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# THE ARENEDIAZONIUM ION AS A DIPOLAROPHILE

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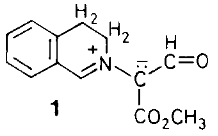
*Summary* *Azomethine ylides (methyl 3-oxido-2-[3,4-dihydroisoquinolinio]-acrylate, 3-methyl-2,4-diphenyloxazolium-5-olate), thiocarbonyl ylides (thiofluorenone S-methylide, thiobenzophenone S-methylide) as well as diazomethane undergo 1,3-dipolar cycloadditions to the NN-bond of 4-nitrobenzenediazonium salt.*

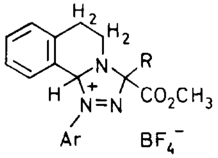
The surprising dienophilic reactivity of the aromatic diazonium nitrogen [1,2] prompted us to explore the NN triple bond of the diazonium ion as an electron-deficient dipolarophile. Two features were responsible for the choice of 1,3-dipoles: *high HOMO energy* and *good quality of the two new σ-bonds* formed in the 1,3-dipolar cycloaddition. We selected azomethine ylides and thiocarbonyl ylides; both harbor carbon functions as termini which allow the generation of two new C-N bonds.



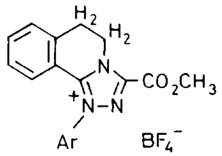
**1**

$+\ Ar{-}\overset{+}{N}{\equiv}N \quad BF_4^-$

**2** Ar = (4)-$NO_2C_6H_4$
**3** Ar = $C_6H_5$



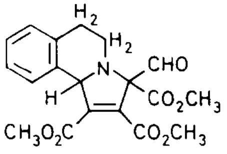
**4** R = CHO
**5** R = H



**6** Ar = (4)-$NO_2C_6H_4$
**7** Ar = $C_6H_5$

The azomethine ylide 1 is isolable in orange crystals.[3,4] The reaction with 2 equiv. of 4-nitrobenzenediazonium fluoborate (2) proceeded at -30°C in acetonitrile and following work-up with dichloromethane/water furnished 57% of the colorless triazolium salt 6 (mp 273-274.5°C).[5] The broad IR absorption at 1080 $cm^{-1}$ indicates $BF_4^-$. The IR band at 1749 $cm^{-1}$ and the $\delta_H(OCH_3)$ at 4.09 ($CD_3CN$) fit an ester group bonded to an electron-poor heteroarene. The low-field shift of the AA'BB' spectrum of $-C_6H_4NO_2$ (δ 7.91, 8.51) compared to 4-nitroaniline (AA'XX', 6.65, 7.99) is likewise significant. The corresponding *N*-phenyl compound 7 (mp 261°C) was isolated in 22% yield.

We regard 4 as the primary product. The easy hydrolytic removal of the formyl group - probably during the aqueous work-up - is analogous to the loss of CHO from the adduct 8 in cold methanol.[4] Autoxidation or hydrogen transfer leads to the 1,2,4-triazolium ions 6 and 7. More astounding is the removal of the ester group of 6 in boiling aqueous acetonitrile; the new tetrafluoborate 9 (mp 223-224°C) shows the triazolium proton at δ 8.84.



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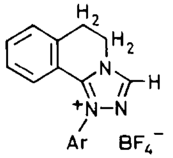

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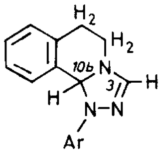

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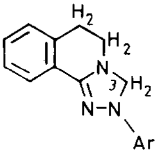
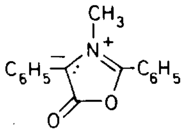


**11**

Ar = $C_6H_4NO_2$-(4)

On assigning the greater nucleophilicity to the exocyclic ylide carbon of 1, one anticipates an adduct with the orientation shown in 4. How can one exclude the product of the opposite regiochemistry ? Reduction of the iminium group of 9 by sodium borohydride afforded 10 (mp 201.5-203.5°C) which exhibits in the $^1$H-NMR spectrum two singlets at δ 6.76 and 6.18 for the 3-H and 10b-H, and the AA'XX' spectrum of $C_6H_4NO_2$ (δ 6.88, 8.04) is back to normal. The regioisomer of 4 should have given rise to 11 by the same reaction sequence; a 3-$H_2$ singlet at higher field would have been appropriate.



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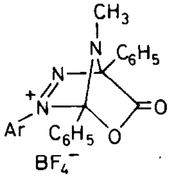

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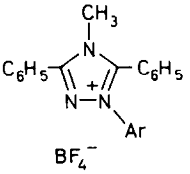
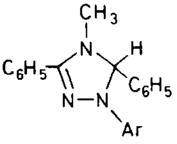


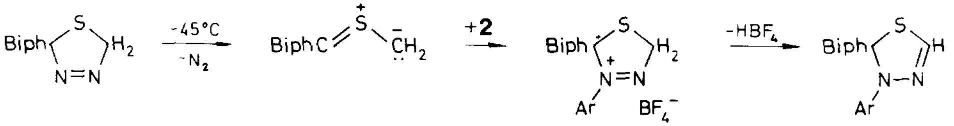
**14**



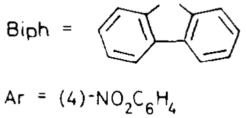
**15**

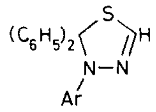
Ar = (4)-$NO_2C_6H_4$

Mesoionic oxazolones (münchnones) are active as azomethine ylides.[6] The reaction of 2 with 3-methyl-2,4-diphenyloxazolium-5-olate (12) in acetonitrile proceeded at room temperature and the evolution of $CO_2$ - the intermediate 13 undergoes a Diels-Alder cycloreversion - was finished after 2 min. Thick-layer chromatography provided 47% of the triazolium salt 14. Due to the onium charge and aromaticity of the ring, the *N*-methyl signal is shifted downfield ($\delta_H$ 3.61); it is found at δ 2.81 in the cyclic benzamidrazone 15 which resulted from the reduction of 14 by sodium borohydride.



16 17 18 19





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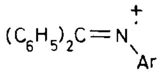

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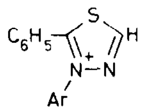

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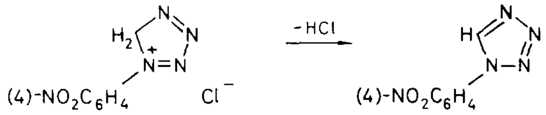
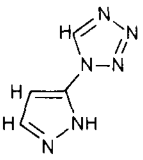
Thiocarbonyl ylides should have very high HO-LU energies because sulfur has the same low electronegativity on the Pauling scale as carbon. Diarylthioketones are converted by diazomethane at -78°C to 1,3,4-thiadiazolines which eliminate $N_2$ at -45°C generating thiocarbonyl methylides.[7,8] Equimolar amounts of thiofluorenone and diazomethane reacted in THF at -78°C in 1 min as testified by the fading of the deep color; in ether as solvent 16 was obtained crystalline.[9] The $N_2$ loss from 16 occurs at -45°C in a first-order reaction with a half-life of 9.1 min. In the presence of 1 equiv. of diazonium salt 2, the thiofluorenone *S*-methylide (17) added to the NN triple bond producing 49% of the spiro-1,3,4-thiadiazoline 19 in orange crystals (mp 257-258°C); λ(max) 392.5 nm (log ε 4.29). A high-field shift of the AA'XX' spectrum of $C_6H_4NO_2$ suggests the shielding influence of the fluorene residue and is in accordance with the addition direction. In 18 and 19 the nucleophilic methylide carbon is bonded to the electrophilic terminal nitrogen of 2.

The analogous reaction of thiobenzophenone *S*-methylide with 2 at -45°C produced only 2.5% of the pure crystalline 20 (mp 162°C) besides 18% benzophenone 4-nitrophenylhydrazone; the origin of the latter has not been studied. In the mass spectrum of 20 the fragment 21 (m/e = 302, 23%) stems from the elimination of HSCN and establishes the structure; loss of phenyl gives rise to the thiadiazolium ion 22.



23 24



25

In 1955 it was reported from this laboratory that the reaction of 4-nitrobenzenediazonium chloride with excess of diazomethane in ether furnished 12% 1-(4-nitrophenyl)tetrazole (24) besides other products.[10] The 5*H*-tetrazolium salt 23 might well be the outcome of a cycloaddition. An argument against the concerted 1,3-dipolar cycloaddition is the regiochemistry, but a two-step process is facing the same difficulty. A similar compound 25 was isolated in 24% yield from pyrazole-3-diazonium chloride and diazomethane.[11]

In the formation of 23 - concerted or non-concerted - C-N and N-N bonds (75 and 39 kcal $\mathrm{mol}^{-1}$) are established as new σ bonds. A somewhat endothermic cycloaddition would not prevent the process as the subsequent aromatization renders the total reaction exothermic.

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