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REARRANGEMENTS ACCOMPANYING THE $AlCl_3$-CATALYSED CYCLISATION OF (1-PHENYLCYCLOPROPYL)ACETYL CHLORIDE

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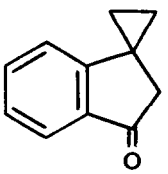
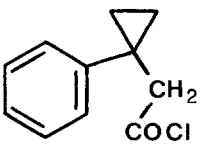
When recently we required the indanone derivative (II), the title reaction seemed to afford a convenient synthetic route. Mild conditions were dictated by the need to avoid the possibility of acid-catalysed scission of the cyclopropane ring, and we initially followed a procedure which had proved successful[1] for the cyclisation of 2-phenylcyclopropanecarbonyl chloride. In this, the acid chloride was treated with $AlCl_3$ in methylene chloride at ca. 5°, and the product mixture was then hydrolysed with refluxing sodium carbonate to destroy any unreacted acid chloride.

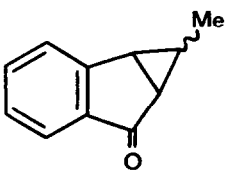
Following this procedure with (1-phenylcyclopropyl)acetyl chloride (I), we were surprised to find that no (II) could be detected in the products, and that a principal volatile component (ca. 30%) was in fact a mixture of the indanones (III), isomeric with the desired ketone.



(II)



(I)

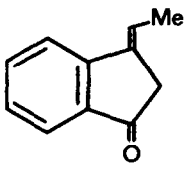


(III)

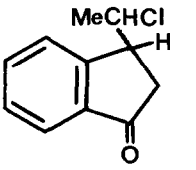
The indanones (III) were separated by preparative gas liquid chromatography, and the major isomer was found to have the methyl group cis to the cyclopentanone ring (n.m.r.).

Three less volatile products were also obtained by a combination of preparative g.l.c. and t.l.c. and the identity of these afforded an insight into the sequence of events which gave rise to (III). In order of decreasing volatility they were found to be the ethylidene-indanone (IV)[2,3] (m.p. 51°), and its diastereomeric HCl adducts (V). Since (IV) could have arisen by acid-catalysed isomerisation of (II), the cyclisation was repeated at a slightly lower temperature (-5°) and its progress was monitored. Shortly after completion of the addition of (I) (20 min), a new product could be isolated in excellent yield, and this indeed proved to be (II) (m.p. 43-45°). Further reaction, however, led to the disappearance of (II)

and its successive replacement by (IV) and then by (V). Transformation of the isomers of (V) into (III) did not occur under the reaction conditions. Instead, it was found to have



(IV)



(V)

been effected by the basic conditions employed during work-up. As expected, this base-promoted 1,3-elimination was stereospecific, the endo-isomer of (III) being formed exclusively from one isomer of (V), the exo-product being formed exclusively from the other.

An interesting feature of this reaction sequence is the direction of addition of HCl to (IV), no doubt influenced by the co-ordination of aluminium to the carbonyl oxygen. Curiously, we have been unable to find reaction conditions, other than those actually starting with (I), under which $AlCl_3$ will promote the addition of HCl to (IV).

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REFERENCES AND FOOTNOTES

1. T.Jacquier and P.Besinet, Bull.Soc.Chim.France, 989, (1957); G.R.Elling, R.C.Hahn, and G.Schwab, J.Am.Chem.Soc., 95, 5659 (1973).

2. The failure to detect any Nuclear Overhauser Effect in the aromatic proton signal on irradiation at the methyl resonance lends support to the stereochemical assignment.

3. The possibility that this might tautomerise to 3-ethylindenone was explored using pyridine/NaOD/D_2O. Instantaneous exchange of the C-2 protons occurred, but the methyl doublet remained unchanged for several hours. Therefore no exchange of the olefinic hydrogen could have occurred, indicating a very low tendency for protonation of the intermediate enol or enolate to form the (antiaromatic) indenone structure.