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3,4-DIAMINOTRIAFULVENES

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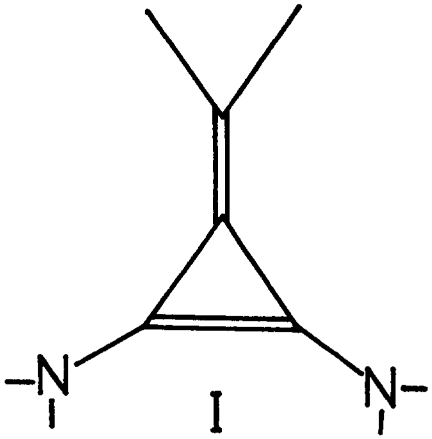
The simplest cross-conjugated 4C4π system, triafulvene (delocalization energy, DE 0.96β) is of interest from the organic and theoretical points of view.[1)] Although the parent triafulvene has not been synthesized yet, some 3,4-di-aryl- or alkyl derivatives with electron-attracting substituents at 1-position have been prepared recently.[1)]



I

However, 3,4-diaminotriafulvene system (I) has not been synthesized so far. We wish to report here first synthesis of 3,4-diaminotriafulvenes and some their properties. 1,2,3-Trispiperizino-cyclopropenium perchlorate (II)[2)] (3 mmol) was added into the solution of malonitrile (3 mmol) and potassium t-butoxide (3 mmol) dissolved in hot dry t-butanol (25 ml). The reaction mixture was kept at 80° with stirring for 21 hr., then filtered. After evaporation under reduced pressure, the residue was extracted with n-hexane. Removing n-hexane from the extract left white crystalline solide (yield 39 %). mp 293° dec (from dimethylformamide-water). The solide was confirmed to be 1,1-dicyano-3,4-dipiperidinotriafulvene (III$_a$) by the elemental analysis (Anal. Calcd. for $C_{16}H_{20}N_4$: C 71.61, H 7.51, N 20.88; Found: C 71.64, H 7.50, N 20.91) and the following spectral data; IR (KBr) 2195 cm^{-1} (ν_{CN}), 1963 (cyclopropene double bond), NMR ($CDCl_3$), τ 8.30

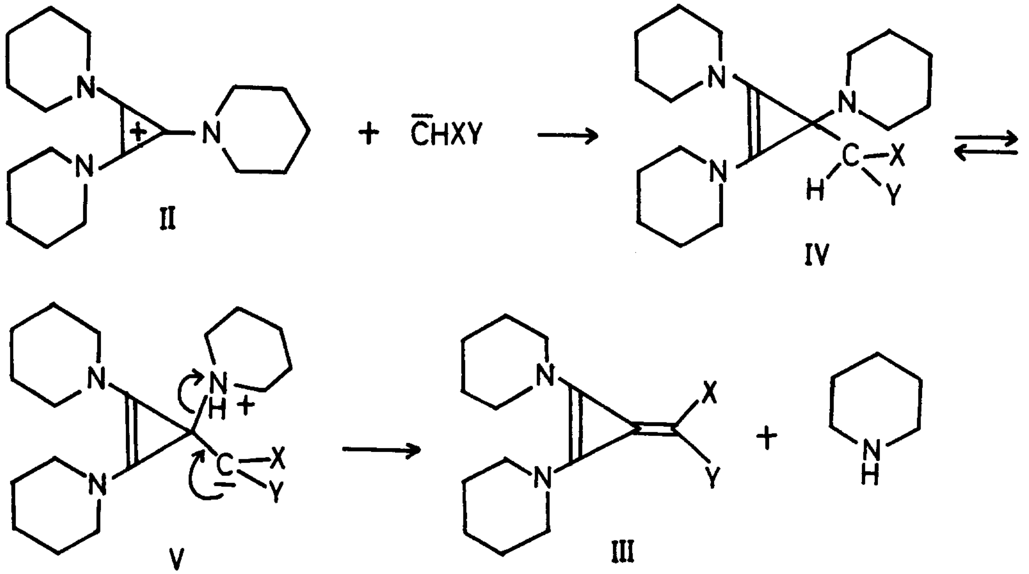
(m 6H), 6.47 (m 4H), UV (CH_3OH) λ_{max} 247 mμ (log ε 3.99) 280 (4.34).

The similar reaction of II with ethylcyanoacetate afforded 1-cyano-1-carbethoxy-3,4-dipiperidinotriafulvene (III_b) in 18 % yield. mp 152° dec (from n-hexane-benzene). Anal. Calcd. for $C_{18}H_{25}N_3O_2$: C 68.54, H 7.99, N 13.33, O 10.14; Found: C 68.29, H 7.97, N 10.14, O 10.71; IR (KBr), 2190 cm^{-1} (ν_{CN}), 1945 (cyclopropene double bond); NMR ($CDCl_3$) τ 8.71 (t 3H), 8.31 (m 12H), 6.36 (m 8H), 5.82 (q 2H); UV (CH_3OH) 227 mμ (log ε 4.17), 294 (4.32).

The reaction of II with other active methylene compounds such as diethylmalonate, dibenzoylmethane and acetylacetone have also been attempted under the above condition, however, the corresponding 3,4-diaminotriafulvene derivatives were not obtained but II was recovered. The reaction leading to the formation of 3,4-diaminotriafulvene derivative (III) is too strange, because we have never encountered any case where the strongly bonded[3)] and poor-leaving amino group is replaced by the carbanions under such a mild condition.

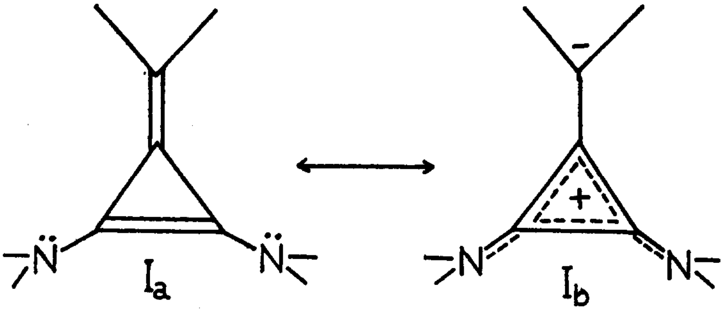
A probable steps of the reaction is supposed to be shown in Scheme I.

Scheme I.



In scheme I, first step (II→IV) is mainly controlled by the nucleophilicity of the carbanion (C̄HXY). The + charge-decrease on the cyclopropenium ring carbon in II due to the conjugation with amino group should weaken the attack of the carbanion. The second step (IV→V) seems to easily take place because of the 1,3-protoropy in alcohol solvent as well as the -charge delocalization in the resultant carbanion (V). The third step (V→III) might become possible due to a change to the more stable system (eg. DE for III_a 3.30β) and good leaving nature of ammonium group. The inertness of the carbanions produced from diethylmalonate, dibenzoylmethane and acetylacetone seems to be responsible for their weaker nucleophilicity.

The stability of 3,4-diaminotriafulvene system should be ascribed to the predominant contribution of the dipolar structure (I_b) in its ground state.



I_a I_b

The contribution of the structure I_b in the ground state of III can be estimated from the solvent effect on the longest wave length $\pi\rightarrow\pi^*$ absorption band (intramolecular CT band).[4)]

Table I. The Solvent Effect on the Longest Wave Length $\pi\rightarrow\pi^*$ Absorption Band (mμ) of III

	Cyclohexane	Dioxane	CH_2Cl_2	CH_3CN	CH_3OH
III_a	288	285	285	282	280
III_b	298	295	298	295	294

As is seen in Table I, both the longest $\pi\rightarrow\pi^*$ transitions of III_a and III_b show blue shift with the increase in the polarity of solvent, indicating the expected predominant contribution of structure I_b in the ground state of

III.[5] Supporting this interpretation, the NMR chemical shifts (III_a τ 6.47, III_b τ 6.36) of the α-methylene protons of piperidine rings in III are not so different from that (τ 6.50) in II. Also HMO method led to the same conclusion as above (contribution of I_b: 82 %).

References and Footnotes

(1) (a) A. Krebs, Angew. Chem., Intern. Ed. Engl., 4, 10 (1965)
(b) G. L. Cross, in "Advances Alicyclic Chemistry", H. Hart and G. J. Karabatos Ed., Vol. 1, p. 53, Academic Press, New York (1966).

(2) Z. Yoshida and Y. Tawara, J. Am. Chem. Soc., 93, 2573 (1971).

(3) HMO calculation shows the π bond order of C-N bond between cyclopropenyl cation ring and amino-group to be 0.38.

(4) The quantum mechanical investigation of the electronic spectra of III will be published later.

(5) The evaluation of both covalent and dipolar structures by combined electronic spectra (intramolecular CT band) and quantum mechanical method has been reported already.[6]

(6) Z. Yoshida, K. Iwata and S. Yoneda, Tetrahedron Letters, 1519 (1971).