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UNEXPECTED REARRANGEMENT INVOLVING AZIDE-OLEFIN CYCLOADDITION IN MORPHINAN SERIES

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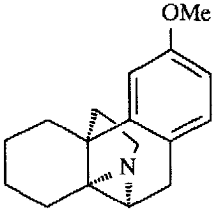
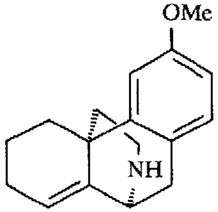
Summary : *Tricyclic azide 3b rearranges into imine 4, instead of the expected morphinan derivative.*

It has been established that aziridine **1** rearranges easily into morphinan **2** [1]. A possible route to aziridine derivatives **1** would be through the intramolecular azide-olefin 1,3-dipolar cycloaddition of tricyclic compounds such as **3b**, followed by nitrogen extrusion in the resulting intermediate triazoline **5** [2].



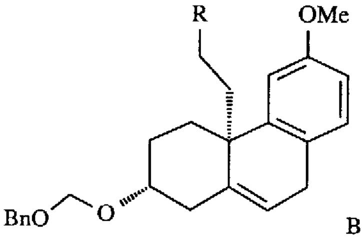
1



2

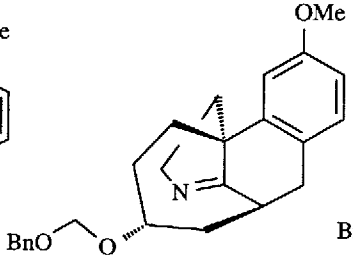
In order to test this methodology, the starting tricyclic azide **3b** was prepared from alcohol **3a** [3] (MsCl/Et_3N then NaN_3; DMF, 60 °C, 20 h). Surprisingly, this azide was found to be very unstable ; it rearranged partially during its preparation, and completely by flash chromatography on silica gel, giving, instead of the expected triazoline, aziridine or morphinan derivatives, the tetracyclic imine **4** [4] (50-55 % overall yield from alcohol **3a**).

It should be noted that this rearrangement does not depend on the stereochemistry of the benzyloxy-methoxy group in compound **3a** : a similar transformation was indeed observed when the starting material, epimeric at C-7, was used.

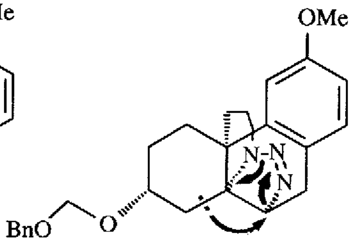


3

a R = OH
b R = N_3



4



5

Unusual structure **4** [5] was unambiguously determined by extensive spectroscopic studies, including 2D NMR experiments (COSY and ^1H-^{13}C heteronuclear shift correlation).

The formation of compound **4** from azide **3b** probably involves the expected intermediate triazoline **5**, which rearranges, as depicted. A somewhat similar rearrangement has been reported by Smith [6].

Acknowledgments. *We thank Drs. A. Guingant and D. Desmaele for stimulating discussions and Mr. C. Chassagnard for NMR spectra recording.*

References and Notes

1. I. Monković, T.T. Conway, H. Wong, Y.G. Perron, J. Patcher, B. Belleau, J. Am. Chem. Soc., **95**, 7910 (1973).
2. For a recent review on azide chemistry, see : E.F.V. Scriven, K. Turnbull, Chem. Rev., **88**, 297 (1988).
3. Preparation of alcohol **3a** [oil, $[\alpha]_D^{20}$ -20° (c = 1.5, EtOH)] will be reported elsewhere.
4. **4** : oil ; $[\alpha]_D^{20}$ +109° (c = 2.5, EtOH) ; MS (CI, NH_3) m/e : 392 (M + H^+) ; IR (neat) 1650, 1610 cm^{-1} ; ^1H NMR (200 MHz, $CDCl_3$) δ : 1.4 (ddd, J = 11.0, 6.0, 1.75 Hz, 1H) 2.2 (ddd, J = 13, 5, 3 Hz, 1H) 2.47 (ddd, J = 15, 9, 8.7 Hz, 1H) 2.8 (dd, J = 15, 2 Hz, 1H) 3.02 (dd, J = 15, 5 Hz, 1H) 3.25 (m, 1H) 3.8 (s, 3H) 3.95 (m, 1H) 4.56 (d, J = 10 Hz, 1H) 4.63 (d, J = 10 Hz, 1H) 4.72 (d, J = 12 Hz, 1H) 4.78 (d, J = 12 Hz, 1H) 6.75 (m, 2H) 7.02 (d, J = 7.5 Hz, 1H) 7.3 (m, 5H) ; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ : 30.7 (t) 32.4 (t) 35.1 (d) 35.5 (t) 39.0 (t) 41.4 (t) 55.3 (q) 56.3 (s) 57.4 (t) 69.6 (t) 73.0 (d) 92.9 (t) 111.9 (d) 112.0 (d) 126.4 (s) 127.5 (d) 127.7 (d, 2C) 128.3 (d, 2C) 130.4 (d) 138.3 (s) 144.5 (s) 158.9 (s) 183.3 (s).
5. Sub-structure related to compound **4** was looked for through "CAS on-line" and showed to be a new tetracyclic type skeleton.
6. P.A.S. Smith, S.S.P. Chou, J. Org. Chem., **46**, 3970 (1981).

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