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SYNTHESES OF 8-(1,2,3,4-TETRACHLOROFULVEN-6-YL)HEPTAFULVENE AND 8-(9-FLUORENYLIDENE)METHYLHEPTAFULVENE

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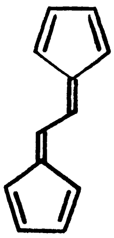
Treatment of [2-(2,3,4,5-tetrachloro-1,3-cyclopentadienyl)vinyl] - tropylium fluoroborate 9 with bases gave 8-(1,2,3,4-tetrachlorofulven-6-yl)heptafulvene 4. In similar way 8-(9-fluorenylidene)methyl heptafulvene 5 was also prepared. 4 is more polar than 5 is, but is less stable. Both 4 and 5 easily gave [8+2]cycloadducts with tetracyanoethylene.

Recently, syntheses of 6,6'-bifulvenyl 1[1] and 8,8'-biheptafulvenyl 2[2] have been reported by Prinzbach et al. and by us, respectively. However, 8-(6-fulvenyl)heptafulvene 3, a vinylog of sesquifulvalene, has been yet unknown. We here report the syntheses of its tetrachloro and dibenzo derivatives, 4 and 5.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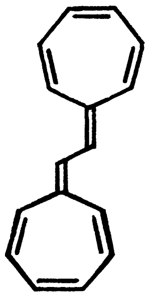
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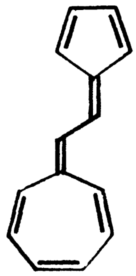
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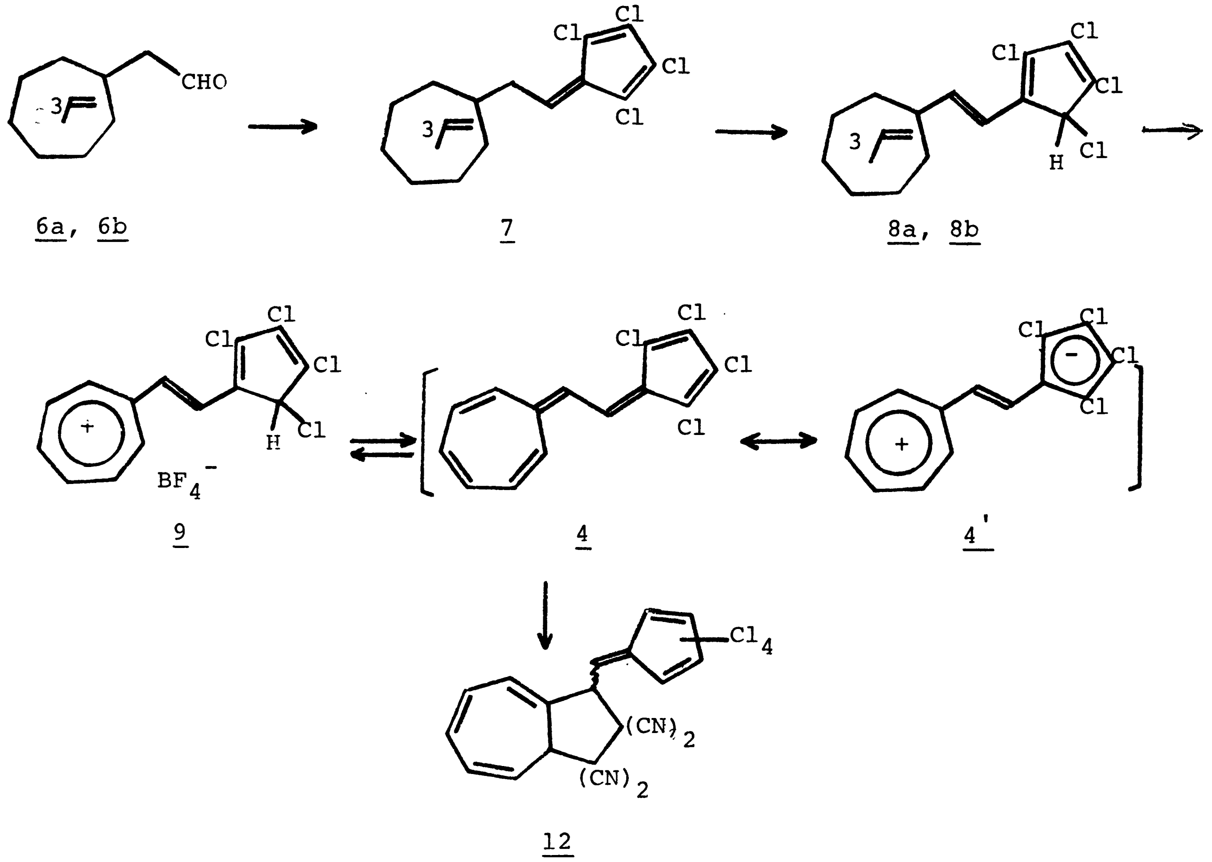
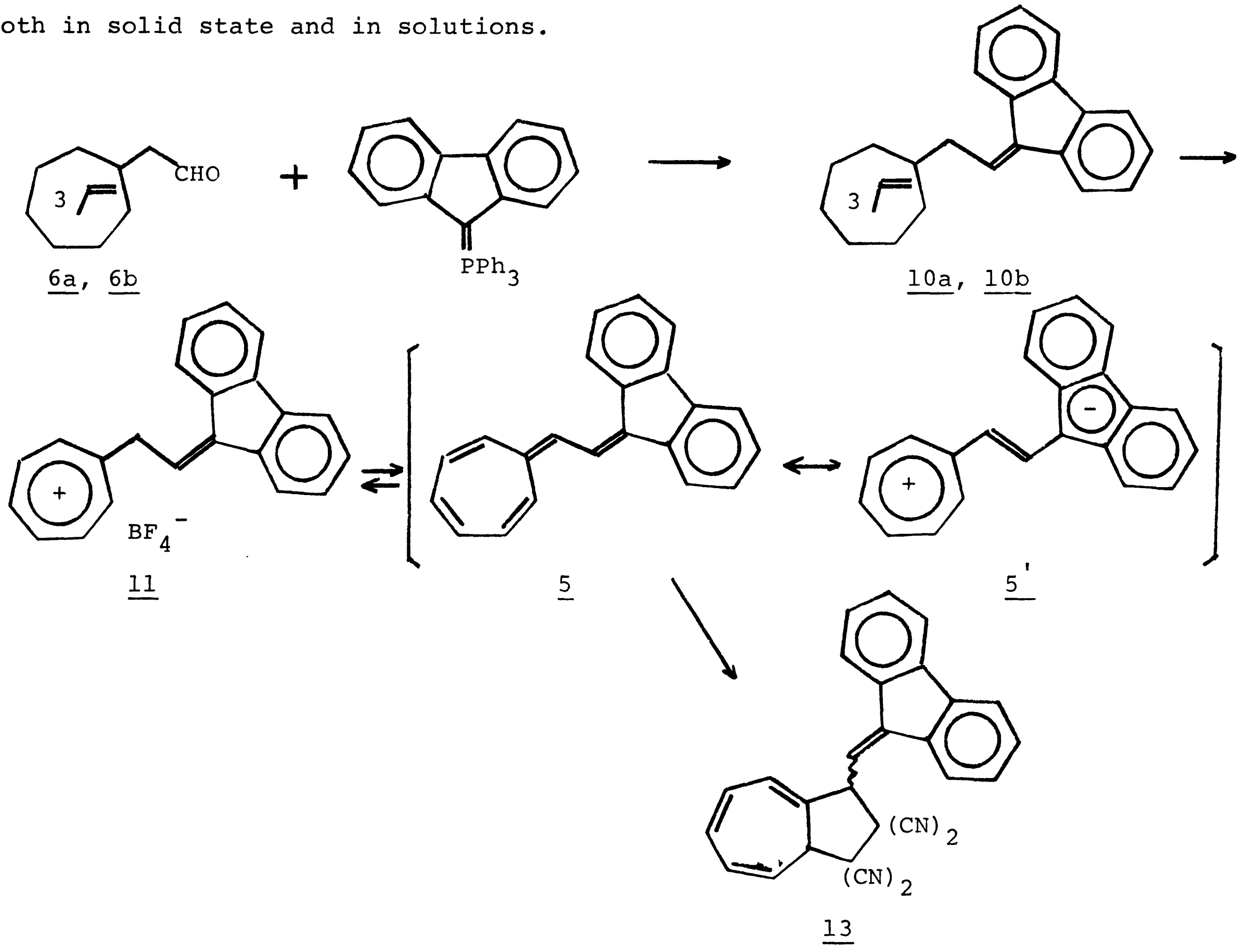
Reaction of a mixture of 1-formylmethyl-and 3-formylmethylcycloheptatriene,[3] 6a and 6b (ca 9:11 by NMR analysis), with tetrachlorocyclopentadiene in hexane at 0°C using triethylamine as a base gave a mixture of 8a and 8b in 32% yield. The ^{1}H-NMR spectrum of the mixture shows the presence of seven olefinic protons and three aliphatic protons, one of the aliphatic protons appearing at ca δ 4.9 ppm, to suggest that 8a and 8b are 1-and 3-[2-(2,3,4,5-tetrachloro-1,3-cyclopentadienyl)vinyl] cycloheptatriene, respectively. 8 may be formed from the initially expected fulvene derivative 7 by base catalysed double bond migration. Treatment of the mixture 8 with triphenylmethyl tetrafluoroborate in methylene chloride at room temperature gave [2-(2,3,4,5-tetrachloro-1,3-cyclopentadienyl)vinyl]tropylium tetrafluoroborate 9 (mp 140°C, deep red prisms from acetonitrile-methylene chloride) in 66% yield. The large coupling constant (J=16.0 Hz, see the Table) between the two olefinic protons indicates their relationship to be trans. Addition of 9 into pyridine at 0°C resulted in deep purple solution and subsequent dilution with water after a few minutes gave 4 in more than 90% yield as dark purple solid. Formation of 4 was also successful by treatment of 9 with triethylamine in methylene chloride. In this case, however, the isolation of 4 was difficult because it rapidly decomposed during chromatographic separation. 4 decomposed at ca 100°C without melting.



Compound 5 was prepared as follows. Reaction of the aldehydes, 6a and 6b, with triphenylphosphonium fluorenylide[4] in refluxing chloroform gave a mixture of 9-(2-cycloheptatrienylethylidene)fluorenes, 10a and 10b, in 82% yield as a pale yellow oil. The ^{1}H-NMR spectrum of the mixture shows the presence of four aliphatic protons at δ 3.68 (m, 2H) and 2.30 ppm (m, 2H) to indicate that 10 is a dibenzofulvene derivative. Treatment of 10 with triphenylmethyl tetrafluoroborate in methylene chloride gave the tropylium salt 11 in 77% yield. Reaction of 11 with triethylamine in methylene chloride gave 5 (mp 154-154.5°C, dark brown needles from n-hexane-ethanol) in 89% yield.

The spectral data of 4, 5, 9, and 11 are listed in the Table. 4 is moderately stable in solid state at room temperature, but is unstable in solutions giving polymeric materials; in chloroform it completely decomposed within 20 min at room temperature, while in pyridine and tetrahydrofuran it is slightly more stable (half-life time in pyridine at 10^{-5} mole concentration was 30 min at 23°C). 5 is stable both in solid state and in solutions.



The chemical shift of the seven-membered ring protons of 4 (δ 6.40 ppm) is ca 0.6 ppm lower than those of 5 (δ 5.83 ppm) to indicate that the contribution of the dipolar resonance form 4' to the resonance hybrid of 4 is greater than 5' to 5 is. The NMR spectra of 4 and 5 in trifluoroacetic acid were identical with those of 9 and 11 in the same solvent, showing that protonation occurred in the five membered ring for 4 and at C-8 of the heptafulvene moiety for 5.

Both 4 and 5 easily reacted with tetracyanoethylene at room temperature to give a 9:1 and 7:2 stereoisomeric mixture of [8+2]cycloadducts, 12 and 13, respectively.

The major isomers of 12 (mp 103-105°C) and 13 (mp 122-123°C) were isolated by repeated recryatalizations from n-heaxane-methylene chloride.

Attempts to prepare the parent hydrocarbon 3 in similar way have been unsuccessful.

Table

The spectral data of 4, 5, 9, 11, 12, and 13

Compound	IR cm^{-1} [a]	UV nm (logε)	^{1}H-NMR ppm (J Hz)	
4	1590, 1530, 1367	516 (4.57) [b]	7.51 d (13.5)	1H [b]
	1237, 1090, 838		7.03 d (13.5)	1H
	750, 692	526 [c]	6.40 m	6H
5	1613, 1574, 1540	231 (4.48) [d]	7.75 m	4H [e]
	1348, 862, 743	254 (4.63)	7.30 m	5H
		433 (4.67)	6.60 d (12.0)	2H
		450 (4.68)	6.25 br. d (11)	1H
			5.83 m	4H
9	1590, 1505, 1240	257 (4.16) [f]	8.96 m	6H [g]
	1060, 745	518 (4.22)	8.01 d (16.0)	1H
			7.47 d (16.0)	1H
			5.27 s	1H
11	1600, 1530, 1450	210 sh (4.53) [f]	9.14 br. s	6H [h]
	1060, 780, 730	284 (4.32)	7.72 m	4H
			7.40 m	4H
			6.78 t (7.0)	1H
			4.90 d (7.0)	2H
12	2260, 1642, 1575	276 (4.40) [d]	6.77 m	2H [e]
	1240, 710, 700	305 sh (4.27)	6.42 m	1H
			6.39 d (10.0)	1H
			6.15 m	1H
			6.00 br.d (10.0)	1H
			5.63 dd (9.5, 4.5)	1H
			3.26 ddd (4.5, 3.0, 1.5)	1H
13	2260, 1605, 1452	216 (4.61) [d]	7.75 m	4H [e]
	785, 730, 710	223 (4.52)	7.35 m	4H
		252 (4.55)	6.8-6.2 m	5H
		261 (4.74)	5.65 m	2H
		285 (4.20)	3.32 narrow m	1H
		305 (4.20)		
		313 (4.20)		
		318 (4.20)		

a) in KBr disk, b) in tetrahydrofuran, c) in pyridine, d) in cyclohexane
e) in $CDCl_3$, f) in conc H_2SO_4, g) in CF_3COOH, h) in $CDCl_3$ at 100 MHz

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