Electrophilic Substitutions on 8-Cyanoheptafulvene

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We wish to report here the first examples of electrophilic substitutions on 8-cyanoheptafulvene (**I**)[1] which is a moderately stable and the simplest derivative of heptafulvenes. The compound **I** is unstable to acids, however, basic conditions were found to be best for obtaining successful results.

Bromination. The addition of one equivalent of bromine to a solution of **I** and a small excess of triethylamine in methylene chloride at 0°C gave, by silica gel chromatography, 8-bromo-8-cyanoheptafulvene (**II**) as orange needles, mp ~50°C decomp., in a 87% yield. The compounds **II** is unstable and is liable to decompose at room temperature. When a mass of **II** was heated at *ca.* 40°C, it decomposed explosively and an evolution of hydrogen bromide was observed. Therefore, we could not obtain successful elemental analytic data. However, the structure was established by means of the spectral data given in the table.

Nitration. When **I** was treated with tetranitromethane in pyridine - ethanol at 10°C for one hour, it gave 8-cyano-8-nitroheptafulvene (**III**) as fine yellowish-brown needles, mp 168°C decomp., in a 16.5% yield. With other nitrating reagents, only polymeric materials were obtained.

Formylation. The Vilsmeyer reaction of **I** was successful in giving 8-cyano-8-formylheptafulvene (**IV**)[2] as red prisms, mp 181—182°C, in a 47% yield.

Trifluoroacetylation. The treatment of **I** with trifluoroacetic anhydride in methylene chloride at 4°C gave 8-cyano-8-trifluoroacetylheptafulvene (**V**) as orange red prisms, mp 213—214°C, in a 20% yield.

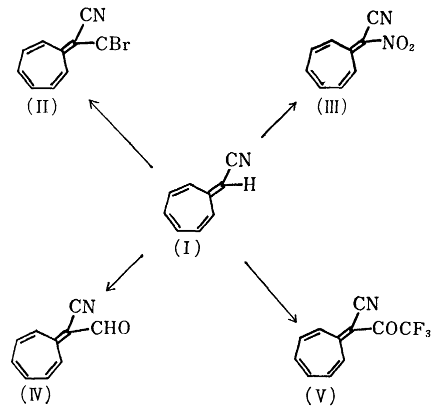
The structures of **III**, **IV**, and **V** were established by their elemental analyses and by their spectral data (see Table 1). The selectivity of the substitution position (C-8) is in accord with the polar character of **I**, which has a high electron density at C-8. The chemical shift of the ring protons of **II** (6.08 ppm) is close to that of **I** (6.13 ppm),[1] however, those of **III**, **IV**, and **V** are 1—1.5 ppm lower, suggesting their larger polar character because of the introduction of electron-withdrawing groups.

From these results, we can say that 8-cyanoheptafulvene (**I**) has an aromatic character.

TABLE 1. SPECTRAL DATA

Compd.	ν_{max} (KBr) cm^{-1}	λ_{max} nm (log ε)	δ ppm (J Hz)[a]
II	2210 1644 1586	246 (*ca* 4.0)[b]	6.61br.d (12) 1H[c]
	1547 1512 753	356 (*ca* 4.3)	6.08 5H
		444sh (*ca* 2.5)	
		484sh (*ca* 2.4)	
		525sh (*ca* 2.3)	
		570sh (*ca* 2.0)	
III	2205 1625 1527	228 (4.20)[d]	7.70—7.25m[e]
	1496 1303 1228	256 (4.01)	
	762	280sh (3.84)	
		438 (4.38)	
IV	2205 1642 1620	219 (4.18)[d]	9.78s 1H[e]
	1520 1490 1270	256 (4.01)	8.87br.d (12) 1H
	1190 756	413 (4.31)	7.63br.d (12) 1H
			7.40—7.00m 4H
V	2205 1648 1618	224 (4.33)[d]	9.02br.d (12) 1H[e]
	1505 1492 1390	255 (4.02)	8.20br.d (12) 1H
	1231 1187 1138	267 (4.03)	7.93—7.50m 4H
	1047 775	436 (4.40)	

a) TMS as internal standard, b) in CH_2Cl_2, c) in acetone, d) in EtOH, e) in $CDCl_3$



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[1] M. Oda and Y. Kitahara, *Chem. Commun.*, **1969**, 352.

[2] This compound has also been synthesized by an other method in our laboratory; *cf.* T. Machiguchi, Ph. D. Dissertation, Tohoku University, 1970.