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REVISION OF THE STRUCTURE OF A REACTION PRODUCT FROM BUTANEDIONE AND ETHANOLAMINE

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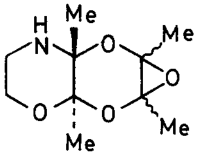
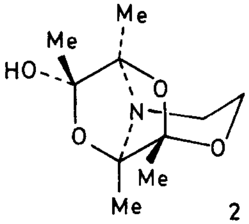
Summary: On the basis of X-ray crystallographic analysis, it is shown that the reaction of ethanolamine with butanedione in excess affords the tricyclic hemiketal 2 and not the epoxy-derivative 1 as we have previously reported.

In a previous paper[1], we reported that the reaction of ethanolamine with butanedione in excess gave 2,3,9,10-tetramethyl-2,3-epoxy-8-aza-1,4,5-trioxadecalin (1). The structure of 1 was assigned on the basis of i.r., ^{1}H and ^{13}C n.m.r., and elemental analysis. We report here a correction of the formerly assigned structure 1 to 5,6,8,9-tetramethyl-1-aza-4,7,10-trioxatricyclo $[4,3,0,1^{5,9}]$decan-8-ol (2) deduced from an X-ray crystallographic analysis. The compound 2, which was formerly identified as 1, was prepared in 70% yield by the reaction of ethanolamine with butanedione in excess (molar ratio=2) in benzene as solvent, after 4 h at room temperature.

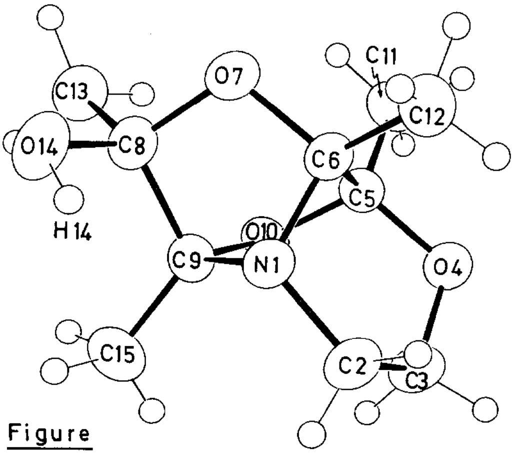


1



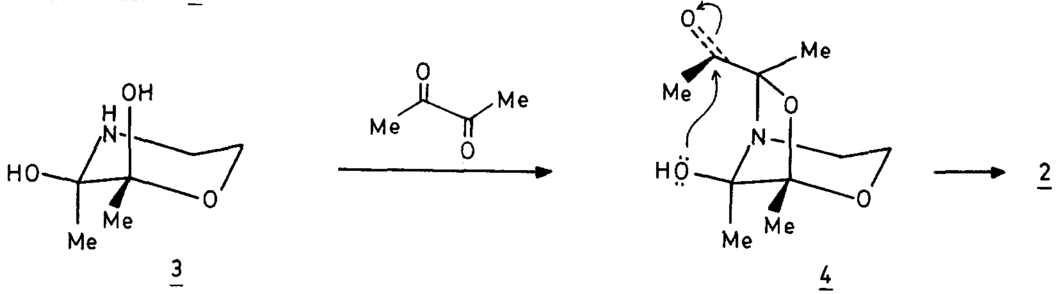
2

The structure of 2 was unambiguosly verified by single crystal X-ray analysis[2,3]. The resulting ORTEP drawing is shown in Figure[4]. Thus, the ^{1}H n.m.r. data should be reinterpreted. The observed long range coupling (1.1 Hz) must be assigned to the methyl group and the OH proton both at C8 in 2. The fixed equatorial position of the N lone pair of electrons with respect to the adjacent methylene group accounts for the highly negative value (-14.9 Hz) of the corresponding geminal coupling.



Figure

The mechanism of the present reaction is considered to proceed by initial 1,2-addition of the ethanolamine to the butanedione generating a cis-2,3-dihydroxymorpholine 3. The formation of the tricyclic hemiketal 2 may arise through the intermediate γ-hydroxyketone 4, formed by 1,1-addition of the 2-aminoethanol moiety in 3 to butanedione[4], with subsequent intramolecular cyclization (Scheme). Conformation 4, shown in the Scheme, should be the most stable on account of the absence of dipolar repulsions between the carbonyl group and the nearer oxigen atoms. This accounts for the exclusive formation of the diastereoisomer 2.



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References and notes

1. B. Alcaide, R. Pérez-Ossorio, J. Plumet, M. Rico and I.M. Rodríguez-Campos, Tetrahedron Lett., 1381 (1986).

2. The system is monoclinic, space group $P2_1$, Z = 2, a = 7.775 (2), b = 9.871 (4), c = 6.893 (2) Å, β = 91.96 (1), V = 528,7 (1) $Å^3$, R = 0.030. This means that the analyzed crystal corresponds to one of the enantiomers and not to the racemate as could be expected from the origin of compound 2. In fact, 2 is optically inactive. Thus, this should be a case of spontaneous optical resolution by crystallization.

3. The atomic coordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

4. Figure is a perspective drawing of the final X-ray model, showing its structural chirality with η = 1.557 (9). See, M. Martínez-Ripoll and J. Fayos, Z. Kristallogr., 152, 189 (1980) and D. Rogers, Acta Cryst., A37, 734 (1981).

5. N-Methylethanolamine reacts with butanedione in this manner. B. Alcaide et al., to be published.

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