

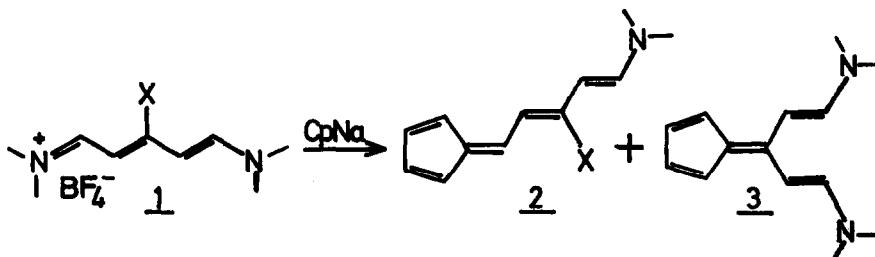
REACTIONS OF 3-SUBSTITUTED PENTACYANINES WITH CYCLOPENTADIENIDE  
AND CYCLONONATETRAENIDE ANIONS

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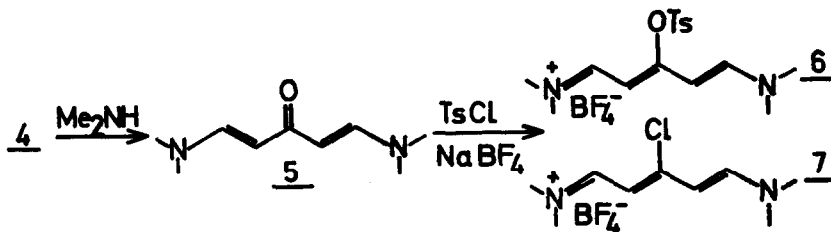
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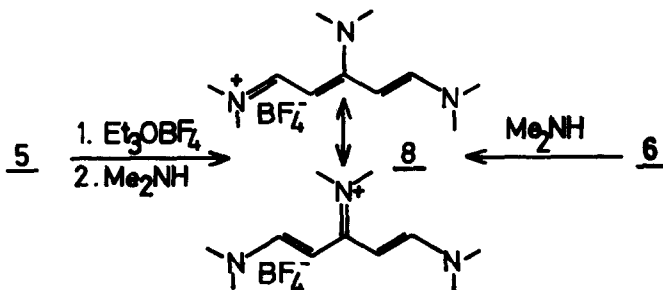
Although it is well known<sup>1)</sup> that the condensation of 1-dialkylamino-penta-1.3-dienylidene-5-dialkylammonium salts (pentacyanines 1, X=H) with sodium-cyclopentadienide leads to 6-(4-dialkylamino-1.3-butadienyl)fulvenes (2, X=H), we expected that the use of substituted pentacyanines with suitable leaving groups at C-3 (1, X=OTs, Cl, N(CH<sub>3</sub>)<sub>2</sub>) would provide 2 as well as 6.6-bis-(2-dialkylaminovinyl)-fulvenes 3, which interested us as potential intermediates for several non-benzenoid aromatics.



Pyrone-4 (4)<sup>2)</sup> served as starting material for the preparation of 3-substituted pentacyanines. Nucleophilic ringopening<sup>3)</sup> of 4 with dimethylamine afforded 1.5-bis-(dimethylamino)penta(1.4)dienone-3 (5). On treatment with p-toluenesulfonylchloride and sodium fluoroborate 5 was converted to a 3:1 mixture of the 3-tosyloxy- and 3-chloro-pentacyanine fluoroborates 6 and 7. The formation of 7, separated from 6 by fractional crystallization (CH<sub>2</sub>Cl<sub>2</sub>), can be understood as nucleophilic displacement of OTs<sup>-</sup> in 6 by chloride ions.



Treatment of 6 with dimethylamine or alkylation of 5 with triethyloxonium fluoroborate, followed by reaction with dimethylamine, produced 1.3-bis-dimethylamino-penta-1.3-dienylidene-5-dimethylammonium fluoroborate 8.

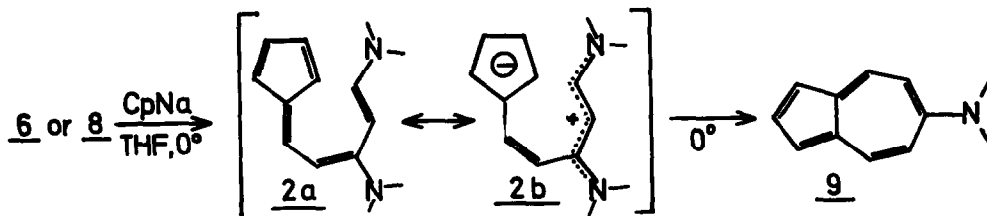


Experimental data<sup>4)</sup> for compounds 5 to 8:

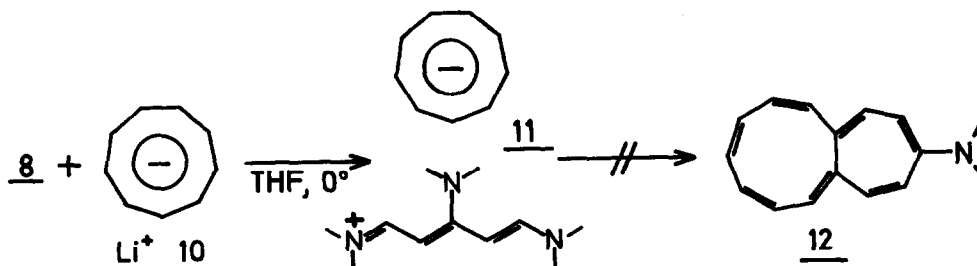
	Yield (%)	mp (°C)	uv in CH <sub>2</sub> Cl <sub>2</sub> nm (log ε)	Solvent	nmr (τ) at 37°		
					H <sub>1</sub> +H <sub>5</sub>	H <sub>2</sub> +H <sub>4</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
(5) pale yellow prisms	93	108-10	350 (4.61) 357 (4.62)	CDCl <sub>3</sub>	2.49(d,13Hz)	5.0(d,13Hz)	7.10(s)
(6) yellow needles	61	112-14	431 (5.01)	CD <sub>3</sub> NO <sub>2</sub>	2.61(broad)	4.46(d,12Hz)	6.78(s) 6.93(s) (OTS:2.12(d,8Hz),2.47(d,8Hz),7.51(s))
(7) orange prisms	21	210-12	440 (4.98)	CD <sub>3</sub> NO <sub>2</sub>	1.99(d,11Hz)	4.0(d,11Hz)	6.60(s) 6.82(s)
(8) pale yellow needles	90	163-65	318 (4.49) 353 (4.41)	CDCl <sub>3</sub>	2.98(d,12Hz)	5.28(d,12Hz)	6.90(s, 6H) 6.97(s,12H)

Surprisingly, reactions of both 6 and 8 with sodium cyclopentadienide in THF at 0° directly afforded 6-dimethylaminoazulene 9 (bronze plates, 41% from 6, 61% from 8; mp:175-177°; uv spectrum in cyclohexane:  $\lambda_{\text{max}}=319(4.70), 375(3.53), 386(3.99), 397(4.19), 490(2.47), 507(2.49), 546(2.30)$  nm(log ε); nmr spectrum in CDCl<sub>3</sub>: doublets centered at 1.99τ (H<sub>4</sub>,H<sub>8</sub>,11 Hz), 2.91τ (H<sub>1</sub>,H<sub>3</sub>,3 Hz), 3.56τ (H<sub>5</sub>,H<sub>7</sub>,11 Hz), triplet at 2.69τ (H<sub>2</sub>,3 Hz), singlet at 6.83τ (N(CH<sub>3</sub>)<sub>2</sub>),<sup>5)</sup> whereas from 7 an orange compound, unstable on work-up, was obtained. Thermolysis of this reaction mixture in toluene (THF was replaced by toluene under nitrogen) produced 6-chloroazulene (blue needles; 24%; mp: 89-91°; uv-spectrum in cyclohexane:  $\lambda_{\text{max}}=242(4.07), 279(4.74), 283.5(4.75), 289(4.80), 306(3.56), 336(3.46), 343(3.40), 352(3.61), 365(2.64), 562.5(2.32), 583(2.41), 608(2.36), 636(2.41), 665(2.11), 703(2.11)$  nm(log ε); nmr spectrum in CDCl<sub>3</sub>: doublets centered at 1.96τ (H<sub>4</sub>,H<sub>8</sub>,10 Hz), 2.70τ (H<sub>1</sub>,H<sub>3</sub>,4Hz), 2.80τ (H<sub>5</sub>,H<sub>7</sub>,10 Hz), triplet at 2.23τ (H<sub>2</sub>,4 Hz). Fulvene 3 could not be detected in the reactions of either 6, 7, or 8 with sodium cyclopentadienide.

The immediate formation of 9 even at 0° (temperatures of 150-250° are required<sup>1)</sup> for the cyclization of (2,X=H) to azulene) indicates a strongly enhanced nucleophilicity of the five-membered ring in 2 (formed directly from 8 or from 6 by nucleophilic exchange of the OTs - group by liberated dimethylamine), in which the dipolar resonance form 2b becomes energetically favorable by resonance stabilization of both its cyclopentadienide and triacyanine systems.



The facile ringclosure to 9 induced us to treat 8 with lithium cyclononatetraenide<sup>6)</sup> 10. A clean reaction formed 1.3-bis-dimethylamino-penta-1.3-dienylidene-5-dimethylammonium cyclononatetraenide 11 (yellow needles, 63%; mp:131-133° dec.; uv spectrum in THF:  $\lambda_{\max}$ =250(4.71),317(4.23),352(4.07) nm (log  $\epsilon$ ); nmr spectrum in CD<sub>3</sub>CN: doublets (12 Hz) centered at 2.98 $\tau$  (2 H), 5.23 $\tau$  (2 H), singlets at 3.17 $\tau$  (9 H), and at 6.98 $\tau$  and 7.09 $\tau$  (18 H).



These spectra, in which the known spectral features of 8 and 10 are superimposed, are proof for the structure of 11. Attempts to convert 11 to 10-dimethylaminononaazulene 12 by various thermolysis conditions were unsuccessful.<sup>7,8)</sup>

#### References

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- 2) R. Willstätter and R. Pummerer, *Ber. dtsch. chem. Ges.* **37**, 3740 (1904).
- 3) Reactions of pyrone-4 with primary amines have been reported by W. Borsche and J. Bonacker, *Ber. dtsch. chem. Ges.* **54**, 2678 (1921) and S. Hünig and G. Köbrich, *Liebigs Ann. Chem.* **617**, 181 (1958).

- 4) Correct elemental analyses were obtained for all the products described, except for 11, which is sensitive to air.
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- 7) The syntheses of a nonafulvene-derivative (K. Hafner and H. Tappe, Angew. Chem. 81, 564 (1969), Angew. Chem. *internat. Edit.* 8, 593 (1969), and of nonafulvalenes (P. J. Garrat and K. A. Knapp, Chem. Commun. 1971, 1084) have recently been reported.
- 8) Similarly, the reaction of hexaalkylguanidinium salts with sodium cyclopentadienide does not lead to fulvenes (U. Müller-Westerhoff, unpublished).