Spiro-α-lactams derived from Adamantane

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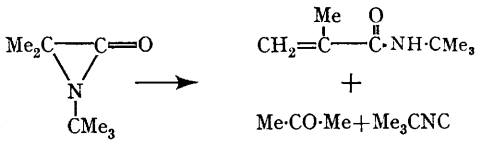
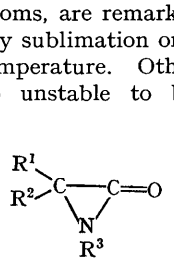
THE first aliphatic α-lactam to be isolated in a pure condition was (I).[1] However, this compound underwent slow decomposition even at room temperature, and in refluxing ether its thermal decomposition was completed in less than 1 hr. to afford *N*-t-butylmethacrylamide as the major product, and acetone and t-butyl isocyanide as the minor products. It was reasoned that if this

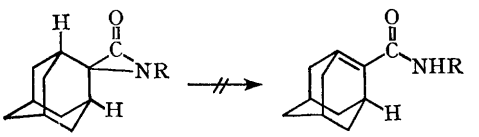


(I)

eliminative isomerization involving β-hydrogen atoms can be avoided, then a thermally more stable α-lactam should be obtained. Indeed, the α-lactams (II),[2] (III),[3] and (IV),† which are devoid of β-hydrogen atoms, are remarkably stable, and can be purified by sublimation or distillation well above room temperature. Other aliphatic α-lactams are too unstable to be isolated and examined. We now report the isolation of two other α-lactams [(V) and (VI)], which contain β-hydrogen atoms, but their involvement in eliminative isomerization is blocked because they occupy bridgehead positions.



(II) $R^1 = Bu^t$, $R^2 = H$, $R^3 = Bu^t$
(III) $R^1 = R^3 = 1$-Adamantyl, $R^2 = H$
(IV) $R^1 = 1$-Adamantyl, $R^2 = H$, $R^3 = Bu^t$



(V) R=Bu^t
(VI) R=1-adamantyl ($C_{10}H_{15}$)

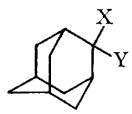
2-Methyleneadamantane (VII)[4] was treated with diborane, and the organoboranes decomposed by alkaline hydrogen peroxide to yield a mixture of alcohols consisting mainly of 2-(hydroxymethyl)-adamantane. A solution of this mixture of alcohols in acetone was added to Jones reagent to afford adamantane-2-carboxylic acid (VIII), in 46% overall yield from (VII). This acid was refluxed with thionyl chloride for 30 min.; the resulting acid chloride (IX) was then allowed to react with bromine in boiling carbon tetrachloride until conversion to (X) was complete (n.m.r.), and the reaction mixture was treated with t-butylamine to obtain, in 76% yield [from (VIII)], the bromoamide (XI). Reaction of (XI) with potassium t-butoxide in ether at 0° afforded the aziridinone (V) as a colourless liquid.

Treatment of crude (X) with 1-aminoadamantane in presence of triethylamine produced (XII) in

† Compound (IV), m.p. 55·0—56·5°, was prepared by a method analogous to that used for the preparation of (III). Its thermal and chemical stability is intermediate between that of (II) and (III). The isolation of (IV) has also been reported by K. Bott, *Angew. Chem. Internat. Edn.*, 1967, **6**, 946.

67% yield [from (VIII)]. When (XII) was allowed to react with potassium t-butoxide in ether at 0°, the aziridinone (VI) was obtained as a white solid (decomposes below its m.p.).

Although the reaction of (XI) and (XII) with one molar equivalent of potassium t-butoxide did not effect complete conversion to the corresponding α-lactams, the use of a 50% excess of base led to complete conversion of the bromo-amides to the α-lactams without the detection of any other carbonyl compounds. This is in sharp contrast to other spiro-α-lactams which could not be isolated either because they were too unstable or because they were inseparable from the starting bromo-amides.[5] The α-lactams (V) and (VI) are considerably more stable than (I), since their complete decomposition at 50° requires as long as 45—60 min. Moreover, in contrast to all other aliphatic α-lactams [except (II), (III), and (IV)] which are said to react "swiftly with methanol at 0°",[2] (V) and (VI) undergo complete decomposition in the presence of methanol at room temperature only after 20—30 min. We are currently studying the nature of the decomposition products, as well as other reactions of these α-lactams.



(VII) X,Y = CH_2
(VIII) X = CO_2H, Y = H
(IX) X = CO·Cl, Y = H

(X) X = CO·Cl, Y = Br
(XI) X = CO·NH·Bu^t, Y = Br
(XII) X = CO·NH·$C_{10}H_{15}$, Y = Br

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