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6,7-DIAZA-DITHIAFULVALENES AND 5-AZA-8a-AZONIA-DITHIAFULVALENES

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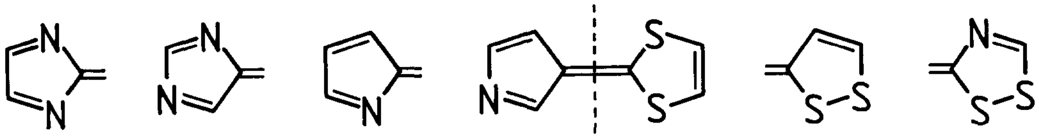
Abstract: 3-Dimethylamino- and 3,5-Bis-dimethylamino-pyrazoles react with 1,2- and 1,3-dithiolium salts to form 6,7-diaza-dithiafulvalenes and 5-aza-8a-azonia-dithiafulvalenes, a new type of heterofulvalenes.

Whereas the reaction of pyrroles, indoles and imidazoles with dithiolium salts and related compounds gives high yields of aza- and diazafulvalenes[1,2] (Scheme 1), pyrazoles fail to undergo a related reaction and 2,3-diazafulvalenes are unknown. Some diazafulvenes derived from pyrazoles[3-6] have been reported, however. The only fulvalene that contains a pyrazole moiety is 2,3,6,7-tetraaza-1,4,5,8-tetraphenylfulvalene-2,3,6,7-tetroxide.[7] Obviously, the 4-position in pyrazoles is much less nucleophilic than the corresponding positions in pyrroles, indoles and imidazoles.

Scheme 1

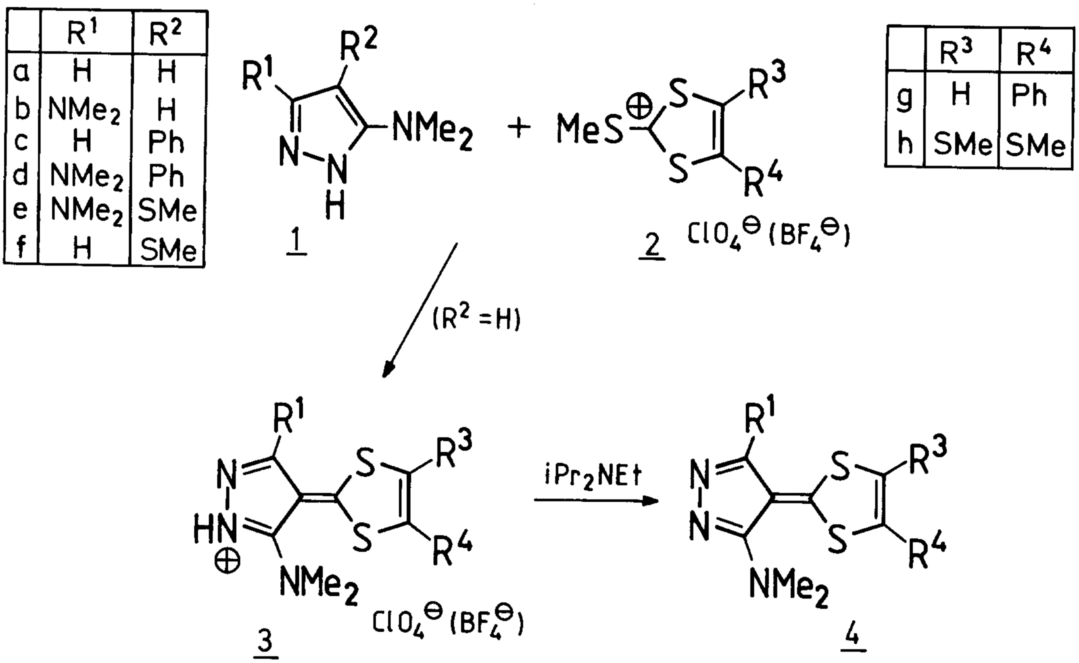


3-Dimethylaminopyrazole (1a) and 3,5-Bis-dimethylamino-pyrazole (1b)[8] are electron-rich pyrazoles and react readily with a number of electrophiles and oxidants. We therefore expected these compounds to react with dithiolium salts to form a new class of azadithiafulvalenes which could be of interest as precursors for organic metals.

Heating of 1a,b with the 1,3-dithiolium salts 2 in acetonitrile gives rise to the red perchlorates (tetrafluoroborates) 3ag,ah,bg,bh which subsequently can be transformed into the orange 6,7-diaza-1,4-dithiafulvalenes 4[9] (Scheme 2). Deprotonation of 3 causes a bathochromic shift. The UV/VIS absorption maxima of 3 and 4 are found in a range that is expected from the data of azadithiafulvalenes.[1] The hypsochromic shift in the spectra of

4bg,bh as compared with those of 4ag,ah can be rationalized by assuming a stronger deviation from coplanarity by virtue of the two dimethylamino groups in the 4b-series rather than the one dimethylamino group in the 4a-series.

Scheme 2

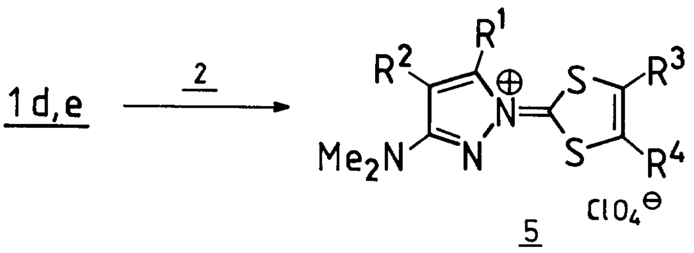


	R^1	R^2
a	H	H
b	NMe_2	H
c	H	Ph
d	NMe_2	Ph
e	NMe_2	SMe
f	H	SMe

	R^3	R^4
g	H	Ph
h	SMe	SMe

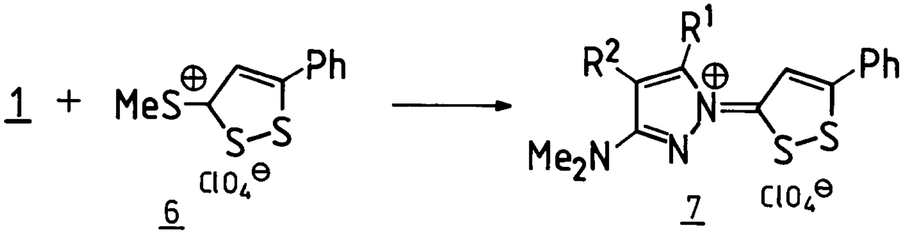
When the 4-substituted pyrazoles 1d,f are reacted with 2, the red azoniafulvalenes 5dg,dh,fg are formed [10] (Scheme 3). Surprisingly, this new

Scheme 3



type of fulvalenes is also obtained from the reaction of 1 with the 1,2-dithiolium salt 6 (Scheme 4). The 5-aza-9a-azonia-1,4-dithiafulvalene

Scheme 4



perchlorates 7 [11] have about the same color as the "normal" fulvalenes 3 although the positive charge in 7 cannot be delocalized in the same way as, eg., in N-protonated 5-aza-1,2-dithiafulvalenes.[1] The azoniafulvalenes 7 can be interpreted as substituted 3-amino-1,2-dithiolium salts. N,N-Dialkylamino-1,2-dithiolium salts, however, are only yellow.[11] From the ^{1}H-NMR spectra of the latter and of 7 it can be concluded that the (bis)dimethylaminopyrazole ring is a weaker electron donor than a dialkylamino group and that a second dimethylamino group in 7 increases the donor effect of the pyrazole ring. In contrast to the diazafulvalenes 3 and their salts 4, where a second dimethylamino group has a hypsochromic effect, in 7 a second dimethylamino group brings about a small bathochromic shift although there is no resonance structure in which one of the dimethylamino groups carries a formal positive charge. In terms of MO theory, azoniafulvalenes such as 7 and 5 are closely related to "normal" fulvalenes. The only difference is the bonding interaction at the central double bond in the HOMO of, eg., 1,2-dithiafulvalenes as compared with the antibonding interaction in 7, leading to a lower bond order.

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9. 3ag(ClO_4): Yield 74%, dark red prisms, m.p. 223-223.5°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 234 (4.29), 282 (sh, 3.76), 360 (sh, 3.68), 440 nm (4.25); 3bg(ClO_4): yield 37%, red needles, m.p. 261-262°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 290 (3.62), 405 nm (4.39); 3ah(BF_4): yield 48%, scarlet needles, m.p. 114.5-115°C, UV/VIS (CH_3CN):λ_{max} ($\log\varepsilon$) = 232 (4.11), 250 (sh, 3.98), 297 (4.01), 464 nm (4.25); 3bh(BF_4): yield 37%, ruby needles, m.p. 165°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 220 (sh, 4.22), 280 (3.79), 300 (3.76), 425 nm (4.22); 4ag: orange-yellow powder, m.p. 163°C (dec.), UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 235 (4.25), 324 (3,53), 412 nm (4.29); 4bg: dark red platelets, m.p. 205-206°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 230 (4.31), 290 (3.59), 398 nm (4.37); 4ah: UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 300 (sh, 3.92), 416 nm (4.11); 3bh: dark red powder, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 300 (sh, 3.63), 396 nm (4.11).
10. 5dg: yield 50%, red needles, m.p. 225.5°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 225 (4.32), 290 (sh, 3.58), 448 nm (4.42); 5dh: yield 23%, dark red needles, m.p. 159°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 305 (sh, 3.84), 466nm (4.37); 5fg: yield 36%, orange-red needles, m.p. 226-227°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 230 (4.28), 247 (sh, 4.22), 309 (3.64), 462 (4.53), 484 nm (sh, 4.44).
11. 7a: yield 57%, metallic-green needles, m.p. 230-230.5°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 231 (sh, 4.03), 328 (4.19), 486 nm (4.41); ^1H-NMR (DMSO-d_6): δ = 3.03 (s; 6 H, NCH_3), 6.92 (d, J = 4 Hz; 1 H, H-7), 7.48 -8.11 (m; 5 H, Ph), 8.70 (d, J = 4 Hz, 1 H, H-6), 8.78 (s; 1 H, H-4); 7b: yield 52%, dark red needles, m.p. 228-228.5°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 234 (sh, 4.13), 334 (4.25), 492 nm (4.21); ^1H-NMR (DMSO-d_6): δ = 2.82 (s; 6 H, NCH_3), 3.03 (s; 6 H, NCH_3), 6.70 (s; 1 H, H-7), 7.50-8.10 (m; 5 H, Ph), 8.30 (s; 1 H, H-4); 7c: yield 60%, dark red needles, m.p. 218.5-219°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 217 (sh, 4.30), 240 (4.17), 335 (4.21), 487 nm (4.44); 7d: yield 34%, dark red prisms, m.p. 263.5-264°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 219 (sh, 4.36), 242 (sh, 4.20), 349 (4.29), 492 nm (4.15); 7e: yield 58%, dark red platelets, m.p. 230-231°C, UV/VIS (CH_3CN): λ_{max} ($\log\varepsilon$) = 215 (sh, 4.65), 342 (4.59), 490 nm (4.51).
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