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REGIOSPECIFIC REDUCTION OF PYRENE TO 1, 9-DIHYDROPYRENE

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The structures of the dihydro products from metal-ammonia reduction of alternate aromatic hydrocarbons correlate to a remarkable degree with predictions of simple MO theory[2,3]; no exceptions are known[4].

We wish to report that treatment of pyrene with lithium in liquid ammonia provides 1, 9-dihydropyrene (I), one of five predicted theoretically equivalent structures (the 1, 3a-, 1, 5-, 1, 6-, 1, 8-, and 1, 9-dihydro isomers), as the primary reduction product; the 1, 6- and/or 1, 8-dihydro structure was previously proposed[6,2].

The nmr spectrum[7] of I (Fig. 1a) exhibited aromatic protons (5H) as a complex multiplet centered at δ 7. 2. Two vinyl protons appeared as a basic four line pattern centered at δ 5. 9, with each of the lines further split into triplets[8] (low field pair $J_{1,(3,3')}$ = 1.5 Hz; high field pair $J_{2,(3,3')}$ = 3. 0 Hz); the remaining vinyl proton appeared as a complex multiplet at δ 5. 6 (1 H). Multiplets were observed in the methylene region at δ 3. 95 (2 H) and at δ 3. 65 (2 H), the former consisting of four considerably broadened lines.

Saturation of the higher field methylene multiplet (Fig. 1b) resulted in collapse of the vinyl complex at δ 5. 9 (2 H) into a sharp AB pattern ($J_{1,2}$ = 10 Hz) assigned to protons H_1 and H_2. In addition, the signal representing the remaining vinyl sharpened to a triplet ($J_{4,5}$ = 3. 5 Hz), indicative of loss of coupling between $H_{3,3'}$ and H_4[9]. Saturation of the low field methylene multiplet (Fig. 1c) removed the major coupling to H_4 without affecting H_1 or H_2. Thus, a single vinyl proton is coupled to both methylenes (one direct, one allylic), a feature characteristic of only the assigned structure, I.

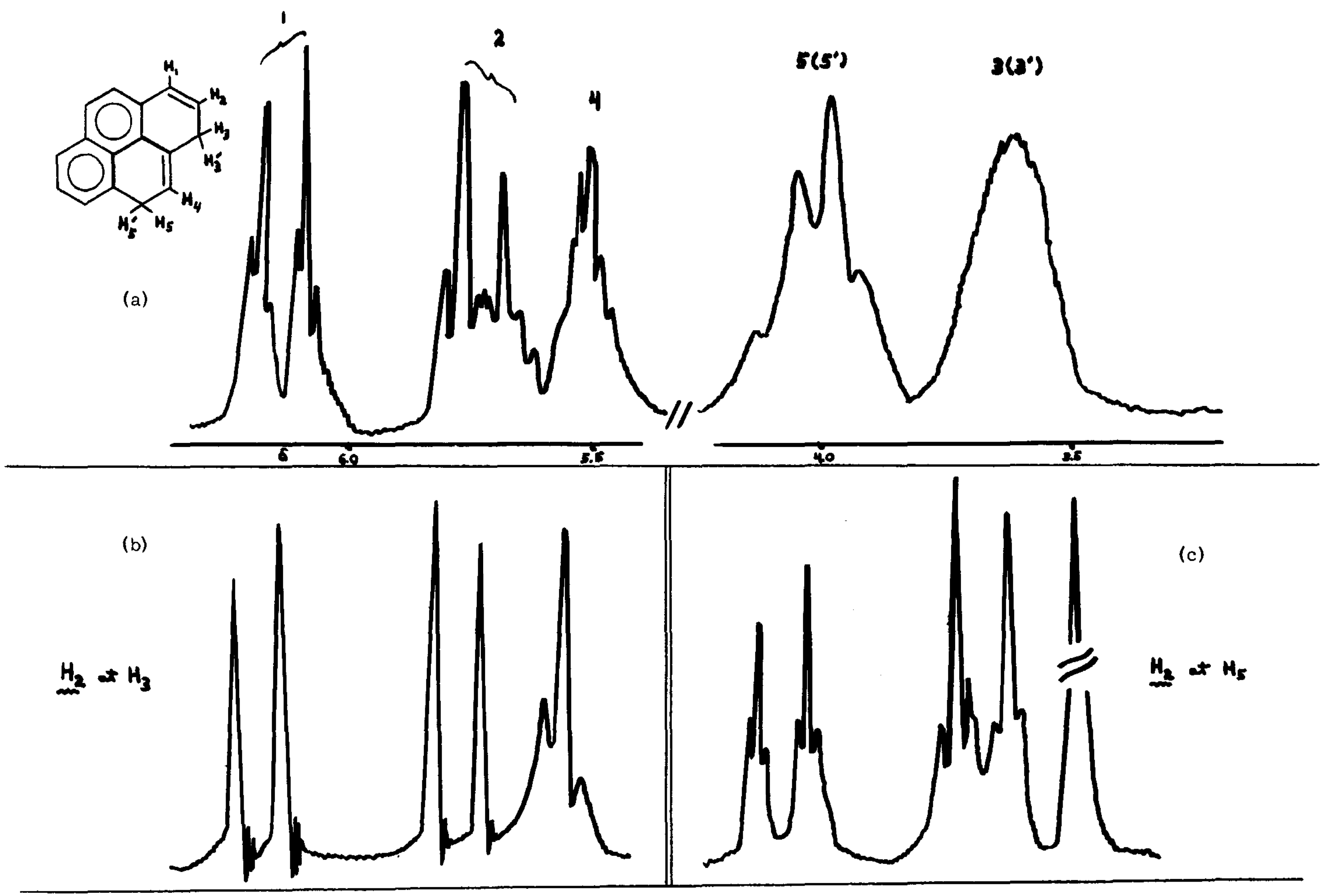

Figure 1: The partial 100 MHz nmr spectrum of 1, 9-dihydropyrene (CCl_4). (a) Vinyl and allylic regions. (b) Vinyl region with saturation of allylic $H_3(H_3')$. (c) Vinyl region with saturation of allylic $H_5(H_5')$.

Previous attempts to characterize I have been severely hampered by the instability of the crude product with respect to air, light, heat, acid, and base, coupled with the difficulty of separating it from relatively large proportions of recovered pyrene. The difficulties have now been obviated by quenching reaction rapidly with solid ammonium chloride, and isolation and recrystallization of the crude product in minimum time. In a typical experiment[10], a solution of pyrene (1.0 g) in tetrahydrofuran (75 ml) was added to liquid ammonia (150 ml) at -33°. Lithium wire (2.5 g-atom) was then added, and after 10 min. reaction was quenched by rapid addition of excess solid NH_4Cl with external cooling. The product, isolated without delay by conventional extraction procedure, contained I (94%), pyrene (5%), and minor amounts of further reduction products (1%), according to nmr analysis. On exposure to air or light or on heating in solution, crude I became black and decomposed to complex mixtures containing increased proportions of pyrene and 4,5-dihydropyrene among other products. However, rapid recrystallization from methanol provided pure I, m.p. 110°. The latter isomerized smoothly to 4,5-dihydropyrene upon warming in methanol in the presence of a drop of conc. hydrochloric acid.

Recovery of large proportions of pyrene from similar reductions quenched with less acidic proton sources[11] (H_2O, ROH) probably results from spontaneous ejection of hydride from the unprotonated monoanion of I, a process for which there is ample precedent[12].

According to simple MO theory[3], the detailed reduction path (radical-anion or dianion intermediate) is unimportant for alternate hydrocarbons. The first proton is expected to add to the pyrenyl carbanion at C-1, the position of highest electron density as determined by the coefficients of the lowest vacant molecular orbital. The second protonation occurs on a monoanionic intermediate in which the electron density is calculated to be highest and equal at seven alternate positions (2, 3a, 5, 6, 8, 9, 10a) and zero at the remaining positions. Two of the resulting predicted structures (1,2- and 1,10a-dihydropyrene) may be rejected by taking into account the perturbation introduced by the adjacent methylene group. Five structures remain as equally probable, and there appears to be no steric or other obvious factor to account for exclusive formation of only one of these, the 1, 9-dihydro isomer (I).

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REFERENCES

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(4) The product of biphenyl, a subject of earlier controversy, has recently been established to be 1, 4-dihydrobiphenyl[5], in agreement with HMO prediction.

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(7) Analyses were performed on a Varian HA-100 spectrometer with CCl_4 as the solvent and TMS as a reference and lock signal.

(8) Since the bond angles between H_1 and $H_{3,3'}$ are presumably the same, it is expected $J_{1,3} = J_{1,3'}$, and since the chemical shift difference between methylene and vinyl protons are large, it is not surprising to observe first order splitting of each of the vinyl signals into triplets.

(9) Although coupling between H_4 and $H_{3,3'}$ was readily observed, the magnitude (1.5-2.0 Hz) proved difficult to determine accurately.

(10) Ammonia was distilled into the reaction vessel through a column of barium oxide as recommended in previous papers in this series.

(11) A minimum of 40-50% pyrene is recovered from comparable reaction quenched with water[2].

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