Chemistry of Heterocyclic Compounds, Vol. 45, No. 5, 2009

REACTIONS OF 1-ARYL- AND 2,3-DIARYL-5-DIAZO-6,6-DIMETHYL-4-OXO-4,5,6,7-TETRAHYDROINDAZOLES WITH N-ETHYL- AND N-PHENYL-SUBSTITUTED MALEIMIDES

I. Strakova[1], M. Turks[1], E. Bizdena[1], S. Belyakov[2], A. Tokmakov[2], and A. Strakovs[1]*

[3+2] Cyclocondensation reactions of a series of 1,3- and 2,3-disubstituted 5-diazo-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles with N-ethyl- and N-phenyl-substituted maleimides have been used to obtain the corresponding 6,6-dimethyl-4,4',6'-trioxo-4,5,6,7-3',3'a,4',5',6',6'a-decahydrospiro-[indazole-5,3'-pyrrolo[3,4-c]pyrazoles]. On boiling these compounds in toluene nitrogen is split off and they are converted into 6',6'-dimethyl-2,4,4'-trioxo-4',5',6',7'-tetrahydro-1'H-spiro[3-azabicyclo-(3.1.0)hexane-6,5'-indazoles].

Keywords: 1,3- and 2,3-substituted 5-diazo-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindazoles, N-ethyl- and N-phenylmaleimides, [3+2] cycloaddition reactions.

In the last decade new methods of synthesis of indazoles have been designed, and include hydrogenated indazoles [1-8]. This is the result of the varied biological action of a large number of synthesized indazole derivatives. Among them have been discovered agonists and antagonists of estrogen receptors [9, 10], dopamine D-3 [11, 12], corticotropin [13], and adenosine [14]; derivatives have been found with antitumor [15], anti-inflammatory [16], and antimicrobial [17] action; inhibitors of HIV proteases [18] and membrane-active substances [19] have been discovered. Indazole derivatives have also been used as ligands [20].

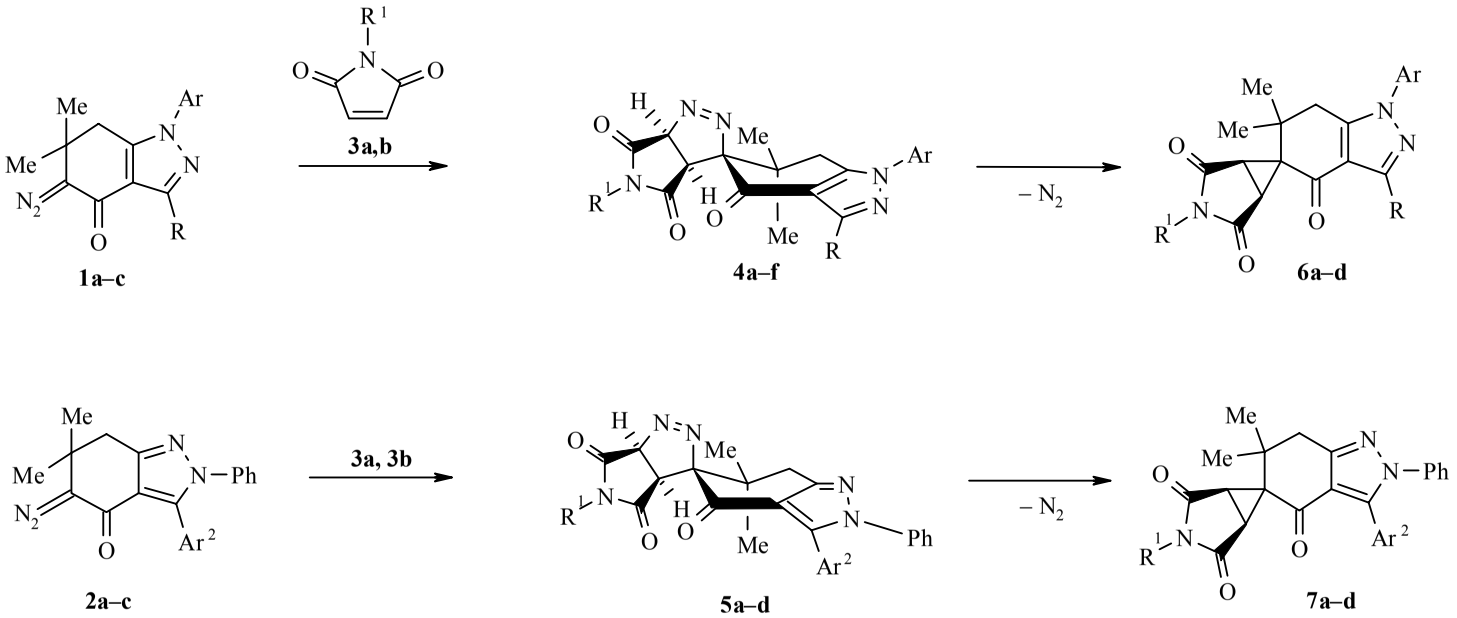
Previously, based on 4,5-dioxo-, 4-chloro-5-formyl-, and 5-diazo-4-oxo derivatives of 4,5,6,7-tetrahydroindazoles obtained by us, we synthesized a series of derivatives of them annelated with heterocycles [21-24].

The interaction of 1-aryl- and 2,3-diaryl-5-diazo-4-oxo-4,5,6,7-tetrahydroindazoles of types **1** and **2** with maleic anhydride and acetylenedicarboxylic acid ester has been carried out. This led to the formation of the corresponding 3-spiropyrazoline and pyrazole derivatives of 4,5,6,7-tetrahydroindazole [25].

* To whom correspondence should be addressed, e-mail: strakovs@latnet.lv.

[1]Riga Technical University, Riga LV-1048, Latvia.
[2]Latvian Institute of Organic Synthesis, Riga LV-1006, Latvia; e-mail: serg@osi.lv.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 695-704, May, 2009. Original article submitted January 4, 2008; revision submitted May 14, 2008.



1 a Ar = Ph, R = H, **b** Ar = 2-pyridyl, R = Me, **c** Ar = Ph, R = Me; **3 a** R^1 = Et, **b** R^1 = Ph; **4**, **6 a** Ar = R^1 = Ph, R = H, **b** Ar = R^1 = Ph, R = Me, **c** Ar = 2-pyridyl, R = Me, R^1 = Ph; **4 d** Ar = Ph, R = H, R^1 = Et, **e** Ar = 2-pyridyl, R = Me, R^1 = Et, **f** Ar = Ph, R = Me, R^1 = Et; **6 d** Ar = 2-pyridyl, R = Me, R^1 = Et; **2 a** Ar^2 = Ph, **b** Ar^2 = C_6H_4Cl-4, **c** Ar^2 = $C_6H_4NMe_2$-4; **5**, **7 a** Ar^2 = R^1 = Ph, **b** Ar^2 = C_6H_4Cl-4, R^1 = Ph; **c** Ar^2 = C_6H_4Cl-4, R^1 = Et; **d** Ar^2 = $C_6H_4NMe_2$-4, R^1 = Ph

In the development of the work mentioned above the reaction of compounds **1a-c** and **2a-c** [26, 27] with N-ethyl- (**3a**) and N-phenylmaleimide (**3b**) is described in the present report. This was carried out according to classical procedures [28, 29] and permitted the synthesis in high yield of the corresponding 6,6-dimethyl-4,4',6'-trioxo-4,5,6,7,3',3'a,4',5',6',6'a,-decahydrospiro [ndazole-5,3'-pyrrolo[3,4-*c*]pyrazoles] **4a-f**, **5a-d**. Compounds **4** and **5** were obtained as racemates. One of the arbitrarily chosen enantiomeric forms is depicted in the Scheme. On boiling products **4**, **5** in toluene or anisole nitrogen is eliminated and 6',6'-dimethyl-2,4,4'-trioxo-4',5',6',7'-tetrahydro-1'H-spiro[3-azabicyclo(3.1.0)hexane-6,5'-indazoles] **6a-d, 7a-d** were formed.

The composition and structure of the obtained compounds **4-7** were confirmed by the results of elemental analysis (Table 1) and data of ^{1}H NMR spectra (Table 2), and for compounds **4b** and **7c** also by data of X-ray structural analysis) (Tables 3, 4, and Figs. 1, 2).

In the ^{1}H NMR spectra of spirocompounds **4** and **5** the signals of the protons of the 7'-CH_2 group have the form of two doublets with J = 16 Hz, and the H-3a and H-6a signals are two doublets with J = 9 Hz, indicating their *cis* disposition. In the spectra of spiro compounds **6** and **7** one two-proton singlet signal is present for the 7'-CH_2 group and also a singlet signal for the protons at positions 3a and 6a. The protons of all the other structural fragments of compounds **4-7** were detected in the expected regions of the spectra.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield %
		C	H	N	M*		
4a	$C_{25}H_{21}N_5O_3$	67.91 / 68.33	4.68 / 4.82	16.17 / 15.93	—	185-187 (dec.)	52
4b	$C_{26}H_{23}N_5O_3$	68.43 / 68.86	4.98 / 4.11	15.44 / 13.73		185-187 (dec.)	80
4c	$C_{25}H_{22}N_6O_3$	66.04 / 66.06	4.81 / 4.88	18.47 / 18.49		196-198 (dec.)	82
4d	$C_{21}H_{21}N_5O_3$	62.08 / 65.17	5.43 / 5.72	16.14 / 17.27		187-188 (dec.)	73
4e	$C_{21}H_{22}N_6O_3$	62.00 / 62.05	5.38 / 5.45	20.14 / 20.70		203-205 (dec.)	85
4f	$C_{22}H_{23}N_5O_3$	65.32 / 64.44	5.46 / 5.41	16.09 / 17.09		176-178 (dec.)	56
5a	$C_{31}H_{25}N_5O_3$	70.43 / 72.22	4.75 / 4.89	13.14 / 13.58		185-187 (dec.)	69
5b	$C_{31}H_{24}ClN_5O_3$	68.27 / 69.21	4.30 / 4.50	12.36 / 13.02		208-210 (dec.)	50
5c	$C_{27}H_{24}ClN_5O_3$	64.35 / 64.61	4.66 / 4.81	13.71 / 13.95		187-190 (dec.)	84
5d	$C_{33}H_{30}N_6O_3$	65.68 / 65.92	5.35 / 5.53	15.19 / 15.37		175-178 (dec.)	96
6a	$C_{25}H_{21}N_3O_3$	72.98 / 72.98	5.14 / 4.99	10.21 / 10.21	411.2 / 411.2	257-258	98
6b	$C_{26}H_{23}N_3O_3$	73.11 / 73.39	5.30 / 5.45	10.02 / 9.87	425.2 / 425.2	244-246	87
6c	$C_{25}H_{22}N_4O_3$	70.37 / 70.41	5.16 / 5.20	13.14 / 13.13	426.2 / 426.2	216-217	99
6d	$C_{21}H_{22}N_4O_3$	66.41 / 66.65	5.85 / 5.86	14.69 / 14.80	378.2 / 378.2	200-201	99
7a	$C_{31}H_{25}N_3O_3$	76.26 / 76.37	5.05 / 5.17	8.71 / 8.62	487.2 / 487.2	246-247	83
7b	$C_{31}H_{24}ClN_3O_3$	71.12 / 71.33	4.56 / 4.63	8.01 / 8.05	521.2 / 521.2	256-257	87
7c	$C_{27}H_{24}ClN_3O_3$	68.20 / 68.42	4.98 / 5.10	8.80 / 8.87	473.2 / 473.2	226-227	89
7d	$C_{31}H_{30}N_4O_3$	74.08 / 74.11	5.71 / 5.83	10.44 / 10.80	530.2 / 530.2	236-237	85

* Average molecular mass of substance.

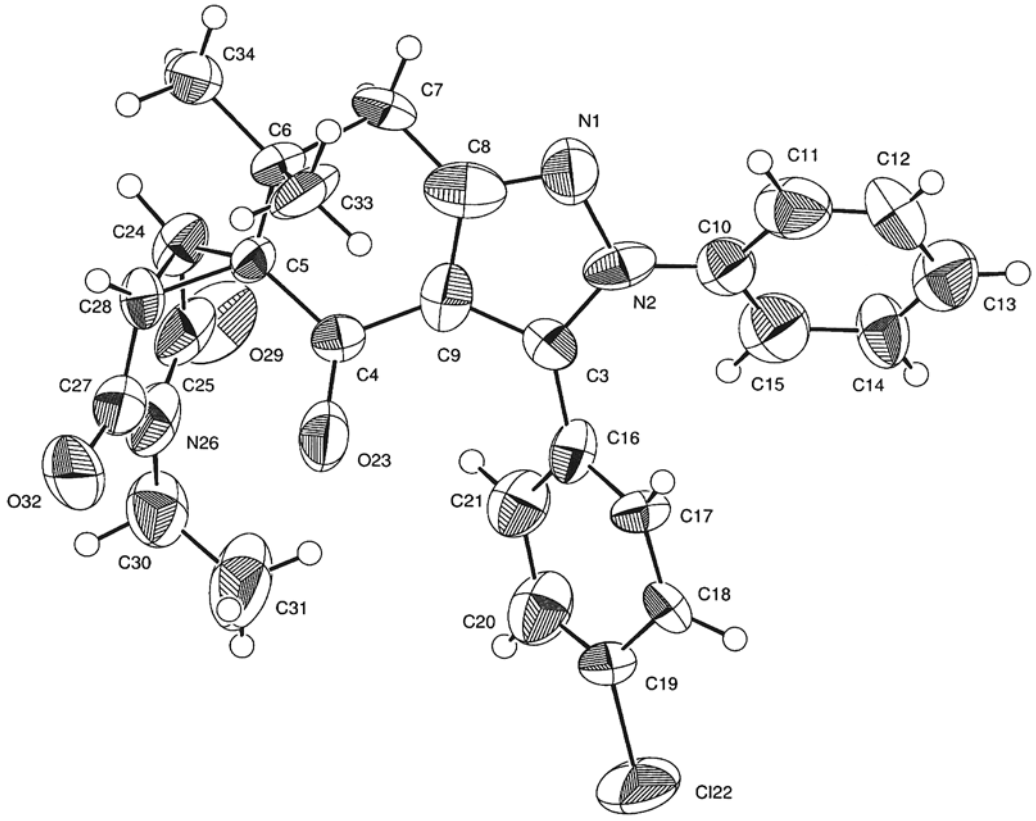


Fig. 1. Spatial model of the compound **7c** molecule with numbering of atoms and ellipsoids of thermal vibrations.

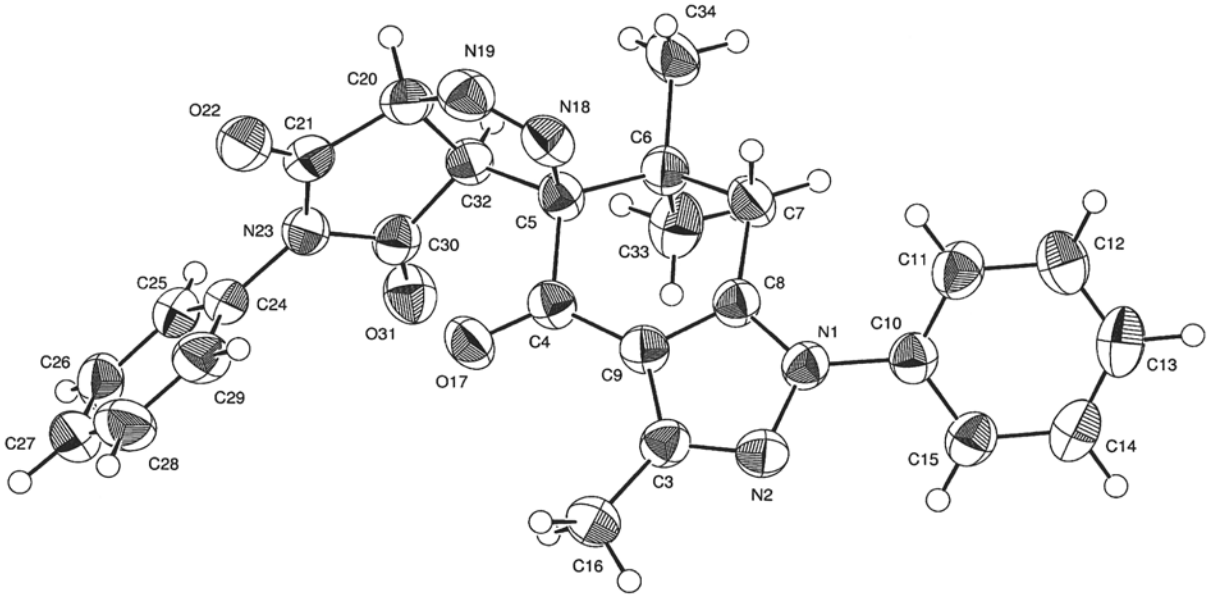


Fig. 2. Spatial model of the compound **4b** molecule with numbering of atoms and ellipsoids of thermal vibrations.

TABLE 2. Data of GLC/HPLC and ^{1}H NMR Spectra of the Synthesized Compounds

Compound	Retention time, min	^{1}H NMR spectrum ($CDCl_3$)*, δ, ppm, (*J*, Hz)
4a	—	1.04 (3H, s, CH_3); 1.27 (3H, s, CH_3); 3.00 (1H, d, *J* = 16.2, H-7'); 3.22 (1H, d, ^3J = 9.2, H-3a); 3.70 (1H, br. d, *J* = 16.0, H-7'); 6.20 (1H, d, ^3J = 9.2, H-6a); 7.50-7.60 (10H, m, C_6H_5); 8.13 (1H, s, H-3')
4b	4.15	1.04 (3H, s, CH_3); 1.27 (3H, s, CH_3); 2.51 (3H, s, 3-CH_3); 2.95 (1H, d, *J* = 16.6, H-7'); 3.20 (1H, d, *J* = 9.2, H-3'a); 3.70 (1H, br. d, *J* = 16.0, H-7'); 6.18 (1H, d, *J* = 9.2, H-6a); 7.50-7.60 (10H, m, C_6H_5)
4c	5.49	1.11 (3H, s, CH_3); 1.30 (3H, s, CH_3); 2.50 (3H, s, 3'-CH_3); 3.22 (1H, d, *J* = 9.0, H-3a); 3.80 and 3.85 (2H, 2d, AB-system, *J* =18.0, H-7'); 6.16 (1H, d, *J* = 9.0, H-6a); 7.27 (1H, ddd, *J* = 4.8, *J* = 2.0, *J* = 1.2, Py); 7.37-7.55 (5H, m, C_6H_5); 7.87 (1H, ddd, *J* = 8.4, *J* = 7.4, *J* = 1.8, Py); 8.02 (1H, d, *J* = 8.2, Py); 8.48 (1H, ddd, *J* = 5.0, *J* =1.8, *J* =1.0, Py)
4d	—	1.02 (3H, s, CH_3); 1.20 (3H, s, CH_3); 1.27 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.97 (1H, d, *J* = 17.0, H-7'); 3.05 (1H, d, *J* = 9.0, H-3a); 3.57-3.68 (3H, m, H-7', $C\underline{H}_2CH_3$); 5.98 (1H, d, *J* = 9.0, H-6a); 7.47-7.57 (5H, m, C_6H_5); 8.10 (1H, s, H-3')
4e	5.31	1.11-1.15 (6H, br. s, CH_3); 1.24 (3H, t, *J* = 7.0, $CH_2C\underline{H}_3$); 2.47 (3H, s, CH_3); 3.06 (1H, d, *J* = 9.0, H-3a); 3.63 (2H,q, *J* = 7.0, $C\underline{H}_2CH_3$); 3.70, 3.90 (2H, 2d, AB-system, *J* = 18.0, H-7'); 5.93 (1H, d, *J* = 9.0, H-6a); 7.28 (1H, dt, *J* = 5.6, *J* = 1.5, Py); 7.86 (1H, dt, *J* = 8.2, *J* = 2.0, Py); 8.00 (1H, d, *J* = 8.4, Py); 8.51 (1H, ddd, *J* = 5.2, *J* = 1.5, *J* = 0.6, Py)
4f	4.62	1.01 (3H, s, CH_3); 1.21 (3H, s, CH_3); 1.27 (3H, t, *J* = 7.2, CH_2-$C\underline{H}_3$); 2.47 (3H, s, 3'-CH_3); 2.93 (1H, d, *J* = 16.6, H-7'); 3.03 (1H, d, *J* = 9.0, H-3a); 3.54-3.68 (3H, m, $C\underline{H}_2CH_3$, H-7'); 5.92 (1H, d, *J* = 9.0, H-6a); 7.54-7.94 (5H, m, C_6H_5)
5a	5.22	1.21 (3H, br. s, CH_3); 1.31 (3H, s, CH_3); 3.10 (1H, d, *J* = 16.0, H-7'); 3.29 (1H, d, *J* = 9.2, H-3a); 3.56 (1H, d, *J* = 16.0, H-7'); 6.14 (1H, d, *J* = 9.2, H-6a); 7.26-7.38 (15H, m, C_6H_5)
5b	5.84	1.05 (3H, br. s, CH_3); 1.30 (3H, br. s, CH_3); 3.19 (2H, br. s, H-7'); 3.70 (1H, d, *J* = 8.2, H-3a); 6.46 (1H, d, *J* = 8.2, H-6a); 7.09 (2H, m, C_6H_4); 7.22-7.33 (4H, m, C_6H_5, C_6H_4); 7.41-7.44 (8H, m, C_6H_5)
5c	8.18	1.11 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 1.20 (6H, br. s, CH_3); 3.05 (1H, d, *J* = 16.2, H-7'); 3.14 (1H, d, *J* = 9.0, H-3a); 3.35-3.44 (1H, br. s, H-7'); 3.52 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 5.92 (1H, d, *J* = 9.0, H-6a); 7.17-7.27 (6H, m, C_6H_5, C_6H_4); 7.33-7.38 (3H, m, C_6H_4)
5d	6.94	1.17 (3H, br. s, CH_3); 1.32 (3H, br. s, CH_3); 2.97 (6H, s, $N(CH_3)_2$); 3.05 (1H, d, *J* = 16.2, H-7'); 3.26 (1H, d, *J* = 9.2, H-3a); 3.56 (1H, br. s, H-7'); 6.13 (1H, d, *J* = 9.2, H-6a); 6.53 (2H, d, *J* = 9.0, C_6H_4); 7.16 (2H, d, *J* = 9.0, C_6H_4); 7.34-7.39 (10H, m, C_6H_5)
6a	16.04	1.11 (6H, s, $2CH_3$); 3.00 (4H, s, H-7',3a,6a); 7.34-7.58 (10H, m, C_6H_5); 8.20 (1H, s, H-3')
6b	15.11	1.20 (6H, s, CH_3); 2.48 (3H, s, CH_3); 2.97 (4H, s, H-7',3a,6a); 7.34-7.52 (10H, m, C_6H_5)
6c	16.03	1.18 (6H, s, CH_3); 2.48 (3H, s, 3'-CH_3); 2.98 (2H, s, H-7'); 3.51 (2H, s, H-3a,6a); 7.25 (1H, ddd, *J* = 7.2, *J* = 4.8, *J* = 1.2, Py); 7.32-7.52 (5H, m, C_6H_5); 7.85 (1H, ddd, *J* = 8.4, *J* = 7.4, *J* = 1.8, Py); 7.97 (1H, dt, *J* = 8.4, *J* = 1.0, Py); 8.45 (1H, ddd, *J* = 5.0, *J* = 1.8, *J* = 1.0, Py)
6d	7.41	1.11 (6H, s, CH_3); 1.15 (3H, t, ^3J = 7.4, $CH_2C\underline{H}_3$); 2.43 (2H, s, 3'-CH_3); 2.78 (2H, s, H-7'); 3.45 (2H, s, H-3a,6a); 3.48 (2H, q, *J* = 7.4, $C\underline{H}_2CH_3$); 7.23 (1H, ddd, *J* = 8.6, *J* = 7.0, *J* = 2.0, Py); 7.84 (1H, ddd, *J* = 7.9, *J* = 7.8, *J* = 2.0, Py); 7.96 (1H, dt, *J* = 8.4, *J* = 1.0, Py); 8.45 (1H, ddd, *J* = 5.0, *J* = 1.8, *J* = 1.0, Py)
7a	24.73	1.18 (6H, s, CH_3); 2.99 (2H, s, H-7'); 3.02 (2H, s, H-3a,6a); 7.13-7.37 (15H, m, $3C_6H_5$)
7b	30.88	1.19 (6H, s, CH_3); 3.00 (2H, s, H-7'); 3.02 (2H, s, H-3a,6a); 7.08-7.23 (8H, m, C_6H_5, C_6H_4); 7.33-7.40 (6H, m, C_6H_5, C_6H_4)
7c	13.58	0.97 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 1.12 (6H, s, CH_3); 2.81 (2H, s, H-7'); 2.96 (2H, s, H-3a,6a); 3.36 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 7.12-7.25 (6H, m, C_6H_5, C_6H_4); 7.32-7.36 (3H, m, C_6H_5)
7d	50.21	1.17 (6H, s, CH_3); 2.96 (6H, s, $N(CH_3)_2$); 2.98 (2H, s, H-7'); 3.00 (2H, s, H-3a,6a); 6.45 (2H, d, *J* = 9.0, C_6H_4); 7.02 (2H, d, *J* = 8.8, C_6H_4); 7.24-7.38 (10H, m, C_6H_5)

*The ^{1}H NMR spectra of compound **5b** were taken in DMSO-d_6.

The six-membered ring of the indazole system in the **7c** molecule has a spatial form close to a twist conformation but the **4b** molecule has an *envelope* conformation. The emergence of the C(6) atom from the plane of the C(4), C(5), C(7), C(8), and C(9) atoms was 0.592(4) Å. The dihedral angle between the planes of the cyclopropane and pyrrole rings in the compound **7c** molecule was 112.3(9)°. In the compound **4b** molecule the dihedral angle between the pyrrole and pyrazole rings was 124.8(5)°. The main bond lengths in the heteroyclic compounds **7c** and **4b** molecules are given in Table 3. In the crystal the molecules of compounds **7c** and **4b** are packed at distances not less than the sums of the van der Waals radii of the contacting atoms. Regretably the low quality of the **7c** crystals did not permit a detailed comparative analysis to be carried out of the geometry of the compounds **7c** and **4b** molecules.

From the results of the X-ray structural analysis it is possible draw the conclusion of a *syn* disposition of the maleimide fragment regarding the keto group in the transition state of the bipolar cycloaddition. The *anti* disposition will not be very likely due to the significant steric difficulties arising on interaction of the dipolarophile with the axial methyl group (Fig. 3)

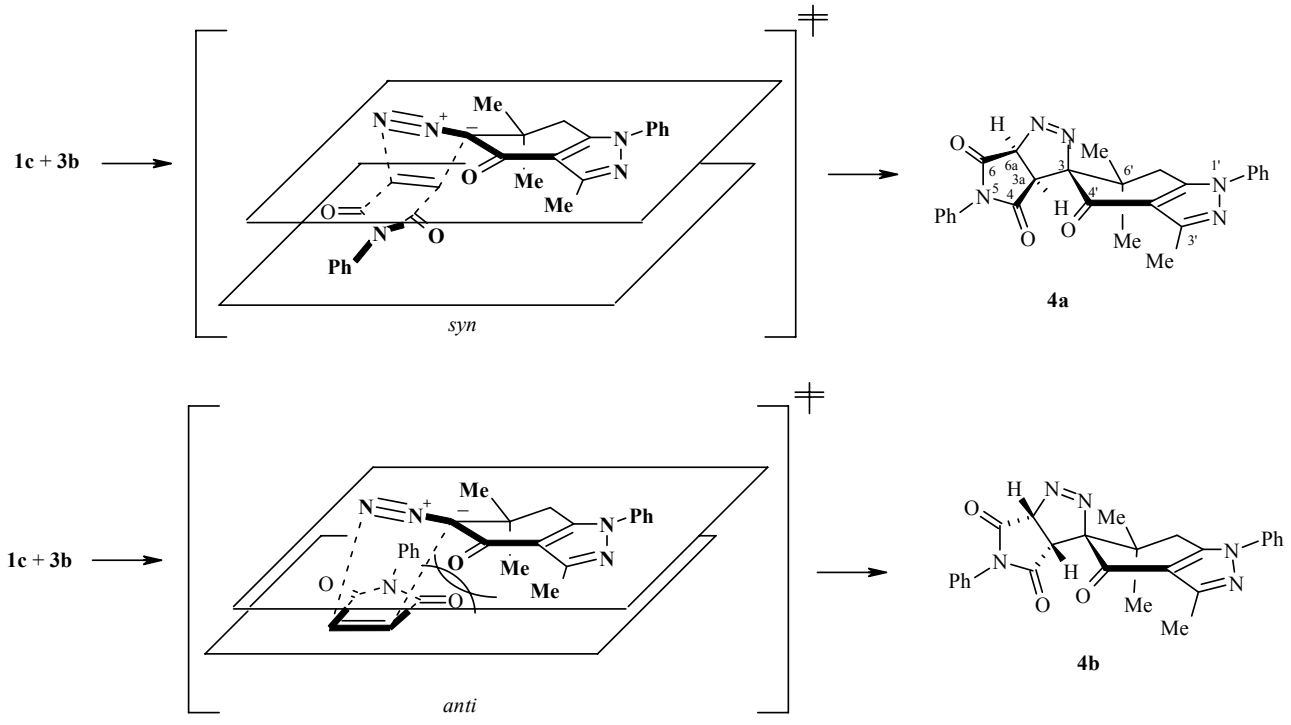


Fig. 3. Scheme for the formation of compounds **4a,b** from the initial **1c** and **3b**.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian Mercury BB spectrometer (200 MHz), internal standard was TMS. HPLC was carried out on an Agilent Technologies 1200 series instrument on a ZORBAX Eclipse XDB-C18 Rapid Resolution HT column (4.6×50 mm; 1.8 μm). Flow rate was 2 ml/min. Gradient A:B = 90%:10% → B (100%) in 10 min, then 3 min B (100%). A = 95 vol. % aqueous 20 mM $AcONH_4$ and 5 vol.% acetonitrile; B = acetonitrile. GLC was carried out on a HP-5 column; phenylmethylsiloxane 5% (Agilent 19091 J-433), film thickness 0.25 μm. Carrier gas was helium, flow rate 1 ml/min. Temperature regime: 1 min 200°C rising at 50°C/min to 310°C; 310°C 50 min.

6,6-Dimethyl-4,4',6'-trioxo-1,5'-diphenyl- (4a), 3,6,6-Trimethyl-4,4',6'-trioxo-1,5'-diphenyl- (4b), 5'-Ethyl-3,6,6-trimethyl-4,4',6'-trioxo-1-(2-pyridyl)- (4e), and 5'-Ethyl-3,6,6-trimethyl-4,4',6'-trioxo-1-phenyl-4,5,6,7,3',3'a,4',5',6',6'a-decahydrospiro[indazole-5,3'-pyrrolo[3,4-*c*]pyrazole] (4f) (General Method). A solution of the appropriate diazoindazole **1** (1 mmol) and substituted maleimide **3** (1 mmol) in CH_2Cl_2 (5-7 ml)

TABLE 3. Main Bond Lengths (*l*) in Heterocyclic Compounds **7c** and **4b**

Bond	*l*, Å	Bond	*l*, Å
Compound **7c**		Compound **4b**	
N(1)−N(2)	1.39(1)	N(1)−N(2)	1.385(4)
N(1)−C(8)	1.33(1)	N(1)−C(8)	1.348(4)
N(2)−C(3)	1.34(1)	N(2)−C(3)	1.317(4)
C(3)−C(9)	1.43(2)	C(3)−C(9)	1.424(4)
C(4)−C(9)	1.47(2)	C(4)−C(9)	1.440(4)
C(4)−C(5)	1.48(1)	C(4)−C(5)	1.560(4)
C(5)−C(6)	1.55(1)	C(5)−C(6)	1.549(4)
C(6)−C(7)	1.58(2)	C(6)−C(7)	1.544(4)
C(7)−C(8)	1.45(2)	C(7)−C(8)	1.490(4)
C(8)−C(9)	1.43(2)	C(8)−C(9)	1.378(4)
C(5)−C(24)	1.56(2)	C(5)−N(18)	1.515(5)
C(5)−C(28)	1.49(1)	C(5)−C(32)	1.546(4)
C(24)−C(25)	1.51(2)	N(18)−N(19)	1.243(4)
C(24)−C(28)	1.50(1)	N(19)−C(20)	1.485(5)
C(25)−N(26)	1.33(2)	C(20)−C(21)	1.524(5)
N(26)−C(27)	1.38(2)	C(20)−C(32)	1.512(5)
C(27)−C(28)	1.47(2)	C(21)−N(23)	1.395(5)
		N(23)−C(30)	1.407(4)
		C(30)−C(32)	1.525(5)

TABLE 4. Crystallographic Data for Compounds **7c** and **4b**

Characteristic	Structure **7c**	Structure **4b**
Empirical formula	$C_{27}H_{24}ClN_3O_3$	$C_{26}H_{23}N_5O_3$
Molecular mass, M_r*	473.94	453.49
Size of crystals, mm	0.08×0.17×0.29	0.21×0.25×0.33
Crystal system	Rhombic	Rhombic
Space group	$P2_1ca$	$Pc2_1b$
Unit cell parameters		
a, Å	9.952(1)	10.3658(4)
b, Å	13.161(1)	12.2077(5)
c, Å	18.094(2)	17.5380(5)
V, Å^3	2369.9(9)	2219.3(1)
Number of molecules in unit cell, *Z*	4	4
Crystal density, *d*, g/cm^3	1.328	1.357
Absorption coefficient, μ, mm^{-1}	0.196	0.092
Number		
independent reflections	2863	2653
reflections with $I > 2\sigma(I)$	1552	1936
refined parameters	297	307
Final convergence factor, *R*	0.098	0.047
Programs used	SIR97 [30], SHELXL97 [31]	SIR97 [30], SHELXL97 [31]

* Precise molecular mass of substance.

was maintained for 6-7 days at 20°C. The resulting solid product **4** was filtered off, and washed on the filter with small portions of cold CH_2Cl_2. Further product **4** was precipitated from the filtrate with hexane. The total amount of compound **4** was recrystallized by dissolving it in boiling CH_2Cl_2 and adding hexane until crystallization began.

6,6-Dimethyl-4,4',6'-trioxo-2,3,5'-triphenyl- (5a), 3-(4-Chlorophenyl)-6,6-dimethyl-4,4',6'-trioxo-2,5'-diphenyl- (5b), 3-(4-Chlorophenyl)-5'-ethyl-6,6-dimethyl-4,4',6'-trioxo-2-phenyl- (5c), 3-(4-Dimethylaminophenyl)-6,6-dimethyl-4,4',6'-trioxo-2,5'-diphenyl-4,5,6,7,3',3'a,4',5',6',6'a-decahydrospiro-[indazole-5,3'-pyrrolo[3,4-*c*]pyrazole] (5d) were obtained analogously to compounds **4a-f** from diazoindazoles **2** and the appropriate N-substituted maleimide **3**.

6',6'-Dimethyl-2,4,4'-trioxo-1',3 -diphenyl- (6a), 3',6',6'-Trimethyl-2,4,4'-trioxo-1',3 -diphenyl- (6b), 3',6',6'-Trimethyl-2,4,4'-trioxo-3-phenyl-1'-(2-pyridyl)- (6c), and 3-Ethyl-3',6',6'-trimethyl-2,4,4'-trioxo-1'-(2-pyridyl)-4',5',6',7'-tetrahydro-1'H-spiro[3-azabicyclo-(3.1.0)hexane-6,5'-indazole] (6d) (General Method). A solution of compound **4** in toluene or anisole was boiled for 1-2 h until the end of nitrogen evolution. Product **6** was precipitated by addition of an excess of hexane to a cooled solution, and was recrystallized from ethanol.

6',6'-Dimethyl-2,4,4'-trioxo-3,2',3'-triphenyl- (7a), 3'-(4-Chlorophenyl)-6',6'-dimethyl-2,4,4'-trioxo-3,2'-diphenyl- (7b), 3'-(4-Chlorophenyl)-3-ethyl-6',6'-dimethyl-2,4,4'-trioxo-2'-phenyl- (7c), and 3'-(4-Dimethylaminophenyl)-6',6'-dimethyl-2,4,4'-trioxo-3,2'-diphenyl-4',5',6',7'-tetrahydro-1'H-spiro[3-azabicyclo-(3.1.0)hexane-6,5'-indazole] (7d) were obtained analogously to spiro compound **6** from compounds **5a-d**. They were recrystallized from ethanol.

X-Ray Structural Investigation of Compounds 7c and 4b. Monocrystals of compounds **7c** and **4b** were grown in ethanol and in 50% ethanol respectively. To initiate crystallization fine crystals of **4b**, obtained by rapid crystallization from CH_2Cl_2, were added to the solution. Analysis was carries out at room temperature on a Nonius KappaCCD automatic diffractometer to $2\theta_{max} = 55^{o}$ ($\lambda_{Mo} = 0.71073$ Å). The principal crystallographic characteristics of the compounds, and also the parameters of refinement of the crystal structures, are given in Table 4.

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