

Reactions of Dienamines with Aryl Azides

H. Cardoen, S. Toppet, G. Smets, and G. L'abbé

Department of Chemistry, Laboratory of Macromolecular and Organic Chemistry,
University of Louvain, B-3030 Heverlee, Belgium

Received March 17, 1972

Sir:

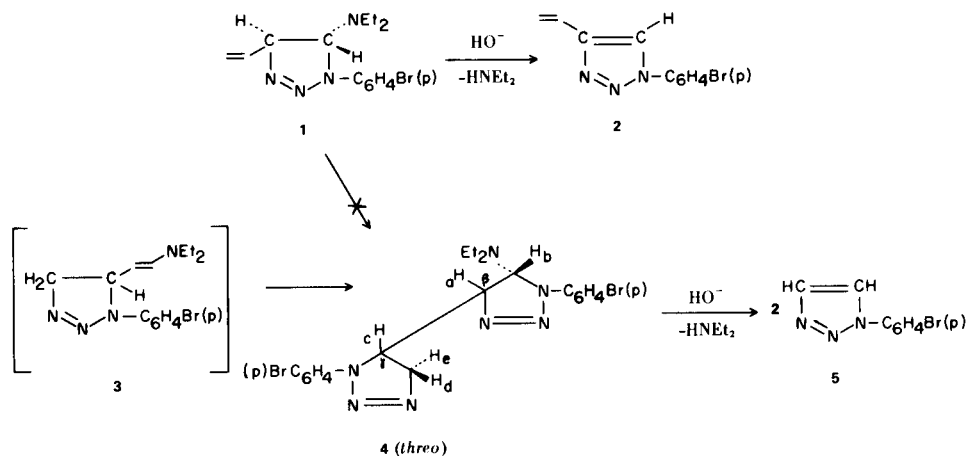
Recently (1), two research groups described the reactions of dienamines with sulfonyl azides which provided a new method for the synthesis of vinyl diazomethanes and the corresponding pyrazoles. Independently, we have obtained similar results from the reaction of *trans*-1-diethylamino-1,3-butadiene (2) with benzenesulfonyl azide. On the contrary, when aryl azides were used as 1,3-dipoles, the reactions with dienamines furnished mono- and bistriazolines. A typical example is described below.

p-Bromophenyl azide reacted with an equimolar amount of *trans*-1-diethylamino-1,3-butadiene (2) in chloroform at room temperature (4 days) and yielded, after crystallization from pentane, two stable adducts: **1** (47%, yellow crystals, m.p. 65°) and **4** (5%, white crystals, m.p. 150-151.5° dec.) (3). Worth mentioning is the nmr spectrum (100 MHz, deuteriobenzene, TMS) of the bistriazoline **4** which shows an ABX pattern (H_c , H_d , and H_e) combined with an AB pattern (H_a and H_b) in the region τ 5.3-7.0. The corresponding chemical shifts and coupling constants (4) are as follows:

$\tau_a = 5.4$	$J_{de} = -17.8 \pm 0.2$ Hz
$\tau_b = 5.7$	$J_{ab} = 4 \pm 0.2$ Hz
$\tau_c = 5.95$	$J_{ac} = 3.7 \pm 0.2$ Hz
$\tau_d = 6.35$	$J_{cd} = 10.3$ Hz
$\tau_e = 6.43$	$J_{ce} = 7.5$ Hz

A point of special interest here is the configuration about the $C_\beta C_\gamma$ carbon atoms. Although the other diastereoisomer is not available for comparison of nmr data, the low vicinal coupling constant, $J_{ac} = 3.7$ Hz, strongly suggests a *threo* (5) configuration for the isolated product, based on the Karplus rule (6). This points to the conclusion that the two azides have attacked the C=C double bonds of the dienamine from opposite sides (7).

Of the two pathways (**1** \rightarrow **4** and **3** \rightarrow **4**) for the formation of **4**, path **1** \rightarrow **4** must be discarded since no reaction occurred when pure **1** was treated with the azide under the same reaction conditions. Hence, enamine **3** is the intermediate in the reaction scheme and its high reactivity towards azides prevents its isolation.



Both adducts **1** and **4** were converted to triazoles, **2** (87%, m.p. 113-114°) and **5** (67%, m.p. 145-146°) respectively, when treated with base (potassium hydroxide) in refluxing methanol. Whereas the reaction **1** → **2** is well known (8), the cleavage of the bistriazolone **4** into two molecules of **5** has no precedence in the literature.

The reactions of dienamines with other types of azides are currently under study.

Acknowledgment.

The authors are indebted to the N.F.W.O. (G. L'a) and to the I.W.O.N.L. (H.C.) for fellowships.

REFERENCES

- (1) M. Regitz and G. Himbert, *Ann. Chem.*, **734**, 70 (1970); D. Pocar and R. Stradi, *Ann. Chim. (Rome)*, **61**, 181 (1971).
- (2) The method of S. Hünig and H. Kahaneck (*Chem. Ber.*, **90**, 238 (1957)), used for the preparation of the dienamine only

furnished the *trans* isomer as shown by the nmr coupling constant $J_{trans} = 13.2$ Hz.

(3) The reaction products were fully characterized by ir, nmr, mass spectra, and micro analysis.

(4) C. N. Banwell, "Nmr for Organic Chemists", D. W. Mathieson, Ed., Academic Press, London and New York, 1967, p. 85.

(5) *Erythro* and *threo* are termed on the basis of steric requirements, necessary for the application of the Karplus rule: $\text{NC}_6\text{H}_4\text{Br}$ and CHNEt_2 are the large groups.

(6) L. M. Jackman and S. Sternhell, "Applications of Nmr in Organic Chemistry", D. H. R. Barton and W. Doering, Eds., Pergamon Press, London, 1969, p. 286.

(7) In the addition of benzonitrile oxide to the same dienamine, both diastereoisomeric bisadducts have been obtained: see P. Caramella and P. Biarchessi, *Tetrahedron*, **26**, 5773 (1970). All attempts to isolate or detect the other diastereoisomer in our case failed. The rather low overall yield of the reaction is due to concurrent tar formation from the dienamine.

(8) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).