrole gives rise to compound VI.

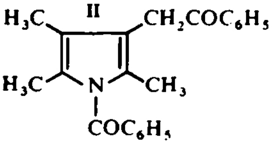
SOME years ago, it was reported that the benzoylation of 2,3,4,5-tetramethylpyrrole gave a compound for which the following structures I–V were suggested on the basis of elemental analysis.[1] More recently, it has been shown to have structure VI using NMR, IR and UV spectroscopy and analogy to the products from 2,5-dimethyl and 2,4-dimethyl 3-acetylpyrroles.[2] We now report more evidence which further supports the structure.

The product was analysed for $C_{22}H_{21}NO_2$. It showed no O—H or H—N but a carbonyl absorption 1685, 1640 cm^{-1} in the IR. The NMR spectrum (Fig 1) in $CDCl_3$ containing TMS as an internal standard showed 3 Me groups having a common chemical shift of δ 1·8, 2 × C_6H_5CO δ 7·35 (multiplet) ppm and an AB type spectrum δ_A 3·35 and δ_B 4·25 ($J_{AB} = 2·5$ Hz). Such a spectrum is not expected from any of the above structures I–V. I–III have CH_2 groups and if the two protons are nonequivalent because of rotation around the C—C bonds of the benzoyl group one expects $J_{AB} \sim$ 12Hz. This is not found and instead the observed value of J_{AB} very strongly supports the presence of a $=CH_2$ group.[3] In the above structure VI the 3 Me groups are not identical although they appear at the same field in the NMR. We therefore, ran the spectrum again in C_6D_6 (Fig 2) containing TMS. In this solvent the three Me groups appear at different fields[4] δ 1·15, δ 1·25 and δ 1·7. Normally $=CH_2$ group have a shift of 4–5 ppm.[3] but in structure VI, a shift to higher field is expected due to the magnetic anisotropy of the phenyl group in the benzoyl side chain.[5] The existence of $=CH_2$ was

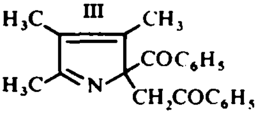
I



II



III



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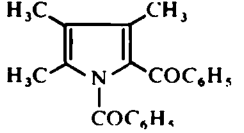
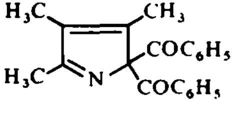
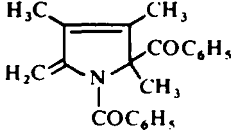


V



VI



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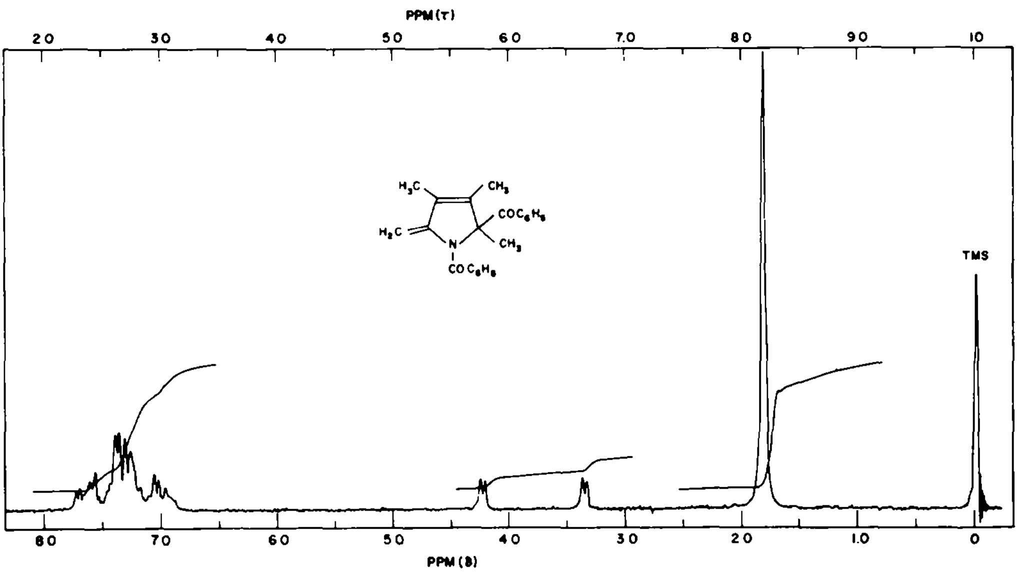


FIG 1. NMR spectrum of VI in $CDCl_3$

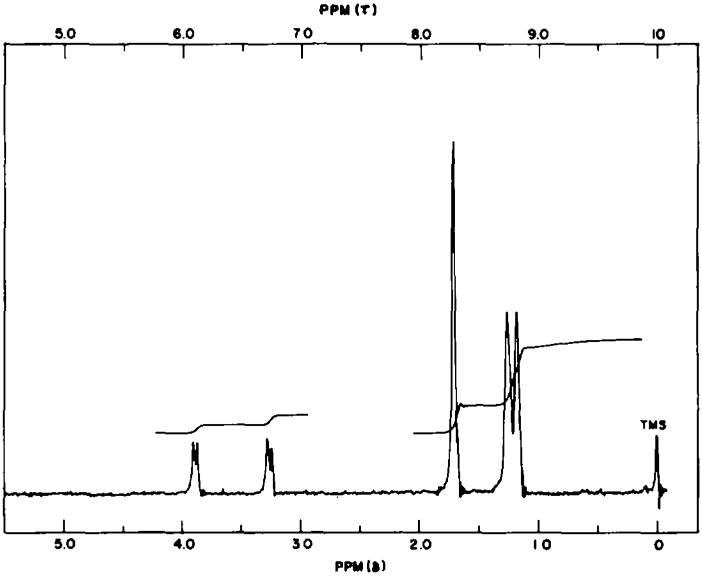


FIG 2. NMR spectrum of VI in C_6D_6

confirmed by Zn/AcOH reduction. NMR of the product gave a quartet at δ 4·65 and a doublet at δ 0·45 showing a $^{\mathrm{H}}{>}$C—CH$_3$ group. Shaking with D$_2$O did not exchange the exocyclic methylene proton.[6] Acid hydrolysis of VI with 1N HCl in ethanol gave 1-benzoyl-2,3,4,5-tetramethylpyrrole VII whose NMR is shown in Fig 3. Its IR spectrum showed no N—H peak but a carbonyl absorption at 1700 cm^{-1}. The NMR

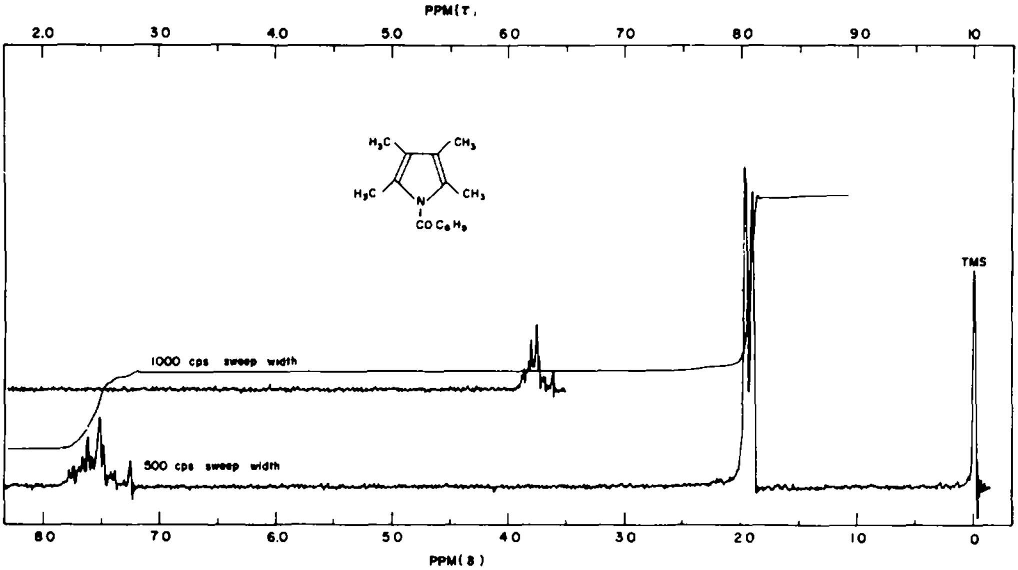
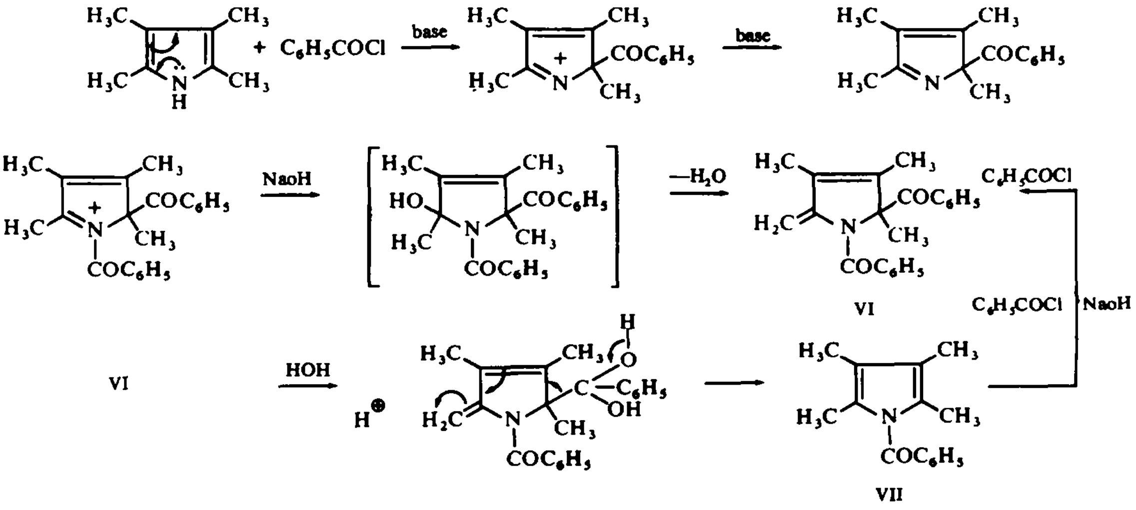


FIG 3. NMR spectrum of VII in $CDCl_3$

spectrum indicates 4 Me groups and one benzoyl group. The two Me peaks do not resolve further even in C_6D_6 indicating 2 pairs of symmetrically placed Me groups. The UV spectrum of VI in ethanol shows a maximum at 232 (ε21000) with a shoulder at 277 (ε7000) and 320 mμ (ε1500) which further support its structure.[7] 1-Benzoyl 2,3,4,5-tetramethylpyrrole was not changed under the conditions under which 2,3,4,5-tetramethylpyrrole was diacylated to give VI. We hence concluded that C-benzoylation is the primary step in the formation of VI. A possible mechanism follows.



EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were determined with a Varian A-60 instrument in $CDCl_3$ and C_6D_6 containing TMS as the internal standard. Chemical shifts are expressed in ppm. IR spectra were taken in KBr on a Perkin-Elmer model 21 spectrophotometer and UV spectrum was measured in ethanol on a Cary model 11.

1,5-Dibenzoyl-2-methylene-3,4,5-trimethyl-Δ^3-pyrroline (VI) 2,3,4,5-Tetramethylpyrrole was benzoylated according to the method of Treibs and Derra-Scherer[1] to give VI (90%) m.p. 141° (lit[1] 140°). (Found: C, 79·89; H, 6·55; N, 4·35. $C_{22}H_{21}NO_2$ requires: C, 79·78; H, 6·35; N, 4·22%).

Zinc-acetic acid reduction of VI. The compound VI (0·331g) was dissolved in AcOH (5 ml) and Zn dust (0·5g) was added in portions and the reaction mixture held at 35° for 1 hr. Zn dust was removed by filtration and washed with AcOH. The combine AcOH extracts were poured into water. The solid which separated was filtered off, washed, dried and crystallized from EtOH giving (0·25g, 75%) as colourless needles, m.p. 172–174° (Found: C, 78·84; H, 7·20; N, 4·34. $C_{22}H_{23}NO_2$ requires: C, 79·25; H, 6·95; N, 4·20%).

1-Benzoyl-2,3,4,5-tetramethylpyrrole (VII). The compound VI (0·331 g) was dissolved in EtOH (5ml) and IN HCl (2·5 ml) was added and the soln heated under reflux for 15 min. EtOH was removed under reduced press. and water was added. The solid which separated was filtered, washed, dried and crystallized from n-pentane giving (0·193g, 85%) as colourless needles m.p. 70° (Found: C, 79·47; H, 7·42; N, 6·37. $C_{15}H_{17}NO$ requires: C, 79·26; H, 7·54; N, 6·16%).

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