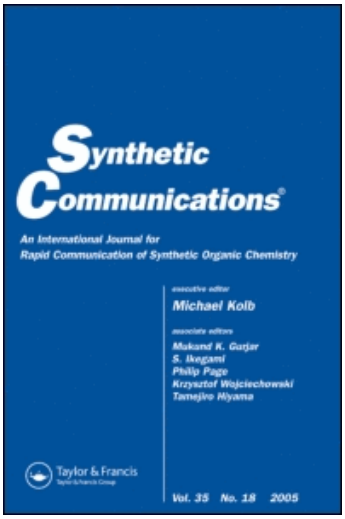

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The Correct Structures of the ortho-Cyclized Products in the Cycloalkylations of 1-m-Methoxybenzyl-4,4a,5,6,7,8-Hexahydronaphthalen-2(3H)-One and 1-m-Methoxybenzyl-Octalins : X-Ray Structure Determination of (±)-4-Methoxy-9a-Carbamorphinan-16-One

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SYNTHETIC COMMUNICATIONS, 22(17), 2509-2512 (1992)

THE CORRECT STRUCTURES OF THE ORTHO-CYCLIZED PRODUCTS IN THE CYCLOALKYLATIONS OF 1-m-METHOXYBENZYL-4,4a,5,6,7,8-HEXAHYDRONAPHTHALEN-2(3H)-ONE AND 1-m-METHOXYBENZYL-OCTALINS : X-RAY STRUCTURE DETERMINATION OF (±)-4-METHOXY-9a-CARBAMORPHINAN-16-ONE

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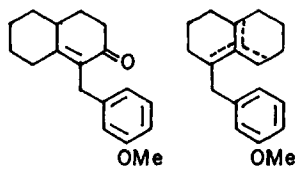
ABSTRACT: The previously assigned (ref.1) ortho-cycloalkylated product from the reaction of **1** and **2** respectively, with ortho-phosphosphoric acid and polyphosphoric acid, has been corrected to (±)-4-methoxy-9a-carbamorphinan-16-one (**6**) and the respective ether **7** by a single crystal X-ray structure determination of **6**.

In 1990 we (S.P. and U.R.G) reported[1] Grew's type cyclization of the methoxybenzyloctalone **1** with orthophosphoric acid resulting in a mixture of a para and an ortho cycloalkylated keto-ethers **3** and **A** (m.p. 120°C) along with a partially aromatized cyclodehydration product **5**. While the structure and stereochemistry of **3** was confirmed through its conversion to ether **4** of known stereostructure, the gross structures of **A** and

the corresponding ether B were assigned as the decahydrobenzo[d,e]anthracene derivatives 9 and 10, respectively, from elemental analyses and spectral data. The polyphosphoric acid catalyzed cyclization of the methoxybenzyloctalins 2 gave a mixture of the stereoisomeric bridged ethers 4 and 8 along with the ether B.



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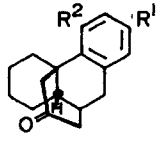
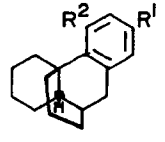
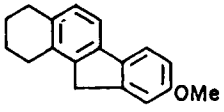




3, R^1 = OMe; R^2 = H 4, R^1 = OMe; R^2 = H

6, R^1 = H; R^2 = OMe 7, R^1 = H; R^2 = OMe



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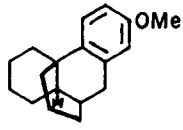

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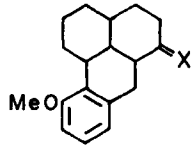

9, X = O

10, X = H_2

The failures in some attempted chemical transformations of A and B mitigated against the correctness of their assigned structures 9 and 10. An X-ray structure determination of A has now established its stereostructure as 6 (Fig.1) and the corresponding ether B as 7. Formation of ortho-cyclization product, as a minor compound, in similar bridged cyclization is known[2].

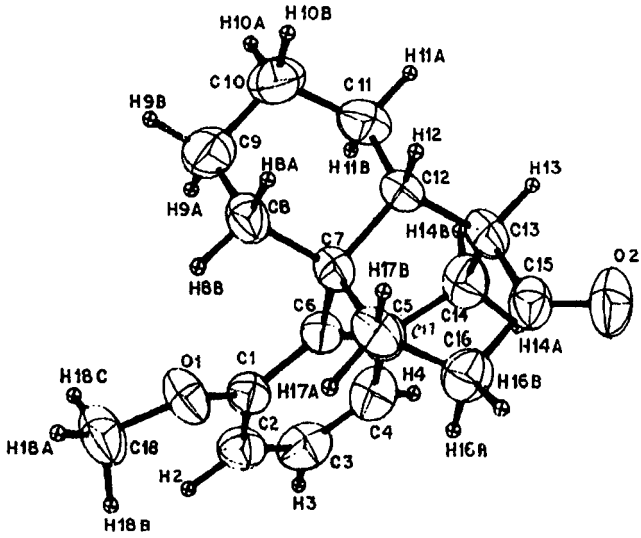

Fig.1 : ORTEP diagram of **6** with all atoms labellings

EXPERIMENTAL

4-Methoxy-9a-carbamorphinan-16-one (6). m.p. 120°C, prepared as described in the original paper[1], was recrystallized from methanol for crystallographic analysis - Crystal data for compound **6** : $C_{18}H_{22}O_2$, M = 270.4, a = 9.607(3), b = 11.170(4), c = 7.518(2) Å, α = 107.35(2), β = 92.99(3), γ = 70.04(3)°, U = 723.4 Å^3, space group PI, Z = 2, D_c = 1.24 g cm^{-3}, μ (Cu-K_α) = 5.85 cm^{-1}. A Rigaku AFCSR diffractometer with a 12 KW rotating anode generator using CuK_α radiation (λ = 1.54184 Å) in the W-2 θ scan mode was used to record 2301 reflections. Lorentz polarisation and absorption corrections were applied. The structure was solved by direct method (MULTAN 88) and refined by full-matrix least-squares analysis with anisotropic thermal parameters to non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms. Refinement converged at

R = 0.049, R_w = 0.0513 for 1730 reflections with $|F_o| \geq 4\sigma(|F_o|)$. Final difference fourier map showed max/min peak heights of 0.2486 and -0.1363 e $\AA^{-3}$ respectively. Atomic coordinates bond lengths and angles, thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Structure factors are available on request from authors.

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