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NEW TYPES OF HETEROFULVALENES AND THEIR WAYS OF FORMATION

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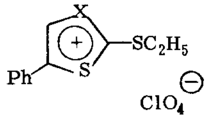
Heterofulvalenes are suitable model compounds for the study of hetero-atom effects in non-alternant cyclic π-systems. Whereas the basic method of their preparation has been published elsewhere[1] we here wish to report a considerable extension of that work and observations which are relevant for the reaction mechanism concerned.

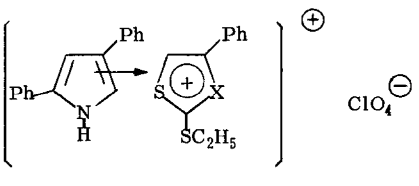
Addition of 1-molar acetonitrile solutions of salts 1 and 2 to equimolar solutions of



1$^{2)}$: X = S ; mp. 116^0 (dec.)

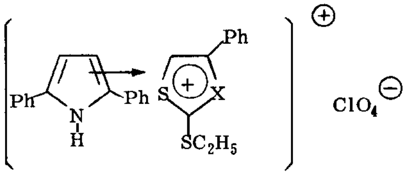
2$^{2)}$: X = Se ; mp. 112^0 (dec.)

2,4-diphenyl-pyrrole in acetonitrile at room temperature produced crystalline, red 1:1 complexes of the starting materials (yield: 50-80%). 2,5-Diphenyl-pyrrole reacted similarly with 1 and 2. It seems appropriate to formulate these compounds as CT-complexes 3-6:



3 : X = Se ; mp. 142^0 (dec.)

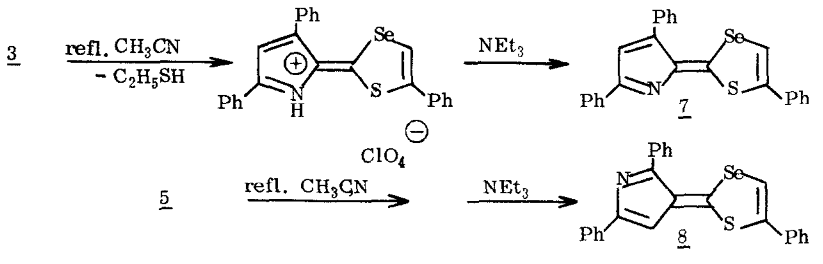
4 : X = S ; mp. 161^0 (dec.)



5 : X = Se ; mp. 128^0 (dec.)

6 : X = S ; mp. 135^0 (dec.)

When recrysallised from acetonitrile compounds 3 - 6 partly underwent further reaction as indicated below. In the cases of 3 and 5 these reactions were complete after 10 hrs. refluxing in acetonitrile. The resulting heterofulvalenes 7 and 8 were isolated as perchlorates which were then deprotonated to yield the stable free bases:

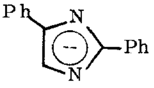


mp. 130°
λ_{max} 485 nm
(log ε 4·53)

mp. 155°
λ_{max} 468 nm
(log ε 4·30)

4 and 6 reacted considerably slower to give the corresponding heterofulvalenes, already obtained by a related method.[1]

In the imidazole series no CT-complexes have been isolated so far, but the anions 9 and 10 could be combined in abs. benzene with the cations of 1, 2 and 11-12 to form the heterofulvalenes 13 - 18 listed in table I (cf. l.c.[1]).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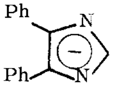
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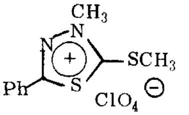
11[3)]

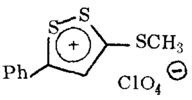
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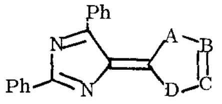
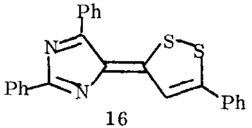
Table I: New 1,3- and 1,4-Diaza-heterofulvalenes[4]


13 - 15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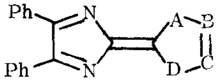

17 - 18

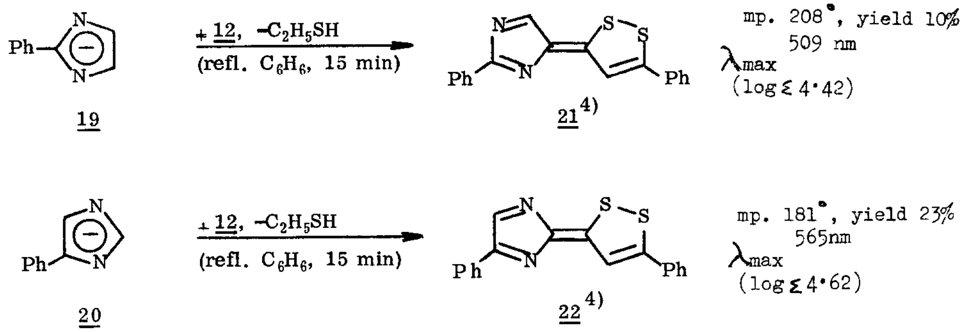
Compound	A	B	C	D	Yield (%)	m.p. (°C)	λ_{max} nm[5)] (log ε) free base	+ a)	++ b)
13	Se	CH	CPh	S	32	200	495 (4·53)	$482^{S(c)}$ (4·43)	442^{S} (4·29)
14	S	CH	CPh	S	12	208	492 (4·51)	460^{S} (4·35)	430^{S} (4·29)
15	NCH_3	N	CPh	S	10	228	440 (4·59)	372^{S} (4·39)	345^{S} (4·41)
16					15	206	542 (4·57)	472^{S} (4·40)	407^{S} (4·46)
17	Se	CH	CPh	S	30	212	528 (4·78)	536^{S} (4·70)	495^{S} (4·36)
18	NCH_3	N	CPh	S	39	183	458 (4·57)	418^{S} (4·37)	380^{S} (4·11)

a) + = monoprot. species, b) + + = diprot. species, c) S = in solution only

While cations 1 and 11 were introduced as new electrophilic agents in the aromatic substitution of azoles, compounds 14-18 constitute the first examples of the hitherto unknown 1,3-diaza-heterofulvalenes. Like their 1,4-diaza-analogues these compounds undergo stepwise and reversible protonation on the addition of perchloric acid (cf. table I).

The question as to what extent phenyl-substituents in the imidazole anion are essential for the electrophilic substitution to occur was also studied; an example is shown in Scheme I:

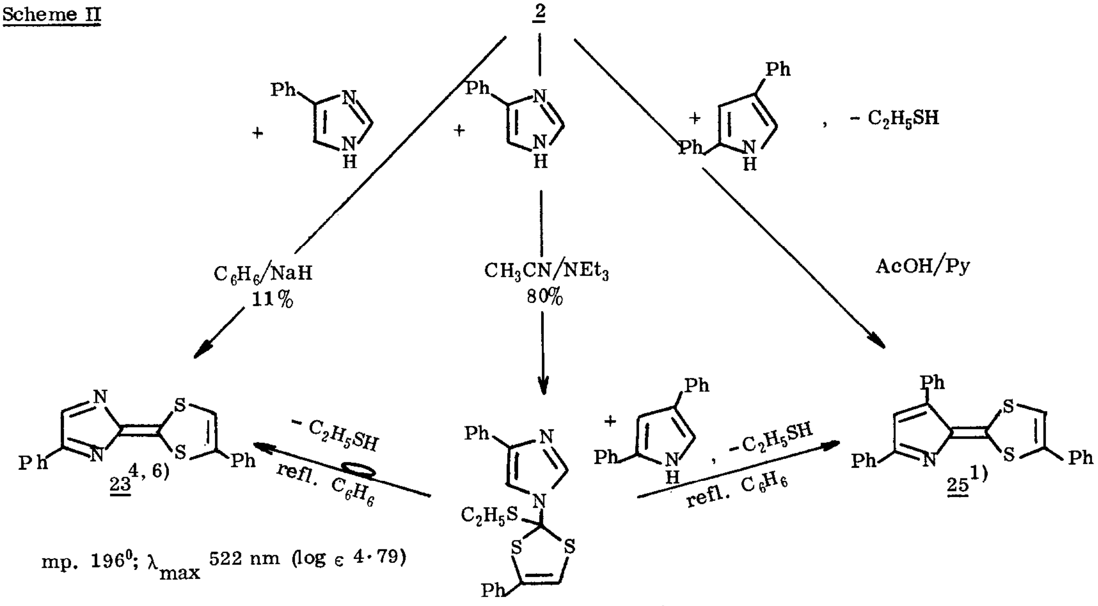
Scheme I



mp. 208°, yield 10%
λ_{max} 509 nm
(log ε 4·42)

mp. 181°, yield 23%
λ_{max} 565nm
(log ε 4·62)

Scheme II



mp. 196°; λ_{max} 522 nm (log ε 4·79)

24 (mp. 111°)

The phenyl imidazol anions 19 and 20 react with 12 under the conditions specified above to give isomeric 1,3- and 1,4-diazafulvalenes 21 and 22 respectively. The imidazole anion itself did not undergo electrophilic substitution by 12 or similar systems under a wide range of reaction conditions. The structure 22 can be unambiguously assigned on the basis of UV-data of the free base and its protonated forms. This implies that 20 has been exclusively substituted in the 2-position - a result which is in marked contrast to the normal behaviour of imidazole and its derivatives, of which it is known that electrophilic substitution takes place in the 4(5)-position, the sole exception being diazotation.[7] In refluxing benzene as solvent 2 reacted similarly with 21 under formation of the corresponding 1,4-diaza-heterofulvalene 23 (cf. Scheme II). However, in acetonitrile at room temperature and in the presence of one equivalent ethyl-diisopropylamine a colourless product was isolated. Analytical and NMR-data suggest structure 24 for this compound. The occurrence of the N-substitution product 24 throws open the question whether in these reactions N-substitution possibly precedes C-substitution. When 24 was refluxed in benzene for 24 hrs it was shown by UV-evidence to have rearranged to give 23 (plus unidentified products). However, the rate of rearrangement (< 10% in 24 hrs.) is too slow to account for the total amount of 23 formed in the 'direct' reaction of 20 with 2 in refluxing benzene. This seems to indicate that under these latter conditions the direct C-substitution should be the dominant mechanism. In refluxing benzene 24 partly dissociates into its components as demonstrated by reaction with 2,4-diphenyl-pyrrole. The sole reaction product was the known 1-azaheterofulvalene 25 (cf. the above scheme). The rearrangement 24 → 23 is thought to follow a similar pattern and should therefore be an inter-molecular reaction.

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References

1. R. Gompper and R. Weiss, Angew. Chem., 80, 277 (1968)
2. Obtained from the corresponding thions by reaction with $OEt_3BF_4/HClO_4$
3. Compound made available by courtesy by Dozent Dr R. Grashey, Universität München
4. Configurations chosen arbitrarily. Due probably to free rotation no cis-trans isomers were found.
5. All UV-measurements in dioxane
6. Details concerning this structural assignment to be published elsewhere.
7. M.S.R. Naidu and H.B. Bensuan, J. Org. Chem., 33, 1307 (1968) and references cited therein.