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MESOIONIC TRIAZOLE BY REACTION OF A SUBSTITUTED 4,4-DICHLORO β-LACTAM WITH PHENYLHYDRAZINE

B. Le Clef, L. Vermylen, H.G. Viehe*
Laboratoire de Chimie Organique

M. Van Meerssche*, G. Germain, J.P. Declercq,
Laboratoire de Chimie Physique et de Cristallographie

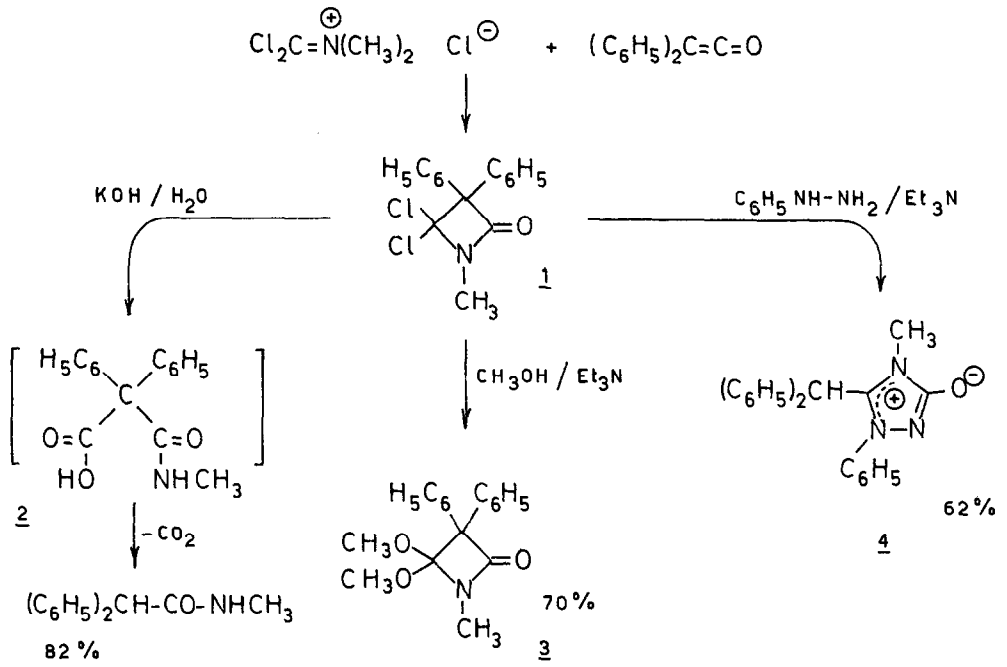
Université de Louvain, Place L. Pasteur, 1 B-1348 Louvain-la-Neuve
Belgium

Summary : β-Lactam 1 undergoes substitution of its chlorine atoms in the presence of methanol but surprisingly produces the triazole 4 upon reaction with phenylhydrazine.

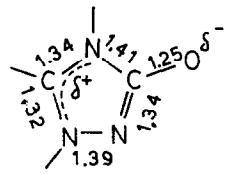
The condensation of diphenylketene and N,N-dimethyl dichloromethyleniminium chloride (Phosgeniminium salt) [1] has recently been described to produce the new β-lactam 1 [2]. Its two reactive centers, the carbonyl and the dichloromethylene groups have now been examined. Hydroxylation and methoxylation lead to chlorine substitution. Thus, when heated in an aqueous KOH solution, 1 gives diphenylacetamide probably via the malonic intermediate 2, whereas stirring 1 in methanol at room temperature in the presence of two equivalents of triethylamine affords 4,4-dimethoxy β-lactam 3. [IR ($CHCl_3$) : $\nu(cm^{-1})$: 1760 (CO) ; NMR ($CDCl_3$) : δ(ppm) : 3.00 (3H,s), 3.10 (6H,s), 7.00-7.20 (10H,m) ; m.p. : 172°]. Phenylhydrazine ($CHCl_3$, 60 hr reflux) produces by cleavage of the C_2-C_3 bond the mesoionic triazole 4 for which the structure proof is derived from X Ray analysis [IR ($CHCl_3$) : $\nu(cm^{-1})$: 1670, 1600 ; NMR ($CDCl_3$) : δ(ppm) : 3.00 (3H,s), 5.90 (1H,s), 7.10-7.80 (15H,m) : UV : λ_{max}(nm) : 290 [3] ; m.p.: 248°]

The crystal data of 4 are as follow : $C_{22}H_{19}N_3O$, monoclinic, space group $P2_1/c$ with a = 11.553(4), b = 14.937(4), c = 17.253(5)Å, β = 143.80(2)° ; V = 1758.4(9) Å^3. Four molecules per unit cell (Z = 4) give D_x = 1.29 g cm^{-3}. The intensity data were recorded on a Picker diffractometer using Ni filtered Cuκα radiation (λ = 1.5418 Å). 2198 reflections were measured of which 1948, with $I > 2.5\sigma(I)$, were used in the structure determination (by MULTAN 74 [4]) and refined [5]. Hydrogen atoms positions were found on a Fourier difference and introduced in the refinement. The final R value is 0.050.

The list of atomic coordinates and molecular dimensions has been deposited with the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, England.



The triazole ring is planar. Bond lengths (Å) into the cycle are in accordance with the following electronic scheme :



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