CHEMISTRY LETTERS, pp. 1215-1218, 1974. Published by the Chemical Society of Japan

CYCLIC CROSS-CONJUGATED HYDROCARBONS HAVING INSERTED p-QUINOID RING. IV.¹⁾ SYNTHESIS OF 3"-METHYL-2",4",5"-TRICYANO-1-CYCLOHEPTA-TRIENYLIDENE-4-CYCLOPENTADIENYLIDENE-2,5-CYCLOHEXADIENE

Kazuko TAKAHASHI, Itsuji OIKAWA, and Kahei TAKASE Department of Chemistry, Faculty of Science, Tohoku University, Aramaki Aoba, Sendai 980

3"-Methyl-2",4",5"-tricyano-l-cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene (IX), a stable derivative of a new cyclic cross-conjugated hydrocarbon, [5.6.7] quinarene, has been synthesized by the hydride abstraction of tetramethylammonium 3-methyl-2,4,5-tricyano-l-(p-tropylphenyl)cyclopentadienide (VIIIb).

Although many synthetic studies of cyclic cross-conjugated hydrocarbons with an inserted p-quinoid structure, named quinarene,²⁾ have recently been described, all compounds which have so far been synthesized are cross-conjugated two-ring hydrocarbons such as [1.6.3] quinarene (I),³⁾ [1.6.7] quinarene (II),^{1,4)} and the corresponding 1-oxa derivatives (III, IV).^{5,6)}

This is the first communication dealing with the successful synthesis and some properties of a three-ring quinarene, 3"-methyl-2",4",5"-tricyano-l-cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene, or 10-methyl-9,11,12-tricyano [5.6.7]quinarene (IX). The method of its preparation opens a route to other similar syntheses of quinarenoid compounds.

The reaction of p-tropylphenyllithium $(VI)^{4,7}$ with 3-methylcyclopent-2-enone in ether, followed by the hydrolysis with dilute sulfuric acid, gave hydrocarbon (VII), mp 105-107°C, 27%, ν max (KBr) 2950w, 1615w, 1500w, 1440m, 1365m, 1000m, 920m, 890s, 820s, and 760-710s cm⁻¹. The position of the double bonds in 5-membered ring of VII was assigned from n.m.d.r. experiment ; δ (CDCl₃, 100 MHz) 2.03(c-H), 3.32(a-H), 5.98(b-H), 6.74(d-H), (Jac=1.5 Hz, Jbc=1.3 Hz, Jcd=0.0 Hz, Jbd=1.3 Hz,



I





Ш



IV



۷



VI



VII



VIIIa: X = Na VIIIb: X = NMe₄

.



ΙX

Me CNH -CN CN X

Jab=1.3 Hz, Jad $\langle 0.5 \text{ Hz} \rangle$, referring the proton coupling constants of methylcyclopentadiene.⁸⁾ VII is stable in solid state for prolonged period below -10°C but polymerizes at room temperature within 24 hr.

Treatment of VII with cyanogen chloride in the presence of sodium hydride and the reaction of the resulting VIIIa with tetramethylammonium bromide followed by the cautious purification, gave VIIIb, colorless prisms, mp 215-217°C, 23%; ν max (KBr) 3030w, 2180s, 1602w, 1520m, 1490s, 1430m, 945s, 830m, and 732m cm⁻¹; λ max (MeCN) 239 nm(log ε 4.50), 255sh(4.46), and 338(4.33); δ (acetone-d₆) 7.58(AA'BB'-m, 4H, benzene), 7.02(br. d, J=6.3 Hz, 1H, tropyl vinyl), 6.7-6.2(m, 2H, tropyl vinyl), 5.68-5.33(m, 2H, tropyl vinyl), 3.36(s, 12H, NMe₄), 2.33(t, J=6.8 Hz, 2H, tropyl methylene), 2.27(s, 3H, C-Me).

VIIIb was then treated with triphenylmethyl perchlorate in acetonitrile to give brownish black needles IX, mp \rangle 300°C, 99%; ν max (KBr) 2200s, 1600s, 1505s, 1485m, 1432m, 1362m, 1255s, 1200m, 832m, 760m, and 732m cm⁻¹. The quinarene (IX) appeared to be quite stable to air, heat, and light in both solid and solution. The electronic spectrum of IX showed absorption bands at λ max (MeCN) 225 nm(log ε 4.55), 260(4.46), 311(4.03), and 552(4.09), in grossly agreement with the calculated transition energies obtained by the application of the semiempirical variable bondlength SCF·LCAO- π -MO·CI method to ∇^{9} (Table 1), although the cyano group would perturb the π -system from that of the parent molecule (V). The longest wavelength maximum (1st band) of IX shifted to long wavelength by 56 nm as compared with that of 8,9-diacetylsesquifulvalene.¹⁰)

Basicity of IX is remarkably weakened by the three cyano groups. IX was not protonated in trifluoroacetic acid but reversibly protonated in conc. sulfuric acid with formation of yellow solution of quinarenium ion (X), λ max (conc. H_2SO_4) 222sh nm(log ε 4.54), 269(4.12), 395(4.31), 470sh(3.70); $\hat{\sigma}$ (conc. H_2SO_4 , 100 MHz, CH_2Cl_2 as internal standard, 5.30 ppm) 9.36-9.00(m, 6H, 7-membered ring), 8.80(br. s, 4H, benzene), 2.62 and 2.75(two br. s, 3H, methyl), the unequivalent methyl signals may be attributable to the presence of different CN-protonated isomers. On the other hand IX was easily methoxylated with methanolic sodium hydrogen carbonate (a weak base) at the 7-membered ring to give a methoxy derivative of VIIIa ; λ max (MeCN-MeOH-NaHCO₃ aq.) 241 nm(log ε 4.50), 255(4.50), 265sh(4.46), 335(4.32). This fact would suggest a larger contribution of dipolar form (IXa) consisting of a feebly basic cyclopentadienide and a significantly acidic tropylium moiety.

Calcd. for V		Observed for IX	
Transition Energy	Oscillator Strength	(in acetonitrile)	
⊿ E (ev)	f (cgs)	⊿ E (ev)	log <i>e</i>
2.12	0.011 (y)		
2.25	0.008 (y)		
2.26	2.45 (z)	2.25	4.09
3.64	0.003 (z)		
3.91	0.008 (y)		
4.09	0.009 (y)		
4.17	0.0003(z)		
4.18	0.079 (z)	3.99	4.03
4.68	0.063 (y)	4.77	4.46

Table 1. Electronic Spectrum of [5.6.7] Quinarene

The authors' thanks are due to Professor T. Nozoe for his encouragement throughout this work.

References

- 1) For part III of this series, see K. Takahashi, N. Hirata, and K. Takase, Tetrahedron Lett., 1285 (1970).
- 2) The name "Quinarene" has been proposed by T. Nozoe for the sake of convenience to designate the polycyclic cross-conjugated hydrocarbons possessing a quinoid structure inserted between the two fulvalene- (fulvene-) carbocycles. The ring size is shown in a bracket; see ref 4 and 7.
- 3) R. Gompper, H. U. Wagner, and E. Kutter, Chem. Ber., <u>101</u>, 4123 (1968).
- 4) K. Takahashi, S. Takenaka, and T. Nozoe, Tetrahedron, <u>30</u>, 2191 (1974).
- 5) a) A. S. Kende, J. Amer. Chem. Soc., <u>85</u>, 1882 (1963); b) R. West and D. C. Zecher,
 ibid., <u>92</u>, 155 (1970); c) B. Föhlish and P. Bürgle, Ann. Chem., <u>701</u>, 67 (1967).
- 6) a) R. van Helden, A. P. ter Borg, and A. F. Bickel, Rec. Trav. Chim., <u>81</u>, 599 (1962); b) T. Nozoe and K. Kitahara, Japanese Pat., 17674 (1964); c) T. Nozoe and K. Takahashi, Bull. Chem. Soc. Japan, <u>40</u>, 1473 (1967); d) P. Bladon, P. L. Pauson, G. R. Proctor, and W. J. Rodger, J. Chem. Soc., 926 (1966); e) C. Jutz and F. Voithenleitner, Chem. Ber., <u>97</u>, 31 (1964).
- 7) K. Takahashi, S. Takenaka, Y. Kikuchi, K. Takase, and T. Nozoe, Bull. Chem. Soc. Japan, <u>47</u>, 2272 (1974).
- 8) V. A. Korenevsky and N. M. Sergeyev, J. Amer. Chem. Soc., <u>94</u>, 8586 (1972).
- 9) H. Yamaguchi and T. Nakajima, Bull. Chem. Soc. Japan, <u>47</u>, in press (1974).
- 10) E. K. Gustorf, M. C. Henry, and P. V. Kennedy, Angew. Chem., 79, 616 (1967).

(Received August 12, 1974)