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SYNTHESIS OF 1,3-BIS(DIAMINOCYCLOPROPENYLIO)CYCLOPENTADIENIDE: TRIPOLAR MESOMERIC COMPOUND

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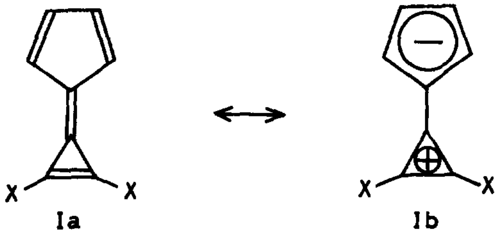
Since the first preparation of calicenes was reported in 1965,[1-5] the physical and chemical properties of calicene represented by both canonical structures of (Ia) and (Ib) have attracted much attention of chemists. However, calicene derivatives so far reported are confined to the substituted ones with alkyl or aryl groups on three-membered ring. Accordingly it is particulary interesting to investigate the chemistry of the electron rich calicenes, in which three-membered ring is replaced with electron donating substituents such as amino group.[6] In view of the paucity of the information on the electronic effect of heteroatom directly attached to the cyclopropenyl ring, an attempt to react 1,2-diamino-3-chlorocyclopropenium ion with cyclopentadienide seemed to be appropriate as an accessible approach to the electron rich calicene. We chosed 1,2-bis(diisopropylamino)-3-chlorocyclopropenium ion[7] (II) as a diaminochlorocyclopropenium component and cyclopentadienide and indenide as a cyclopentadienide component. We wish to communicate that both reactions have led to the exclusive formation of a new type of tripolar mesomeric compounds (III, IV).

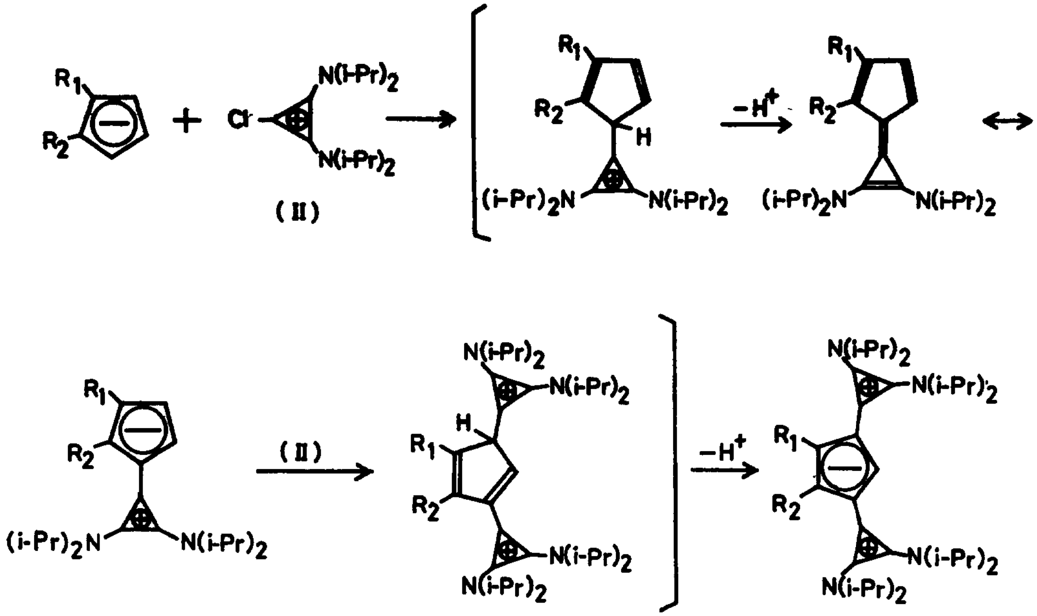


Ia Ib

To a solution of sodium cyclopentadienide (2 mmole) in 10 ml THF was added (II) (371 mg, 1 mmole) in 5 ml CH_2Cl_2 at room temperature in argon atmosphere. After stirring for 1 hr, the reaction mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with saturated $KClO_4$ solution, dried over anhydrous Na_2SO_4, and subsequent recrystalization from CH_2Cl_2-Et_2O gave pale green crystals (III) in 54 % yield. mp 207° (dec). Anal. Calcd for $C_{35}H_{59}N_4ClO_4$: C, 66.16; H, 9.37; N, 8.82. Found: C, 66.34; H, 9.50; N, 8.77. ir (KBr) 2970, 1895, 1510, 1480, 1338 and 1095 cm^{-1}. uv (CH_3OH) λ_{max} 245 nm (log ε 4.34), 275 (4.09, sh), 367 (4.70) and 384 (4.73). nmr ($CDCl_3$) δ 7.18 (1H, multiplet), 6.67 (2H, multiplet), 4.10 (8H, sesquitet) and 1.46 (48H, doublet).

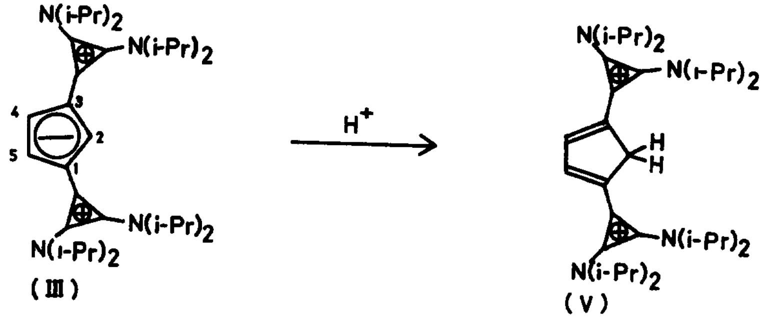
To a suspension of lithium indenide (6 mmole) in 10 ml THF was added (II) (742 mg, 2 mmole) in 10 ml CH_2Cl_2 at room temperature in argon atmosphere and the mixture was stirred for 3 hr. After work up, olive crystals (IV) were obtained in 63 % yield, mp 254° (dec). Anal. Calcd for $C_{39}H_{61}N_4ClO_4$. C, 68.34: H, 8.97, N, 8.18. Found. C, 67.63, H, 8.97; N, 7.96. ir (KBr) 2975, 1895, 1512, 1473, 1458, 1309 and 1093 cm^{-1}. uv (CH_3OH) λ_{max} 252 nm (log ε 4.34), 274 (4.36), 329 (4.02), 397 (4.57, sh) and 412 (4.60). nmr (d_6-DMSO) δ 7.50 ∿ 7.38 (2H, multiplet), 7.43 (1H, singlet), 7.00 ∿ 6.86 (2H, multiplet), 4.20 (8H, sesquitet), 1.38 (48H, doublet). Microanalyses and spectral data of the products indicates that the five-membered ring is replaced with two diaminocyclopropenium groups at 1 and 3 positions. Mono-substituted compound (calicene itself) has never been isolated by change of solvent and the ratio of the electrophile (II) to cyclopentadienide. Diaminocalicene should exist as a reaction intermediate, which is considered to be a most plausible precursor of the tripolar mesomeric systems (III) and (IV). The exclusive formation of tripolar mesomeric system suggests that reactivity of the most probable intermediate, diaminocalicene towards the electrophile (II) should be markedly enhanced due to the strong electron donating effect of the amino-group compared with that of cyclopentadienide or indenide.

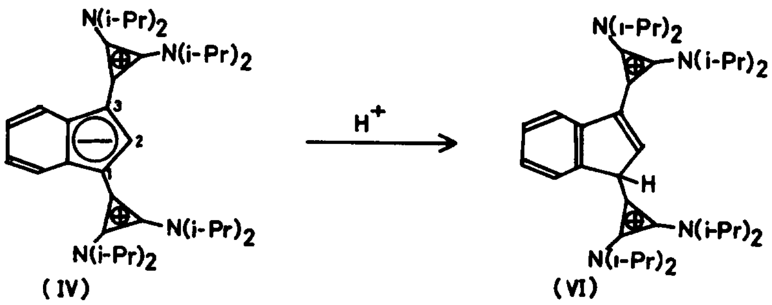
In strong acid such as trifluoroacetic acid or perchloric acid, protonation of (III) took place at the 2-position to give a stable adduct (V). The position of protonation was determined by the nmr and ir spectra. On the contrary, the (IV) was protonated at the 1-position, to afford (VI). The reason for the formation of (VI) is considered to be due to the larger stability of (VI) than the



(III) $R_1=R_2=H$

(IV) $R_1,R_2=-(CH)_4-$





alternative proton adduct at the 2-position, because the latter one should be destabilized due to its quinonoid structure.

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