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8-OXOHEPTAFULVENE VII. HOMOPOLYMERIZATION AND STEREOCHEMISTRY OF ADDUCTS OF 8-OXOHEPTAFULVENE WITH OLEFINS

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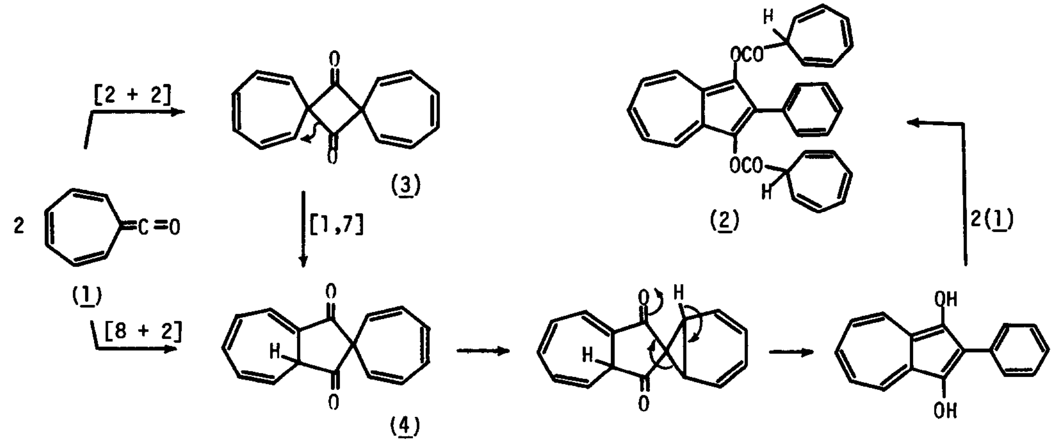
We have already reported[2] that the reactions of 8-oxoheptafulvene with several olefins and carbonyl compounds afforded the corresponding adducts, their rearrangement products or their decarboxylation products We now studied the homopolymerization, and further reactions of 8-oxoheptafulvene with several olefins to investigate the stereochemistry of the addition reaction because the properties of the ketene moiety may be affected by the cyclic conjugated unsaturated moiety

When the reddish solution of 8-oxoheptafulvene (1) obtained by the reaction of 7-cycloheptatrienecarbonyl chloride with triethylamine in anhydrous n-hexane or ether at room temperature was stirred for 2 hr, the solution became dark brown. After the precipitated triethylamine hydrochloride was removed, the product was isolated by column chromatography on silica gel using benzene as solvent, and unstable blue crystals (2), mp around 70°C, were obtained in a poor yield (ca. 2%) as only isolable pure product. The compound (2) was determined as 1,3-di(cycloheptatrienylmethanoyloxy)-2-phenylazulene, corresponding to the tetramer of 1, from the following spectral data; molecular formula, $C_{32}H_{24}O_4$ (mass spectr obs, 472.1684, calcd, 472.1673),[3] UV λ_{max}^{EtOH} 244 nm (log ε 4.30), 269 (4.32), 302 (4 53), 351 (3.29), 378 (3.08), 620 (2 47), 660^{sh}(2.42), IR (KBr) 1760 cm^{-1}, NMR ($CDCl_3$) δ 2.78 (t,d, J=5 5, 1.0 Hz, 2H), 5.35 (d,d, J=9 0, 5 5 Hz, 4H), 6.18 (d,m, J=9 0 Hz, 4H), 6.56 (t, J=3 0 Hz, 4H), 6.89 (d,d, J=9.5, 9.5 Hz, 2H), 7 1~7.7 (m, 6H) and 7 92 (d, J=9.5 Hz, 2H)

The mechanism of the formation of the azulene (2) can be rationalized by two possible pathways depicted below the one is initiated by dimerization of 1 by the mode of [2 + 2] cycloaddition at each ketene group to form cyclobutane-1,3-dione (3) followed by [1,7] shift[4]

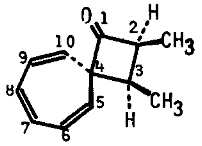


of one of the cyclobutane bond to cycloheptatriene moiety to give cyclopentanedione derivative (4) and successive rearrangement of one of cycloheptatriene to phenyl, and esterification of resulting dihydroxyazulene by 8-oxoheptafulvene afforded 2. The other path involves the initial dimerization of 1 by the mode of [8 + 2] cycloaddition to give the intermediary dione (4).

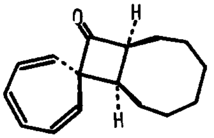
The reaction of 8-oxoheptafulvene (1) with *cis*-2-butene afforded a single isolable product , *cis*-2,3-dimethylspiro[3.6]deca-5,7,9-triene-1-one (5) as colorless oil, bp 60~70°C/ 0.001 mmHg, in 31.4% yield, whose structure was assigned by the following spectral data, MW (mass spectr.) 174, IR (neat), 1760 cm^{-1}, NMR (CDCl$_3$) δ 0.62 (d,J=7.2 Hz, Me$_3$), 0.91 (d, J=7.2 Hz, Me$_2$), 2.02 (d,q, J=10.5, 7.2 Hz, H$_3$), 3.55 (d,q, J=10.5, 7.2 Hz, H$_2$), 5.26 (d, J=9.0 Hz, H$_5$ or H$_{10}$), 5.35 (d, J=9.0 Hz, H$_{10}$ or H$_5$), 6.06~6.44 (m, H$_6$ and H$_9$), 6.51 (m, H$_7$ and H$_8$) However, 1 did not react smoothly with *trans*-2-butene, and a small amount of azulene (2) and 2.2% of *cis*-adduct (5) were obtained, and no *trans*-adduct could be isolated.[5]

8-Oxoheptafulvene (1) reacted smoothly with *cis*- and *trans*-cyclooctene to give single stereoisomeric products, *cis*-2,3-hexamethylenespiro[3.6]deca-5,7,9-triene-1-one (6; 67.3%) and the *trans* isomer (7, 88.1%), both as colorless oils, respectively. NMR spectra of 6 and 7 show H$_2$ protons at δ 3.36 (d,d,d, J=10.0, 10.0, 3.0 Hz) and 3.09 (d,d,d, J=9.5, 9.5, 5.5 Hz), respectively, from the coupling constants the stereochemistry could not be clarified. However, the stereochemistry of 6 and 7 can be deduced from the comparison of their IR spectra in the 1500~1400 cm^{-1} region:[6] the *cis* compound (6) shows two bands at 1465 and 1445 cm^{-1}, whereas the *trans* isomer (7) shows only one band at 1445 cm^{-1}.

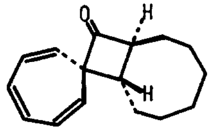
It has been shown that 8-oxoheptafulvene reacted with cyclopentadiene or indene to yield



(5)



(6)



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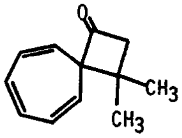

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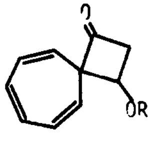
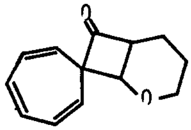


(9)

a, R = CH_2CH_3
b, R = $(CH_2)_3CH_3$
c; R = $CH_2CH(CH_3)_2$



(10)

regiospecific adducts.[2] Furthermore, it became clear that 1 reacted with isobutene to give a regiospecific adduct, 3,3-dimethylspiro[3.6]deca-5,7,9-triene-1-one (8) in 9% yield as colorless oil; IR (neat) 1777 cm^{-1}, NMR (CCl_4), δ 1.10 (s, 2Me), 2.70 (s, CH_2), 4.9~5.1 (m, H_5 and H_{10}), 6.2~6.45 (m, H_6~H_9), accompanied with a small amount of azulene (2).[5]

Similarly, 1 reacted with enol ethers (ethylvinyl, butylvinyl and isobutylvinyl ethers)

Table 1. Yields and physical properties of the compounds (9 and 10)

Compound	Yield (%)	MW (mass sp.)	IR ν_{CO}* (cm^{-1})	NMR δ (J, Hz) (in CCl_4)
(9a) colorless oil	77.8	190	1775	1.16 (t, J=7.0, Me), 2.7~3.3 (m, H_2), 3.39 (q, J=7.0, $-OCH_2-$), 3.82 (d,d, J=6.5, 5.5, H_3), 5.07 (d,m, J=9.0, H_5 or H_{10}), 5.36 (d,m, J=9.0, H_{10} or H_5), 6.19 (m, H_6 and H_9), 6.39 (m, H_7 and H_8)
(9b) colorless oil	65.9	218	1775	0.91 (t, J=6.0, Me), 1.1~1.9 (m, 4H), 2.75~3.25 (m, H_2), 3.32 (t, J=6.0, $-OCH_2-$), 3.78 (d,d, J=6.5, 5.5, H_3), 5.10 (d,m, J=9.0, H_5 or H_{10}), 5.33 (d,m, J=9.0, H_{10} or H_5), 6.20 (m, H_6 and H_9), 6.39 (m, H_7 and H_8)
(9c) colorless oil	66.9	218	1775	0.9 (d, J=6.0, 2Me), 1.81 (m, J=6.0, $-\overset{|}{C}H-$), 2.75~3.3 (m, H_2 and $-OCH_2-$), 3.78 (d,d, J=6.5, 5.5, H_3), 5.09 (d, J=9.0, H_5 or H_{10}), 5.36 (d, J=9.0, H_{10} or H_5), 6.21 (m, H_6 and H_9), 6.42 (m, H_7 and H_8)
(10) colorless crystals mp 71~72°C	40.9	202	1775	1.3~2.2 (m, 4H), 3.0~3.3 (m, H_2), 3.3~3.7 (m, $-OCH_2-$), 3.72 (d, J=5.5, H_3), 5.13 (d, J=9.0, H_5 or H_{10}), 5.38 (d, J=10.0, H_{10} or H_5), 6.18 (m, H_6 and H_9), 6.49 (t, J=5.5, H_7 and H_8)

* Taken in neat except for (10; in KBr).

and 2,3-dihydropyran to give the corresponding regiospecific [2 + 2] cycloadducts (9a-c, 10), whose yields and physical data are shown in Table 1. The compounds (9) are unstable and easily polymerize to give resinous products on standing in the air, whereas the compound (10) is rather stable.

These results are in accord with prediction of the Woodward-Hoffmann orbital symmetry conservation rule[7] as well as with the observed cycloaddition of various ketenes to olefins.[6,8,9]

References and Footnotes

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3) High resolution mass spectrum of 2 was measured by Mr. Y. Kato of Naka Work, Hitachi Ltd., to whom the authors are indebted.

4) The facile [1,7] shifts on cycloheptatriene ring system were observed in some cases; ref., 1, N. Morita, T. Asao, N. Iwagame and Y. Kitahara, Chem. Lett., 1973, 67, E. E. Waali and W. M. Jones, J. Amer. Chem. Soc., 95, 8114 (1973).

5) As 8-oxoheptafulvene (1) is very unstable, it easily decomposes or polymerizes in the reaction with less reactive olefins[9] yielding a minute amount of azulene (2).

6) It has been reported that *cis* and *trans* isomers of bicyclo[6.2.0]decane system are easily distinguished by their IR spectra, R. Montaigne and L. Ghosez, Angew. Chem., 80, 194 (1968), Angew. Chem., internat. Edit., 7, 221 (1968).

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