OLEFINIC CYCLIZATION OF α-CARBAMOYL-α-THIOCARBOCATION

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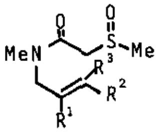
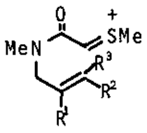
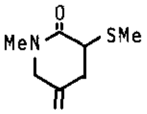
The α-carbamoyl-α-thiocarbocation ($R\overset{+}{S}=CHCONR'_2$), the Pummerer reaction intermediate of α-sulfinylacetamide [$RS(O)CH_2CONR'_2$], was found to behave as a highly reactive initiating center for cationic olefin cyclization. Thus, treatment of N-(2-methyl-2-propenyl)-N-methyl-α-(methylsulfinyl)acetamide (Ia) with $(CF_3CO)_2O$ in CH_2Cl_2 caused the cyclization through a Pummerer reaction intermediate (A, R^1=Me, R^2=R^3=H) to give the six-membered lactams II and III in 43 and 35% yields. Under the same reaction conditions, N-2-butenyl-N-methyl-α-(methylsulfinyl)acetamide (Ib) afforded the five-membered lactam IV in 92% yield and N-(3-methyl-2-butenyl)-N-methyl-α-(methylsulfinyl)acetamide (Ic) gave a mixture of the five-membered lactams V and VI (ca. 4:1) in 93% yield. Treatment of N-2-propenyl-N-methyl-α-(methylsulfinyl)acetamide (Id) by a similar method to that employed for the cyclization of Ia-c did not afford a cyclized product but a Pummerer rearrangement product VII. However, further treatment of VII with CF_3COOH (in the absence of CH_2Cl_2) caused the cyclization to give the five-memered lactams VIII and IX in 9 and 39% yields. Similar treatment of X derived from N-2-propenyl-N-methyl-α-(phenylsulfinyl)acetamide (Ie) gave the tricyclic compound XI in 33% yield along with the five-membered lactams XII (21%) and XIII (14%).



(Ia) R^1=Me, R^2=R^3=H
(Ib) R^1=R^3=H, R^2=Me
(Ic) R^1=H, R^2=R^3=Me



(A)



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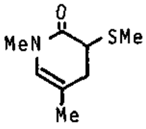

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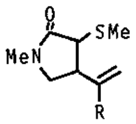
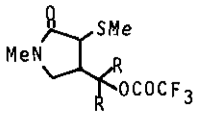
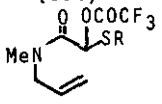


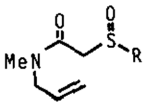
(IV) R=H
(V) R=Me



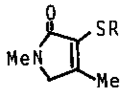
(VI) R=Me
(VIII) R=H



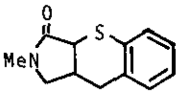
(VII) R=Me
(X) R=Ph



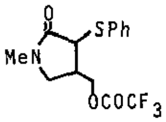
(Id) R=Me
(Ie) R=Ph



(IX) R=Me
(XIII) R=Ph



(XI)



(XII)