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NONBENZENOID AROMATIC DICYCLOPENTA[a,f]NAPHTHALENE DIANIONS.

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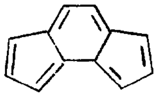
The syntheses of the 4n π-electron hydrocarbon pentalene and its benzologs have received considerable attention.(1-4) While pentalene itself is unknown its dianion(2) and several uncharged derivatives(3,4) have been prepared. Of the two pentalene mono-benzologs, the neutral s-indacene is known(5) together with the dianions of both s and as-indacene (1).(1b,6) Attempts to convert as-indacene (1) dianion into a fully conjugated ferrocene polymer having possible unusual conductive properties have led only to dimeric ferrocene products.(6) We report here a conceptually parallel study with the synthetic objective of a conjugated ferrocene polymer 3 derived from a pentalene dibenzolog, the dicyclopenta[a,f]naphthalenide dianion 2. Ferrocene dimer formation from 2 might be less likely than from as-indacenide dianion due to the absence of attractive interactions between iron atoms that may play a role in the formation of the as-indacene ferrocene dimer.



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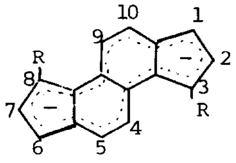
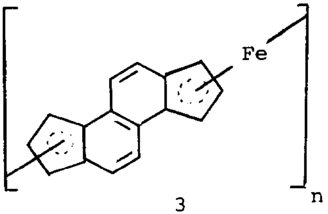


2a R = H

2b R = C_6H_5



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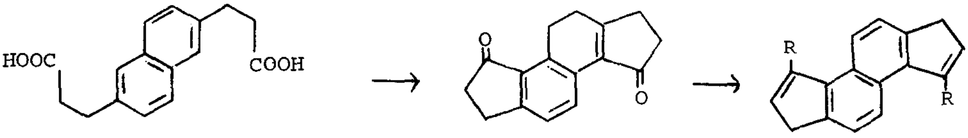
Alkylation of 2,6-di(bromomethyl)naphthalene(7) with sodiodiethyl malonate in hot ethanol-benzene gave a tetraester(8) (m.p. 67-70°, ν_{CO}^{KBr} 1745 and 1725 cm^{-1}) which was saponified with 3N sodium hydroxide in aqueous methanol followed by decarboxylation of the resulting acid$^{(8)}$ at 250-300° *in vacuo*. The naphthalene-2,6-*bis*-propionic acid 3 thus obtained was characterized as its diethyl ester,$^{(8)}$ m.p. 113-115°, $\nu_{CO}^{CHCl_3}$ 1725 cm^{-1}. Cyclization of 3 to the



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4

5a R=H

5b $R=C_6H_5$

diketone 4$^{(8)}$ (m.p. 243-245°, ν_{CO}^{KBr} 1685 cm^{-1}) proceeded at 120° over 3.5 hr. in polyphosphoric acid. Alternatively the diacid chloride of 3 yielded 4 on treatment with aluminum chloride in methylene chloride at 0°. The diketone 4, obtained in an overall 30% yield from di(bromomethyl)naphthalene, displayed an A_2B_2 pattern in the nmr ($CDCl_3$-CF_3COOH) at τ 6.6-7.3 (CH_2CH_2) and doublets at τ 2.40 (J=9 Hz, H_5, H_{10}) and τ 0.82 (J=9 Hz, H_4 and H_9 deshielded by the C_3 carbonyl). Reduction of 4 with sodium borohydride-lithium bromide in refluxing isopropyl alcohol gave a mixture of epimeric diols (m.p. 165-185° dec.) which suffered facile dehydration with p-toluenesulfonic acid in benzene at 60°. The resulting 2,7-dihydrodicyclopenta[a,f]naphthalene 5a$^{(8)}$ (m.p. 158-160°) was obtained as a colorless, moderately stable solid in 87% overall yield from 4. The structure and isomeric purity of 5a was suggested by nmr signals ($CDCl_3$) at τ 6.53 (H_1, H_6, t, J=1.5 Hz), τ 3.35 (H_2, H_7, d of t, J=6 and 1.5 Hz), τ 2.54 (H_3, H_8, d of t, J=6 and 1.5 Hz), τ 2.40 ($H_{5(4)}$, $H_{10(9)}$, d, J=9 Hz), and τ2.06 ($H_{4(5)}$, $H_{9(10)}$, d, J=9 Hz) and by hydrogenation to hexahydrodicyclopenta-[a,f]naphthalene$^{(8)}$ (m.p. 169-170°). Aqueous base catalyzed isomerization of 5a to an equilibrium mixture of three double bond isomers demonstrated the absence of double bond migration during the formation of 5a.

Addition of two equivalents of butyl-lithium to a solution of 5a in THF at -78°, gradual warming of the solution to 25°, and evaporation of the solvent gave solid lustrous bronze colored dilithio dicyclopenta[a,f]naphthalenide 2a. The structure of 2a was confirmed by quenching with deuterium oxide to give a mixture of dideuterated isomers of diene 5a and by its nmr spectrum which displayed signals (THF) at τ 3.53 (H_2, H_3, H_7, H_8, m), τ 3.90 (H_1, H_6, d of d, J=2.5 Hz, J=2.0 Hz), τ 2.97 (H_5, H_{10}, d, J=5.5 Hz) and τ 2.73 (H_4, H_9, d, J=5.5 Hz). Charge densities estimated by correction of this spectrum for ring current effects correlate well with values obtained by an SCF calculation (Table I).(6,9)

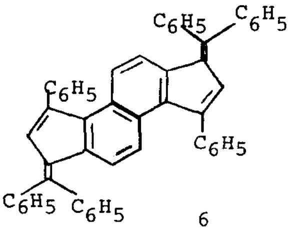
Table I

NMR Chemical Shifts (τ) and Charge Densities (ρ) on Dicyclopenta[a,f]-naphthalene Dianions

ring position	τ_{obs}	τ_{corr}[a]	ρ_{exptl}[b]	ρ_{calc}[c]
1	3.90	4.53	-.21	-.24
2	3.53	3.94	-.15	-.16
3	3.53	4.40	-.19	-.22
4	2.97	4.06	-.12	-.09
5	2.93	3.69	-.09	-.07

a. Chemical shifts corrected for ring current effects, see ref. 9.
b. Calculated from τ_{corr} by method of Katz, Balogh and Schulman.[6b]
c. SCF-MO calculation.

Treatment of the diketone 4 with phenyl-lithium followed by p-toluenesulfonic acid catalyzed dehydration yielded the diphenyl diene(8) 5b (m.p. 233-234°; nmr ($CDCl_3$), τ 2.33 (H_5, H_{10}, d, J=9 cps), τ 2.64 (H_4, H_9, d, J=9 cps), τ 2.52 (10 ArH, m), τ 3.52 (H_2, H_7, t, J=2 cps) and τ 6.47 (H_1, H_6, J=2 cps). Unlike 5a, 5b failed to isomerize with aqueous base although in D_2O-DMF complete deuterium exchange occurred at the methylene carbons. Butyl-lithium in THF similarly converted 5b to its dianion 2b which displayed nmr signals (THF) at τ 2.37 (2H, m), τ 2.7-3.2 (10H, m), τ 3.48 (H_2, H_7, d, J=3.5 Hz) and τ 3.96 (H_1,H_6, d, J=3.5 Hz). Confirmation of these chemical shift assignments was obtained by conversion of the aforementioned 5b-d_4 to 2b-d_2 which no longer displayed a τ 3.96 signal. The dianion 2b reacted readily at 25° with benzophenone to give the novel orange *bis*-fulvene 6(8) [m.p. 275-280° dec., $\lambda_{max}^{C_6H_{12}}$ 266 mμ (ε 31,200), 277 (34,200), 340 (27,200) and 403 (19,500)].



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Attempts to oxidize the dienes 5 or the dianions 2 to neutral 4n π-electron hydrocarbons have thus far been unsuccessful. Studies of the formation of conjugated ferrocene polymers from 2 are in progress.

Acknowledgement. We are indebted to Professor W. A. Little for the SCF calculation.

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