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2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** copolymerizes readily by a radicalar mechanism with maleic anhydride, an air and heat sensitive isolable charge-transfer monomer **2** being formed as intermediate. Similarly, a (more stable) adduct **4** has been prepared from **1** and TCNE. In opposition, acrylic acid adds onto the  $\Delta^4$ -oxazoline endocyclic double bond giving the acrylate **5**. The hydrolysis and hydrogenation of **1** are also reported.

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### Introduction.

Very few important applications of  $\Delta^4$ -oxazolines have been reported [1]: for example, the formation of 2-keto- $\Delta^4$ -oxazoline is a classical method for protecting amino groups in peptide chemistry [2] whereas  $\Delta^3$ -pyrrolines and furanes are respectively prepared from the reaction of acetylene dicarboxylates and ethyl fumarate with 5-carboxylate- $\Delta^4$ -oxazoline [3,4].

Up to now,  $\Delta^4$ -oxazolines have never been used in macromolecular chemistry. This is in strong opposition to  $\Delta^2$ -oxazolines, which interact easily with acrylic acid [5],  $\beta$ -propiolactone [6], or glutaric and succinic anhydrides [7] forming alternating 1:1 or 2:1 copolymers.

Moreover, few 2-imino- $\Delta^4$ -oxazolines are known, Dimroth rearrangements [8] and exchange of imino groups with isocyanates and thiocyanates [9] being their most typical reactions. Therefore, the easy availability of a 4-methoxy-2-

imino- $\Delta^4$ -oxazoline **1** in our laboratory [10] prompted us to study the chemistry of this novel oxazoline derivative; the presence of an alkoxy group being a favourable factor for modifying the reactivity of the ring towards electrophilic reagents.

### Results.

#### Formation of Charge-Transfer Complexes.

a) Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with Maleic Anhydride.

The iminoxazoline **1** reacted vigorously with maleic anhydride at room temperature in the absence of solvent to give a deep brown viscous material. When the same reaction was run under nitrogen in dry toluene as solvent ( $T = 60^\circ$ ), a dark solution was obtained from which a brown polymer corresponding to a (1:1) copolymer of both reagents could be isolated. This copolymer **3** was prepared in

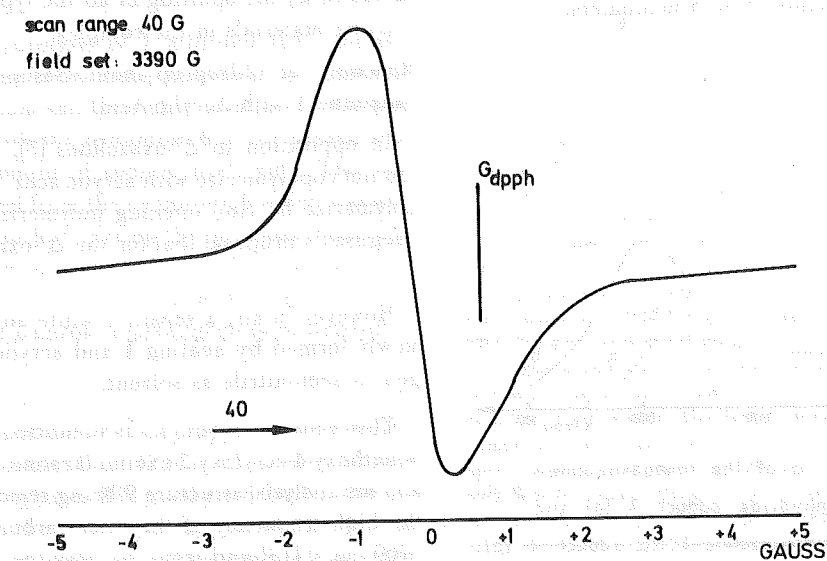


FIG. 1: EPR spectrum of the "oxazoline-maleic anhydride" copolymer **3** in DMSO ( $g = 2.0051$ )

various solvents and resulted probably from a radical chain process as shown by the presence of a pmr signal in dimethylsulfoxide ( $g = 2.0051$  from Figure 1) as well as in the solid phase (spins concentration)  $2 \times 10^{16}$  spins per gram for polymer **3**.

The ir spectrum (potassium bromide) of the copolymer **3** (see Experimental) revealed the presence of a saturated cyclic anhydride function and of an imino group: therefore the endocyclic double bond of both monomers participated in the polymerization process. Moreover, the infrared studies revealed also that some of the resulting oxazolidinyl groups rearranged themselves to cyclic urea (a typical case of Dimroth rearrangement) during the reaction as shown by the presence of an additional absorption at  $\nu = 1675 \text{ cm}^{-1}$ .

The isolation of the intermediate monomeric (1:1) adduct **2** was a difficult task owing to its high sensitivity to oxygen and to heat. An unstable violet product could however be isolated by reaction of maleic anhydride vapours with the oxazoline **1** under vacuum, followed by careful washing of the unreacted starting material with heptane and chloroform (see Experimental). The violet powder was stable under a nitrogen atmosphere but readily polymerized in the presence of air. Its elemental analysis fitted with a (1:1) oxazoline **1**-maleic anhydride adduct but its molecular weight could not be measured owing to the instability of this compound.

Structure of the adduct **2** is therefore formulated as a charge-transfer complex as shown by the groups initially present in the infrared spectrum of the starting materials (potassium bromide mull) the slight shift of the characteristic absorption of the  $\Delta^4$ -oxazoline double bond in the complex ( $\text{C}=\text{C}$  oxazoline =  $1665 \text{ cm}^{-1}$ ,  $\text{C}=\text{C}$  oxazoline in **2**,  $1660 \text{ cm}^{-1}$ ) being due to the weak interaction between the endocyclic double bonds of both monomers.

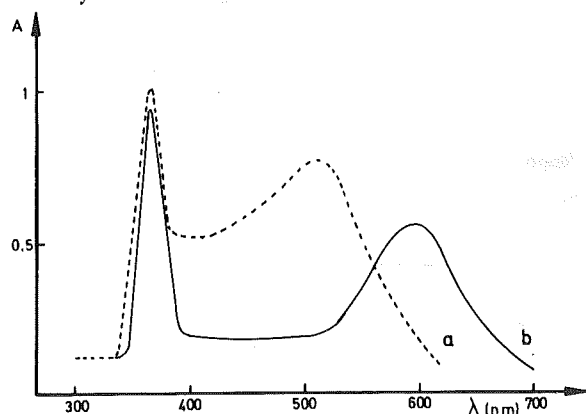


FIG. 2 : UV spectra of the iminoxazoline - maleic anhydride adduct **2** (a) and of the iminoxazoline-TCNE adduct **4** (b). Solvent: acetonitrile; Concentration: 0.016 mole/L.

The adduct **2** (as well as the copolymer **3**) appeared to be paramagnetic as shown by pmr spectroscopy ( $g = 2.0051$ ; calculated number of spins in the solid: 5.17<sup>17</sup> spins/g): a radical polymerization mechanism is thus further supported by these observations.

Moreover, the elemental analysis and the infrared spectrum of the polymerization product of **2** (prepared in the presence of air at room temperature or by heating under nitrogen) were identical: therefore, oxygen does not participate in a stoichiometric reaction with **2** and acts as an initiator for the radical polymerization process.

In fact, the reaction between maleic anhydride and 2-isopropylimino-5-methoxy- $\Delta^4$ -oxazoline **2** was reminiscent of the thermal or oxygen induced polymerizations of the intermediate charge transfer complexes between maleic anhydride and vinylalkyl groups [11].

#### b) Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **2** with Tetracyanoethylene.

Tetracyanoethylene (TCNE) formed a dark brown paramagnetic adduct **4** ( $g = 2.0050$  in methanol) with the iminoxazoline **1** (yield, 55%). In opposition to the complex **2** obtained from maleic anhydride, the TCNE adduct was not air sensitive and its preparation did not require an inert atmosphere.

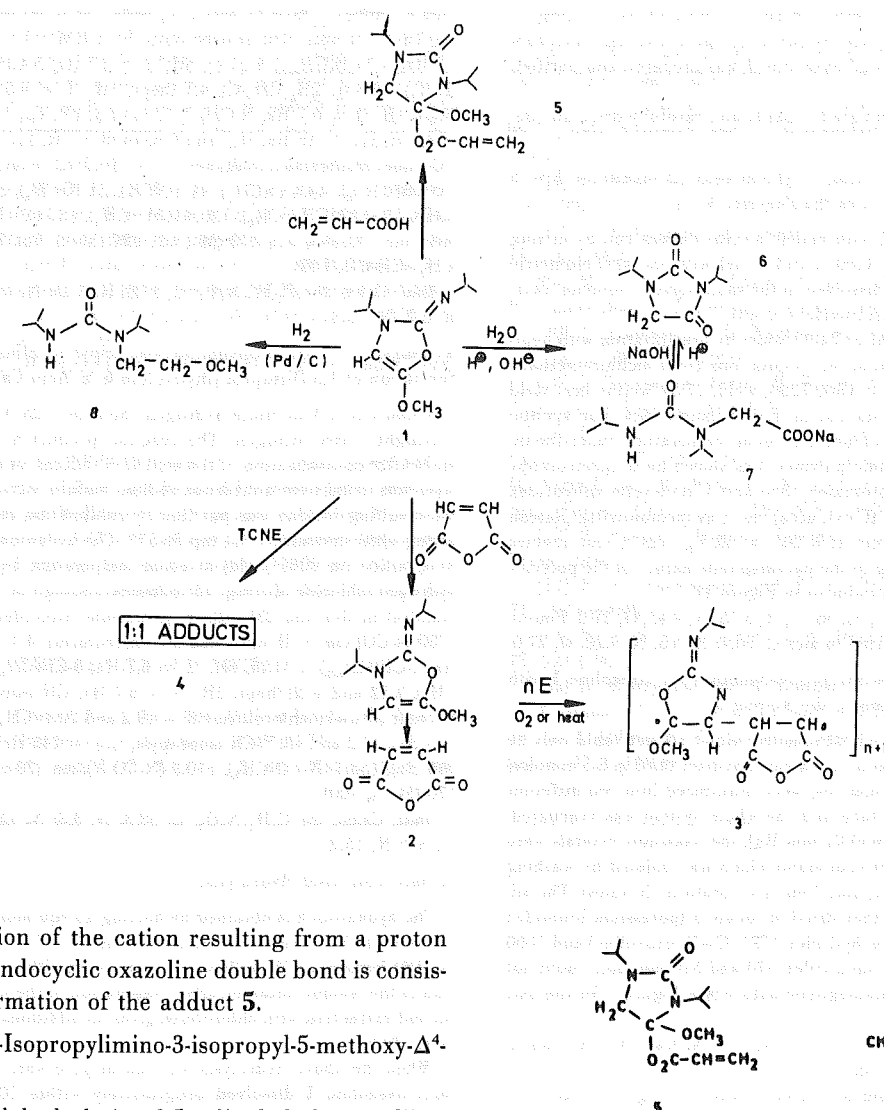
Elemental analysis and mass spectrometry determinations were in agreement with a 1:1 addition product, the uv spectra of the adducts **2** and **4** presenting the characteristic features of charge transfer complexes (Figure 2): TCNE being a stronger acceptor than maleic anhydride, its adduct absorbed at a longer wavelength (590 nm) than the maleic anhydride complex (510 nm). However, other (1:1) addition products were probably formed from TCNE as shown by the splitting of all the typical ir bands of the starting materials in the complex.

#### Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with Acrylic Acid.

In opposition to  $\Delta^2$ -oxazolines [5], the  $\Delta^4$ -oxazoline **1** did not copolymerize with acrylic acid, therefore, **1** did not polymerize by ring opening polymerization according to Saegusa's proposal [5a] for the  $\Delta^2$ -oxazolines.

However in air, a sensitive white addition product was slowly formed by heating **1** and acrylic acid under nitrogen in acetonitrile as solvent.

This addition product was identified as 1,3-diisopropyl-4-methoxy-4-acryloxy-2-oxoimidazoline **5** as shown by ir and ms analysis, structure **9** being rejected on the basis of the high frequency of the ester carbonyl group ( $\nu \text{ C}=\text{O}$ ,  $1760 \text{ cm}^{-1}$ ) [13] and from the easy thermal elimination of methyl acrylate (identified by ms) during attempted purification of **5** by preparative gc. Moreover, the efficient elec-



tronic stabilization of the cation resulting from a proton addition to the endocyclic oxazoline double bond is consistent with the formation of the adduct **5**.

#### Hydrolysis of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1**.

Acid catalysed hydrolysis of **1** afforded the 1,3-diisopropylhydantoin **6** in 90% yield. Moreover, an unstable carboxylic acid sodium salt (probable structure **7** was also detected together with the hydantoin **6** in the presence of a stoichiometric amount of sodium hydroxide. This salt was reversibly formed from the hydantoin **6** which was also quantitatively obtained by stirring the iminoxazoline **1** at  $70^\circ$  in distilled water during 30 hours. The formation of the carboxylic acid sodium salt **7** from **1** seems to be directly related to the Dimroth rearrangement of heterocycles [8].

Catalytic hydrogenation of 2-isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** on (Pd/C) afforded 1,3-diisopropyl-(2-methoxyethyl)urea **8** in good yield (90%). The acetyl type C-O link in the heterocycle appeared therefore as the more reactive site of the ring. This feature explained also the easy ring transformation of the iminoxazoline **1** to the hydantoin **6**.

#### EXPERIMENTAL

Melting points (uncorrected) were determined on a Leitz Wetzlar microscope. The ir, uv and ms spectra were recorded using a Perkin-Elmer 197, Varian Techtron 635 and Varian MAT-112 spectrometers respectively. The  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra (in deuterioacetonitrile with tetramethylsilane as internal standard (unless otherwise stated)) were determined on a Varian HA 100 and a Brücker HF 90 instrument. The pmr spectra were measured on a Varian E-12 spectrometer working in the X band ( $\nu = 9.55 \text{ GHz}$ ); the magnetic field was modulated at 100 kHz. The  $g$  values were calculated by using the 1,1-diphenyl-2-picrylhydrazyl signal as reference and the spin concentrations were estimated when comparing signals intensities with the "Strong Pitch" standard ( $3.10^{15}$  spins/cm) from Varian. Gas liquid chromatography analysis were accomplished on a Varian chromatograph 1700 (coupled with MAT-112 spectrometer) or a 2100 with FFAP or Silicone SE 30 (15%) on chromosorb W30-60 columns (length: 4 feet, diameter: 1/8 inch) using helium as the carrier gas and programming the temperature from  $70$  to  $240^\circ$  ( $15^\circ/\text{min}$ ). Molecular weight determinations were run in chloroform at  $40^\circ$  with Dampfdruck-Osmometer Knauer instrument; the standard being a solution of polystyrene (MW = 1700) in chloroform. All experiments were carried out under nitrogen atmosphere (unless otherwise specified).

Maleic anhydride, tetracyanoethylene and acrylic acid are all commercial products. They were purified by conventional processes. 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** was prepared and purified as reported in ref [10].

All the solvents were reagent-grade quality and carefully dried and degassed just before use.

Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with Maleic Anhydride. Preparation of the Polymer **3**.

The copolymerization of **1** with maleic anhydride was run by mixing solutions of the oxazoline **1** (0.005-0.015 mole) with the stoichiometric amount of maleic anhydride dissolved in the same solvent (toluene, dioxane, acetonitrile or dimethylsulfoxide) (10 ml).

The polymer was isolated after 24-90 hours by precipitation with heptane-ether and purified by three reprecipitations from dichloromethane with heptane-ether (1:1) ( $M_n = 1800-7200$ , yield, 27-52%) (the best yield and the highest  $M_n$  were obtained in dimethylsulfoxide). The spontaneous polymerisation of the adduct **2** at room temperature under the influence of air led also the same polymer **3** as shown by ir spectroscopy and analysis; ir (potassium bromide): 1860 and 1785 (cyclic anhydride), 1745 (C=N, imino) and 1675 (C=O, urea)  $\text{cm}^{-1}$ ; uv (acetonitrile): plateau from 400 nm with a maximum at  $\lambda_{205} = 32 \text{ Lg}^{-1}\text{cm}^{-1}$ ; nmr spectra could not be registered owing to the paramagnetic nature of the polymer (the pmr spectrum being reproduced in Figure 1).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_5$ : C, 56.75; H, 6.75; N, 9.45; O, 27.0. Found: (from a sample of **3** polymerized in air): C, 56.4; H, 6.5; N, 9.20; O, 27.0.

Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with Maleic Anhydride. Preparation of the Adduct **2**.

The isolation of the air and heat sensitive violet adduct could only be achieved by vapour phase reaction: maleic anhydride (0.83 g, 8.5 mmoles) and oxazoline **1** (1.68 g, 8.5 mmoles) were introduced into two different flasks connected by a glass tube and the whole system was evacuated. After 50 hours under vacuum (0.01 mm Hg), the oxazoline crystals were covered by a layer of a violet compound which was isolated by washing with 5 ml of heptane (5 times) and 2 ml of chloroform (3 times). The adduct (0.175 g, 7% yield) was then dried *in vacuo*; ir (potassium bromide): 1850 and 1780 (C=O, cyclic anhydride), 1725 (C=N, oxazoline) and 1660 (C=C, oxazoline)  $\text{cm}^{-1}$ ; uv (acetonitrile): 370 and 510 nm; nmr could not be registered owing to its paramagnetic nature (see Figure 1 for the pmr spectrum).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_5$ : C, 56.75; H, 6.75; N, 9.45; O, 27.0. Found: C, 56.6; H, 6.7; N, 9.4; O, 27.0.

The molecular weight could not be determined owing to instability.

Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with TCNE. Preparation of the Adduct **4**.

Equimolar amounts (1.6 mmoles) of the reactants were dissolved in acetonitrile (10 ml) and heated under nitrogen at 60° (66 hours). The solvent was then evaporated under vacuum at room temperature and the product (0.88 mmole, 55%) was "recrystallised" in a (70:30) carbon tetrachloride-chloroform mixture; ir (potassium bromide): 2220 and 2200 (C=N, oxazoline), 1765 and 1725 (C=N imino), 1665 and 1620 (C=C, oxazoline), 1580 and 1550 (C=C TCNE)  $\text{cm}^{-1}$  [15]; uv (acetonitrile): 370 and 590 nm (Figure 1); nmr: could not be registered owing to the paramagnetic nature of the "adduct"; ms: (70 eV),  $m/z$  326 ( $M^+$ , 22), 198 (oxazoline **1**, 40), 113 ( $M-213$ , 100).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$ : C, 58.9; H, 5.5; N, 25.8. Found: C, 58.8; H, 5.5; N, 25.7.

Reaction of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1** with Acrylic Acid. Preparation of 1,3-Diisopropyl-4-acryloxy-4-methoxy-2-oximidazole **5**.

Equimolar amounts of oxazoline **1** and acrylic acid (7.5 mmoles) were dissolved in acetonitrile (10 ml) and the solution was heated during 75 hours at 60° under nitrogen. Evaporation of the solution *in vacuo* at room temperature afforded **5** as white solid (100%), mp 63°; ir (potas-

sium bromide): 1760 (CO, acrylate), 1670 (CO, urea) and 1620 (C=C acrylate)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuterioacetone):  $\delta$  HMDS = 1.13 (d, 6H,  $^3J = 6.5$  Hz, =NCH( $\text{CH}_3$ )), 1.27 (d, 6H,  $^3J = 6.7$  Hz, N-CH( $\text{CH}_3$ )), 3.72 (s, 3H,  $\text{OCH}_3$ ), 3.98 (s, 2H,  $\text{CH}_2\text{-C}$ ), 4.1 (hept, 1H,  $^3J = 6.5$  Hz, =N-CH), 4.34 (hept, 1H,  $^3J = 6.7$  Hz, N-CH), 5.72 (d of d, 1H,  $J_{MX} = 2$  Hz,  $H_x$ ), 6.25 (d of d, 1H,  $J_{AM} = 16$  Hz,  $H_A$ ) and 6.65 (d of d, 1H,  $J_{AX} = 10$  Hz,  $H_A$ ) ppm;  $^{13}\text{C}$  nmr (deuterioacetone):  $\delta = 20.7$  (2 lines, -NCH( $\text{CH}_3$ )) and =NCH( $\text{CH}_3$ )), 44.4 (NCH $_2$ ), 49 (NCH), 51 ( $\text{OCH}_3$ ), 52.6 (=N-CH), 67.6 ( $\text{CH}_2\text{-C-O}$ ), 129 (CH=CH $_2$ ), 130.4 (CH=CH $_2$ ), 157 (C=N) and 170.1 (COO) ppm; ms: (70 eV),  $m/z$  270 ( $M^+$ , 12), 227 (M-43, 46), 170 (M-100, 55), 55 ( $\text{CH}_2=\text{CH-CO}$ , 100).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_4$ : C, 57.8; H, 8.15; N, 10.9. Found: C, 57.8; H, 8.2; N, 10.8.

Hydrolysis of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1**. Formation of 1,3-Diisopropylhydantoin **6**. a. Acid Catalyzed Hydrolysis.

A solution of **1** in dilute hydrogen chloride (1.25 *N*) was heated at 50° overnight under nitrogen. The reaction product **6** was extracted with ether after neutralization of the acid with sodium bicarbonate. The ether layer was dried over anhydrous sodium sulfate. After removal of ether, the resulting residue was purified by sublimation *in vacuo* (30°/1 mm) giving white crystals (90%), mp 56-57°. The hydantoin **6** was more readily obtained (in 90% yield) at room temperature by bubbling gaseous hydrogen chloride during 15 minutes through a solution of **1** (2.5 mmoles) in dioxane (20 ml); ir (potassium bromide): [14] 1690 (2-CO), 1750 (4-CO)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.19 (d, 6H,  $^3J = 6.7$  Hz, 1-CH( $\text{CH}_3$ )), 1.31 (d, 6H,  $^3J = 6.7$  Hz, 3-CH( $\text{CH}_3$ )), 3.73 (s, 24, ring  $\text{CH}_2$ ), 4.32 and 4.28 (hept, 2H,  $^3J = 6.7$  Hz, CH isopropyl groups) ppm;  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta = 19.2$  and 20.1 ( $\text{CH}_3$  isopropyls,  $^1J_{\text{CH}} = 128$  Hz), 43.2 and 43.7 (CH isopropyls,  $^1J_{\text{CH}} = 142$  Hz), 44.7 ( $\text{CH}_2$ ,  $^1J_{\text{CH}} = 146$  Hz), 155.7 (N-CO-CH $_2$ ), 170.2 (N-CO-N); ms: (70 eV),  $m/z$  184 ( $M^+$ , 6), 170 (M-14, 100).

Anal. Calcd. for  $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_2$ : C, 58.8; H, 8.8; N, 15.2. Found: C, 59.2; H, 8.7; N, 15.2.

b. Base Catalyzed Hydrolysis.

The hydantoin **6** is obtained by heating an equimolar solution of **1** and sodium hydroxide (2.5 mmoles) in methanol-water (1:1) (15 ml) during 180 minutes at 75° followed by extraction with chloroform. Acidification of the residue obtained after evaporation of the solvent followed by a second extraction with chloroform gives an additional amount of **6** (total yield, 90%).

When the above hydrolysis was run in pure water (15 ml) at 75°, the iminooxazoline **1** dissolved progressively within 10 hours. Extraction with chloroform without acidification gave **6** (20%) whereas the salt **7** (contaminated with some sodium hydroxide) was obtained by evaporation of the solvent. Treatment of **7** with an acid and extraction by chloroform afforded a second crop of **6** (65%); ir (potassium bromide): 1600 (CO urea and COO $^-$ ), 1400 (COO $^-$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuterium oxide):  $\delta$  1.05 and 1.2 (d, 12H,  $^3J = 6.3$  Hz,  $\text{CH}_3$  of two isopropyl groups), 3.9 (s, 2H, N-CH $_2$ -COONa) and 4.2 (m, 2H, two CH isopropyl) ppm (NB: the  $\text{CH}_2$  groups of **7** ( $\delta$  3.9 ppm) and Na glycinate ( $\delta$  3.6 ppm) are not exchanged in the presence of deuterio sodium hydroxide whereas the  $\text{CH}_2$  group of **6** is exchanged within 5 minutes under the same conditions);  $^{13}\text{C}$  nmr (internal TMS, deuterium oxide):  $\delta$  20.8 ( $^1J = 125.6$  Hz) and 23.7 ( $^1J = 126$  Hz) ( $\text{CH}_3$  of two isopropyls), 46.5 ( $^1J = 135.5$  Hz,  $\text{CH}_2$ ), 43.9 ( $^1J = 139.1$  Hz) and 47.6 ( $^1J = 138.3$  Hz) (two CH isopropyls) 160.5 (NCON) and 179.4 (COONa) ppm; ms: (70 eV)  $m/z$  184 ( $M^+$  -40(NaOH), 44 (M-140, 100).

Every attempt to isolate the free acid corresponding to **7** led to the recovery of the hydantoin **6**. In fact, an equilibrium between **6** and **7** took place at 70°.

Satisfactory analysis of the salt **7** could not be obtained as the salt remained contaminated by sodium hydroxide and decomposed to the hydantoin **6** during tentative purification.

Catalytic Hydrogenation of 2-Isopropylimino-3-isopropyl-5-methoxy- $\Delta^4$ -oxazoline **1**. Preparation of 1,3-Diisopropyl-(2-methoxyethyl)-urea **8**.

A solution of **1** (2.5 mmoles) in methanol or cyclohexane (5 ml) was stir-

red in the presence of Pd/C (10% Pd) (100 mg) as catalyst under hydrogen pressure (100 bars) at 50° during 60 hours. After evaporation of the solvent, **8** was isolated in 90% yield as a liquid which was purified by column chromatography on silicagel (0.3-0.5 mm Merck) (elution solvent: 2-propanol-benzene 15:85); ir (liquid film): 3450 (NH), 1640 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.01 (d, 6H,  $^3J = 7.0$  Hz, ( $\text{CH}_3$ ) $_2$ CHNCH $_2$ ), 1.04 (d, 6H,  $^3J = 6.7$  Hz, ( $\text{CH}_3$ ) $_2$ CHNH), 3.33 (t, 2H,  $A_2B_2$ , N-CH $_2$ ), 3.30 (s, 3H,  $\text{OCH}_3$ ), 3.38 (t, 2H,  $A_2B_2$ , -CH $_2$ O-), 3.71 (m, 1H, ( $\text{CH}_3$ ) $_2$ CH-NH), 4.35 (hept, 1H,  $^3J = 7.0$  Hz, ( $\text{CH}_3$ ) $_2$ CH-NCH $_2$ ) and 5.45 (d, 1H,  $^3J = 5.8$  Hz, NH);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  20.6 ( $^1J = 124$  Hz) and 23.5 ( $^1J = 124$  Hz) ( $\text{CH}_3$  isopropyls), 42.1 ( $^1J = 140$  Hz) and 45.7 ( $^1J = 142$  Hz) (CH isopropyls), 42.3 ( $^1J = 138$  Hz, N-CH $_2$ ), 58.9 ( $^1J = 140.4$  Hz, O-CH $_3$ ), 75.2 ( $^1J = 142$  Hz, O-CH $_2$ ) and 159.0 (CO) ppm; ms: (70 eV),  $m/z$  202 ( $M^+$ , 9), 72 (M-230, 100).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{22}\text{N}_2\text{O}_2$ : C, 59.5; H, 11.0; N, 13.85. Found: C, 59.6; H, 11.0; N, 13.9.

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#### REFERENCES AND NOTES

- [1a] J. Frump, *Chem. Rev.*, **71**, 483 (1971); [b] K. H. Scholz, H. G. Heine and W. Hartmann, *Ann. Chem.*, 1319 (1976).
- [2] J. C. Sheehan and F. S. Guziec, *J. Am. Chem. Soc.*, **94**, 6561 (1972).

[3] K. J. Niklas and C. Huisgen, Thesis der Universität, München, 1965.

[4] J. W. Lown, R. K. Smalley, G. Dallas and T. W. Maloney, *Can. J. Chem.*, **48**, 103 (1970).

[5a] T. Saegusa and Y. Kimura, *Macromolecules*, **10**, 236 (1977); [b] T. Bala Krijhnan and R. Repiyasamy, *Makromol. Chem., Rapid Commun.*, **1**, 307 (1980).

[6] L. B. Rivas and A. S. Pooley, *Bol. Soc. Chil. Quim.*, **27**, 318 (1982); *Chem. Abstr.*, **97**, 6844 (1982).

[7] S. Kobayashi, M. Isobe and T. Saegusa, *Macromolecules*, **15**, 703 (1982).

[8a] M. Wahren, *Z. Chem.*, **9**, 241 (1969); [b] E. Vowinkel and P. Gleichenhagen, *Tetrahedron Letters*, 143 (1974).

[9] T. Kumamoto, T. Nagaoka and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **39**, 1765 (1966).

[10] J. Drapier, A. Feron, R. Warin, A. J. Hubert and Ph. Teyssié, *Tetrahedron Letters*, 559 (1979).

[11a] R. Vukovic, J. Kuresevic and D. Fles, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3835 (1979) and references therein; [b] Z. Meic, D. Viric-Topic, R. Vukovic, V. Kuresevic and D. Fles, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3035 (1981) and references therein.

[12] R. Foster, "Organic Charge-transfer Complexes", Academic Press, 1969.

[13] R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

[14] N. A. S. Paul and P. J. A. Demoen, *Bull. Soc. Chem. Belg.*, **75**, 524 (1966).

[15a] B. Moszynska and A. Tramer, *J. Chem. Phys.*, **46**, 820 (1967); [b] J. Stanley, D. Smith, B. Latimer and J. P. Deulin, *J. Phys. Chem.*, **70**, 2011 (1966); [c] T. Takenaka and S. Hayashi, *Bull. Chem. Soc. Japan*, **37**, 1216 (1964).