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A NOVEL REACTION OF 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE WITH HEPTAFULVENES. FORMATION OF 1,2-DICYANOAZULENES

Shigeyasu Kuroda,[1] Makoto Funamizu and Yoshio Kitahara*

Department of Chemistry, Faculty of Science, Tohoku University,
Aramaki Aoba, Sendai 980, Japan

Toyonobu Asao

Department of Chemistry, College of General Education, Tohoku University,
Kawauchi, Sendai 980, Japan

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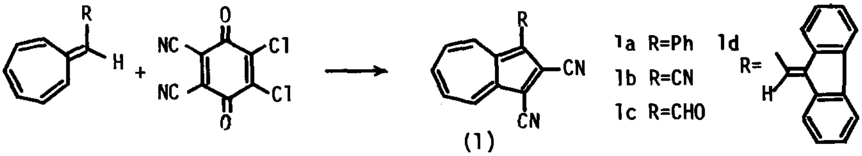
2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is well known useful oxidizing reagent in organic synthesis and has powerful ability in complex formation with unsaturated compounds.[2] However, only one report on the cycloaddition of DDQ has appeared,[3] in spite of p-benzoquinone often serves as dienophile.

We now report a novel reaction of DDQ with heptafulvenes to form 1,2-dicyanoazulenes involving a cycloaddition and successive unusual cleavage of DDQ moiety.

When two molar equivalents of DDQ were added to each solutions of 8-phenyl-,[4] 8-cyano-,[5] 8-formyl-,[6] and 8-(9-fluorenylidenemethyl)-heptafulvene[7] in methylene chloride at room temperature, the solutions were immediately became dark brown and no complexes precipitated. After stirring for 30 min., the reaction products were separated by column chromatography on silica gel to give the corresponding 3-substituted 1,2-dicyanoazulenes (1) in low yields.



8-Bromo-8-cyanoheptafulvene[8] also reacted with DDQ to give 1,2,3-tricyanoazulene (1b) in 7.4% yield.

The yields and the physical properties of the new compounds were shown in Table 1.[9]

This novel reaction can be rationalized by the following mechanism which involves the initial (8 + 2)cycloaddition of DDQ with heptafulvenes followed by attack of base (water) and oxidative cleavage, although the intermediary cycloadducts and another cleaved fragment, dichloromaleic acid, have not been isolated.

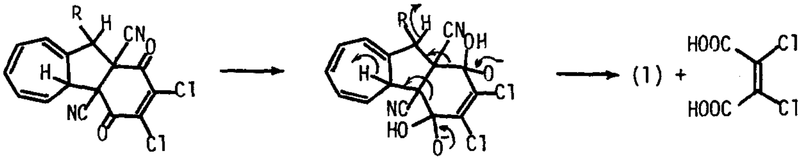


Table 1. Yields and physical properties of the new 3-substituted 1,2-dicyanoazulenes.

Compounds	1b	1c	1d
yields (%)	17.5	5	8
color	violet needles	purple needles	green needles
mp °C	200~200.5	274~275	169~170
MW (mass sp.)	203	206	354
UV $\lambda_{max}^{CH_2Cl_2}$ nm (log ε)	254 (4.48), 275 (4.41), 299 (4.41), 309 (4.44), 345 (4.04), 365 (3.60), 515sh (3.42), 592 (2.97)	238 (4.35), 246 (4.33), 290 (4.86), 316 (4.91), 345 (3.93), 368 (3.78), 379 (3.79), 440 (2.74), 546 (3.12)	261 (4.52), 300 (4.35), 620 (3.22)
IR (KBr) cm^{-1}	2235vs, 1582s, 1431vs	2250m, 1680s, 1590w	2230s, 1640w, 1590m, 1440s
NMR ppm (in DMSO-d_6)	8.96 (d,m, J=10 Hz, 2H) 8.59 (t,m, J=10 Hz, 1H) 8.20 (t,m, J=10 Hz, 2H)	10.56 (s, 1H) 9.92 (d, J=10 Hz, 1H) 9.14 (d, J=9 Hz, 1H) 8.70 (t, J=ca 10 Hz, 1H) 8.36 (t, J=ca 9 Hz, 2H)	8.87 (d, J=10 Hz, 1H) 8.78 (d, J=10 Hz, 1H) 8.29 (m, 1H) 8.05 (s, 1H) 8.00 (m, 2H) 7.7~7.9 (m, 4H) 7.2~7.5 (m, 3H) 6.95 (m, 1H)

References and Footnotes

1) Present Address: Department of Chemistry, College of General Education, Tohoku University, Kawauchi, Sendai 980, Japan.

2) D. Walker and J. D. Hiebert, Chem. Rev., 67, 153 (1967).

3) R. Noyori, N. Hayashi and M. Kato, Tetrahedron Lett., 1973, 2983.

4) 8-Phenylheptafulvene was obtained by the treatment of benzyltropylium tetrafuloroborate[10] with triethylamine in methylene chloride at -30~ -20°C as reddish solution, but it could not be isolated in pure state because of its instability.

5) M. Oda and Y. Kitahara, Chem. Commun., 1969, 352.

6) M. Oda and Y. Kitahara, Chem. & Ind., 1969, 920.

7) S. Kuroda, M. Oda and Y. Kitahara, Chem. Lett., 1974, 773.

8) M. Oda and Y. Kitahara, Bull. Chem. Soc. Japan, 44, 296 (1971).

9) 1,2-Dicyano-3-phenylazulene (1a) (λ max in CH_3CN nm, 245, 280sh, 298sh, 308, 354, 594) was identified by direct comparison of ir spectrum with that of authentic specimen provided by Prof. Mukai; T. Mukai et al., unpublished result.

10) R. W. Murray and M. L. Kaplan, Tetrahedron Lett., 1965, 2903; 1967, 1307.