SUBSTITUTED 1,2-DIAZA-7-OXASPIRO[4,4]NONEN-6-ONES; PREPARATION, NMR SPECTRA, AND CRYSTAL STRUCTURE

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Dedicated to the memory of Professor František Šorm.

Diazomethane adds to substituted 3-methylene-2(3H)-dihydrofuranones (Ia—Ii) to give the coresponding title dihydropyrazolospirodihydrofuranones (IIa—IIf, IIi, and IIj) or (IIIa, IIIg, and IIIh). NMR spectra of the adducts are discussed in some detail and the crystal structure has been solved for (4R*, 5S*)-5-benzoyloxy-1,2-diaza-7-oxaspiro[4.4]non-1-en-6-one (IIa).

Addition of diazomethane to an activated double bond is a well established concerted[1] (leading to pyrazolines) or step-wise[2] (leading directly to cyclopropanes)
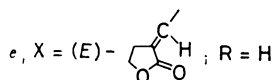

I
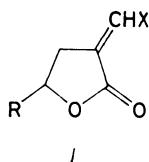
a, X = (Z) - OCOC$_6$H$_5$; R = H
b, X = (E) - OCOC$_6$H$_5$; R = H
c, X = (E) - C$_6$H$_5$; R = H
d, X = (E) - OSO$_2$C$_6$H$_4$-p-CH$_3$; R = H
e, X = (E) - [structure] ; R = H
f, X = (E) - OSO$_2$CH$_3$; R = H
g, X = (Z) - OSO$_2$C$_6$H$_4$-p-CH$_3$; R = H
h, X = (Z) - OSO$_2$C$_6$H$_5$; R = H
i, X = (E) - OSO$_2$C$_6$H$_4$-p-CH$_3$; R = CH$_3$

II
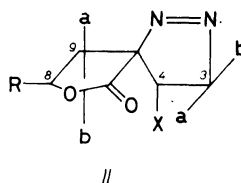
a, (4R*,5S*)- ; X = OCOC$_6$H$_5$; R = H
b, (4R*,5R*)- ; X = OCOC$_6$H$_5$; R = H
c, (4R*,5R*)- ; X = C$_6$H$_5$; R = H
d, (4R*,5R*)- ; X = OSO$_2$C$_6$H$_4$-p-CH$_3$; R = H
e, (4R*,5R*)- ; X = [structure] ; R = H
f, (4R*,5R*)- ; X = OSO$_2$CH$_3$; R = H
i, (4R*,5R*,8R*)- ; X = OSO$_2$C$_6$H$_4$-p-CH$_3$; R = CH$_3$
j, (4R*,5R*,8S*)- ; X = OSO$_2$C$_6$H$_4$-p-CH$_3$; R = CH$_3$
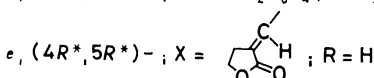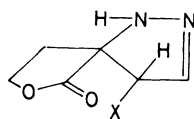
III

a, $(4R^*, 5R^*)-$; X = $OCOC_6H_5$

g, $(4R^*, 5R^*)-$; X = $OSO_2C_6H_4$-p-CH_3

h, $(4R^*, 5R^*)-$; X = $OSO_2C_6H_5$

SCHEME 1

1,3-dipolar cycloaddition reaction in which the configuration at the double bond is fully retained in the adducts[1,2].

We now wish to report that diazomethane adds to various substituted 3-methylene-2($3H$)-dihydrofuranones (I) yielding either the corresponding substituted 1,2-diaza-7-oxaspiro[4.4]non-1-en-6-ones (II) or the tautomeric substituted 1,2-diaza-7-oxaspiro[4.4]non-2-en-6-ones (III), as shown in Scheme 1.

EXPERIMENTAL

Melting points were determined on a PHKM 05 (G.D.R.) melting point apparatus. Infrared spectra were recorded with a Unicam SP 1000 spectrometer (wavenumbers in cm^{-1}). Ultraviolet spectra (in ethanol) were obtained with a Unicam SP 1800 spectrophotometer. ^{1}H and ^{13}C NMR spectra of the compound IIa were taken on and homonuclear COSY and NOESY experiments were carried out with a Bruker AM 400 (9·4 T) spectrometer; all other NMR spectra were measured with a Tesla BS 567 (2·35 T) spectrometer. Selected chemical shifts (in deuteriochloroform) are reported in ppm (δ-scale) relative to an internal tetramethylsilane reference; coupling constants (J) are given in Hz.

The starting compounds were prepared as follows: (Z)- and (E)-3-(benzoyloxymethylene)-2($3H$)-dihydrofuranone (Ia) and (Ib), resp., (E)- and (Z)-3-(p-toluenesulfonyloxymethylene)-2($3H$)-dihydrofuranone (Id) and (Ig), resp., (E)-3-(methanesulfonyloxymethylene)-2($3H$)-dihydrofuranone (If), and (Z)-3-(benzenesulfonyloxymethylene)-2($3H$)-dihydrofuranone (Ih) according to lit.[3]; (E)-3-(phenylmethylene)-2($3H$)-dihydrofuranone (Ic) was prepared according to lit.[4], (E,E)-(oxydimethylidine)bis(dihydro-2($3H$)-furanone) (Ie) according to lit.[5], and (E)-3--(p-toluenesulfonyloxymethylene)-5-methyl-2($3H$)-dihydrofuranone (Ii) according to lit.[6]. Diazomethane was prepared from N-nitroso-N-methylurea and its ethereal solution was dried over potassium hydroxide pellets for two hours before use.

The crystals of the compound IIa suitable for X-ray studies were obtained by recrystallization from ethanol in the form of well developed colourless needles. The experimental density of the crystals was determined by the flotation method in a H_2O–K_2HgI_4 mixture. The space group and preliminary lattice parameters were obtained from Weissenberg and precession photographs. Final values of the lattice parameters were determined from 15 diffractions in the range $11 < 2\Theta < 26°$, collected on a Syntex P2$_1$ diffractometer and are summarized in Table I. The dimen-

sions of the crystal used for data collection were $0.28 \times 0.31 \times 0.48$ mm. Diffraction intensities were measured with $0-2\Theta$ scan techniques using graphite monochromatized MoK_{α}-radiation, $\lambda = 0.7107$ Å. The crystal stability during the data collection was checked by measuring two standard reflexions after every fifty ones measured; no significant decrease in their intensities was detected. Of 1 618 diffractions measured, maximum $2\Theta = 54°$, $0 < h < 9$, $0 < k < 12$, $-13 < l < 12$, 1 236 with $I \geqq 2.5\sigma(I)$ were classified as observed and used in the structure solution and refinement. The data were corrected for L_p-factor but no absorption correction was applied. The structure was solved by direct methods in a straightforward manner and all atoms, except hydrogens, were refined anisotropically by a block-diagonal matrix least-squares procedure with weight $w = 1/\sigma^2 |F_o|$. The refinements were performed on $|F_o|$ and stopped when the average shifts of the refined parameters were less than 0.3σ. Hydrogen atoms were positioned theoretically and refined isotropically. Final residuals R and R_w are 0.037 and 0.034, resp., for observed reflexions and 0.053 and 0.035, resp., for all data. A final electron density map showed maximum residual density of 0.14 eÅ^{-3}. All the programs employed during the structure solution and refinement, including atom scattering factors, were part of the XTL program system supplied by Syntex Corp. The final atomic parameters, including B_{eq}, are given in Table II.

General Procedure for Preparation of 1,2-Diaza-7-oxaspiro[4.4]non-1-en-6-one (*IIa—IIf, IIi* and *IIj*) and 1,2-Diaza-7-oxaspiro[4.4]non-2-en-6-one (*IIIa, IIIg, and IIIh*)

A solution of approx. 0.015 mol of diazomethane in 30 ml of diethylether was added to a solution of 0.01 mol of a compound *I* in either benzene or dichlorometane and kept standing at ambient

TABLE I

Basic crystallographic data of *IIa*

Formula	$C_{13}H_{12}N_2O_4$
Molecular weight	260.25
$F(000)$	544
Crystal system	monoclinic
Space group	$P2_1/c$ No. 14
Lattice parameters	$a = 8.738(2)$ Å
	$b = 11.842(3)$ Å
	$c = 12.832(4)$ Å
	$\beta = 105.22(3)°$
Unit cell volume	$1\ 281.2(7)$ Å^3
D_m	1.31 Mg m^{-3}
D_x	1.35
Z	4
Temperature	293 K
μ	0.11 mm^{-1}

*   A list of structure factors and anisotropic temperature factors of atoms other than hydrogen can be obtained from the author (Z. Ž.) upon request.

temperature until all starting compound *I* dissapeared as indicated by thin-layer chromatography on silica gel. The solvent was removed in vacuo, leaving a nearly quantitative yield of a white solid or syrup which was crystallized.

TABLE II

Final atomic parameters of *IIa* and their e.s.d.'s in parenthesis. The values of positional parameters have been multiplied by 10^4. The average temperature factor B_{eq} is defined as $B_{eq} = \doteq \frac{1}{3}[B_{22} + (1/\sin^2 \beta)(B_{11} + B_{33} + 2B_{13} \cos \beta)]$

Atom	x	y	z	B_{eq}
N(1)	8925(3)	3550(2)	2957(2)	5·5(1)
N(2)	8173(3)	4222(2)	2253(2)	5·5(1)
C(3)	6600(4)	3801(2)	1667(2)	4·5(1)
C(4)	6314(3)	2784(2)	2308(2)	3·6(1)
C(5)	8002(3)	2482(2)	2995(2)	3·7(1)
C(6)	8174(3)	2164(2)	4204(2)	4·0(1)
O(7)	8569(2)	1067(2)	4374(2)	5·0(1)
C(8)	8581(4)	527(3)	3331(3)	5·8(2)
C(9)	8770(4)	1486(3)	2564(3)	5·3(2)
O(10)	5294(2)	3139(1)	2997(1)	3·7(1)
C(11)	4678(3)	2313(2)	3511(2)	3·8(1)
O(12)	4948(2)	1326(2)	3397(2)	5·3(1)
C(13)	3709(3)	2770(2)	4228(2)	3·7(1)
C(14)	2960(3)	2011(3)	4780(3)	4·9(2)
C(15)	2106(3)	2420(3)	5493(3)	5·4(2)
C(16)	1997(4)	3552(3)	5668(3)	5·5(2)
C(17)	2720(4)	4301(3)	5113(3)	5·3(2)
C(18)	3579(3)	3916(2)	4399(2)	4·3(1)
O(19)	8004(2)	2760(2)	4944(2)	5·2(1)
H3a	5890(30)	4400(20)	1640(20)	6·3(7)
H3b	6660(30)	3650(20)	920(20)	5·9(7)
H4b	5810(20)	2160(20)	1860(20)	4·1(6)
H8a	9500(30)	30(20)	3480(20)	7·9(8)
H8b	7540(30)	140(20)	3090(20)	7·1(8)
H9a	9800(30)	1570(20)	2630(20)	7·1(8)
H9b	8330(30)	1300(20)	1760(20)	5·5(6)
H14	3030(30)	1230(20)	4630(20)	6·1(7)
H15	1620(30)	1850(20)	5870(20)	5·6(7)
H16	1330(30)	3870(20)	6220(20)	6·9(7)
H17	2690(30)	5100(20)	5230(20)	5·7(7)
H18	4090(30)	4420(20)	4030(20)	4·3(6)

(4R^*,5S^*)-4-*Benzoyloxy*-1,2-*diaza*-7-*oxaspiro*[4,4]*non*-1-*en*-6-*one* (IIa) (2·15 g; 82·5%) was obtained from 2·2 g *Ia* in benzene after 100 h standing and crystallization from water; mp 120 to 124°C (decomposition). IR spectrum (KBr): 1 705 (C=O, benzoyl) and 1 760 (C=O, γ-lactone). UV spectrum: λ_{max} 245 nm (log ε 4·13). ^{13}C NMR spectrum: 169·6 (C-6); 166·4 (C-11); 133·8 (C-16); 129·8 (C-14, C-18); 128·8 (C-15, C-17); 128·5 (C-13); 93·0 (C-5); 81·2 (C-3); 72·2 (C-4); 66·2 (C-8); 31·4 (C-9). ^{1}H NMR spectrum: 2·29 ddd, 1 H (H-9b, J(9a, 9b) = 13·4, J(8a, 9b) = 2·5, J(8b, 9b) = 6·3; 2·75 ddd, 1 H (H-9a, J(9a, 8a) = 8·9, J(9a, 8b) = 9·8); 4·56 m, 1 H and 4·62 m, 1 H (H-8b and H-8a, resp., J(8a, 8b) = 9·0); 4·76 dd, 1 H (H-3b, J(3b, 4b) = 6·4, J(3a, 3b) = 19·0); 5·04 dd, 1 H (H-3a, J(3a, 4b) = 2·1); 5·29 dd, 1 H (H-4b); 7·38—7·43 m, 2 H (H-15 and H-17); 7·53—7·58 m, 1 H (H-16); 7·92—7·95 m, 2 H (H-14 and H-18). Complete analysis and assignment of H-3, H-4, H-8, and H-9 signals is supported by simulation and homonuclear COSY experiments, as well as by NOESY and phase sensitive NOESY experiments wherein correlation has shown between H-4b and the signal at δ 2·29 which was, accordingly, assigned to H-9b. The magnitudes of ^3J(H, H) coupling constants are also in agreement with the assignment. For $C_{13}H_{12}N_2O_4$ (260·3) calculated: 58·98% C, 4·65% H, 10·76% N; found: 59·81% C, 4·73% H, 10·80% N.

(4R^*,5R^*)-4-*Benzoyloxy*-1,2-*diaza*-7-*oxaspiro*[4,4]*non*-1-*en*-6-*one* (IIb) (2·2 g; 85%) was prepared from 2·2 g *Ib* in benzene in 72 h; m.p. 90—91°C (ethanol, with decomposition). IR spectrum (KBr): 1 705 (C=O, benzoyl) and 1 758 (C=O, γ-lactone). UV spectrum: λ_{max} 245 nm (log ε 4·18). ^{13}C NMR spectrum: 170·7 (C-6); 165·4 (C-11); 134·0 (C-16); 129·8 (C-14, C-18); 128·7 (C-15, C-17); 128·5 (C-13); 97·1 (C-5); 84·3 (C-3); 69·8 (C-4); 67·6 (C-8); 27·7 (C-9). ^{1}H NMR spectrum: 2·70 ddd, 1 H (H-9a, J(9a, 9b) = 14·0, J(9a, 8a) = 8·2, J(9a, 8b) = 8·7); 2·96 ddd, 1 H (H-9b, J(9b, 8a) = 4·0, J(9b, 8b) = 7·0); 4·66 m, 1 H (H-8a, J(8a, 8b) = 8·6); 4·72 m, 1 H (H-3a, J(3a, 3b) = 18·7, J(3a, 4a) = 5·2); 4·91 m, 1 H (H-8b); 5·27 m, 1 H (H-3b, J(3b, 4a) = = 1·4); 5·62 dd, 1 H (H-4a). Complete analysis of ^{1}H NMR of the spiroheterocyclic moiety is supported by simulation; assignments have been made on the basis of coupling constants and a comparison with the spectrum of the compound *IIa*. For $C_{13}H_{12}N_2O_4$ (260·3) calculated: 59·98% C, 4·65% H, 10·76% N; found: 60·12% C, 4·48% H, 10·89% N.

(4R^*,5R^*)-4-*Phenyl*-1,2-*diaza*-7-*oxaspiro*[4,4]*non*-1-*en*-6-*one* (IIc) (1·35 g; 63%) was obtained from 1·75 g *Ic* in benzene in 150 h; m.p. 92—95°C (ethanol, with decomposition). ^{13}C NMR spectrum: 173·4 (C-6); 138·8 (C-ipso); 129·2 (C-ortho); 128·0 (C-para); 127·7 (C-meta); 98·7 (C-5); 86·2 (C-3); 67·3 (C-8); 43·7 (C-4); 30·0 (C-9). ^{1}H NMR spectrum: 2·00 m, 1 H (H-9b, J(9b, 9a) = = 13·7, J(9b, 8b) = 8·7, J(9b, 8a) = 9·2); 2·38 ddd, 1 H (H-9a, J(9a, 8b) = 2·8, J(9a, 8a) = 7·0); 3·62 dd, 1 H (H-4a, J(4a, 3b) = 5·6, J(4a, 3a) = 6·6); 4·42 dt, 1 H (H-8b, J(8b, 8a) = 8·7); 4·79 m, 1 H (H-8a); 5·08 d, 1 H (H-3b, J(3b, 3a) = 0·0); 5·09 d, 1 H (H-3a). For $C_{12}H_{12}N_2O_2$ (216·2) calculated: 66·66% C, 5·59% H, 12·96% N; found: 66·78% C, 5·63% H, 13·13% N.

(4R^*,5R^*)-4-(*p*-*Toluenesulfonyloxy*)-1,2-*diaza*-7-*oxaspiro*[4,4]*non*-1-*en*-6-*one* (IId) (2·65 g; 85%) was prepared from 2·7 g *Id* in dichloromethane in 72 h; m.p. 66·5—68°C (tetrachloromethane, with decomposition). ^{1}H NMR spectrum: 2·49 s, 3 H (CH$_3$); 2·75—2·93 m, 2 H (H-9a, H-9b); 4·44—4·99 m, 5 H (H-8a, H-8b, H-4a, H-3a, H-3b); 7·26—7·81 m, 4 H (C$_6$H$_4$). For $C_{13}H_{14}O_5$. .N$_2$S (310·3) calculated: 50·32% C, 4·55% H, 9·03% N; found: 50·08% C, 4·69% H, 9·17% N.

(4R^*,5R^*)-4-[(*E*)-2(3*H*)-*Dihydrofuranone*-3-*methylidinoxy*]-1,2-*diaza*-7-*oxaspiro*[4,4]*non*-1-*en*-6- -*one* (IIe) (1·8 g; 71%) was obtained from 2·1 g *Ie* in dichloromethane in 120 h; m.p. 126—129°C (water, with decomposition). ^{1}H NMR spectrum: 2·78 dt, 2 H (CH$_2$ in the substituent X, ^3J = = 7·5, ^4J = 2·6); 2·76—2·90 m, 2 H (H-9a, H-9b); 4·36 t, 2 H (OCH$_2$ in the substituent X); 4·50—5·20 m, 5 H (H-8a, H-8b, H-3a, H-3b, H-4a); 7·30 t, 1 H (=CH in the substituent X). For $C_{11}H_{12}N_2O_5$ (252·2) calculated: 52·39% C, 4·80% H, 11·11% N; found: 52·07% C, 4·61% H, 11·17% N.

(4R^*, 5R^*)-4-*Methanesulfonyloxy*-1,2-*diaza*-7-*oxaspiro*[4.4]*non*-1-*en*-6-*one* (IIf) (2·1 g;   90%) was prepared from 1·9 g *If* in dichloromethane in 72 h; m.p. 71·5—73·5°C (water, with decomposition). ^{1}H NMR spectrum 2·86—2·98 m, 2 H (H-9a, H-9b); 3·08 s, 3 H (CH$_3$); 4·60—5·30 m, 5 H (H-8a, H-8b, H-3a, H-3b, H-4a). For C$_7$H$_{10}$N$_2$O$_5$S (234·3) calculated: 35·88% C, 4·30% H, 11·96% N; found: 35·63% C, 4·17% H, 12·02% N.

A mixture of (4R^*,5R^*,8R^*)- and (4R^*,5R^*,8S^*)-8-*methyl*-4-(p-*toluenesulfonyloxy*)-1,2-*diaza*--7-*oxaspiro*[4.4]*non*-1-*en*-6-*one* (IIi) and (IIj), respectively, (3·2 g; 99%) was prepared from 2·8 g *Ii* in dichloromethane in 48 h; a syrup consisting of 70% *IIj* and 30% *IIi* as indicated by the corresponding methyl-doublets in ^{1}H NMR spectrum at 1·52 (J = 6·5) and 1·66 (J = 7·0), respectively. Because of facile decomposition of the mixture, no attempt was made to separate the individual components. For C$_{14}$H$_{16}$N$_2$O$_5$S (324·4) calculated: 51·84% C, 4·97% H, 8·64% N; found: 51·56% C, 4·90% H, 8·39% N.

(4R^*,5R^*)-4-*Benzoyloxy*-1,2-*diaza*-7-*oxaspiro*[4.4]*non*-2-*en*-6-*one* (IIIa) (2·05; 79%) was obtained from 2·2 g *Ia* in benzene after 100 h and crystallization from a mixture of carbon tetrachloride and dichloromethane (3 : 1); m.p. 115—117°C. IR spectrum (nujol) broad 3 440 and 3 540 (NH), 1 620 and 1 640 (H bonded C=O). ^{13}C NMR spectrum: 172·9 (C-6); 165·5 (C=O, benzoyl); 139·1 (C-3); 133·9 (C-*para*); 130·0 (C-*ortho*); 128·7 (C-*meta*); 128·5 (C-*ipso*); 83·2 (C-4); 69·1 (C-5); 65·0 (C-8); 34·9 (C-9). ^{1}H NMR spectrum: 2·61 t, 2 H (H-9a, H-9b); 4·42 t, 2 H (H-8a, H-8b); 6·11 d, 1 H (H-4, J(4, 3) = 1·2); 6·93 d, 1 H (H-3); 7·35—7·61 m, 3 H (H-*para*, H-*meta*); 7·95—8·05 m, 2 H (H-*ortho*); 11·70 s, 1 H (N–H). For C$_{13}$H$_{12}$N$_2$O$_4$ (260·3) calculated: 59·98% C, 4·65% H, 10·76% N; found: 59·83% C, 4·67% H, 10·67% N.

(4R^*,5R^*)-4-(p-*Toluenesulfonyloxy*)-1,2-*diaza*-7-*oxaspiro*[4.4]*non*-2-*en*-6-*one* (IIIg) (2·5 g; 80%) was obtained from 2·7 g *Ig* in dichloromethane in 72 h; m.p. 63—65°C (water-ethanol 3 : 1), with decomposition). ^{1}H NMR spectrum: 2·32 s, 3 H (CH$_3$); 3·29 t, 2 H (H-9a, H-9b, J(9,8) = = 6·2); 4·66 t, 2 H (H-8a, H-8b); 6·45 d, 1H (H-3, J(3, 4) = 2·5); 7·10—7·70 m, 4 H (C$_6$H$_4$); 8·02 d, 1 H (H-4); 14·72 s, 1 H (N–H). For C$_{13}$H$_{14}$N$_2$O$_5$S (310·3) calculated: 52·32% C, 4·55% H, 9·03% N; found: 50·07% C, 4·32% H, 8·89% N.

(4R^*, 5R^*)-4-*Benezenesulfonyloxy*-1,2-*diaza*-7-*oxaspiro*[4.4]*non*-2-*en*-6-*one* (IIIh) (2·5 g; 85%) was prepared from 2·5 g *Ih* in dichloromethane in 24 h; m.p. 52—54°C (water, with decomposition). ^{1}H NMR spectrum: 3·26 t, 2 H (H-9a, H-9b, J(8, 9) = 6·5); 4·70 t, 2 H (H-8a, H-8b); 6·39 d, 1 H (H-3, J(3, 4) = 1·3); 7·35—7·85 m, 5 H (C$_6$H$_5$); 7·98 d, 1 H (H-4); 11·20 broad s, 1 H (N–H). For C$_{12}$H$_{12}$N$_2$O$_5$S (296·3) calculated: 48·64% C, 4·08% H, 9·45% N; found: 48·40% C, 3·81% H, 9·18% N.

RESULTS AND DISCUSSION

Whereas diazomethane addition to compounds *Ia*—*Ii* proceeds readily and is completed in days (the rate of addition increasing in the series *Ic* < *Ia*, *Ib* < *Id*, *Ig*, *Ii* < < *Ij* < *Ih*), no addition takes place with *I* (X = NR$_2$, N$_3$, or OC$_2$H$_5$). All compounds *I* with (Z)-configuration add diazomethane to give the corresponding *III* whereas all starting compounds (E)-*I* give adducts with the tautomeric structure *II* (with *Ia*, an adduct with the structure *IIIa* separates in the reaction mixture but tautomerizes to *IIa* when crystallized from water).

At ambient temperature, only adducts *IIa*, *IIb*, *IIc*, and *IIe* are stable; all other prepared compounds *II* and *III* are unstable, more so in the solid state than in solu-

tion. In the solid state, the half-lives are in the range of few hours — few days, the stability increasing in the series *IIIh* < *IIf* < *IIi*, *IIj* < *IIIg*, *IId* ≪ *IIa*, *IIb*, *IIc*, and *IIe*.

As shown by the crystal structure of the compound *IIa*, configuration of the starting double bond is retained in the adduct.

In ^{1}H NMR spectra of compounds *II*, diastereotopic protons a and b (H-9a, H-9b; H-8a, H-8b; H-3a, H-3b) give rise to complicated patterns. On the other hand, ^{1}H NMR spectra of compounds *III* are deceptively simple at 100 MHz, the symmetry nonequivalent protons a and b giving rise to patterns resembling symmetry equivalence. This shows the N=N double bond anisotropy to be the decisive influence producing large differences in behaviour of a proton a and the corresponding proton b in structures *II*. Complete assignment of proton signals in compounds *II* presents an interesting challenge; The two spin systems H-3, H-4 and H-8, H-9 are mutually isolated and scalar ^{1}H–^{1}H coupling that might have related them is not available. Hence dipolar (through-space) ^{1}H coupling was used via NOESY and phase sensitive NOESY to determine the relation. The stable compound *IIa*, the crystal structure of which has been determined, was used for these experiments at 400 MHz. Both NOESY and phase sensitive NOESY spectra of *IIa* showed a correlation (through-space coupling) between the absorption at δ 5·29 (assigned easily to H-4b) and the absorption at δ 2·29 (assigned therefore to H-9b). The assignment of the other proton signals has been made on the basis of information derived from homonuclenar COSY experiments, the magnitude of scalar coupling constants, and chemical shifts. Dihedral angles H(9b)C(9)C(8)H(8a) (132°), H(9b)C(9)C(8)-H(8b) (−25°), H(9a)C(9)C(8)H(8a) (−11·6°), and H(9a)C(9)C(8)H(8b) (−168·7°) as well as H(4b)C(4)C(3)H(3b) (−35·6°) and H(4b)C(4)C(3)H(3a) (56·7°), calculated from the structural data of the compound *IIa* could not be brought cnsistently into agreement with the observed ^3J(H, H) coupling constants; the situation in the solid state could thus not be used quantitatively for assigning the ^{1}H NMR signals to the individual protons. In compounds *IIa* and *IIb*, the relative configuration at the carbon atom C-4 is well characterized by the chemical shifts of protons H-4b (δ 5·29) and H-4a (δ 5·62), respectively. Model inspection reveals that, compared to the compound *IIa*, in the ^{1}H NMR spectrum of the diastereomer *IIb*, of the protons H-8 and H-9, the proton H-9b should experience the greatest change. It has been therefore assigned the signals centered at δ 2·96. In the compound *IIc*, the highest--field absorption at δ 2·00 has been assigned to the proton H-9b, based on the N=N double bond anisotropy influence and expected shielding by the benzene ring. Tautomeric *IIa* and *IIIa* differ also considerably in solid state infrared spectra, the former showing no N—H bond and no hydrogen-bonded carbonyls, the latter exhibiting both features.

Diazomethane addition to the compounds *Ii* is about 40% stereoselective, as apparent from ^{1}H NMR spectra of the mixture of adducts *IIi* and *IIj*. The assignment

of the $(4R^*,5R^*,8S^*)$-structure *IIj* to the major product is based on model inspection (sterically less hindered approach) and the expected N=N double bond anisotropy effect. ^{13}C NMR spectra were analysed empirically, with the help of APT and known spectra of starting compounds *I* (refs[3,6,7]).

The decomposition of *II* and *III* has been looked into and the results will be published elsewhere. Suffice it to say here that it proceeds with initial liberation of the acid HX (X being the substituent in *II* and *III*) and intermediary formation of the corresponding pyrazolenine that, apparently, undergoes a sigmatropic rearrangement followed by decarboxylation.

TABLE III

Selected interatomic distances (.10 nm) and bond angles (°) in *IIa* with e.s.d's in parentheses

Atoms	Bond length	Atoms	Bond angle
N(1)–N(2)	1·252(4)	C(5)–N(1)–N(2)	111·9(2)
N(2)–C(3)	1·469(4)	N(1)–N(2)–C(3)	113·4(2)
C(3)–C(4)	1·516(4)	N(2)–C(3)–C(4)	104·9(2)
C(4)–C(5)	1·548(4)	C(3)–C(4)–C(5)	102·9(2)
C(5)–N(1)	1·508(4)	C(3)–C(4)–O(10)	108·1(2)
C(5)–C(6)	1·565(4)	C(5)–C(4)–O(10)	111·1(2)
C(5)–C(9)	1·530(4)	C(4)–C(5)–N(1)	103·0(2)
C(6)–O(7)	1·348(4)	C(4)–C(5)–C(6)	116·7(2)
O(7)–C(8)	1·485(4)	C(4)–C(5)–C(9)	114·5(2)
C(8)–C(9)	1·540(5)	N(1)–C(5)–C(6)	108·7(2)
C(4)–O(10)	1·472(4)	N(1)–C(5)–C(9)	110·2(2)
O(10)–C(11)	1·368(3)	C(6)–C(5)–C(9)	103·7(2)
C(11)–O(12)	1·208(3)	C(5)–C(6)–O(7)	110·2(2)
C(11)–C(13)	1·505(4)	C(5)–C(6)–O(19)	129·2(3)
C(6)–O(19)	1·223(3)	C(6)–O(7)–C(8)	109·3(3)
		O(7)–C(8)–C(9)	106·6(3)
		O(7)–C(6)–O(19)	120·5(3)
		C(8)–C(9)–C(5)	101·9(3)
		C(4)–O(10)–C(11)	117·5(2)
		O(10)–C(11)–C(13)	113·2(2)
		O(10)–C(11)–O(12)	121·3(2)
		O(12)–C(11)–C(13)	125·5(3)
		C(11)–C(13)–C(14)	119·2(2)
		C(11)–C(13)–C(18)	122·2(3)
		Benzene ring	
av. C–C	1·394(5)	av. C–C–C	120·0(5)

The structure of the compound *IIa* (Fig. 1) confirms the expected presence of only one tautomer. The bond lengths (Table III) correspond to the expected state of hybridization of the atoms involved. Thus, the distance N(1)—N(2) (1·252(4) Å) is typical for the double bond and the same is valid for the bond lengths C(6)—O(19) and C(11)—O(12) (1·223(3) and 1·208(3) Å, respectively)[7]. The geometry of the dihydropyrazolospirodihydrofuranone moiety can be compared to the relevant fragment in the adduct (*IV*) of diazomethane to a *trans*-decaline-type α-exomethylene-butyrolactone[8]; this comparison is presented in Table IV. Unlike the structure *IV*,
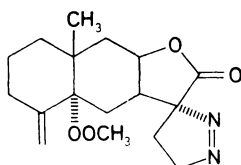
IV

where the pyrazoline ring is approximately planar, both the rings in structure *IIa* deviate significantly from planarity (plane A is defined by the atoms N(1), N(2), C(3), C(4), and C(5); $0·5222X - 0·4820Y - 0·7035Z = -1·0036$; distances of the atoms from the best plane are (Å): N(1) $-0·046(3)$, N(2) $-0·036(3)$, C(3) $0·100(3)$, C(4) $-0·121(3)$, C(5) $0·102(3)$; the plane B is defined by the atoms C(5), C(6), O(7),
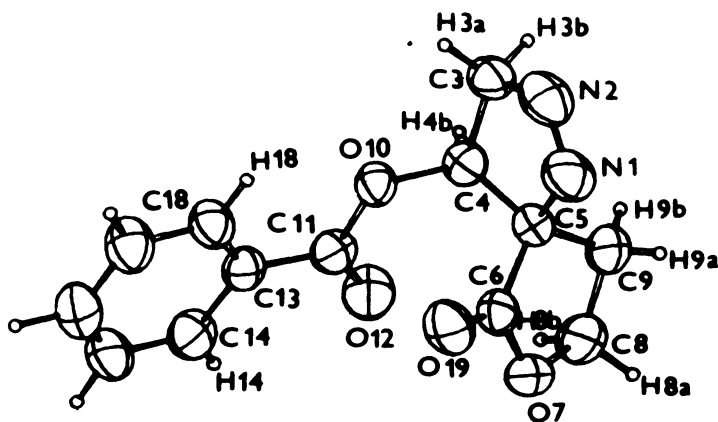

FIG. 1

A perspective view of the molecule of *IIa*. The nonhydrogen atoms are represented as thermal ellipsoids at 50% probability level. Hydrogen atoms have been assigned arbitrary thermal parameters for the sake of clarity

TABLE IV

Comparison of bond lengths (.10 nm) in the structure of *IIa* with the relevant structure *IV*

Parameter	*IIa*	*IV*[a]	Parameter	*IIa*	*IV*[a]
N(1)–N(2)	1·252(4)	1·250(5)	C(6)–O(7)	1·348(4)	1·349(4)
N(2)–C(3)	1·469(4)	1·461(7)	C(6)–O(19)	1·223(3)	1·205(5)
C(3)–C(4)	1·516(4)	1·523(6)	O(7)–C(8)	1·485(4)	1·484(4)
C(4)–C(5)	1·548(4)	1·524(6)	C(8)–C(9)	1·540(5)	1·530(5)
N(1)–C(5)	1·508(4)	1·532(5)	C(9)–C(5)	1·530(4)	1·531(5)
C(5)–C(6)	1·565(4)	1·524(5)			

[a] Data from ref.[8].

C(8), and C(9); $0.9174X + 0.2265Y + 0.3271Z = 7.4990$; distances of the atoms from the best plane are (Å): C(5) $-0.131(3)$, C(6) $0.038(3)$, O(7) $0.076(2)$. C(8) $-0.159(4)$, C(9) $0.176(4)$, O(19) $0.132(2)$). In both *IV* and *IIa*, the lactone and the
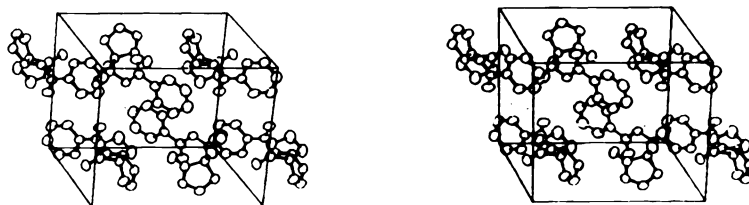

FIG. 2

A stereoscopic view of the packing arrangement in *IIa*. Hydrogen atoms are omitted for clarity

pyrazoline rings are mutually almost orthogonal (dihedral angle between the planes A and B: $82.0(3)°$). A stereoscopic view showing the structure and crystal packing of the compound *IIa* (hydrogen atoms are omitted for clarity) is displayed in Fig. 2.

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