

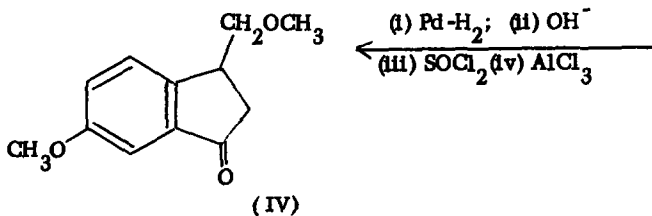
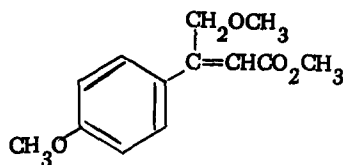
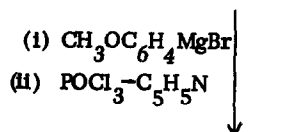
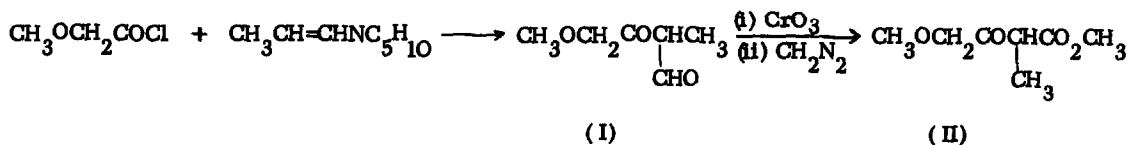
COMMENT ON A PAPER BY SAMIR CHATTERJEE.

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All claims in the paper cited (Tetrahedron Lett. 3249 (1979)) should be accepted as fact after, but not before, verification by independent experiment.

A recent letter¹ purported to describe the synthesis of a potential intermediate for synthesis of aconitine. A chart of the earlier stages claimed is shown below.



The substance (I) is described as having ν_{max} 1730, 1715 cm^{-1} . These frequencies would indeed be expected for isolated aliphatic formyl and keto groups, but (I) is an acyclic enolizable β -ketoaldehyde and such substances in general exist predominantly² as α -hydroxymethylene ketones and show infra-red absorption characteristic of this form. Further, such substances on chromic oxidation tend to be destroyed by cleavage and not oxidized smoothly (and without decarboxylation) to β -keto acids (a 93% overall yield from

(I) to (II) was claimed).

The conversion of (II) to (III) requires (i) an abnormal reaction of a β -keto ester with a Grignard reagent (the normal outcome³ is formation of the magnesium enolate of the β -keto ester) and (ii) a so-called "dehydration" involving the wholly unexplained disappearance of a C-methyl group. The formulation of (III) is no clerical error since evidence is presented indicating the presence of an olefinic hydrogen in (III) and of two hydrogens adjacent to the carbonyl group in the derived indanone (IV) (it might be added that the indanone is assigned a boiling-point much higher than that ascribed to the ester (III), instead of the appreciably lower boiling-point that it would certainly have).

Numerous other improbabilities (and one impossibility) could be indicated in S. Chatterjee's letter. Other readers are invited to examine that letter and to form their own opinions. Mine is expressed in the synopsis (above).

¹ S. Chatterjee, Tetrahedron Lett., 3249 (1979). This letter was addressed from the Department of Chemistry, The Johns Hopkins University. Professor A. Nickon (personal communication) states that the work in question was not conducted in that department and that the letter is therefore not a contribution from that University.

² V. A. Gindin, B. A. Erschov, A. K. Kol'tsov and R. S. Noi, Doklady Akad. Nauk. SSSR 214 (1), 97 (1974) and numerous earlier papers.

³ T. Zerewitinoff, Ber. dtsch. chem. Ges., 41, 2233 (1908).

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