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[7+1]- AND [11+1]-CYCLOREACTIONS OF DIAZO-AZOLES WITH 1-NUCLEOPHILE-1-ELECTROPHILES (YLIDES) TO 3H-PYRAZOLO[5,1-c][1,2,4]TRIAZOLES AND 3H-[1,2,4]TRIAZOLO[4,3-b]INDAZOLES [1)]

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Diazo-azoles react as 1,7- or 1,11-dipoles with ylides such as diazoalkanes or such of the phosphonium-, sulfonium-, pyridinium- and sulfene-type to form 3H-pyrazolo[5,1-c][1,2,4]triazoles and 3H-[1,2,4]-triazolo[4,3-b]indazoles in a [7+1]- or [11+1]-cycloreaction.

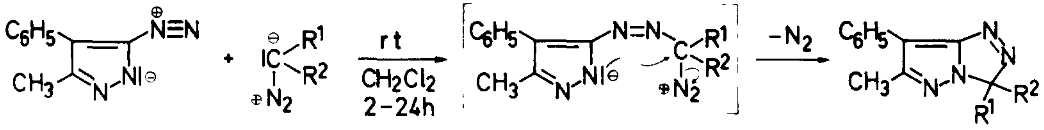
In cycloaddition reactions with carbenes, these usually act as transient 1,1-species.

The criteria of cycloaddition reactions as given by Huisgen[2)] are not fulfilled when instead of the carbene its precursor already reacts with the substrate. In a primary addition and subsequent intramolecular substitution for instance, the same cycle is formed as on formal participation of the carbene. Such and other reactions of two or more components, which irrespective of the mechanism lead to the formation of cycles, are proposed to be designated as cycloreactions. Consequently cycloaddition reactions represent a subset of cycloreactions.

In the reactions of diazo-azoles **1** and **4** [3)] with diazoalkanes **2a** - **2d** [4)] in dichloromethane at room temperature we found examples of [7+1]- and [11+1]-cycloreactions. Under loss of nitrogen 3H-pyrazolo[5,1-c][1,2,4]triazoles **3a** - **3c** and 3H-[1,2,4]triazolo[4,3-b]indazoles **5b** - **5d** are formed, respectively (see scheme 1 and table 1).

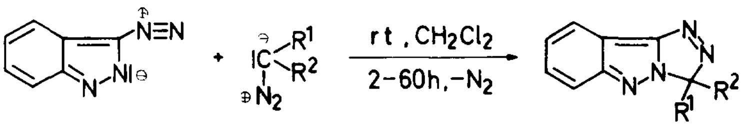
Scheme 1

[7+1]cycloreaction



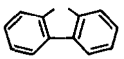
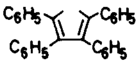
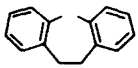
1 2a-c 3a-c

[11+1]cycloreaction



4 2b-d 5b-d

Table 1 : Yields and melting points of 3H-azolo[1,2,4]triazoles 3 and 5 [a].

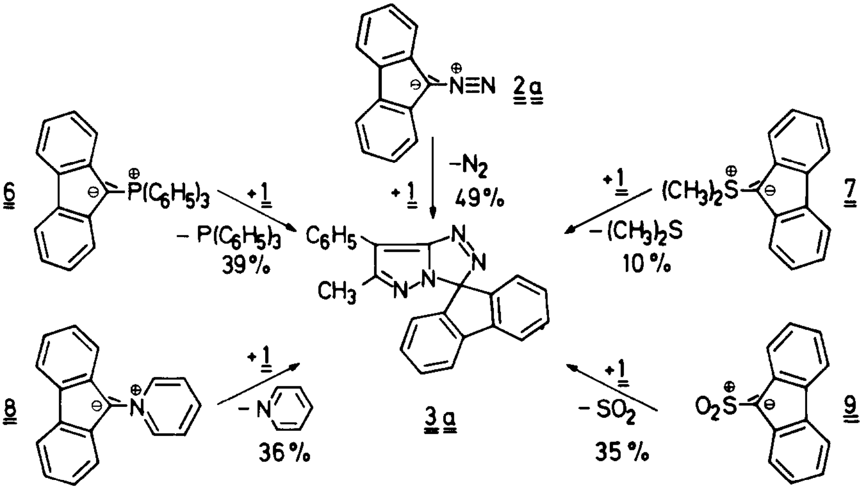
2, 3, 5	R^1	R^2	yield [%] 3	yield [%] 5	m.p. [°C] 3	m.p. [°C] 5
a			49	-	197-199	-
b	C_6H_5	C_6H_5	28	87	156-158	204-205
c			40	42	182-184	190-192
d			-	54	-	153-155

[a] The analytical data (microanalyses and UV, IR, ^{1}H-NMR, ^{13}C-NMR) of all products are in accordance with the assigned structures.

Herein the diazoalkane 2 reacts ylid-like as a 1-nucleophile-1-electrophile[5]. The new, disubstituted 3H-azolo[1,2,4]triazoles 3a - 3c and 5b - 5d are yellow compounds which exhibit strong fluorescence in the long wavelength UV region. At their melting points they decompose partially with elimination of nitrogen.

In the cycloreactions with diazo-pyrazole 1 we used other 1-nucleophile-1-electrophiles which are analogous to 2a, such as the phosphonium-, sulfonium- and pyridinium-ylides 6 6), 7 7), 8 8) and the sulfene 9 9). Under loss of triphenylphosphane, dimethylsulfide, pyridine or sulfur dioxide, respectively, we obtained the same 3H-spiro-pyrazolo[5,1-c][1,2,4]triazole 3a which we had prepared from 1 and 2a (see scheme 2).

Scheme 2



The comparison between reactions of diazo-containing ylides and diazo-free ylides confirms the two-step mechanism of the cycloreaction which is shown in scheme 1. Thus, the eliminated nitrogen in reactions 1 or 4 with 2a - 2d must originate from the diazoalkanes.

References and notes :

1) Reactions with diazo-azoles, 2nd communication. This work was supported by the Deutsche Forschungsgemeinschaft, the BASF Aktiengesellschaft and the Haarmann+Reimer GmbH. - 1st communication : G. Ege, K. Gilbert and H. Franz, Synthesis 1977, 556.

2) R. Huisgen, Angew. Chem. 80, 329 (1968); Angew. Chem. Int. Ed. Engl. 7, 321 (1968).

3) General procedure for the preparation of diazo-azoles : See ref. 1).

4) M. Regitz, Diazoalkane, Thieme, Stuttgart, 1977.

5) We define a 1-nucleophile-1-electrophile as a compound in which a special atom first reacts as a nucleophile and afterwards as an electrophile. The type of the [n+1]cycloreaction, with ylides as 1-nucleophile-1-electrophiles, is known for the cases n = 2, n = 4 and n = 9; for n = 2 see : A.W. Johnson, Ylid Chemistry, Academic Press, New York, 1966; C.D. Gutsche, Org. Reactions 8, 364 (1958); n = 4 : G.F. Bettinetti and L. Capretti, Gazz. Chim. Ital. 95, 33 (1965); n = 9 : R. Huisgen and R. Fleischmann, Liebigs Ann. Chem. 623, 47 (1959).

6) L.A. Pinck and G.E. Hilbert, J. Am. Chem. Soc. 69, 723 (1947).

7) A.W. Johnson and R.B. LaCount, ibid. 83, 417 (1961).

8) L.A. Pinck and G.E. Hilbert, ibid. 68, 2011 (1946).

9) In situ generated according to : L.A. Paquette, J.P Freeman and R.W. Houser, J. Org. Chem. 34, 2901 (1969).

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