# Interaction of 4,5-diphenyl-2,3-dihydro-2,3-pyrroledione with ethoxycarbonylmethylenetriphenylphosphorane: synthesis and crystal structure of 4,5-diphenyl-*Z*-2-ethoxycarbonylmethylene-2,3-dihydro-3-pyrrolone

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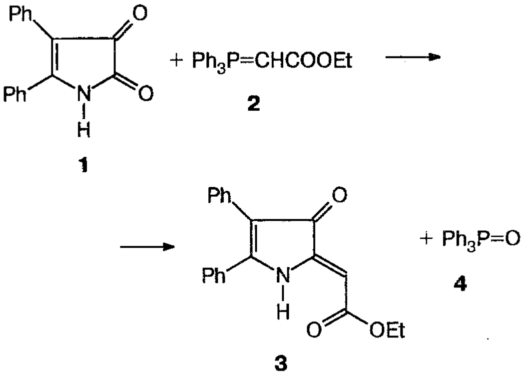
1-Unsubstituted 4,5-diphenyl-2,3-dihydro-2,3-pyrroledione interacts with ethoxycarbonylmethylenetriphenylphosphorane regioselectively to give 4,5-diphenyl-*Z*-2-ethoxycarbonylmethylene-2,3-dihydro-3-pyrrolone. The crystal and molecular structure of the latter was studied by X-ray analysis.

**Key words:** 2,3-dihydro-2,3-pyrroledione, alkoxycarbonylmethylenetriphenylphosphorane, Wittig reaction, crystal and molecular structure.

There is information in the literature concerning reactions of benzo[*b*]-2,3-dihydropyrrole-2,3-diones, *i.e.*, isatins, with Wittig reagents, proceeding at the ketonic carbonyl group with the formation of *E*-3-methylene-2,3-dihydroindoline-2-ones.[1] The interaction of phosphoranes with 2,3-dihydropyrrole-2,3-diones, which are not fused with a benzene ring at their [*a*]-side, has not been studied yet. It should be noted that annelation of pyrroledione oxa-analogs, 2,3-dihydrofuran-2,3-diones, with benzene changes the reaction direction of these compounds with triphenylphosphoranes, so that 5-aryl-2,3-dihydrofuran-2,3-diones react[2] at their carbonyl group in position 2 and benzo[*b*]-2,3-dihydro-2,3-furandiones, coumarandiones, react at their carbonyl group in position 3 with the formation[3] of methylene derivatives and triphenylphosphine oxide, respectively.

1-Unsubstituted 4,5-diphenyl-2,3-dihydropyrrole-2,3-dione (**1**) reacts with ethoxycarbonylmethylenetriphenylphosphorane (**2**), taken in proportion 1:1, under boiling in benzene for 0.5 h. The reaction proceeds regioselectively to give in a high yield 4,5-diphenyl-*Z*-2-ethoxycarbonylmethylene-2,3-dihydro-3-pyrrolone (**3**), which is a product of Wittig reaction at lactam carbonyl rather than at ketone group of pyrroledione **1**, as well as triphenylphosphine oxide (**4**).

Since the reaction between compounds **1** and **2** can lead to formation of several stereo- and regioisomers, we studied the structure of compound **3** by the X-ray analysis.



The general appearance of molecule **3** is shown in Fig. 1. Bond lengths and valence angles are given in Tables 1 and 2. The fragment CHCOOPh is planar and coplanar with the heterocyclic plane. The angle between the corresponding planes is equal to 7°. Carbonyl group C(6)=O(3) is *cis*-oriented toward nitrogen atom N(1). The planar structure is probably stabilized by the formation of a united conjugated system, which explains the red color of the crystals. In addition to that, the binding between the carbon atoms C(1)=C(2) and C(4)=C(5) (1.36 and 1.34 Å, respectively) as well as in the carbonyl groups C(3)=O(1) and C(6)=O(3) (1.23 and 1.21 Å, respectively) has a clearly marked double bond character. The other geometric molecular parameters have the usual values. Thus, any significant influence of the

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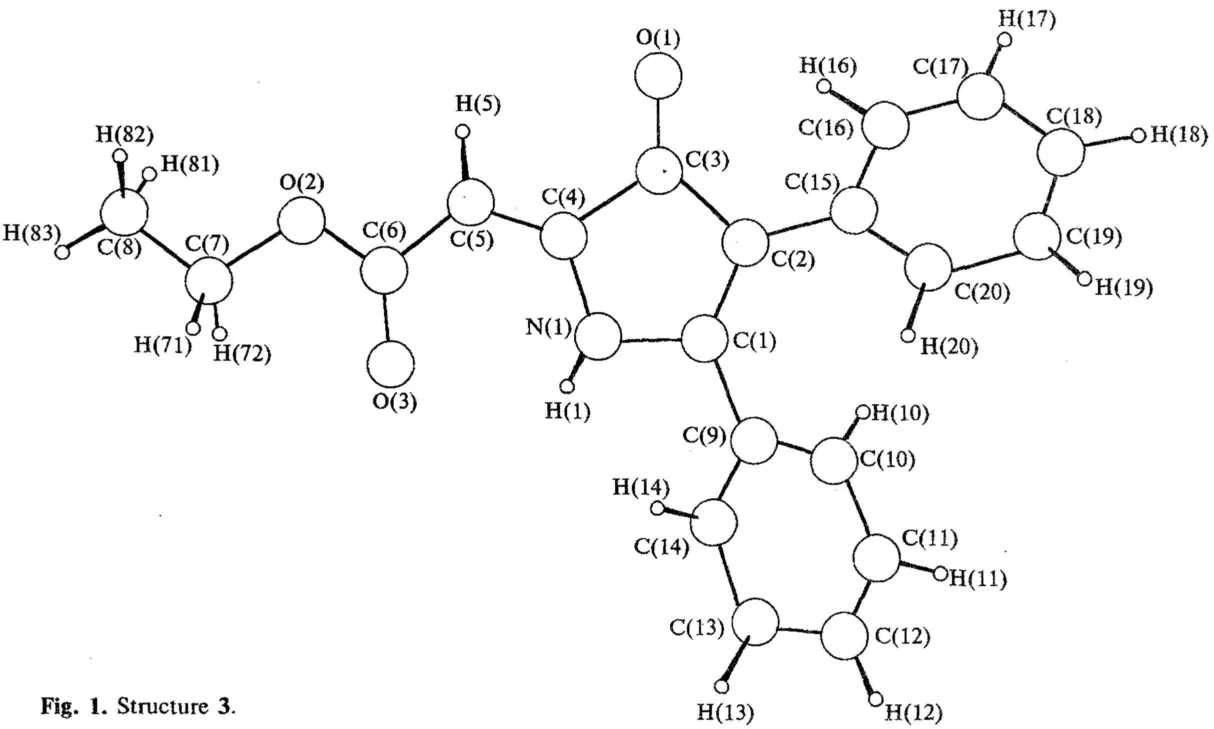

**Fig. 1.** Structure **3**.

**Table 1.** Bond lengths in structure **3**

| Bond | $d$/Å | Bond | $d$/Å |
|---|---|---|---|
| O(1)—C(3) | 1.226(7) | O(2)—C(6) | 1.343(9) |
| O(2)—C(7) | 1.46(1) | O(3)—C(6) | 1.21(1) |
| N(1)—C(1) | 1.40(1) | N(1)—C(4) | 1.375(9) |
| C(1)—C(2) | 1.357(8) | C(1)—C(9) | 1.468(9) |
| C(2)—C(3) | 1.468(9) | C(3)—C(4) | 1.50(1) |
| C(2)—C(15) | 1.47(1) | C(4)—C(5) | 1.34(1) |
| C(5)—C(6) | 1.47(1) | C(7)—C(8) | 1.49(1) |
| C(9)—C(10) | 1.39(1) | C(9)—C(14) | 1.39(1) |
| C(10)—C(11) | 1.38(1) | C(11)—C(12) | 1.37(1) |
| C(12)—C(13) | 1.38(1) | C(13)—C(14) | 1.39(1) |
| C(14)—H(14) | 0.91(7) | C(15)—C(20) | 1.39(1) |
| C(15)—C(16) | 1.39(1) | C(16)—C(17) | 1.39(1) |
| C(17)—C(18) | 1.37(1) | C(18)—C(19) | 1.38(1) |
| C(19)—C(20) | 1.38(1) | | |

conjugation between the ethoxycarbonylmethylene fragment and the heterocycle on molecular bond lengths is not observed.

Phenyl substituents are twisted with respect to the heterocyclic plane (torsion angles C(10)C(9)C(1)C(2) and C(16)C(15)C(2)C(1) are equal to 42 and 34°, respectively; the phenyl ring planes form an angle of 47° between them).

There are no intermolecular hydrogen bonds in the crystal. The minimum intermolecular contact between the atoms O(1) and N(1) belonging to molecules connected by a sliding reflection plane *n* is equal to 3.13 Å. This value does not unambigously indicate the presence of a hydrogen bond.

**Table 2.** Valence angles in structure **3**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| C(6)—O(2)—C(7) | 115.7(6) | C(1)—N(1)—C(4) | 109.4(6) |
| N(1)—C(1)—C(2) | 112.1(6) | N(1)—C(1)—C(9) | 116.0(6) |
| C(2)—C(1)—C(9) | 132.0(6) | C(1)—C(2)—C(3) | 106.3(6) |
| C(1)—C(2)—C(15) | 129.1(6) | C(3)—C(2)—C(15) | 124.5(6) |
| O(1)—C(3)—C(2) | 130.1(6) | O(1)—C(3)—C(4) | 124.1(6) |
| C(2)—C(3)—C(4) | 105.7(6) | N(1)—C(4)—C(3) | 106.1(6) |
| N(1)—C(4)—C(5) | 127.9(7) | C(3)—C(4)—C(5) | 126.0(7) |
| C(4)—C(5)—C(6) | 122.8(7) | O(2)—C(6)—O(3) | 124.0(7) |
| O(2)—C(6)—C(5) | 111.0(7) | O(3)—C(6)—C(5) | 125.0(7) |
| O(2)—C(7)—C(8) | 107.2(7) | C(1)—C(9)—C(14) | 120.4(7) |
| C(1)—C(9)—C(10) | 122.2(7) | C(9)—C(10)—C(11) | 122.2(7) |
| C(10)—C(9)—C(14) | 117.4(7) | C(10)—C(11)—C(12) | 118.7(8) |
| C(11)—C(12)—C(13) | 121.5(8) | C(12)—C(13)—C(14) | 118.5(8) |
| C(9)—C(14)—C(13) | 121.7(7) | C(17)—C(18)—C(19) | 119.1(8) |
| C(2)—C(15)—C(16) | 122.7(6) | C(2)—C(15)—C(20) | 120.0(6) |
| C(16)—C(15)—C(20) | 117.3(7) | C(15)—C(16)—C(17) | 121.0(7) |
| C(16)—C(17)—C(18) | 120.7(8) | C(18)—C(19)—C(20) | 120.6(8) |
| C(15)—C(20)—C(19) | 121.2(7) | | |

## Experimental

IR spectra were recorded on an UR-20 spectrometer in Vaseline oil and in 0.01 *M* solution in $CHCl_3$, cell of 0.4 mm width. $^1H$ NMR spectra were recorded with a Bruker WP-80SV (80 MHz) instrument in chloroform-d; the internal standard was HMDS. The homogeneity of compound **3** was confirmed by TLC on Silufol plates in a benzene—ethyl acetate (5:1) system.

The investigation of compound **3** by X-ray analysis was carried out on an automatic four-circle KM-4 diffractometer (KUMA DIFFRACTION), Mo-Kα radiation, graphite mono-

**Table 3.** Atomic coordinates (×$10^4$, for H atoms — ×$10^3$) in structure **3**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 1435(2) | −3386(4) | 2127(0) |
| O(2) | 1148(2) | 734(5) | 8965(7) |
| O(3) | 2448(3) | 736(5) | 9373(6) |
| N(1) | 2968(3) | −1255(6) | 1229(8) |
| C(1) | 3309(3) | −2043(6) | 2245(8) |
| C(2) | 2800(3) | −2969(6) | 2758(8) |
| C(3) | 2051(4) | −2748(6) | 2060(9) |
| C(4) | 2184(4) | −1567(6) | 1130(8) |
| C(5) | 1634(5) | −935(7) | 389(9) |
| C(6) | 1805(5) | 248(7) | 9537(8) |
| C(7) | 1249(4) | 1923(8) | 8100(10) |
| C(8) | 461(6) | 2290(10) | 7560(10) |
| C(9) | 4133(4) | −1745(6) | 2555(9) |
| C(10) | 4416(4) | −1708(7) | 3880(10) |
| C(11) | 5193(4) | −1432(7) | 4170(10) |
| C(12) | 5703(5) | −1210(8) | 3110(10) |
| C(13) | 5447(4) | −1182(8) | 1790(10) |
| C(14) | 4659(4) | −1457(7) | 1520(10) |
| C(15) | 2937(4) | −4025(6) | 3781(8) |
| C(16) | 3650(4) | −4704(7) | 3907(9) |
| C(17) | 3770(5) | −5648(9) | 4930(10) |
| C(18) | 3181(5) | −5960(8) | 5820(10) |
| C(19) | 2466(5) | −5328(8) | 5691(9) |
| C(20) | 2343(4) | −4376(7) | 4683(9) |
| H(1) | 311(3) | −41(6) | 114(7) |
| H(5) | 111(3) | −126(5) | 45(6) |
| H(71) | 149(3) | 274(6) | 856(7) |
| H(72) | 165(3) | 171(5) | 740(6) |
| H(81) | 51(4) | 320(7) | 701(8) |
| H(82) | 9(4) | 260(8) | 835(8) |
| H(83) | 21(4) | 152(6) | 719(7) |
| H(10) | 409(3) | −192(6) | 463(6) |
| H(11) | 540(4) | −134(7) | 529(8) |
| H(12) | 622(4) | −113(7) | 331(8) |
| H(13) | 581(4) | −95(6) | 94(7) |
| H(14) | 447(3) | −149(6) | 67(7) |
| H(16) | 410(3) | −449(6) | 312(7) |
| H(17) | 425(3) | −608(6) | 492(6) |
| H(18) | 329(4) | −661(7) | 667(9) |
| H(19) | 208(3) | −565(6) | 626(6) |
| H(20) | 182(4) | −390(6) | 455(6) |

chromator. 1108 independent reflections were measured, from which 997 with $I > 3\sigma(I)$ were used for calculations. The structure was solved by a direct statistical method, hydrogen atoms were objectively localized from a difference synthesis of electron density. The MSM refinement was carried out in full-matrix anisotropic (for H atoms — in isotropic) approximation until $R = 0.028$. The calculations were executed using a CSD program package.[4] Red prismatic well edged crystals of compound **3** belong to orthorhombic system, $a = 17.052(6)$, $b = 9.846(3)$, $c = 9.880(4)$ Å, $V = 1658.7$ Å$^3$, mol. weight 319.35, $d_{calc} = 1.286$ g cm$^{-3}$, $Z = 4$; space group $Pbn2_1$ ($Pna2_1$). Atomic coordinates are given in Table 3.

***Z*-2-Ethoxycarbonylmethylene-4,5-diphenyl-2,3-dihydro-3-pyrrolone (3).** A solution of 0.01 mol of compound **1** and 0.01 mol of compound **2** in 100 mL of benzene was boiled for 0.5 h (the reaction course was monitored by TLC), and the solvent was removed. The residue was dissolved in 25 mL of benzene and chromatographed on a column of silica gel (40—100 μm), collecting the first red fraction. Yield 2.55 g (80 %), m.p. 127.5—128.5 °C (from heptane). Found (%): C, 75.17; H, 5.45; N, 4.40. $C_{20}H_{17}NO_3$. Calculated (%): C, 75.22; H, 5.36; N, 4.38. IR (ν/cm$^{-1}$): 3350 (NH); 1670 br (C(3)=O, COOEt). IR spectrum of the solution: 3285 (NH); 1665 br (C(3)=O, COOEt). $^1$H NMR (δ): 1.28 (t, 3 H, Me, $J$ = 8 Hz); 4.23 (q, 2 H, $CH_2O$, $J$ = 8 Hz); 6.01 (s, 1 H, CH); 7.06—7.71 (m, 10 H, 2 Ph); 8.59 (s, 1 H, NH).

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