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THE ONE-ELECTRON REDUCTION OF CARBONIUM IONS. IX.
FORMATION OF INTRAMOLECULAR CYCLIZATION PRODUCTS BY THE CHROMOUS-ION REDUCTION OF POLYMETHYLENEBISTROPYLIUM IONS

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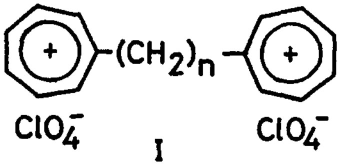
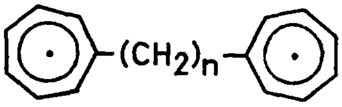
Although the chemistry of the biradical has attracted much interest since the classical study on the "Chichibabin's hydrocarbon",1) there have been rather few reports on the biradical having a simple polymethylene chain.2) We now wish to report on the syntheses of a series of stable dications with two tropylium rings connected by the polymethylene chain, I,3) and on their one-electron reduction which gave the products supposed to have been derived from the biradical intermediate, II.


I


II

The polymethylenebistropylium salts, I ($n = 4 \sim 6$), were synthesized by hydride abstraction with triphenylmethyl perchlorate from α,ω-dicycloheptatrienylalkane, which had been obtained by the reaction of 7-ethoxycyclohepta-1,3,5-triene with polymethylenebis-Grignard reagents. The salt, I ($n = 3$), was synthesized similarly from 1,3-dicycloheptatrienylpropane, which had been obtained by the Clemmensen reduction of dicycloheptatrienylacetone reported by Yagihara and Kitahara.4) The salts, I ($n = 1,2$), were prepared by the methods similar to those reported by Kitahara et al.5) Properties of I ($n = 1 \sim 6$) are listed in Table 1.

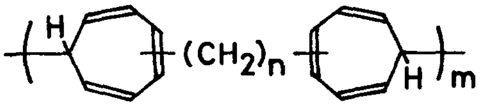
Table 1. Properties of Polymethylenebistropylium Perchlorates (I)[a]

n	mp, °C (dec)	UV: $\lambda_{max}^{H_2SO_4}$, nm (log ε)	NMR: τ_{CF_3COOH}, ppm
1	>200	281 (4.07), 289 (4.10), 298 (4.01)	0.72 (lit, 0.62[c]) (s, 12H, $-C_7H_6^+$), 4.43 (lit, 4.35[c]) (s, 2H, +⟩-CH_2-⟨+)
2	~229[b]	288 (4.04), 294 (4.05), 301 (4.05)	0.73 (lit, 0.67[d]) (m, 12H, $-C_7H_6^+$), 5.98 (lit, 5.92[d]) (s, 4H, +⟩-CH_2-)
3	>200	290 (4.00), 295 (4.00), 302 (4.05)	0.80 (s, 12H, $-C_7H_6^+$), 6.34 (t, 4H, +⟩-CH_2-), 7.47 (m, 2H, $-CH_2-$)
4	184.0-186.2	295 (4.06), 301 (4.03)	0.84 (s, 12H, $-C_7H_6^+$), 6.50 (m, 4H, +⟩-CH_2-), 7.84 (m, 4H, $-CH_2-$)
5	133.8-135.1	296 (4.08), 301 (4.06)	0.86 (s, 12H, $-C_7H_6^+$), 6.57 (t, 4H, +⟩-CH_2-), 8.10 (m, 6H, $-CH_2-$)
6	146.0-148.5	296 (4.07), 301 (4.05)	0.85 (s, 12H, $-C_7H_6^+$), 6.54 (t, 4H, +⟩-CH_2-), 8.25 (m, 8H, $-CH_2-$)

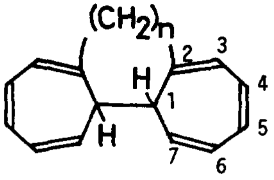
a) All gave satisfactory elemental analyses. b) Violent explosion. c) Ref. 5a. d) Ref. 5b.

We have already shown that the substituted tropylium ions are readily reduced with Cr(II) to give the dimers quantitatively, by the one-electron reduction mechanism.[6] Thus, the reduction of the dications, I (n=1~6) (2×10^{-3}M), with 10-fold excess of Cr(II) was carried out in 12N H_2SO_4[7] under nitrogen atmosphere at 20-25°C for 1-2 hr. The ordinary work-up gave the oily product[8] (68-100% yield) which is supposed to be a mixture of oligomers and/or polymers with the structure III (n=1~6) on the basis of its NMR (olefinic ring protons centered at τ 3.5, 4.0, and 4.8, plus methine and methylene protons with intensities almost in accord with the supposed structure), IR (3020, 1380, and 700 cm^{-1} for the cycloheptatrienyl bands), and UV (λ_{max}^{EtOH} 260 nm for n=6 as the representative case) spectral data.

In the case of n=2~4, however, the intramolecular cyclization product, IV, was isolated from the crude product by repeated preparative TLC on silica gel in 8.7, 8.1, and 7.4% yields for n=2, 3, and 4, respectively. This clearly indicates the generation of the polymethylenebiscycloheptatrienyl biradical intermediate, II, in the course of reduction.[9] The properties of IV are given in Table 2.



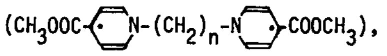
III



IV

Table 2. Properties of 2,2'-Polymethylenobiscyclohepta-2,4,6-trien-1-yl (IV)

n	mp, °C	MS: m/e (M^+)	NMR: τ_{CCl_4}, ppm
2	(oil)	208	3.58 (m, 4H, $H^{4,5}$), 4.07 (m, 4H, $H^{3,6}$), 4.91 (m, 2H, H^7), 7.64 (br, 4H, $>C{-}CH_2{-}$), 8.13 (d, 2H, H^1)
3	51.0-54.5	222	3.54 (t, 4H, $H^{4,5}$), 3.80 (d of d, 2H, H^6), 4.00 (d, 2H, H^3), 4.57 (d of d, 2H, H^7), 7.51 (t, 4H, $>C{-}CH_2{-}$), 7.77 (d, 2H, H^1), 8.33 (m, 2H, $-CH_2-$)
4	73.1-77.1	236	3.49 (t, 4H, $H^{4,5}$), 3.79 (d of d, 2H, H^6), 3.99 (d, 2H, H^3), 4.47 (d of d, 2H, H^7), 7.51 (br, 4H, $>C{-}CH_2{-}$), 7.87 (d, 2H, H^1), 8.27 (br, 4H, $-CH_2-$)

With respect to the association of the stable polymethylenebispyridinyl biradical , Itoh and Kosower[2b] reported, on the basis of spectral data, that a considerable fraction of the biradical exists in the closed form (by intramolecular association) for n=3 and 4, while only the open form (by intermolecular association) is assumed for n=2 and 5. Chemically substantiating these spectral findings, the present results indicate that two factors are important for the intramolecular coupling, that is, (a) the face-to-face π-interaction[10] between the two cycloheptatrienyl rings, and (b) the formation of a medium-sized (i.e., six- to eight-membered) ring when the two rings are connected at the "ortho" position, while the biradicals which can not satisfy these steric requirements would couple intermolecularly to give III.[11]

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References

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7) The acidity of more than 6N seems necessary for complete dissolution of the dications in the aqueous medium.

8) Especially when n = 3 and 6, an elastic solid, supposedly a high molecular-weight polymer, was formed besides the oil.

9) The mechanism in which the chromium complex or the carbanion is involved seems unlikely from analogy with the reduction of the alkyltropylium ions (Ref. 6). In addition, no protonolysis product from such an intermediate, e.g., α,ω-dicycloheptatrienylalkane, has ever been detected.

10) This interaction is supposed to be rather weak compared with the case of the pyridinyl radical, because of the quite effective delocalization of the unpaired electron in the cycloheptatrienyl radical.

11) A considerable fraction of monoradicals which were first formed by the reduction might proceed on to couple with another mono- or biradical species, thus, also resulting in the formation of III.