

REACTIONS OF 8-BROMO-8-CYANOHEPTAFLUENE

Shigeyasu Kuroda and Toyonobu Asao

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

Makoto Funamizu, Hiroshi Kurihara and Yoshio Kitahara\*

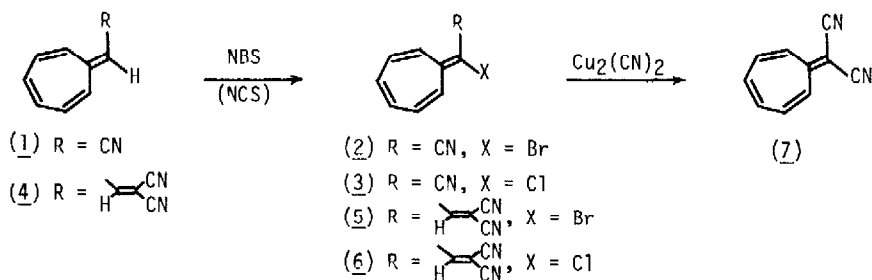
Department of Chemistry, Faculty of Science, Tohoku University  
Aramaki Aoba, Sendai 980 Japan

(Received in Japan 6 November 1975; received in UK for publication 16 December 1975)

Studies on the reactions of 8-substituted and 8,8-disubstituted heptafulvenes have revealed that the electrophilic<sup>1</sup> and nucleophilic<sup>2</sup> substitutions occurred at 8-position and at seven-membered ring, respectively, halogen added at seven-membered ring under photo-irradiation,<sup>3</sup> and cycloaddition with dienophiles, enamines and benzyne occurred at 1,8-position of heptafulvenes<sup>4</sup>

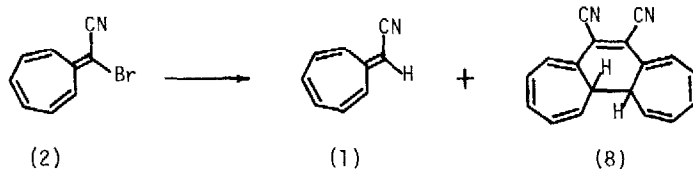
However, reactions of 8-haloheptafulvene having reactive substituents at 8-position have not been studied. In the present paper, further preparation of 8-haloheptafulvenes, and nucleophilic, coupling and cycloaddition reactions of 8-bromo-8-cyanoheptafulvene have been studied, the results will be reported herein.

The reaction of 8-cyanoheptafulvene (1)<sup>5</sup> with 1.5 equivalents of NBS in methylene chloride at ice cooling temperature for a few minutes afforded unstable known 8-bromo-8-cyanoheptafulvene (2)<sup>1</sup> in 93% yield after a careful chromatographic separation on silica gel under nitrogen atmosphere. The reaction of 1 with NCS also gave 8-chloro derivative (3) as fairly stable crystals in 54% yield. Similarly, 8-bromo- and 8-chloro-(2',2'-dicyanovinyl)heptafulvenes (5 and 6) were obtained from the corresponding heptafulvene (4)<sup>6</sup> in the yields of 47.5% and 83.5%, respectively. Physical properties of these 8-haloheptafulvenes are shown in Table 1.



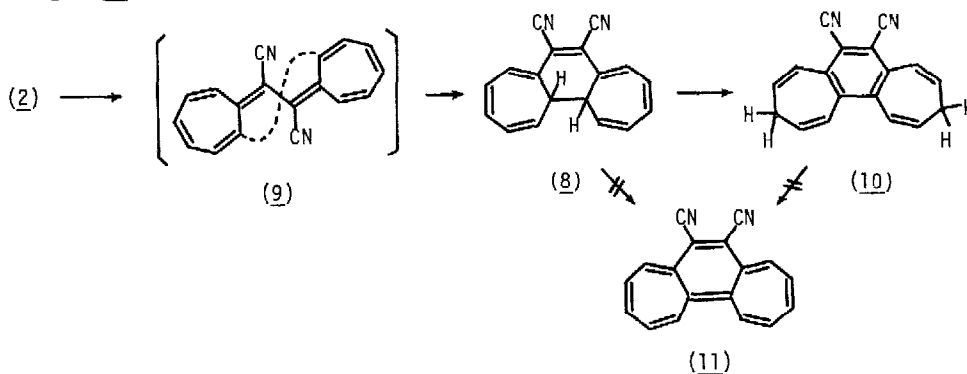
A reaction of 8-bromo-8-cyanoheptafulvene (2) with excess  $\text{Cu}_2(\text{CN})_2$  in refluxing pyridine gave 8,8-dicyanoheptafulvene (7)<sup>7</sup> in 9% yield, the reaction is the first example of nucleophilic substitution at theoretically less reactive 8-position of heptafulvenes

Attempted Ullmann coupling of 2 using copper, zinc or zinc-copper in pyridine afforded an unexpected reduction product,<sup>8</sup> 8-cyanoheptafulvene (1), however, the reaction in dimethylformamide afforded tricyclic product (8), in 40.5% yield, accompanying 1

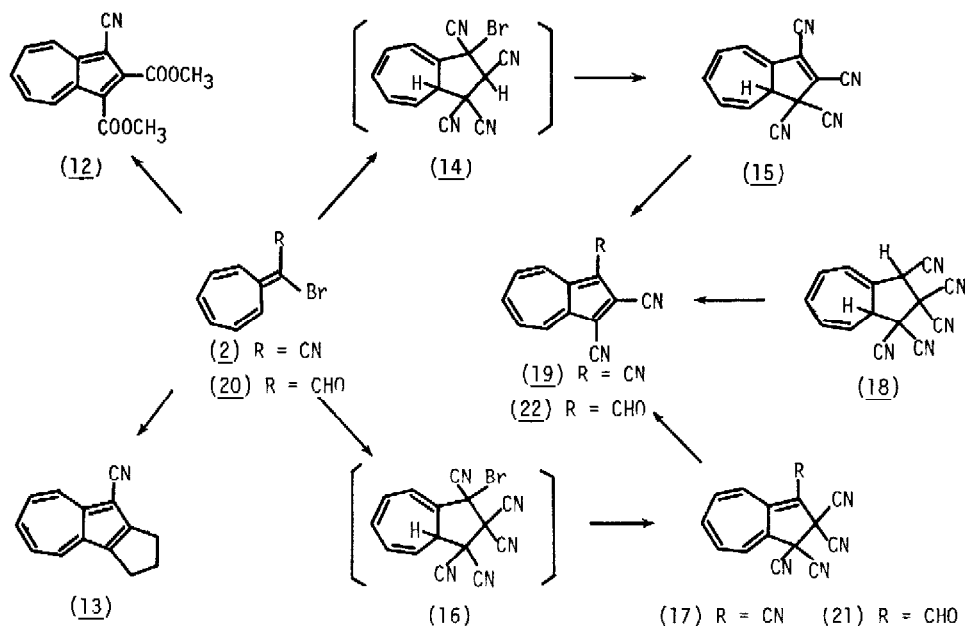


The mechanism of the formation of 8 can be rationalized as shown below which involves the initial Ullmann coupling of 2 giving 9 followed by a thermal conrotatory electrocyclic reaction, although the intermediate (9) was not isolated<sup>9</sup>

Further thermal isomerization of 8 afforded a mixture of sigmatropic rearrangement products mainly consists of the compound (10). However, attempted synthesis of fully conjugated compound (11) from 8 or 10 was unsuccessful



Since the reaction of 1 with dimethyl acetylenedicarboxylate (DAC) or enamines has been reported to give azulenes by [8 + 2] cycloaddition followed by dehydrogenation,<sup>4a,c</sup> the similar cycloaddition of 2 was studied in the expectation to obtain the corresponding azulenes in higher yield by the facile elimination of hydrogen bromide from the initially formed adducts. However, the reaction of 2 with DAC and cyclopentanone morpholinoenamine afforded the azulenes (12)<sup>4</sup> and (13),<sup>4</sup> respectively, in lower yield than in the case of 8-cyanoheptafulvene (1), which must be due to instability of 2 and steric hindrance of bulky bromine atom for the cycloaddition



In the reaction of **2** with tri- and tetracyanoethylene, 1,1,2,3-tetracyano-1,8a-dihydroazulene (**15**) and 1,1,2,2,3-pentacyano-1,2-dihydroazulene (**17**) were obtained respectively, after a rapid chromatographic separation on silica gel, which must be formed by the elimination of hydrogen bromide from the initial [8 + 2] cycloadducts (**14** and **16**). However, rechromatography of not only **15** and **17** but also cycloadduct (**18**)<sup>10</sup> of **1** and tetracyanoethylene on silica gel afforded 1,2,3-tricyanoazulene (**19**)<sup>11</sup> although in very low yields. The same reaction also occurred on alumina column. The reaction of 8-bromo-8-formylheptafulvene (**20**)<sup>12</sup> and tetracyanoethylene afforded an unstable compound (**21**), mp 203-204°C, whose treatment with silica gel afforded 1,2-dicyano-3-formylazulene (**22**)<sup>11</sup> in 4.7% yield.

This unusual decyanogen reaction of **17** and **21** is the first example in our knowledge, and the following mechanism can be tentatively proposed:

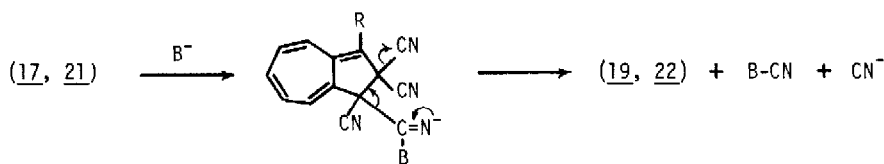


Table 1 Physical properties of the products

Compound	Color mp (°C)	Uv $\lambda_{\max}$ nm (log $\epsilon$ ) [a]	Nmr $\delta$ ppm (J in Hz) [b]	Molecular ions at m/e
<u>3</u>	red needles 68-69	242(4.09) 354(4.24)	6.32(m, 4H) 6.74(m, 2H)	163, 164
<u>5</u>	reddish purple needles 124-125	273(3.95) 473(4.44)	6.80(m, 6H) 7.70(s, 1H)	258, 260
<u>6</u>	reddish purple needles 146-147	275(3.81) 283(3.78) 477(4.43)	6.75(m, 6H) 7.66(s, 1H)	215, 216
<u>8</u>	reddish orange plates 186-187	240(4.51) 294(4.06) 409(4.31)	2.15(d, J=6.0, 2H) 5.11(d,d, J=6.0, 9.0, 2H) 6.31(m, 2H) 6.95(m, 6H)	256
<u>15</u>	orange solid		3.85(m, 1H) 5.80(d,d, J=4.0, 10.0, 1H) 6.53(m, 2H) 7.01(m, 2H)	
<u>17</u>	red needles 200.5	366(4.73) 382 <sup>Sh</sup> (3.60)	6.85(m, 4H) 7.40(m, 1H)	255

[a] in  $\text{CH}_2\text{Cl}_2$ , [b] in  $\text{CDCl}_3$  except 17 (in  $\text{DMSO}-d_6$ )

## References and Footnote

- 1) M. Oda and Y. Kitahara, Bull. Chem. Soc. Japan, 44, 296 (1971)
- 2) Y. Kitahara, K. Doi and T. Kato, *ibid.*, 39, 2444 (1966)
- 3) M. Oda, M. Funamizu and Y. Kitahara, Chem. & Ind., 75 (1969)
- 4) (a) M. Oda, H. Tani and Y. Kitahara, Chem. Commun., 739 (1969), (b) M. Oda and Y. Kitahara, Bull. Chem. Soc. Japan, 43, 1920 (1970), (c) M. Oda and Y. Kitahara, Synthesis, 367 (1971), (d) M. Oda, Y. Kayama and Y. Kitahara, Chem. Commun., 505 (1971)
- 5) M. Oda and Y. Kitahara, Chem. Commun., 352 (1969)
- 6) C. Jutz, Chem. Ber., 97, 2050 (1964)
- 7) T. Mukai, T. Nozoe, K. Osaka and N. Shishido, Bull. Chem. Soc. Japan, 34, 1384 (1961)
- 8) The similar reductions in case of the Ullmann reaction have often been observed, cf. R. G. R. Bacon and H. A. O. Hill, Quart. Rev., 19, 95 (1965)
- 9) 8,8'-Biheptafulvenyl itself has been synthesized (S. Kuroda, M. Oda and Y. Kitahara, Angew. Chem. 85, 93 (1973), Angew. Chem., intern. Ed., 12, 76 (1973)), and the compound is also thermally unstable to give a tricyclic compound, unpublished result
- 10) Y. Kitahara and M. Oda, "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," The Jerusalem Symposium on Quantum Chem. and Biochem., III, p. 284, Jerusalem 1971
- 11) S. Kuroda, M. Funamizu, Y. Kitahara and T. Asao, Tetrahedron Letters, 1973 (1975)
- 12) The compound (20) was obtained by the reaction of 8-formylheptafulvene and NBS, but it was quite unstable, therefore, the compound was used for the cycloaddition without complete purification