

SUBSTITUTED CYCLONONATETRAENES AND NONAFULVENES

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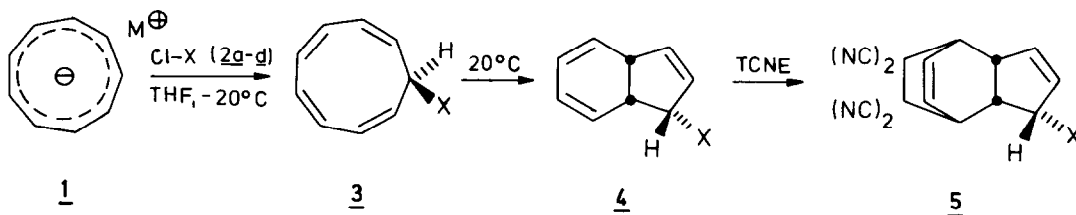
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**Summary:** Reaction of cis,cis,cis,cis-[9]annulene anion (1) with electrophiles (2a-d) leads to substituted cis,cis,cis,cis-1,3,5,7-cyclononatetraenes (3a-d) which are precursors for the preparation of 10- and 10,10'-donor-substituted nonafulvenes (e.g. 7b'-e'). The influence of solvent and temperature on the <sup>1</sup>H-nmr spectra of the nonafulvenes 7b'-h' has been investigated.

Although the properties of cis,cis,cis,cis-[9]annulene anion (1) and its mono-trans-isomer have been studied in recent years <sup>1)</sup> not much is known about the reactions of these aromatic anions <sup>2)</sup>. Therefore, we report on reactions of 1 which lead to nonafulvenes with donor substituents at C<sup>10</sup>. They provide a gradual transition between the unsubstituted nonafulvene (7a') <sup>3)</sup> and 10,10'-bis(dimethylamino)nonafulvene (7i') <sup>4)</sup> whose UV- and <sup>1</sup>H-nmr spectroscopic behaviour is strikingly different.

Substituted cyclononatetraenes

Reaction of cis,cis,cis,cis-[9]annulene anion (1) with Cl-X 2a-d in tetrahydrofuran (THF) at -20°C led to the new cis,cis,cis,cis-cyclononatetraenes 3a-d in 70-90% yields.



3e and 3f were accessible by methanolysis and by hydrolysis, respectively, of 3d in THF at -10°C. The constitution of the cyclononatetraenes 3 was revealed by means of their <sup>1</sup>H-nmr spectra and the formation of the corresponding nine-membered ring anions 6a,b,c,e and the dianion 6g, e.g. with

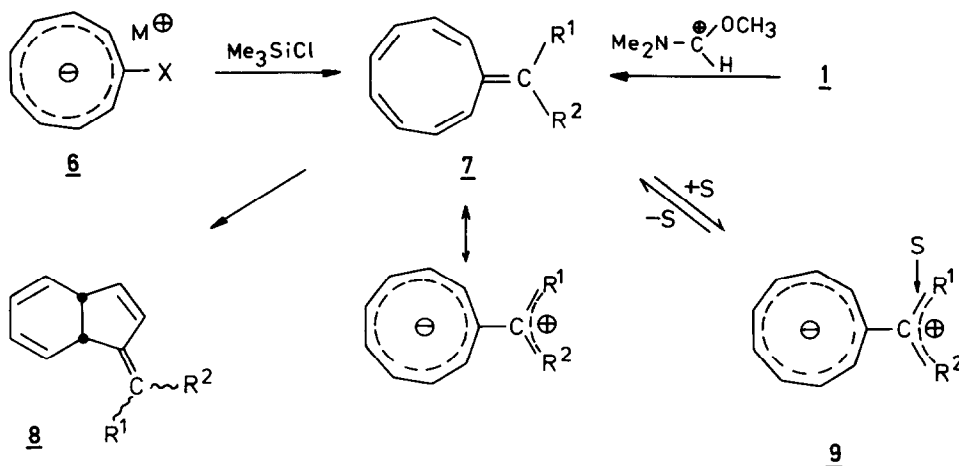
sodium bis(trimethylsilyl)amide <sup>5)</sup>. The all-cis configuration was proven by valence isomerizations to give only the cis-dihydroindenes 4. 4a,e,f had been synthesized before <sup>1a,6)</sup>. 4b,c and d reacted with tetracyanoethylene to the adducts 5 (mp: (5b) 210°C; (5c) 212°C; (5d) 205°C). 4b,c and d have coupling constants  $J_{8,9}$  characteristic of the cis ring juncture ( $J_{8,9}$ : (4b) 12 Hz; (4c) 12 Hz; (4d) 12.5 Hz) <sup>7)</sup>.

#### 10,10'-Donor-substituted nonafulvenes

Reaction of the nine-membered ring anions <sup>5)</sup> 6b,c,e and of the dianion 6g with trimethylsilylchloride in THF at -78°C led to the nonafulvenes 7b'-e'; 7f' was synthesized from 1 and  $(\text{CH}_3)_2\text{N}-\overset{\ominus}{\text{C}}\text{H}-\text{OCH}_3$  <sup>8)</sup> at -20°C. Structural proof resulted from the <sup>1</sup>H- and <sup>13</sup>C-nmr spectra (Tab.1), the combustion analyses and the valence isomerization products 8. Reaction of 1 with  $(\text{CH}_3)_2\text{N}-\overset{\ominus}{\text{C}}(\text{OC}_2\text{H}_5)_2$  resulted in a mixture of 10,10'-bis(ethoxy)nonafulvene 7g' ( $\text{R}^1=\text{R}^2=\text{OC}_2\text{H}_5$ ) and 10-dimethylamino-10'-ethoxynonafulvene 7h' ( $\text{R}^1=\text{N}(\text{CH}_3)_2$ ,  $\text{R}^2=\text{OC}_2\text{H}_5$ ) which we were unable to separate so far <sup>9)</sup>.

<u>7</u>	$\text{R}^1$	$\text{R}^2$	<sup>1</sup> H-nmr ( $\delta$ )	<sup>13</sup> C-nmr ( $\delta$ )
a'	H	H	ref. <sup>3)</sup>	ref. <sup>3)</sup>
b'	CH <sub>3</sub>	OSi(CH <sub>3</sub> ) <sub>3</sub>	ref. <sup>5a)</sup>	ref. <sup>5a)</sup>
c'	C <sub>6</sub> H <sub>5</sub>	OSi(CH <sub>3</sub> ) <sub>3</sub>	0.0 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ); 5.47 (dd, J=13 and 3.5 Hz, 1H, H <sup>2</sup> or H <sup>7</sup> ); 5.6-6.2 (m, 6H, vinyl-H); 6.47 (d, J=13 Hz, H <sup>8</sup> ); 7.2-7.8 (m, 5H, aromatic H)	-
d'	OCH <sub>3</sub>	OSi(CH <sub>3</sub> ) <sub>3</sub>	0.30 (s, 9H, Si(CH <sub>3</sub> ) <sub>3</sub> ); 3.63 (s, 3H, OCH <sub>3</sub> ); 5.7-6.3 (m, 8H, vinyl-H)	-
e'	OSi(CH <sub>3</sub> ) <sub>3</sub>	OSi(CH <sub>3</sub> ) <sub>3</sub>	0.32 (s, 18H, 2Si(CH <sub>3</sub> ) <sub>3</sub> ); 5.47 (dd, J=12.5 and 3.5 Hz, 2H, H <sup>2</sup> , H <sup>7</sup> ); 5.6-6.1 (m, 4H, H <sup>3</sup> -H <sup>6</sup> ); 6.12 (d, J=12.5 Hz, 2H, H <sup>1</sup> , H <sup>8</sup> )	-
f'	H	N(CH <sub>3</sub> ) <sub>2</sub>	2.85 (s, 6H, N(CH <sub>3</sub> ) <sub>2</sub> ); 5.27 (dd, J=13.1 and 5.4 Hz, 1H, H <sup>2</sup> or H <sup>7</sup> ); 5.74 (d, J=12.7 Hz, 1H, H <sup>7</sup> or H <sup>2</sup> ); 5.89 (d, J=12.7 Hz, 1H, H <sup>1</sup> or H <sup>8</sup> ); 6.08 (m, 2H, H <sup>4</sup> , H <sup>5</sup> ); 6.16 (s, 1H, H <sup>10</sup> ); 6.28 (m, 2H, H <sup>3</sup> , H <sup>6</sup> ); 6.52 (d, J=12.2 Hz, 1H, H <sup>8</sup> or H <sup>1</sup> )	107.5 (C <sup>9</sup> ) 114.4, 123.7, 127.4, 127.5, 128.3, 128.8, 131.7 (C <sup>1</sup> -C <sup>8</sup> ) 146.4 (C <sup>10</sup> )
i'	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	ref. <sup>4)</sup>	-

Tab.1: Nmr spectra of the nonafulvenes 7 in CDCl<sub>3</sub> at 0°C with TMS as the internal standard.



Quite remarkably, however, none of the new nonafulvenes 7b'-h' showed a downfield shift of the  $^1\text{H}$ -nmr signals from the olefin into the [9]annulene anion region either in donor solvents (e.g.  $\text{CH}_3\text{CN}$ ) or at lower temperatures ( $-97^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2$ ) as observed by Hafner and Tappe with 7i'. Even in  $\text{CH}_2\text{Cl}_2/\text{HMPA}=5:1$  at  $-86^\circ\text{C}$  the  $^1\text{H}$ -nmr spectra of 7b'-h' correspond to the olefin spectra at  $0^\circ\text{C}$  (Tab.1). Apparently only in the case of the bis-dimethylamino compound 7i' solvation can lead to an equilibrium of the nonafulvene with its (most probably) twisted and strongly solvated <sup>10)</sup> isomer (conformer <sup>4)</sup> 9i'. This should be due both to the steric hindrance in 7i' and the favorable electronic stabilization of the charges in the dipole 9i' <sup>4)</sup>. Finally, it is interesting to note that this situation corresponds largely to results which we have found in comparable systems <sup>5,11)</sup>.

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