Chemistry of 2-methylene-2,3-dihydro-3-furanones
13*. Interaction of 2-methoxycarbonylmethylene-5-phenyl-2,3-dihydro-3-furanone with acetone azine

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[3+2]-Cycloaddition of 2-methoxycarbonylmethylene-5-phenyl-2,3-dihydro-3-furanone to acetone azine has been studied. This results in a monospirocycloadduct, *viz.*, 9,9-dimethyl-6-methoxycarbonyl-2-phenyl-1-oxa-7,8-diazaspiro[4.4]nona-2,6-dien-4-one. Its structure has been confirmed by X-ray diffraction analysis.

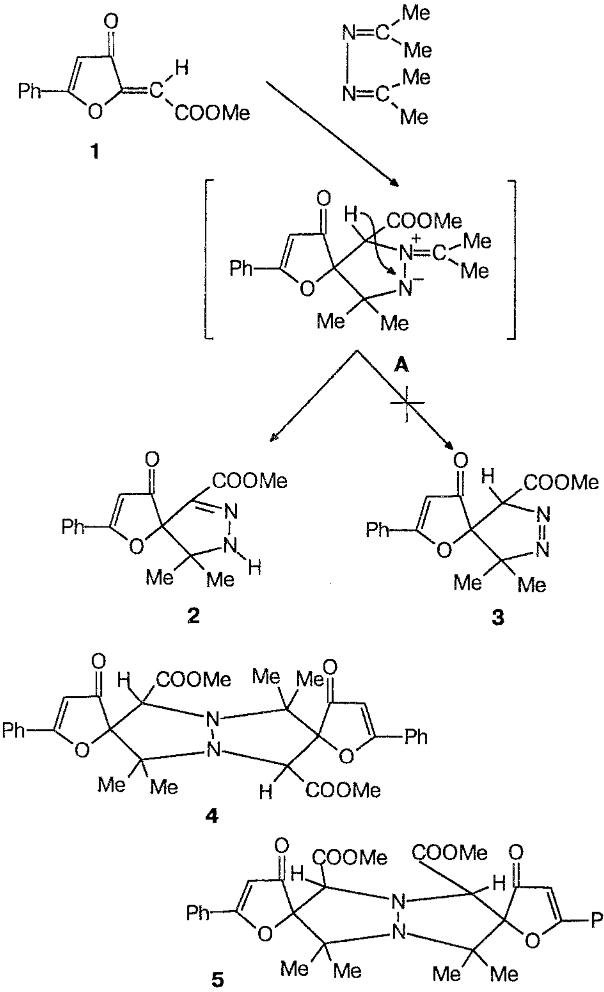
Key words: 2-methylene-2,3-dihydro-3-furanones, acetone azine, [3+2]-cycloaddition, 1-oxa-7,8-diazaspiro[4.4]nona-2,6-dien-4-one, crystal and molecular structure.

It is known that electron-deficient azines, for example hexafluoroacetone azine, readily enter a cycloaddition reaction with electron-rich alkenes to quantitatively form the "criss-cross" products, 1,5-diazabicyclo[3.3.0]octanes. Azomethinimines are isolated as intermediate 1:1 cycloadducts in this case.[2,3] The reactions of azines with electron-deficient alkenes (acrylates, maleic anhydride, *N*-phenylmaleimide) occur in an analogous way. These reactions are carried out under more drastic conditions (longer heating at 125–130 °C), which leads to the formation of only the criss-cross cycloaddition products.[2,3]

It was of interest to study the possibility of the reaction of 2-acetylmethylene-2,3-dihydro-3-furanones having an electron-deficient alkene fragment with azines. The most interesting reaction is that with azines that have a C-methyl group and can behave as nucleophiles in the enhydrazine form.[3]

Interaction of 2-methoxycarbonylmethylene-5-phenyl-2,3-dihydro-3-furanone (**1**) with acetone azine (brief boiling in ethanol) gave a product whose structure did not correspond to the criss-cross *bis*-spirocycloadducts (**4**) or (**5**). The selection between structures **2** and **3** could only be made by using the X-ray analysis data, which established that the product had the structure of 9,9-dimethyl-6-methoxycarbonyl-2-phenyl-1-oxa-7,8-diazaspiro[4.4]nona-2,6-dien-4-one (**2**). It seems likely that the [3+2]-cycloaddition of acetone azine to **1** proceeds *via* the elimination of propylene in the intermediate azomethinimine (A) (Scheme 1).

Scheme 1



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* For the previous communication see Ref. 1.

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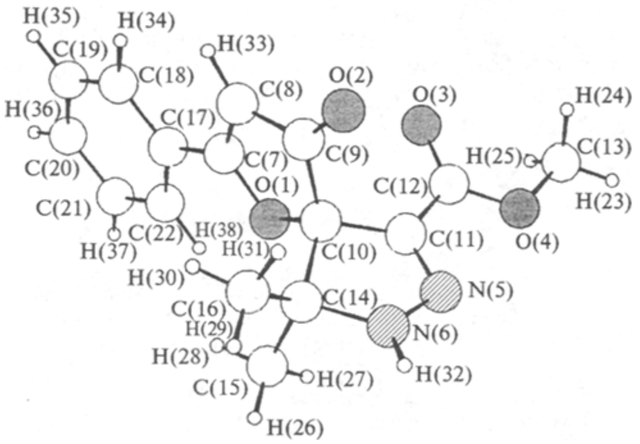


Fig. 1. Molecular structure of compound **2**.

Benzaldehyde, izopropylidenehydrazone, and acetophenone azine could not be involved in the interaction with furanone **1**.

Figure 1 shows the molecular structure of compound **2**. The structure of the pyrazoline spiro-fragment was established unambiguously: the C(11) atom is planar, the C(11)—N(5) double bond length is 1.299 Å, the hydrogen atom is reliably localized at the N(6) atom.

The phenyl and furan spiro-rings are coplanar; however, the possible conjugation between them does not affect the C(7)—C(17) bond length, which is equal to 1.464 Å. The pyrazoline cycle is not planar and has an envelope conformation. Bending along the N(6)...C(10) line in the direction opposite to the O(2) atom is 21.9°. The C(10)—C(14) (1.585 Å) bond is considerably longer than *r* $C(sp)^3$—$C(sp)^3$, (1.54 Å). The increase in the C(10)—C(9) (1.537 Å) bond length (*r* $C(sp)^3$—$C(sp)^2$ 1.50 Å) is nearly the same (0.04 Å). The lengthening of the C(9)—C(10) and C(10)—C(14) bonds, and the loss of planarity of the pyrazoline ring seem to be the result of steric strains arising between the O(2) atom and the C(16) methyl group. The methoxycarbonyl group and the N(6)—N(5)—C(11)—C(10) plane are almost coplanar. The O(3)—C(12)—C(11)—C(10) torsion angle is 3.2°. There are no hydrogen bonds in the crystal.

Experimental

The IR spectrum was recorded on an UR-20 spectrometer. The ^1H NMR spectrum was obtained on a RYa-2310 spectrometer (60 MHz) in $CDCl_3$ solution, HMDS as the internal standard. The ^{13}C NMR (δ) spectrum was recorded on a Bruker HX-90 spectrometer (90 MHz) in $CDCl_3$. The mass-spectrum (*m/z*, % of the maximum peak) was recorded on a Varian MAT-311 spectrometer, direct injection mode, emission current 1000 mA, energy of ionizing electrons 70 eV. The reactions were monitored, and the purity of the compounds was checked by TLC on Silufol UV-254 plates in the solvent system benzene—ether—acetone, 10:9:1, spots were visualized by iodine vapor. The starting azines were prepared according to the known procedures,[4,5] 2-methoxycarbonylmethylene-5-phenyl-2,3-dihydro-3-furanone (**1**) was obtained as described in Ref. 6. The crystals of **2** are triclinic: a = 9.973(4), b = 11.710(4), c = 7.329(3) Å, α = 97.98(3), β = 102.88(3), g = 111.08(4)°, V = 757 $Å^3$, Z = 2, d_{calc}= 1.317 $g \cdot cm^{-3}$, space group $P\bar{1}$.

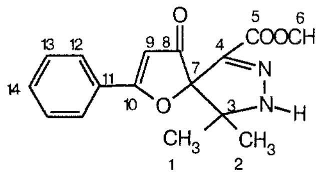
The experiments were carried out on a four-circle KM-4 diffractometer (KUMA-DIFFRACTION, Poland) with χ-geometry; $\theta/2\theta$ scan technique, Mo-radiation, graphite monochromator. A total of 2207 reflections were measured, 1252 independent reflections with $I > 4\sigma(I)$ were used in the calculations. The structure was solved by the direct statistical method and refined in a full-matrix anisotropic (for H atoms isotropic) approximation; the refinement was completed at R = 0.0425. The errors in the bond length determination (σ) were from 0.008 to 0.009 Å.

All calculations were performed on a PC AT 286 computer using the package of CSD programs.[7] Table 1 lists the atomic coordinates.

Table 1. Atomic coordinates

Atom	*x/a*	*y/b*	*z/c*	*B*(*i/e*)
O(1)	0.6384(4)	0.2175(3)	0.0530(5)	3.12(13)
O(2)	1.0336(4)	0.3609(4)	0.2133(6)	4.1(2)
O(3)	0.7889(5)	0.0967(4)	−0.1964(6)	4.8(2)
O(4)	0.8094(5)	−0.0647(3)	−0.0777(6)	4.3(2)
N(5)	0.8281(6)	0.0539(4)	0.2744(7)	3.9(2)
N(6)	0.8331(6)	0.1294(5)	0.4311(7)	4.5(2)
C(7)	0.6744(6)	0.3260(5)	−0.0123(8)	2.9(2)
C(8)	0.8221(6)	0.3986(5)	0.428(8)	3.3(2)
C(9)	0.8999(6)	0.3357(5)	0.1514(8)	3.0(2)
C(10)	0.7755(6)	0.2190(5)	0.1738(8)	2.7(2)
C(11)	0.7951(6)	0.0986(5)	0.1254(8)	2.9(2)
C(12)	0.7981(6)	0.0448(5)	−0.0644(8)	3.4(2)
C(13)	0.8088(4)	−0.1253(6)	−0.2606(10)	5.0(3)
C(14)	0.7656(4)	0.2197(5)	0.3868(8)	3.1(2)
C(15)	0.6028(7)	0.1624(7)	0.3898(10)	5.8(3)
C(16)	0.8493(8)	0.3420(6)	0.5294(10)	5.3(3)
C(17)	0.5451(7)	0.3437(5)	−0.1241(8)	3.3(2)
C(18)	0.5705(7)	0.4526(6)	−0.1973(9)	4.4(3)
C(19)	0.4473(9)	0.4698(7)	−0.2977(10)	5.1(3)
C(20)	0.3059(9)	0.3847(8)	−0.3280(10)	5.7(3)
C(21)	0.2807(7)	0.2784(6)	−0.2569(11)	5.4(3)
C(22)	0.4006(6)	0.2581(5)	−0.1558(9)	4.1(2)
H(23)	0.815(4)	−0.204(4)	−0.259(6)	5.5(10)
H(24)	0.888(4)	−0.074(4)	−0.290(6)	5.3(10)
H(25)	0.711(4)	−0.142(3)	−0.353(6)	5.6(10)
H(26)	0.589(4)	0.143(4)	0.502(6)	6.1(11)
H(27)	0.549(4)	0.069(4)	0.287(7)	7.1(12)
H(28)	0.559(5)	0.230(4)	0.369(7)	7.1(12)
H(29)	0.848(5)	0.338(4)	0.664(7)	7.2(12)
H(30)	0.807(5)	0.408(4)	0.502(7)	9.1(14)
H(31)	0.964(5)	0.369(4)	0.532(7)	7.5(12)
H(32)	0.844(5)	0.114(4)	0.540(7)	7.2(12)
H(33)	0.872(3)	0.479(3)	0.005(5)	3.2(8)
H(34)	0.683(4)	0.518(3)	−0.169(5)	3.6(8)
H(35)	0.473(4)	0.552(4)	−0.327(6)	5.8(11)
H(36)	0.217(4)	0.392(3)	−0.406(6)	5.4(10)
H(37)	0.179(4)	0.216(3)	−0.276(5)	3.8(8)
H(38)	0.384(3)	0.183(3)	−0.114(4)	2.1(7)

9,9-Dimethyl-6-methoxycarbonyl-2-phenyl-1-oxa-7,8-diazaspiro[4.4]nona-2,6-dien-4-one (2). A mixture of 1.15 g (5 mmol) of compound **1** and 1.12 g (10 mmol) of acetone azine was boiled for 5 min in 25 mL of ethanol (monitored by TLC). The residue was washed with ethanol and ether and recrystallized from ethanol. Yield 0.80 g (53 %), m.p. 211—212°C; IR, ν/cm^{-1}: 3302 (NH), 1713 ($\underline{CO}$OMe), 1672 (CO), 1588, 1562, 1524, 1447, 1408, 1344, 1375; ^{1}H NMR, δ: 1.35 (s, 6 H, 2 CH_3); 3.62 (s, 3 H, OCH_3); 6.02 (s, 1 H, CH); 7.30—8.00 (m, 5 H, C_6H_5); 13.17 (br. s, 1 H, NH); ^{13}C NMR, δ: 20.41 (C(1)), 23.14 (C(2)), 52.07 (C(6)), 71.18 (C(7)), 77.09 (C(3)), 94.91 (C(9)), 101.47 (C(4)), 127.21, 128.38, 128.97, 133.00 (C(11)—C(14)), 161.47 (C(10)), 184.16 (C(8)), 198.26 (C(5)).



Mass-spectrum, *m/z* (I_{rel}(%)): 302 $[M+2]^+$(4), 301 $[M+1]^+$(23), 300 $[M]^+$(100), 285 $[M-CH_3]^+$(10), 272 $[M-N_2]^+$(3), 269 $[M-OCH_3]^+$(3), 244 $[M-Me_2CN]^+$(23), 241 $[M-COOCH_3]^+$(24), 229 $[M-Me_2CN_2]^+$(5), 213 $[M-Me_2CN-OCH_3]^+$(18), 212 $[M-Me_2CN-CH_3OH]^+$(28), 195 $[M-PhCO]^+$(23), 185 $[M-Me_2CN-COOCH_3]^+$(7), 147 $[PhCOCH_2\text{–}CO]^+$(34), 105 $[PhCO]^+$(59), 102 $[PhC{\equiv}CH]^+$(52), 77 $[Ph]^+$(48), 56 $[Me_2CN]^+$(55). Found (%): N, 9.51. $C_{16}H_{16}N_2O_4$. Calculated (%): N, 9.33. Mol. weight 300.32.

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