isobutylamine. After 12 h the precipitate was filtered off, dried, and recrystallized from ethyl acetate. The product obtained was identical in every respect (mp, IR, PMR, and mass spectra) with adduct IVa. Yield 1.4 g (90%).

Hydrolysis of Salt IVa. Adduct IVa (0.5 g, 1 mmole) was dissolved in 10 ml of an aqueous solution of NaOH (2 M), the solution was then neutralized with hydrochloric acid (2 M). The white precipitate formed was filtered off, dried, and recrystallized from ethanol, mp 164-166°C. The product obtained had identical mp, IR, PMR, and mass spectra to those of a known sample of 4,4'-benzylidenebis(3-methyl-1-phenyl-5-pyrazolone) (V).

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SPIROBUTYROLACTONE DERIVED FROM 1-PHENYL-3-METHYL-2-PYRAZOLIN-5-ONE

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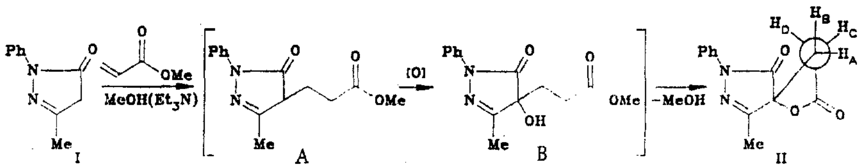
X-ray diffraction and NMR spectral examination have shown that 1-phenyl-3-methyl-2-pyrazolin-5-one reacts with methyl acrylate in methanol to give spiro[(1-phenyl-3-methyl-2-pyrazolin-5-one)-4,5'-butyrolactone]. The conformation has been shown to be the same in the crystal and in solution, the pyrazoline ring has been found to be nonplanar, the reasons for the acoplanarity established, stabilizing and destabilizing interactions studied, and the orientation of the phenyl substituent relative to the pyrazolin-5-one ring determined.

The reaction of 1-phenyl-3-methyl-2-pyrazolin-5-one (I) with methyl acrylate has given the novel spiro[(1-phenyl-3-methyl-2-pyrazolin-5-one)-4,5'-butyrolactone] (II), the formation of which may be rationalized as oxidation of the intermediate monoalkylated compound A by atmospheric oxygen, followed by cyclization of the hydroxyacid ester B:



The signals in the ^{1}H NMR spectrum of the spirolactone (II) were assigned on the basis of descreening of the CH_2CO protons as compared with CH_2C, which is in accordance with the high absolute $^2J_{gem}$ value for the CH_2CO protons, and on the descreening of the and H_D protons by the CO group in the pyrazoline ring, as in [1]. The observed values for ^3J are in accordance with the dihedral angles found by x-ray diffraction analysis*: $^3J_{BD}$ (162.7°) > $^3J_{AC}$ (42.5°)

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*In the x-ray structural examination, atoms H_A, H_B, H_C, and H_D are designated 1-H, 2-H, 3-H, and 4-H (Fig. 1 and Table 1).

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TABLE 1. Atom Coordinates ($\times 10^4$) in the Spirolactone (II)

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	3917(1)	3324(1)	7943(2)	$C_{(11)}$	2535(2)	699(1)	12630(3)
$O_{(2)}$	3710(1)	5730(1)	4544(2)	$C_{(12)}$	3466(1)	946(1)	11604(3)
$O_{(3)}$	2604(1)	4593(1)	5525(2)	$C_{(13)}$	3401(1)	1516(1)	9961(3)
$N_{(1)}$	2331(1)	2451(1)	7693(2)	1-H	2611(14)	3428(13)	2256(28)
$N_{(2)}$	1317(1)	2546(1)	6675(2)	2-H	3506(16)	2730(12)	3494(33)
$C_{(1)}$	2545(1)	3596(1)	5366(2)	3-H	4172(14)	4348(11)	1982(27)
$C_{(2)}$	3051(2)	3135(2)	7185(4)	4-H	4673(14)	4034(12)	4036(28)
$C_{(3)}$	1413(1)	3209(1)	5437(3)	5-H	−137(23)	3377(20)	4657(47)
$C_{(4)}$	508(1)	3529(1)	4140(3)	6-H	712(21)	3516(19)	2916(43)
$C_{(5)}$	3474(1)	4922(1)	4473(3)	7-H	347(33)	2911(28)	3497(62)
$C_{(6)}$	4003(1)	4144(1)	3346(2)	8-H	790(15)	1798(14)	10028(30)
$C_{(7)}$	3170(1)	3362(1)	3449(2)	9-H	894(18)	815(14)	12638(33)
$C_{(8)}$	2396(1)	1851(1)	9354(2)	10-H	2562(17)	272(13)	13832(33)
$C_{(9)}$	1453(1)	1602(1)	10372(3)	11-H	4166(18)	713(13)	12092(35)
$C_{(10)}$	1535(2)	1026(1)	11999(3)	12-H	4065(15)	1698(13)	9279(30)

TABLE 2. Bond Lengths ℓ (Å) in Spirolactone (II)

Bond	l	Bond	l
$O_{(1)}-C_{(2)}$	1,206(3)	$C_{(6)}-C_{(7)}$	1,517(2)
$O_{(2)}-C_{(5)}$	1,195(1)	$C_{(6)}-H_{(3)}$	0,99(2)
$O_{(3)}-C_{(5)}$	1,363(2)	$C_{(6)}-H_{(4)}$	0,96(2)
$O_{(3)}-C_{(1)}$	1,437(1)	$C_{(7)}-H_{(1)}$	1,06(2)
$C_{(1)}-C_{(2)}$	1,524(3)	$C_{(7)}-H_{(2)}$	1,00(2)
$C_{(1)}-C_{(3)}$	1,491(2)	$C_{(8)}-C_{(9)}$	1,388(2)
$C_{(1)}-C_{(7)}$	1,538(2)	$C_{(9)}-C_{(10)}$	1,377(2)
$N_{(1)}-C_{(2)}$	1,363(3)	$C_{(9)}-H_{(8)}$	0,89(2)
$N_{(1)}-N_{(2)}$	1,423(1)	$C_{(10)}-C_{(11)}$	1,377(2)
$N_{(1)}-C_{(8)}$	1,415(1)	$C_{(10)}-H_{(9)}$	0,94(2)
$N_{(2)}-C_{(3)}$	1,271(2)	$C_{(11)}-C_{(12)}$	1,378(2)
$C_{(3)}-C_{(4)}$	1,483(2)	$C_{(11)}-H_{(10)}$	1,02(2)
$C_{(4)}-H_{(5)}$	0,89(3)	$C_{(12)}-C_{(13)}$	1,379(2)
$C_{(4)}-H_{(6)}$	0,86(3)	$C_{(12)}-H_{(11)}$	0,98(2)
$C_{(4)}-H_{(7)}$	1,01(4)	$C_{(8)}-C_{(13)}$	1,381(2)
$C_{(5)}-C_{(6)}$	1,497(2)	$C_{(13)}-H_{(12)}$	0,97(2)

TABLE 3. Valence Angles (ω) in (II)

Angle	ω°	Angle	ω°
$C_{(1)}O_{(3)}C_{(5)}$	110,3(1)	$C_{(5)}C_{(6)}C_{(7)}$	103,9(1)
$C_{(2)}N_{(1)}N_{(2)}$	111,8(2)	$C_{(5)}C_{(6)}H_{(3)}$	110,0(9)
$C_{(8)}N_{(1)}N_{(2)}$	119,2(1)	$C_{(5)}C_{(6)}H_{(4)}$	104(1)
$C_{(2)}N_{(1)}C_{(8)}$	127,0(2)	$C_{(7)}C_{(6)}H_{(3)}$	114,0(9)
$N_{(1)}N_{(2)}C_{(3)}$	108,0(2)	$C_{(7)}C_{(6)}H_{(4)}$	115(1)
$C_{(2)}C_{(1)}C_{(3)}$	100,9(1)	$H_{(3)}C_{(6)}H_{(4)}$	109(1)
$C_{(2)}C_{(1)}O_{(3)}$	110,6(2)	$C_{(1)}C_{(7)}C_{(6)}$	102,1(1)
$C_{(2)}C_{(1)}C_{(7)}$	112,3(2)	$C_{(1)}C_{(7)}H_{(1)}$	107(1)
$C_{(3)}C_{(1)}O_{(3)}$	114,5(1)	$C_{(1)}C_{(7)}H_{(2)}$	112(1)
$C_{(3)}C_{(1)}C_{(7)}$	114,0(1)	$C_{(6)}C_{(7)}H_{(1)}$	109(1)
$O_{(3)}C_{(1)}C_{(7)}$	104,8(1)	$C_{(6)}C_{(7)}H_{(2)}$	114(1)
$N_{(1)}C_{(2)}O_{(1)}$	126,9(2)	$H_{(1)}C_{(7)}H_{(2)}$	112(2)
$N_{(1)}C_{(2)}O_{(1)}$	128,4(3)	$N_{(1)}C_{(8)}C_{(9)}$	120,1(1)
$N_{(1)}C_{(2)}C_{(1)}$	104,6(2)	$N_{(1)}C_{(8)}C_{(13)}$	119,7(1)
$C_{(1)}C_{(3)}N_{(2)}$	112,7(1)	$C_{(9)}C_{(8)}C_{(13)}$	120,2(2)
$C_{(1)}C_{(3)}C_{(4)}$	123,9(2)	$C_{(8)}C_{(9)}C_{(10)}$	119,1(2)
$N_{(2)}C_{(3)}C_{(4)}$	123,4(2)	$C_{(9)}C_{(10)}C_{(11)}$	121,0(2)
$O_{(3)}C_{(5)}O_{(2)}$	120,3(2)	$C_{(10)}C_{(11)}C_{(12)}$	119,4(2)
$O_{(3)}C_{(5)}C_{(6)}$	110,0(1)	$C_{(11)}C_{(12)}C_{(13)}$	120,5(2)
$O_{(2)}C_{(5)}C_{(6)}$	129,8(2)	$C_{(12)}C_{(13)}C_{(8)}$	119,7(2)

and $^3J_{BD}$ (35.9°) > $^3J_{BC}$ (84.3°). The signals in the ^{13}C NMR spectrum were assigned on the basis of descreening of the methylene carbon in the CH_2CO group, and an increase in its coupling constant in comparison with CH_2C, together with comparison with the spectra of the pyrazolinone (I) [2, 3] and its spiroepoxide [4]. In the chemical ionization mass spectrum of the spirolactone (II), the ion peak $[M+1]^+$ is seen, and its fragmentation under electron impact is in agreement with the breakdown of both the pyrazolinone (I) [5] and the lactone, with peaks $[M-28]^+$, $[M-56]^+$, and $[M-57]^+$. The IR spectrum of the spirolactone (II) also confirms the presence of the pyrazolinone moiety [2] and the ester group.

Spirans of other types, coupled at the 4 position of the pyrazolinone (I), have been reported previously [1, 4, 6].

The stereochemistry of the molecule of (II) is controlled for the most part by two factors, namely repulsion of the electron envelopes of the covalently nonbonded atoms, and $n-\pi^*$ conjugation. Thus, in the crystal the butyrolactone ring in (II) has the envelope conformation, bent along the $C_{(1)}...C_{(7)}$ axis by 27° with the more sterically favored pseudoequatorial conformation of the methyl substituent. There is also the possibility of conversion of the lactone ring in solution with the resulting conformational equilibrium:

II

IIc

The results of an x-ray diffraction examination of (II) (Tables 1-3) were therefore used to construct a geometrical model of the form (IIc), according to which there is strong repulsion between the CH_3 group and the axial hydrogen, the [H(Me)...*a*-H] distance being 2.1 Å (the sum of the H...H van der Waals radii is 2.34 Å [7]). There is therefore little likelihood that form (IIc) is preferred to (II), and it may therefore be concluded that the conformation is the same in solution as in the crystal, in agreement with the $^3J_{vic}$ values (see above).

The geometry of the butyrolactone ring in the crystal is clearly optimal in solution also. In fact, further screening of the bonds in projection $C_{(7)} \rightarrow C_{(6)}$ (Fig. 1) results in shortening of the intramolecular contacts 1-H...3-H and 2-H...4-H, which in the actual molecule have values of 2.35 Å. If, however, the rotation is reversed, due to an increase in the torsion angle $C_{(1)}C_{(7)}C_{(6)}C_{(5)}$, steric hindrance also arises, since the distances $C_{(5)}$...1-H and $C_{(1)}$...4-H are decreased, amounting in (II) to 2.82 Å (the sum of the van der Waals radii for C...H is 2.87 Å [7]). An unusual feature of the structure of (II) is the nonplanarity of the pyrazolinone ring, the bending along the $C_{(1)}...N_{(2)}$ axis being 13.6°. This bending, together with the increase in one of the angles at the spiro-atom $C_{(3)}C_{(1)}C_{(7)}$ (114.0(1)°) clearly results in a decrease in the repulsion between atoms 1-H...6-H and 1-H...$C_{(13)}$ (the corresponding distances in (II) are 2.37(3) and 2.62(2) Å).

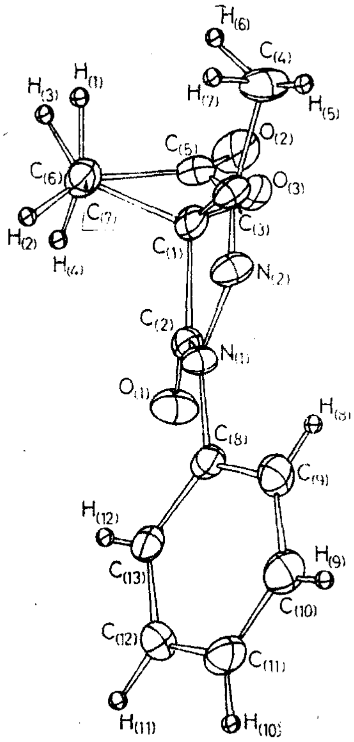

Fig. 1. Molecule of the spirolactone (II) with 30% probability ellipsoids of thermal vibration for the nonhydrogen atoms.

The dihedral angle between the benzene ring and the averaged mean plane of the pyrazolinone ring (τ) is 30°. This opening is due to a competition between electronic ($n(N)-\pi^*(Ph)$) and steric factors. The former is at a maximum when $\tau = 0°$, and the latter at a minimum when $\tau = 90°$. When $\tau = 30°$, the repulsion between atoms $O_{(1)}...C_{(13)}$ (2.997(2), $O_{(1)}...1$-H 2.51(2), and $N_{(2)}...8$-H 2.58(3) Å is the least possible (the sums of the van der Waals radii are O...C 3.0, O...H 2.47, and N...H 2.67 Å [7]). Most of the structural parameters for (II) are in agreement with the geometry of analogous fragments [8].

Attention is drawn to the low pyramidicity of $N_{(1)}$ (sum of valence angles 358°), and to the $N_{(1)}-C_{(2)}$ bond length of 1.363(2) Å, which is 0.015-0.02 Å shorter than the N—H bond in an N-alkylamides [9]. This is surprising in view of the fact that in (II) the unshared electron pair at $N_{(1)}$ is involved in conjugation with imino-, phenyl, and carbonyl groups, i.e., the $n(N)-\pi^*$ (C=) interaction is expected to be less pronounced than in N—H- and N-alkylamides. In conclusion, it should be noted that the crystals of (II) are chiral, since the space group $P2_12_12_1$ is noncentrosymmetric.

EXPERIMENTAL

The IR spectrum was recorded on a Specord IR-75 in chloroform. PMR spectra were obtained on a Bruker WM-400 spectrometer in $CDCl_3$, internal standard TMS. Mass spectra were obtained on a Hitachi M-80 at 70 and 12 eV (peaks of relative intensity >10% are given).

X-Ray Structural Examination of Spirolactone (II). The principal crystallographic data for (II) are: $C_{13}H_{12}N_2O_3$; M = 244.27; a = 12.221(3); b = 14.353(3); c = 6.740(2) Å; V = 1182.3 Å^3; d_{calc} = 1.38 g/cm^3; Z = 4, space group $P2_12_12_1$. The intensities of 1167 reflexions with $I > 2\sigma(I)$ were measured on a DAR-UM automatic diffractometer ($0.054 \leq \sin(\theta/\lambda) \leq 0.6$; ($\theta/2\theta$ method, Cu Kα irradiation). Absorption was neglected ($\mu_{Cu\ K\alpha} = 10.5\ cm^{-1}$).

Direct method, Fourier synthesis, full-matrix least squares approximation (O, N, and C atoms) and isotropic (H atoms) to R = 0.029, using the program described in [10]. The molecular diagram was constructed using the ELLIDS program [11]. Geometric modelling of conformation (IIc) was carried out with the Viking suite of programs [12].

Spiro[(1-phenyl-3-methyl-2-pyrazolin-5-one)-4,5'-butyrolactone] (II). A mixture of 1.74 g (10 mmole) of the pyrazolinone (I), 0.86 g (10 mmole) of methyl acrylate, and 0.05 ml of triethylamine in 30 ml of dry methanol was kept for four months at 20°C. The solvent was then removed, and the residue distilled in vacuo to give 1.2 g of a viscous, yellow liquid, bp 210-220°C (2 mm), which was dissolved in 5 ml of dry ether, and the solution kept in the refrigerator for one month. There was obtained 0.32 g (13%) of colorless needles of (II), mp 146-147°C (from ether), readily soluble in chloroform, methanol, and DMSO, moderately soluble in ether and dioxane, and insoluble in pentane.

IR spectrum: 1807, 1790 (OCO), 1720 (CON), 1656 (C=N), 1595 cm^{-1} (Ph). ^{1}H NMR spectrum: 2.21 (3H, s, CH_3), 2.36 (1H, d.d.d., $^3J_{AB}$ = 13.4 Hz, $^3J_{AC}$ = 9.8 Hz, $^3J_{AD}$ = 10.10 Hz, H_A); 2.52 (1H, d.d.d, $^3J_{BD}$ = 9.8 Hz, $^3J_{BC}$ = 3.9 Hz, H_B); 2.73 (1H, d.d.d, $^2J_{CD}$ = −17.8 Hz, H_C); 3.13 (1H, d.d.d, H_D); 7.21 (1H, t, p-H), 7.41 (2H, t, m-H) and 7.83 ppm (2H, d, o-H) (Ph). ^{13}C NMR spectrum: 12.15 (Me, ^1J = 129.4 Hz), 26.58 ($\underline{C}H_2C$, ^1J = 135.5 Hz, ^2J = 3.7 Hz); 27.66 ($\underline{C}H_2CO$, ^1J = 137.9 Hz, ^2J = 4.9 Hz), 83.26 (spiro-C); 118.49, 125.58, 128.91, and 137.1 (Ph); 157.32 (C=C, ^2J = 4.9 Hz), 169.46 (NC=O); 174.51 ppm (OC=O). Chemical ionization mass spectrum in isobutane: m/z 245 $[M + H]^+$. Electron impact at 70 eV, m/z (relative intensity, %): M^+ 244 (100), 216 (18), 188 (18), 187 (33), 105 (15), 93 (18), 92 (27), 91 (27), 77 (80), 66 (10), 65 (16), 56 (20), 55 (27), 46 (22); at 12 eV: M^+ 244 (100), 216 (12), 188 (5). Found, %: C 63.9; H 4.9; N 11.5. $C_{13}H_{12}N_2O_3$. Calculated, %: C 63.9; H 4.9; N 11.5.

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