Monatshefte für Chemie 119, 1121—1124 (1988)

Monatshefte für Chemie
Chemical Monthly
© by Springer-Verlag 1988

Novel Reactions with Hetaryldieneamines as Activated Olefins

A. Messmer, Gy. Hajós, G. Timári, and **A. Gelléri**

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary

(Received 7 July 1987. Accepted 5 August 1987)

In the presence of appropriate reagents, hetaryldieneamines were found to react with only one of their two double bonds. Reaction with aryldiazonium salts resulted in hydrazone **2** while azodicarboxylic ester afforded substitution product **3**. In reactions with benzofuroxan and arylazides, hetaryldieneamines reacted as enamines to yield quinoxaline (**4**) and *v*-triazole derivatives (**5**), respectively.

(Keywords: Cycloaddition; Dieneamine; Diels Alder reaction of inverse electron demand)

Neue Reaktionen mit Hetaryldienaminen als aktivierte Olefine

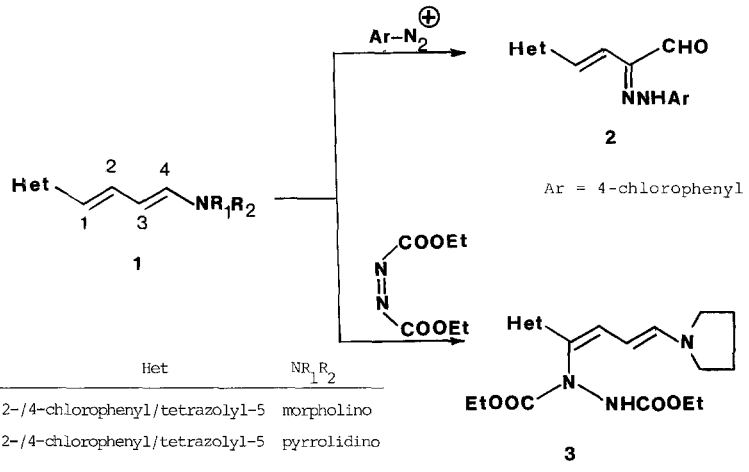
Mit entsprechenden Reagenzien traten Hetaryldienamine nur mit einer der zwei Doppelbindungen in Reaktion. Die Umsetzung mit Aryldiazoniumsalzen führte zum Hydrazon **2**, während Azodicarbonsäureester das Substitutionsprodukt **3** ergab. In Reaktionen mit Benzofuroxan und mit Arylaziden reagierten die Dienamine **1** als Enamine und es entstanden Chinoxalin- (**4**) bzw. Triazolderivate (**5**).

Introduction

Recently we have published [1] that hetaryldieneamines **1**—available from fused azolium and azinium salts [2–4]—easily undergo cycloaddition of [4 + 2] and [6 + 4] type. The latter reaction allowed, i.a., elaboration of a simple route to hetarylazulenes. In both of these cycloadditions, dieneamines take part as diene components contributing with their both double bonds.

We found now that these push-pull hetaryldieneamines can also react with certain reagents used commonly as dienophiles in such an unexpected manner as if they had only one double bond (e.g. as an enamine or ethenylhetarene).

Scheme 1



	Het	NR_1R_2
a	2-/4-chlorophenyl/tetrazolyl-5	morpholino
b	2-/4-chlorophenyl/tetrazolyl-5	pyrrolidino

Results and Discussion

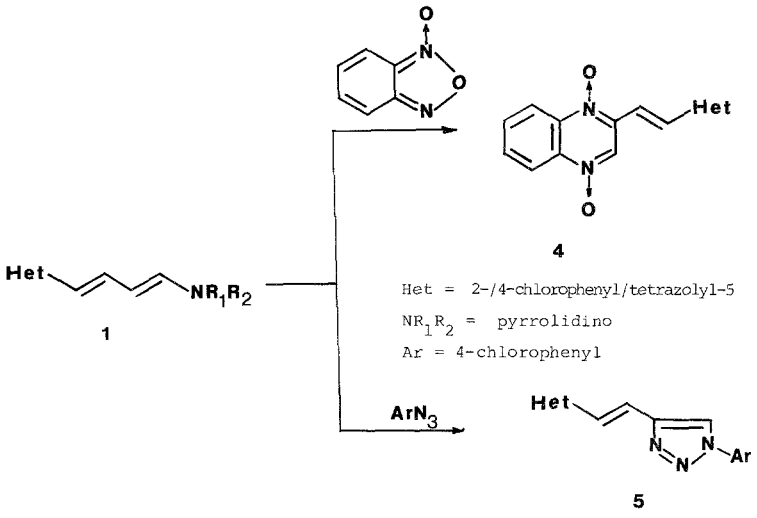
Reaction of **1** with aryldiazonium salt known as dienophile in other cases [5] led to formation of hydrazone **2** which can be rationalized by an electrophilic attack of the diazonium salt at the electron rich C-3 carbon atom followed by hydrolysis of the amine moiety. An analogous behaviour of enamines has been reported [6].

Similarly, an unexpected behaviour of dieneamine **1** with azodicarboxylic ester was found [7]. This reaction afforded, instead of the expected cycloadduct, a hydrazino-substituted dieneamine **3** the structure of which was unambiguously proved by ^{1}H-NMR: the observed coupling constant ($J_{3,4} = 13$ Hz; a typical value for such double bonds of dieneamines [8]) and the chemical shift of the central proton of the three neighbouring ones (5.8 ppm) could not be assigned to an alternative structure implying C-4 substitution.

Both of the above cases showed that dieneamine **1** reacted with only one of its double bonds. This finding prompted us to study the reactivity of **1** with 4-pi systems especially preferred for a *Diels-Alder* reaction of inverse electron demand. Such a reaction has earlier been reported: benzofuroxane was found to react with diethylaminobutadiene to give rise to quinoxalylenamines [9].

We found now that hetaryldieneamine **1** also reacted with this reagent and yielded hetarylethenylquinoxaline (**4**) in good yield. While in the cited work, however, the 3,4-double bond of the diene chain reacted, in our case regiospecific formation of the reverse product formed by contribution of the 1,2-double bond of **1** was found. This difference (compared to the

Scheme 2



earlier findings with simple dieneamines) is probably due to the presence of the hetaryl group diminishing the electronic density of the 3,4-double bond to a considerable extent.

Arylazides generally known as reactive 1,3-dipoles also easily gave cycloadducts with **1** and yielded hetarylethenyl-*v*-triazoles. Earlier results [10] showed that in such reactions always the nitrogen of arylazides adjacent to the aryl group is directed to the carbon atom of the dipolarophile bearing the amino function. On this basis, for the product of this cycloaddition, structure **5** was supposed.

Experimental Part

The nmr spectra were obtained on a Varian XL-100 equipment, the ir spectra on a Specord 75 apparatus. Melting points are uncorrected.

Reaction of Hetaryldieneamines (**1**) *with Aryldiazonium Salts*

A solution of *p*-chlorophenyldiazonium fluoroborate (0.24 g, 1 mmol) in acetonitrile (5 ml) was added in one portion to a solution of dieneamine **1 a** (0.32 g, 1 mmol) in dichloromethane (5 ml). An orange precipitate was first formed and disappeared then rapidly. The resulting solution was evaporated and the solid residue was triturated with chloroform. Pale yellow crystals deposited which were filtered off and were recrystallized from aquous dimethyl sulfoxide to give 0.21 g (52%) of hydrazone **2**; m.p. 208–209 °C.

Anal. calcd. for $C_{17}H_{12}Cl_2N_6O$ (387.2): N 21.69, Cl 18.39. Found: N 21.45, Cl 18.49. ^{1}H-NMR (*DMSO-d_6*): 9.56 (d, 1 H, H-4, J = 2.5 Hz), 7.92 (dd, 1 H, J = 16 Hz and 2.5 Hz), 7.98 (d, 1 H, H-1), 8.15–7.72 (AA′BB′, 4 H, H-tetrazolylaryl), 7.51–7.39 (AA′BB″, 4 H, H-hydrazinoaryl) ppm.

1-[2-(4-Chlorophenyl)tetrazolyl-5]-1-(1,2-diethoxycarbonylhidrazino)-4-pyrrolidino-butadiene (**3**)

Diethyl azodicarboxylate (0.44 g, 2.6 mmol) was added dropwise to a dry-ice-cold and stirred solution of 1-[2-(4-chlorophenyl)tetrazolyl-5]-4-pyrrolidinobutadiene (**1 b**) (0.6 g, 2 mmol) in dichloromethane (10 ml). The mixture was stirred at − 80 °C for additional 30 min and was then evaporated *in vacuo* to give a red oil. Trituration with ethanol afforded a solid which was filtered, washed thoroughly with ethanol and ether and finally recrystallized from ethanol to give 0.57 g (60%) of yellow needles, m.p. 161–162 °C.

Anal. calcd. for $C_{21}H_{26}N_7O_4Cl$ (475.88): C 52.95, H 5.50, N 20.59, Cl 7.45. Found: C 52.53, H 5.70, N 20.57, Cl 7.53. ^{1}H-NMR ($CDCl_3$): 8.04 and 7.50 (AA'BB', 4 H, H-*Ar*), 7.36 (d, 1 H, H-2, $J_{2,3} = 12$ Hz), 7.16 (s, 1 H, NH), 6.94 (d, 1 H, H-4, $J_{3,4} = 13$ Hz), 5.80 (dd, 1 H, H-3), 4.22 (qq, 4 H, —CH_2— ethyl), 3.38 and 1.97 (m, 8 H, H-pyrrolidine), 1.24 (t, 6 H, CH_3) ppm.

2-[1-(2-/4-Chlorophenyl/tetrazolyl-5)ethenyl]quinoxaline-1,4-dioxide (**4**)

A solution of dieneamine **1 b** (0.48 g, 1.5 mmol) and benzofuroxane (0.27 g, 2 mmol) in acetonitrile (8 ml) was refluxed for 8 h. The crude product separated as red crystals (0.31 g, 59%) was filtered and then purified by chromatography on silica (as eluent, a mixture of chloroform—acetone—ether—*t*-butanol in a ratio of 14 : 2 : 3 : 1 was used; $R_f = 0.35$) to give 0.08 g (23%) of product, m.p. 207–208 °C.

Anal. calcd. for $C_{17}H_{10}ClN_6O$ (349.77): N 24.03, Cl 10.47. Found: N 23.67, Cl 10.45. ^{1}H-NMR (*DMSO-d*$_6$): 9.27 (s, 1 H, H-3), 8.09–7.68 (m, 8 H, H-*Ar*), 6.87 and 6.28 (dd, 2 H, H-ethylene) ppm.

trans-1-[2-(4-Chlorophenyl)tetrazolyl-5]-2-[1-(4-chlorophenyl)-v-triazolyl-4]-ethylene (**5**)

A solution of dieneamine **1 b** (0.32 g, 1 mmol) and 4-chlorophenylazide (0.22 g, 1.5 mmol) in acetonitrile (10 ml) was refluxed for 8 h. A yellow precipitate deposited which was recrystallized from dimethylformamide to give 0.20 g (51%) of colorless needles, m.p. 220–222 °C.

Anal. calcd. for $C_{17}H_{11}Cl_2N_7$ (384.24): N 25.52, Cl 18.46. Found: N 25.67, Cl 18.80. ^{1}H-NMR (trifluoroacetic acid): 8.7 (s, 1 H, H-triazolyl), 7.88 and 7.69 (2 s, 2 H, H-ethenyl, $J = 16.5$ Hz), 8.2–7.5 (m, 8 H, H-aryl).

References

[1] *Messmer A, Hajós Gy, Timári G* (1988) Monatsh 119: 1113
[2] *Gelléri A, Messmer A* (1973) Tetrahedron Lett 14: 4295
[3] *Hajós Gy, Messmer A* (1984) J Heterocyclic Chem 21: 809
[4] *Mörler I, Kröhnke F* (1971) Liebigs Ann Chem 744: 65
[5] *Carlson BA, Sheppard WA, Webster OW* (1975) J Am Chem Soc 97: 5291
[6] *Shvedov VJ, Almuchova LB, Grinev AN* (1965) Zh Org Chim 1: 879
[7] *Schmidt RR, Wagner A* (1982) Synthesis 958
[8] *Jackman LM, Sternhell S* (1969) Application of NMR spectroscopy in organic chemistry, 2nd edn. Pergamon Press, New York, p 185
[9] a) *Devi P, Sandhu PS, Thyagarajan G* (1979) J Chem Soc Chem Comm 710; b) *Borah HN, Devi P, Shandhu JS, Baruah JN* (1984) Tetrahedron 40: 1617
[10] *Meilahn MK, Cox B, Munk ME* (1975) J Org Chem 40: 819