CHEMISTRY LETTERS, pp. 873-876, 1977. Published by the Chemical Society of Japan

SYNTHESIS OF ISO-π-ELECTRONIC HETEROANALOGUES OF HEPTAFULVALENE[1]

Kazuo KATO,* (the late) Yoshio KITAHARA,* Noboru MORITA,** and Toyonobu ASAO**#

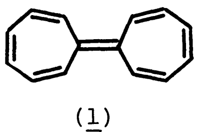
* Department of Chemistry, Faculty of Science, Tohoku University,
Aramaki, Aoba, Sendai 980

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

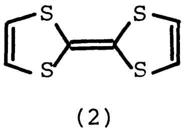
Several iso-π-electronic oxa- and thia-heteroanalogues of heptafulvalene were synthesized by the reaction of the corresponding heterocyclic ketones with 8-oxoheptafulvene. These fulvalenes were found to be polyolefinic by comparison of their physical and chemical properties with those of heptafulvalene.

Heptafulvalene (1), typical cross conjugated carbocyclic unsaturated compound, has been of interest in connection with theoretical field and was reported as moderately stable deeply colored crystals,although the compound showed polyolefinic properties rather than aromatic ones.[2]

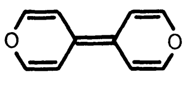
Tetrathiafulvalene (2), 4,4'-bispyranylidene (3),and their derivatives was also reported as stable iso-π-electronic heteroanalogues of 1.[3] However, the compound containing hetero atoms in one ring of 1 has been unknown.



(1)



(2)

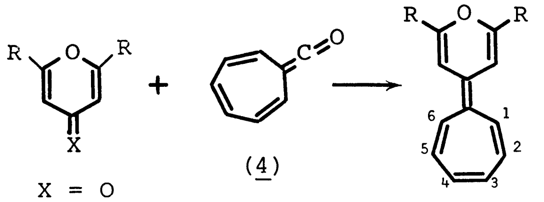


(3)

On the other hand, we have reported that 8-oxoheptafulvene is a very useful reagent to introduce a cycloheptatrienylidene moiety by the reaction with carbonyl compounds.[4]

In this communication, we wish to report the synthesis and some of the properties of several iso-π-electronic heteroanalogues of 1 having one carbocyclic heptafulvene moiety.

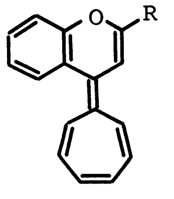
The preparation of the oxaheptafulvalenes (4H-pyranylidenecycloheptatrienylidene) can be illustrated generally as in the following scheme; 8-oxoheptafulvene (4) generated in situ by the reaction of 7-cycloheptatrienylcarbonyl chloride with triethylamine in hexane or benzene reacted with 4H-pyran-4-one or 4H-pyran-4-thione derivatives at room temperature to give the corresponding deeply colored heteroheptafulvalenes (5a~d, 6a,b,and 7) according to (2 + 2) cycloaddition followed



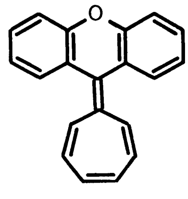
X = O
X = S

(4)

(5)
a, R=H c, R=C_6H_5
b, R=CH_3 d, R=$COOCH_3$



(6)
a, R=iso-Pr
b, R=C_6H_5

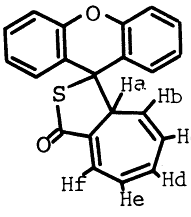


(7)

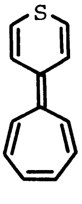
by the elimination of CO_2 or COS.

The yields of the heteroheptafulvalenes from the thiones are generally better than those from the ketones, thus the compounds (5a~d and 6a,b) were obtained from the ketones in the yields of 0, 0.2, 25, 75, 8, and 42%, and from the thiones in 51, 25, 73, quantitative, 82, and 57%, respectively. These differences may be attributed to the more facile reactivity of the reagent (4) toward thiocarbonyl group which has a strongly polarized character compared to carbonyl group.[3b)] The compound (7) was obtained from xanthone in 8% yield with a recovery of large amount of the ketone. However, the reaction of xanthothione with 4 afforded (8 + 2) cycloadduct (8) in 86% yield instead of 7. 8 ; mp 149~150°C, colorless crystals, $\nu_{C=O}$ 1670 cm^{-1}, NMR ($CDCl_3$) δ 2.75 ppm (d,d, J=4, 2 Hz, Ha), 4.95 (d,d, J=10, 4 Hz, Hb), 5.80 (d,d,d, J=10, 4, 2 Hz, Hc), 6.50 (m, Hd,e), 6.89 (d,d, J=4, 2 Hz, Hf), 7.0~7.35 (m, 2H), 7.6~7.78 (m, 6H).

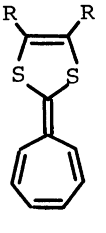
Furthermore, 4H-thiopyran-4-one, 1,3-dithiol-2-thione, and its 4,5-dimethoxycarbonyl derivative reacted with 4 to give the corresponding deeply colored fulvalenes (9 and 10a,b) in 25, 47, and 12% yields, respectively. However, 4 did not react with N-substituted 4-pyridones and azaheptafulvalenes could not be obtained.



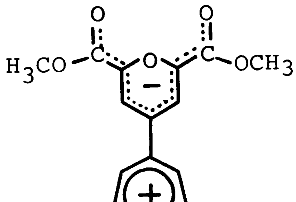
(8)



(9)



(10)
a, R=H
b, R=$COOCH_3$



(5d')

Heteroheptafulvalenes obtained here are labile except 5d, although these compounds are rather stable in solutions. Therefore, their elemental analyses could not be performed except 5d. However, all the parent peaks in their mass spectra are in accord with the corresponding molecular weights and the structures are assumed from their NMR spectra shown in Table 1. UV spectra of the heteroheptafulvalenes show maxima at around 340~400 nm with a tailing to longer wave-length. NMR and IR spectra of 5a, 9, and 10a are shown in Figs.1 and 2, respectively. It is observed that seven-membered ring protons in these three compounds resonate at a little higher field than those in 1.

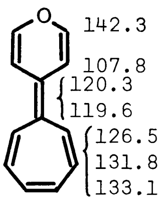
Table 1. Data of ^{1}H-NMR and UV maxima of heptafulvalene and heteroheptafulvalenes

Compounds	^{1}H-NMR δ ppm (J in Hz)*	$\lambda_{max}^{CCl_4}$ nm (log ε)
1	5.7~5.9 (m, 8H), 5.9~6.05 (m, 4H)	362 (4.32)
5a	5.3~5.8 (m, 6H), 5.85 (d,d, J=5, 2, 2H), 6.48 (d,d, J=5, 2, 2H)	355 (4.18)
5b	1.99 (s, Me), 5.1~5.8 (m, 8H)	356 (3.96)
5c	5.5~5.8 (m, H-2~5), 6.0 (d, J=10, H-1,6), 6.45 (s, 2H), 7.2~7.5 (m, 6H), 7.6~7.8 (m, 4H)	407 (4.49)
5d	3.93 (s, Me), 5.6~6.0 (m, H-2~5), 6.12 (d, J=11, H-1,6), 6.90 (s, 2H)	406 (4.56)
6a	1.2 (d, Me), 2.55 (-CHMe$_2$), 5.69 (s, 1H), 5.8 6.2 (m, H-1~5) 6.20 (d, J=10, H-6), 6.8~7.2 (m, 3H), 7.73 (m, 1H)	367 (4.10)
6b	5.8~6.2 (m, H-1~5), 6.30 (d, J=10, H-6), 6.45 (s, 1H), 6.8~7.5 (m, 6H), 7.5~7.9 (m, 3H)	397 (4.29)
7	5.8~6.35 (m, H-1~6), 6.9~7.3 (m, 6H), 7.6 (d,d, J=6, 1, 2H)	363 (4.30)
9	5.5~5.85 (m, 6H), 5.95 (d,m, J=11, 2H), 6.4 (d,m, J-11, 2H)	380 (4.44)
10a	5.35~5.7 (m, 6H), 6.3 (s, 2H)	356 (4.13)
10b	3.82 (s, Me), 5.3~5.6 (m, 4H), 5.7 (m, 2H)	338 (4.26) 450 (3.06)

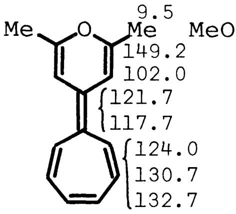
* The NMR were measured with Hitachi R-22 (90 MHz) spectrometer in CCl$_4$ except 5a, 5c, 5d, and 10b in CDCl$_3$, and numbering of protons is for cycloheptatrienyliden moiety.

The compound (5d) was obtained as stable brown needles, mp 142~143°C, and the extreme stability may be attributed to a contribution of a dipolar structure (5d').

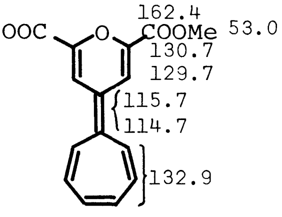
Data of ^{13}C-NMR spectra of 5a, 5b, and 5d are also shown below with those of heptafulvalene (1) and 8,8-dicyanoheptafulvene.[5] The signals of pinch bond carbon of these heteroheptafulvalenes are observed at somewhat higher field than those of 1 and sesquifulvalene (146.5 and 138.6 ppm).[6]



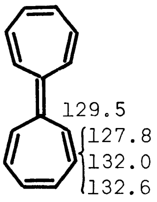
(5a)



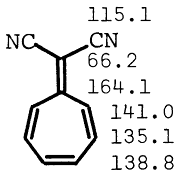
(5b)

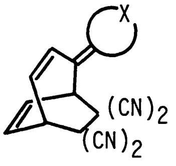


(5d)

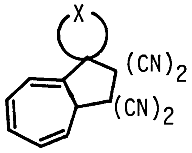


(1)





(4 + 2)



(8 + 2)

The heteroheptafulvalenes easily reacted with TCNE to give regiospecific (4 + 2) or (8 + 2) cycloadducts depend on the substrates and thus, the compounds 5b, 7, and 10a,b gave (4 + 2) adducts and 5a and 6a afforded (8 + 2) adducts. These adducts are unstable except an adduct of 5d, mp 130~132°C (decomp.). The structures of

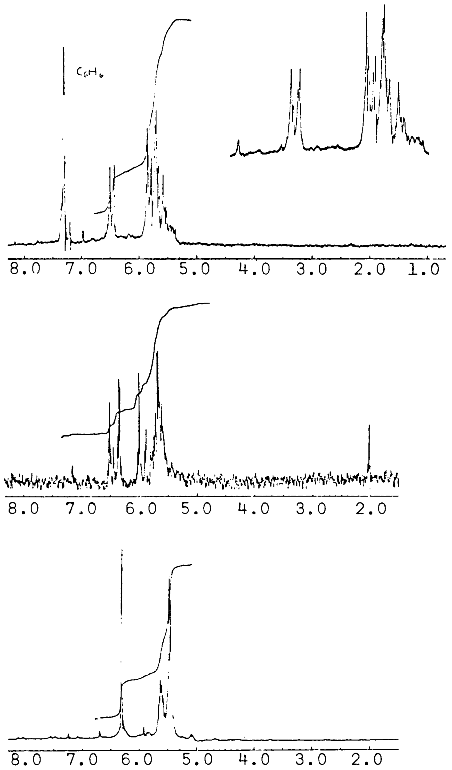


Fig. 1. NMR spectra (90 MHz) of 5a (top, in $CDCl_3$), 9 (middle, in CCl_4), and 10a (bottom, in CCl_4).

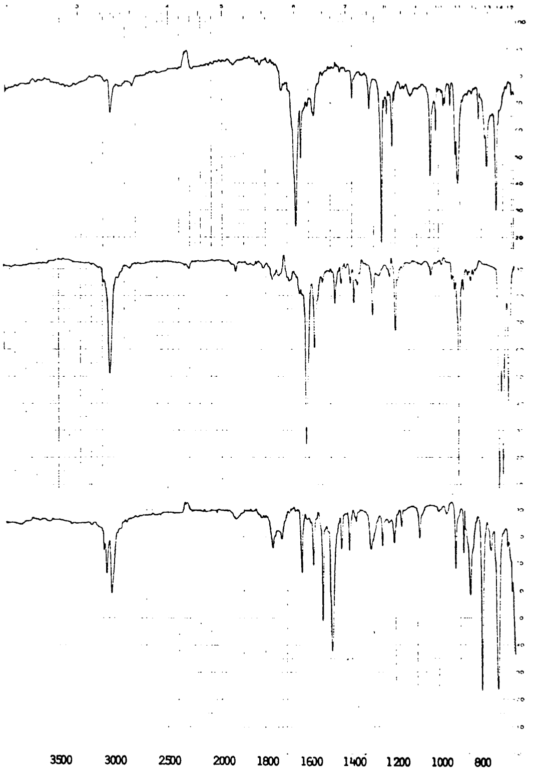


Fig. 2. IR spectra of 5a (top), 9 (middle), and 10a (bottom) in CCl_4.

these adducts were easily assigned by their NMR spectra. However, in the reaction of the heteroheptafulvalenes with tetracyano-p-quinodimethane (TCNQ), formation of CT-complexes was not clearly observed at the present stage.

REFERENCES AND NOTES

To whom all correspondeces should be addressed.

1) Part VIII in the series of "8-Oxoheptafulvene"; the preceding Part VII, N. Morita, T. Asao, and Y. Kitahara, Tetrahedron Lett., 2821 (1975).

2) W. von E. Doering and H. Krauch, Angew. Chem., 68, 661 (1956); W. von E. Doering, "Theoretical Organic Chemistry," (Kekule Symposium), Butterworth, London, 1959, p. 44; P. Coppens, Mol. Cryst. Liq. Cryst., 9, 25 (1969).

3) Cf. a) A. F. Garito and A. J. Heeger, Accounts of Chem. Res., 7, 232 (1974); b) E. Campaigne, "The Chemistry of the Carbonyl Group," ed. by S. Patai, Interscience, New York, N.Y., 1966, p. 917.

4) N. Morita, T. Asao, and Y. Kitahara, Tetrahedron Lett., 2083 (1974); and references cited therein.

5) The authors wish to thank Professor Takase and Dr. Yasunami of Tohoku University, and JEOL Ltd., for the ^{13}C-NMR measurments.

6) R. Hollenstein, A. Mooser, M. Neuenschwander, and W. v. Philipsborn, Angew. Chem., 86, 595 (1974); Angew. Chem., Intern. Ed., 13, 551 (1974); K. M. Rapp and J. Daub, Tetrahedron Lett., 2011 (1976).

(Received May 25, 1977)