

SYNTHESIS OF IMINOAZIRIDINES FROM CARBODIIMIDES AND DIAZOESTERS :

A new example of transition metal salt catalysed reactions of carbenes

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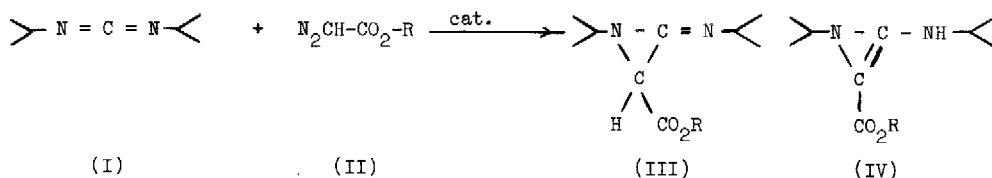
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Summary : Alkyl diazoacetates react with N,N'-diisopropylcarbodiimide in the presence of transition metal salts (e.g. copper triflate or rhodium (II) acetate) to give 1-isopropyl-2-alkoxycarbonyl-3-isopropylimino-aziridine in good yield. The reaction takes place at room temperature without formation of the formal dimer of the carbene (maleate and fumarate).

The cyclopropanation of multiple-bonds through cycloaddition of carbenes generated by decomposition of diazoesters is a classical procedure for the synthesis of three-membered rings^{1a,b}. The reaction is less generally applied to unsaturated heteroatomic compounds, but aziridines have been prepared from imines by this procedure^{2a,b,c}.

In the particular case of carbodiimides, MARTVON and coworkers³ observe the 1,3-dipolar addition of diazomethane on a C=N bond of the substrate. The isolated product is a triazoline which rearranges spontaneously to the corresponding triazole.

In a general investigation of the catalytic activity of transition metal derivatives in the reactions of diazocompounds on nitrogen-containing unsaturated compounds^{4a,b}, we have observed the specific formation of the iminoaziridine (III) in good yield during the reaction of diazoacetic acid esters (II) with N,N'-diisopropylcarbodiimide (I). The reaction takes place catalytically in the presence of copper (II) trifluoromethanesulphonate (copper triflate) or of rhodium (II) acetate.



According to a reported procedure^{4a}, the diazoester (0.01 M) is slowly introduced into a solution of catalyst (0.00025 M) in carbodiimide (0.02 M). Nitrogen evolution is observed immediately at the beginning of addition of the reactant. After 24 h, the excess of carbodiimide is removed by distillation under vacuo. The product (III) of the reaction is collected

as a colorless oil which solidifies in white needles. The compound is purified by crystallization in pentane at -10°C . (M.P. ($\text{R}=\text{CH}_3$) : $39.5 - 40^{\circ}\text{C}$; ($\text{R}=\text{C}_2\text{H}_5$) : $47-49^{\circ}\text{C}$; ($\text{R}=\text{n},\text{C}_4\text{H}_9$) : $57-59^{\circ}\text{C}$). The yield is of 70 % calculated on the diazoester. Maleate and fumarate (the usual by-products of the reactions of diazoesters) are completely absent even in the raw material as shown by G.L.C. In fact only a single compound could be detected beside the diimide in excess and the missing 30 % may be accounted for by the presence of polymeric residue in the distillation flask.

In the absence of catalyst, the nitrogen evolution is observed only at 150°C and runs to completion within 180 minutes (yield : 15 %).

Identification of product (III, $\text{R}=\text{CH}_3$) : The elemental analysis corresponds to the formula ($\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_2$). (Calculated : C, 60.6; H, 9.15; N, 14.14 % ; found : C, 60.6; H, 9.5; N, 14.4 %) The mass spectrum shows a main peak at $M/e = 198$ (calculated : 198) and fragments at $M/e = 183$ ($\text{M}^+ - \text{CH}_3$), 155 ($\text{M}^+ - \text{C}_3\text{H}_7$), 139 ($\text{M}^+ - \text{CH}_3 - \text{CO}_2$), 72 ($\text{CH} - \text{CO}_2 - \text{CH}_3$). The i.r. spectrum shows the absence of the typical cumulene absorption at 2148 cm^{-1} and the presence of two new bands at 1725 ($\text{C}=\text{O}$ ester) and 1665 ($\text{C}=\text{N}$ - imine) cm^{-1} . This last absorption band allows the rejection of formula IV.

The ^1H n.m.r. spectrum (100 MHz, TMS as reference) shows sing lets at δ (ppm) = 5.33 ($\underline{\text{H}}$ aziridine), 3.71 ($\underline{\text{CH}}_3\text{-O}$), two heptuplets ($\underline{\text{CH}}$ isopropyl) at 4.14 ($^3\text{J} = 6.7$) ($\text{C} = \text{N} - \underline{\text{CH}}$) and 3.64 ($^3\text{J} = 6.3$) ($\underline{\text{N}} - \underline{\text{CH}}$) and two doublets (corresponding $\underline{\text{CH}}_3$ isopropyl) at 1.16 ($^3\text{J} = 6.7$) and 1.03 ($^3\text{J} = 6.3$ Hz).

The ^{13}C n.m.r. spectrum (total decoupling, TMS as reference) shows signals at 150.9 ppm ($\underline{\text{C}}=\text{O}$), 147 ($\underline{\text{C}}=\text{N}$), 58.6 ($\underline{\text{CH}}_3\text{-O}$), 84.6 ($\underline{\text{CH}}$ aziridine) as well as the typical peaks of both isopropyl groups (46.7 and 45.2 for the two different $\underline{\text{CH}}$ isopropyl moieties and 25 and 20.7 for the corresponding $\underline{\text{CH}}_3$ groups).

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