of 3b,28-diacetoxy-18a,19a-epoxylupane (1) with TosOH. 3β,28-Diacetoxy- $18\alpha,19\alpha$ -epoxylupane  $^1$  (1) (1.0 g),  $18\alpha$ OH.H<sub>2</sub>O (0.15 g) and  $18\alpha$ O (0.2 g) in dry benzene (25 ml) were refluxed for 35 min and worked up. Chromatography on silica plates gave 3\beta,28diacetoxy-18,19-secolup-13(18)-en-19-one (0.8 g) identical with the compound above, and  $3\beta$ ,28-diacetoxy-lupa-12,19(21)-diene (10), crystallised from EtOH (0.11 g), m.p. 124 °C, Typicalises from Electric (0.11 g), in.p. 124 (7, M+),  $[\alpha]_D - 6^\circ$  (c 1.0); m/e (% rel. int.) 524 (7, M+), 464 (12), 451 (21), 404 (5), 391 (6), 274 (11), 261 (24), 225 (5), 215 (11), 214 (15), 213 (7), 203 (11), 202 (25), 201 (100), 200 (11), 199 (18), 190 (16), 189 (25), 187 (21), 185 (17), 171 (21);  $\delta$  (CCl<sub>4</sub>) 5.4 (1 H, m, C-21 proton), 5.2 (1 H, m, C-12 proton), 4.35 (1 H, m, 3αH), 3.92 (2 H, AB quart. J 11 Hz, C-28 protons), 2.9 (1 H, br. s, C-18 proton), 1.95 (6 H, s, acetyl protons), 1.1-0.8 (group of 7 methyls). Anal. C<sub>34</sub>H<sub>53</sub>O<sub>4</sub>: C, H.

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Derivatives and Reactions of Glutacondialdehyde. VI. Isoxazoline Formation from the Glutacondialdehyde Anion

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The formation of pyridines  $^1$  and pyrylium salts  $^2$  as well as 3-formyl-2(1H)-pyridinethiones  $^3$  from the glutacondial dehyde anion (1) is well-known, while the formation of other heterocyclic systems from 1 has not been reported.

Baumgarten reported 4 the reaction of 1 and hydroxylamine to give the dioxime of glutacondialdehyde to which he assigned the structures 2a or 2b:

$$\begin{bmatrix} 0 & & & \\ & & & \\ & & & \end{bmatrix}^{\Theta} + H_2NOH \longrightarrow$$

HON = CH - CH = CH - CH = CH - NHOH

or

HON=CH-CH2-CH=CH-CH=NOH

2Ь

As a part of our interest in the chemistry of 1 we have reinvestigated this reaction, and found that the anion 1 reacts with hydroxylamine in a more interesting manner than could be anticipated.4 In this contribution we wish to report that the correct structure of the reaction products is 3, thus giving a new synthesis of the ∆2-isoxazoline system:

The UV spectrum of the product showed bands at  $\lambda_{\rm max} = 215$  nm (log  $\varepsilon = 3.44$ ) indicating the absence of a highly conjugated system as in the simple glutacondialdehyde derivatives.6 The mass spectrum of the compound is in accordance with structure 3. The molecular ion peak is seen at m/e = 128, while dominant fragment ion peaks are seen at m/e = 59 and 70. The fragmentation of 3 can be rationalized in the following way:

$$HON-CH=CH_2^{-1} \leftarrow ON^{-1}$$

m/e = 59(66%)m/e = 128(6.4%)m/e = 70(100%)

The <sup>1</sup>H NMR spectrum of 3 shows in the cases of H(4a) and H(4b) the usual pattern of nonequivalent ring protons. The chemical shift and coupling constants are given in Table 1. The values of the coupling constants and chemical shift are in close agreement with values in similar compounds as reported by several authors. The <sup>13</sup>C NMR spectrum of 3 consists of five lines as stated in Table 1. The assignment of the lines has been done by recording the gated decoupled spectrum.

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Table 1. Chemical shift $\delta(i)$ and coupling constants $J_{ij}$ in 3	Table 1.	Chemical	$\mathbf{shift}$	$\delta(i)^a$	and	coupling	constants	$J_{ii}$	in	3
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Atom (i)	$\delta(\mathrm{i})$	Atoms (i, j)	$ J_{f ij} $ (Hz)
H(3)	7.4 (7.4)	H(3), H(4a)	1.7 (1.7)
$\mathbf{H}(\mathbf{4a})$	3.0 (3.0)	$\mathbf{H}(3),  \mathbf{H}(4\mathbf{b})$	1.7 (1.7)
$\mathbf{H}(\mathbf{4b})$	2.6 (2.6)	$\mathbf{H}(4\mathbf{a}),\ \mathbf{H}(4\mathbf{b})$	17.8 (17.8)
$\mathbf{H}(5)$	4.6 (4.6)	H(4a), H(5)	10.0 (10.0)
$\mathbf{H}(6)$	2.5 (2.5)	H(4b), H(5)	7.4 (7.4)
$\mathbf{H}(7)$	$6.6 \ (7.2)$	$\mathbf{H}(5),  \mathbf{H}(6)$	5.7
H(8)	11.0 (10.5)	$\mathbf{H}(6),  \mathbf{H}(7)$	5.4
C(3)	147.1 (146.9)		
C(4)	40.3 (40.0)		
C(4) C(5)	74.7 (75.2)		
C(6)	30.3 (34.6)		
C(7)	146.0 (146.0)		

a Relative to TMS.

The NMR spectrum of the reaction product before purification consisted of two sets of lines, which we assigned to the two isomers, syn and anti, in ratio 1:1. After distillation only one of the isomers was obtained with m.p. 87-89 °C. The values in brackets in Table 1 are the ones associated to the other isomer. The differences of the chemical shifts in the two compounds have been used in the assignment of the lines.

The mechanism for the formation of 3 are similar to well-known syntheses of isoxazolines and can be explained by assuming 2a or 2b as an intermediate. The C(3)-C(4) double bond in 2a or 2b may after isomerization add the hydroxylamine moiety to give 3:

$$2a \text{ or } 2b = \begin{bmatrix} HON = \overset{5}{C}H - \overset{4}{C}H = \overset{3}{C}H - \overset{2}{C}H \\ H - O & & & \\ & & \\ & & & \\ & &$$

We have shown 6 that addition of for example an alcohol to the C(3)-C(4) double bond in the acetals of 1 readily takes place.

Experimental. Microanalyses were carried out in the Microanalytical Department of the University of Copenhagen by Mr. Preben Hansen.

Instrumentation: UV, Beckman ACTA III; MS, AEI-MS 902; <sup>13</sup>C NMR and <sup>1</sup>H NMR, Jeol.

2-Isoxazolin-5-yl acetaldehyde oxime 3. Following the reported procedure,4 the sodium salt of glutacondialdehyde (1) (15 g) and hydroxylamine was refluxed in absolute ethanol. Evaporation of the ethanol and continuous extraction of the residue with ether yielded nearly colourless crystals, 4.2 g (34 %). Distil-

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lation of the crude product yielded as the main fraction (b.p. 136-138 °C/0.5 mmHg) colourless crystals of 3, m.p. 87-89 °C. The distillate as well as the crude product gave rise to only one spot by TLC on silica gel with different solvents as eluents. (Baumgarten reported a yield of 32 % and m.p. 88 °C). Anal. C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>: C, H, N.

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