Although this elimination reaction was forseen in the thermolysis of some particular salts 2,6,7 it was not noticed during the study of the base-induced decompositions of N-alkoxy-pyridinium salts carried out so far. This gives a fifth possible reaction for nucleophiles on theses derivatives, that can be distinguished from the substitution at C_{α} by the fact that the N-oxide produced is accompanied here by an olefinic compound and not by an alcohol.

We have studied the decomposition of salts $\underline{1}$ and $\underline{2^8}$ by 2.5 N NaOH at 25°C. Owing to the high solubility of pyridine N-oxide in water, the resulting heterocyclic products were continuously extracted by CHCl $_3$ over 24 hours and analyzed by quantitative VPC. In fact the reaction was achieved within a few minutes, as shown by the NMR study performed in 2.5 N NaOD in D $_2$ O; the deuterium content reported below was deduced from the spectra recorded after 15 min.

Decomposition Products

+	N-oxide	Deoxy-heterocycle	Deuteration in -2 and -6
1: Pyrn-och ₂ ch ₂ co ₂ h, no ₃	78 %	3 %	95 %
$\underline{2}$: 3,5-Lut \dot{n} -OCH ₂ CH ₂ CO ₂ H, NO $\frac{1}{3}$	89 %	4 %	96 %

The results given above show that the decomposition according to eq. 2 is highly predominant, the classical decomposition being here very reduced. The nucleophilic substitution at C_{α} would normally also produce an N-oxide but here it is not observed to any detectable extent as shown in NMR by the ratio acrylate / N-oxide = 1, and by the absence of hydracrylate signals.

The high percentage observed for deuteration implies a fast and almost complete base-catalyzed exchange of the -2 and -6 hydrogen atoms in $\underline{1}$ and $\underline{2}$ prior to elimination⁹, and shows that abstraction of the β -proton does not result from an intramolecular transfer affecting an ylide such as $\underline{3}$, for if this was the case the deuteration of the produced M-oxide would not exceed 50 %.

The competition between the two types of alkaline decomposition shown by eq. 1 and 2, notably in terms of the nature of the base, is presently being studied.

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SYNTHESIS OF IMINOAZIRIDINES FROM CARBODIIMIDES AND DIAZOESTERS:

A new example of transition metal salt catalysed reactions of carbenes

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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 l-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^{la,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 ha,b, we have observed the specific formation of the iminoaziridine (III) in good yield during the reaction of diazocetic 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. (R=CH $_3$): 39.5 - 40° C; (R=C $_2$ H $_5$): 47-49° C; (R=n,C $_4$ H $_9$): 57-59° 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,R=CH₃): The elemental analysis corresponds to the formula $(c_{10}H_{18}N_2O_2)$. (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 (M⁺ - CH₃), 155 (M⁺ - C₃H₇), 139 (M⁺ - CH₃-CO₂), 72 (CH-CO₂-CH₃). 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 (C=0 ester) and 1665 (C=N - imine) cm⁻¹. This last absorption band allows the rejection of formula IV. The H¹ n.m.r. spectrum (100 MHz, TMS as reference) shows sing lets at δ (ppm) = 5.33 (H aziridine), 3.71 (CH₃-O), two heptuplets (CH isopropyl) at 4.14 (3 J = 6.7) (C = N - CH[<]) and 3.64 (3 J = 6.3) (N - CH^{</2}) and two doublets (corresponding CH₃ isopropyl) at 1.16 (3 J = 6.7) and 1.03 (3 J = 6.3 Hz). The C¹³ n.m.r. spectrum (total decoupling, TMS as reference) shows signals at 150.9 ppm (C=O), 147 (C=N), 58.6 (CH₃-O-), 84.6 (CH aziridine) as well as the typical peaks of both isopropyl

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DIASTEREOTOPIC gem-DIMETHOXY GROUPS WITH A RING-PUCKERED MEISENHEIMER-TYPE 6-ADDUCT

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Equivalence of the gem-dialkoxy groups of 6-adducts is a firm notion in chemistry since the time of Meisenheimer. 1However, this situation, when it is recognized that it simply relies on the planarity (or mean planarity) of the ring for all systems reported so far, such as with cyclohexadiene $(\underline{1})^2$ or cycloheptatriene $(\underline{2})^3$ systems, is open to question.

We report, therefore, the first of-adduct where ring puckering induces nonequivalence of the gem-dialkoxy groups. Thus, during our efforts towards the total synthesis of zoanthoxanthins, 4 the idea was to induce ring puckering in a type-2 adduct by inhibiting negative charge dispersal on the seven-membered ring 3 through benzene annelation.

The idea, though unprofitable with 2-methoxy-4,5-benzotropone, where

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reluctancy towards o-quinoid forms resulted in resistance to potassium methoxide addition, worked well with 2-methoxy-3-nitro-4,5-benzotropone. In fact, on the mixing of a ca. 2.5 M solution of 2-methoxy-3-nitro-4,5-benzotropone (3) in dried DMSO with the five-fold excess of a concentrated methanolic solution of potassium methoxide, orange crystals of 4, m.p. 189° from DMSO, precipitated. The structure of 4, which is the first o-adduct isolated from troponoids, is supported by elemental analysis, by the observation that on acidification of a DMSO solution of 4, 3 is immediately reformed in quantitative yield, and, finally, by the 'H nmr