Tetrahedron Letters,Vol.23,No.10,pp 1103-1104,1982 0040-4039/82/101103-02$03.00/0
Printed in Great Britain

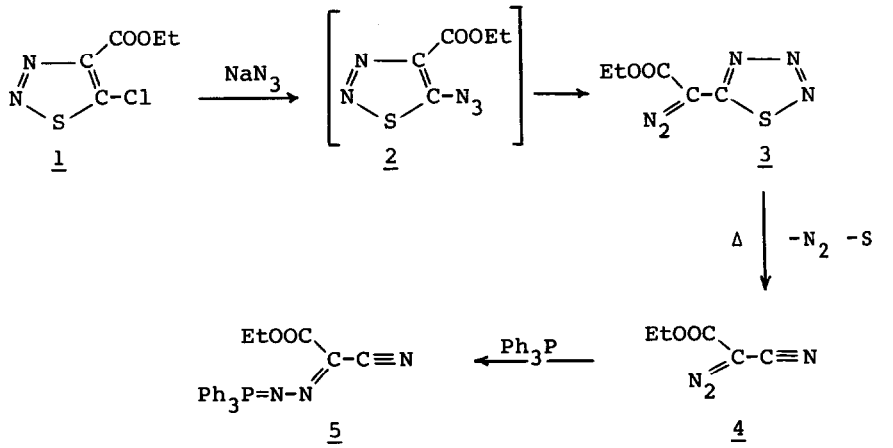
SPONTANEOUS RING TRANSFORMATION OF A 5-AZIDO-1,2,3-THIADIAZOLE

Gerrit L'abbé, Martine Deketele and Jean-Paul Dekerk
Department of Chemistry, University of Leuven
Celestijnenlaan 200F, B-3030 Heverlee, Belgium.

ABSTRACT. The reaction of 4-carbethoxy-5-chloro-1,2,3-thiadiazole (1) with sodium azide results in the formation of ethyl α-thiatriazolyldiazoacetate (3) instead of the corresponding azide (2). Two plausible mechanisms for this new rearrangement are formulated.

Unlike the corresponding ketones, α-diazothioketones and thioacyl azides are unknown. During their preparation, they cyclize to 1,2,3-thiadiazoles and 1,2,3,4-thiatriazoles respectively.[1] With this in mind we have observed an interesting rearrangement in our attempts to prepare the unknown 5-azido-1,2,3-thiadiazoles.

When 4-carbethoxy-5-chloro-1,2,3-thiadiazole[2] 1 was treated with sodium azide under the conditions normally used to prepare the azide (acetone/water, 0°C), a pale yellow oil having structure 3 was obtained in 73% yield. Although the IR (neat, 2125 and 1695 cm^{-1}) and ^1H NMR spectra ($CDCl_3$, triplet at δ 1.42, quartet at 4.49 ppm) are consistent with both structures 2 and 3, the ^{13}C NMR spectrum ($CDCl_3$) definitely rules out structure 2 in favour of structure 3. Indeed, the C_4 (δ 149.3) and C_5 (δ 152.5) ring carbon absorptions of 1 have shifted to δ 64.5 and 167.3 ppm respectively in the product. The high-field resonance at δ 64.5 cannot be attributed to a carbon absorption of a thiadiazole nucleus,[3] but is at the expected position for a diazoalkane. For instance, methyl phenyldiazoacetate exhibits a diazo carbon absorption at δ 62.7 ppm.[4]

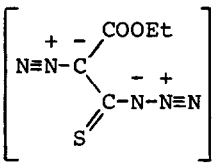


Confirmation of structure 3 was obtained by thermolysis of the product at 60°C (5 h) in chloroform solution, giving a quantitative yield of ethyl α-cyanodiazoacetate 4 as a pale yellow liquid. The diazonitrile was converted into the yellow phosphazine 5 (mp 168-169°C) on treatment with triphenylphosphine. This compound was also obtained directly when 3 was allowed to react with triphenylphosphine in ether at room temperature (yield 66%). The structures of 4 and 5 were unambiguously assigned on the basis of the following characteristic spectral data:

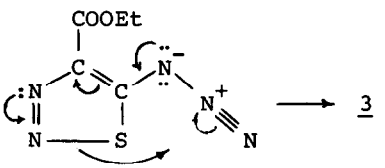
4: IR (neat) 2220 (s, C≡N), 2140 (vs, C=N_2), 1720 (s br, C=O) cm^{-1}
^{13}C NMR ($CDCl_3$) δ 51.1 (br, CN_2), 107.5 (C≡N), 161.4 (C=O)

5: IR (KBr) 2195 (m, C≡N), 1720 (s, C=O) cm^{-1}
^{13}C NMR ($CDCl_3$) δ 113.4 (C≡N), 117.1 (d, C=N-N=P, $^3J_{CP}$ = 51.7 Hz), 162.9 (C=O).

Mechanistically, the formation of 3 from 2 can be explained by assuming the open-chain intermediate 6 in which the thioketone function is flanked both by a diazo and an azide function. The azide group of this unstable intermediate would then cause cyclization to 3. An alternative mechanism involves a concerted valence isomerization as shown on structure 2*. This is referred to as a bond-switch mechanism.[5]



6



2*

Further experiments are being carried out to examine the generality of this rearrangement by varying the substituent at the 4-position of the 1,2,3-thiadiazole.

ACKNOWLEDGEMENT. M. Deketele and J-P. Dekerk are indebted to the I.W.O.N.L. and the N.F.W.O. (Belgium) respectively for a fellowship. Financial support from the University (Research Grants) and from the Ministry of National Education is gratefully acknowledged.

REFERENCES.

1. K. A. Jensen and C. Pedersen, Adv. Heterocycl. Chem., 3, 263 (1964); E. C. Taylor and I. J. Turchi, Chem. Rev., 79, 181 (1979); R. Huisgen, Angew. Chem. Int. Ed. Engl., 19, 947 (1980).
2. J. Goerdeler and G. Gnad, Chem. Ber., 99, 1618 (1966).
3. J. H. Looker, N. A. Khatri, R. B. Patterson, and C. A. Kingsbury, J. Heterocycl. Chem., 15, 1383 (1978).
4. M-H. Bui-Nguyen, H. Dahn, and J. F. McGarrity, Helv. Chim. Acta, 63, 63 (1980).
5. For other examples of bond switch, see E. Klingsberg, Lect. Heterocycl. Chem., 1, S-19 (1972); A. J. Boulton, ibid., 2, S-45 (1974); K. Akiba, S. Arai, T. Tsuchiya, Y. Yamamoto, and F. Iwasaki, Angew. Chem. Int. Ed. Engl., 18, 166 (1979); K. Akiba, T. Kobayashi, and S. Arai, J. Am. Chem. Soc., 101, 5857 (1979).

(Received in UK 23 December 1981)