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REACTION OF SUBSTITUTED 1,2,8,9-TETRA-AZADISPIRO[4.1.4.3]TETRADECA-1,8-DIEN-6-ONES AND 1,2,8,9-TETRAAZADISPIRO[4.1.4.2]TRIDECA-1,8-DIEN-6-ONES WITH CHLORINE

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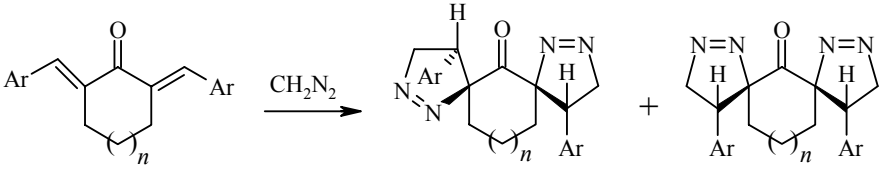
Reaction of 4,11-diaryl-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-ones and -dispiro-[4.1.4.2]trideca-1,8-dien-6-ones with chlorine gives substituted dispirocyclic compounds containing a 3-chloro-1-pyrazoline fragment which loses nitrogen on heating to give spirocyclic chlorocyclopropanes.

Keywords: diazomethane, pyrazolines, cyclopropane.

It has previously been shown that the reactions of bi- and spirocyclic 2-pyrazolines with halogenating agents give substituted 3-halo-1-pyrazolines which lose nitrogen on heating to give substituted 1-halocyclopropane-1-carboxylates [1-7]. The halogenation of spirocyclic 1-pyrazolines, obtained from diazomethane and itaconic acid imides gives spirocyclic mono- and dihalocyclopropanes [8] while the chlorination of 4'-arylspiro[1,2,3,4-tetrahydronaphthalene-2,3'-(1'-pyrazolin)]-1-ones gives the corresponding 3-chloro-1-pyrazolines which lose nitrogen on heating to form spirocyclic chlorocyclopropanes [9].

In this work we have studied the reaction of the 4,11-diaryl-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-ones **1a-c** and the 4,11-diaryl-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-ones **2a-c** with chlorine and subsequent thermolysis of obtained 3-chloro-1-pyrazolines. The pyrazolines **1a-c** and **2a-c** were prepared by the reaction of diazomethane with 2,6-bis[(*E*)-arylmethylidene]-1-cyclohexanones **3a-c** and 2,5-bis[(*E*)-arylmethylidene]-1-cyclopentanones **4a-c** respectively. Using ^{1}H NMR spectroscopy it was shown that the reaction mixture of dienes **3a-c** and **4a-c** with diazomethane contains two diastereomer compounds in the ratios 4:1 and 5:1 respectively. The main isomers **1a-c** and **2a-c** were separated by recrystallization.



3a-c, **4a-c** **1a-c**, **2a-c** **1'a-c**, **2'a-c**

a Ar = Ph, **b** Ar = 4-ClC_6H_4, **c** Ar = 4-MeOC_6H_4, **1**, **3** n = 1; **2**, **4** n = 0

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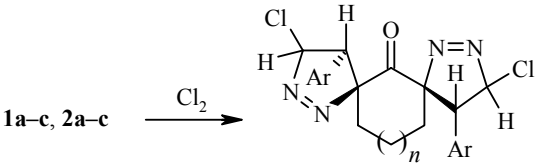
The structure of the pyrazolines **1a-c** and **2a-c** was shown from spectroscopic data. Hence the ^{1}H NMR spectrum of the pyrazoline **1a** shows: a signal for the pyrazoline ring methine group proton as a double doublet at 3.90 ppm (J = 9 and J = 3 Hz), signals for the CH_2 group protons at 4.69 ppm (dd, J = 18 and J = 9 Hz) and 5.05 ppm (dd, J = 18 and J = 3 Hz), and also signals for the aromatic and cyclohexane rings protons. It has previously been shown that, in the product of addition of diazomethane to the structurally similar 2-benzylidene-1-tetralone, the aryl group occurs in a *trans* position relative to the carbonyl group [9].

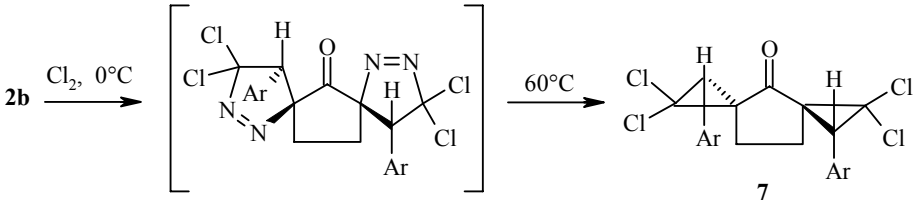
The reaction of the spiropyrazolines **1a-c** and **2a-c** with excess chlorine in chloroform at -10ºC gives 63-84% yields of the substituted 3,10-dichloro-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-ones **5a-c** and 3,10-dichloro-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-ones **6a-c**.



5a–c, **6a–c**

5, **6 a** Ar = Ph, **b** Ar = 4-ClC_6H_4, **c** Ar = 3-Cl-4-$MeOC_6H_3$; **5** n = 1, **6** n = 0

The composition and structure of the compounds were established by their spectroscopic and elemental analytical data. The ^{1}H NMR spectra of the reaction mixture showed signals for only one of the possible diastereomers: signals for the cyclohexane ring protons at 1.68-2.27 ppm, doublet signals for the H-4 and H-11 group protons at 3.73-4.23 ppm, and signals for the H-3 and H-10 protons at 6.28-6.37 ppm (d, J = 5 Hz). The ^{13}C NMR spectra show signals for the quaternary carbon atoms of the pyrazoline rings at 104.0-105.0, the C-3 and C-10 atom signals at 96.5-98.4 ppm, and the carbonyl carbon atom signal at 197-204 ppm. It should be noted that chlorination of pyrazolines **1c** and **2c** with donor substituents in the ring also chlorinates the aromatic ring. The chloro-substituted pyrazolines are unstable at room temperature and slowly decompose hence satisfactory elemental analytical data could not be obtained for all of the compounds.



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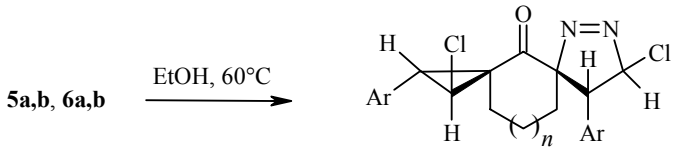
Ar = 4-ClC_6H_4

The chlorination of the pyrazoline **2b** at 0ºC also gives a tetrachloro-substituted pyrazoline which loses nitrogen at 60ºC to form 1,1,6,6-tetrachloro-2,7-bis(4-chlorophenyl)dispiro[2.1.2.2]nonan-4-one (**7**).

Heating the chloropyrazolines **5a,b** and **6a,b** in ethanol for 0.5 h gives a good yield of the products of extrusion of nitrogen from only one of the pyrazoline rings, i.e. compounds **8a,b** and **9a,b**. According to ^{1}H NMR spectroscopy the reaction mixtures contains only a single stereoisomer.



8a,b, **9a,b**

8, **9 a** Ar = Ph, **b** Ar = 4-ClC_6H_4; **8** n = 1, **9** n = 0

The composition and structure of the compounds were determined from spectroscopic and elemental analytical data. The IR spectra of the compounds show absorption stretching bands for the carbonyl groups at 1690-1710 cm^{-1}. The ^1H NMR spectra show signals for the pyrazoline ring protons at 3.73-4.00 and 6.21-6.33 ppm and doublet signals for the protons of the cyclopropane ring at 2.95-3.15 and 3.50-3.75 ppm (J = 6 Hz). The main interactions between the protons were obtained from the ^1H–^1H NOESY spectra of compound **8b** (Figure 1) in which cross peaks are present corresponding to interaction of both cyclopropane ring protons with the *ortho* protons of the aromatic ring and also cross peaks relating to interaction of both pyrazoline ring protons with the *ortho* protons of the second aromatic ring. Hence we deduce that the chlorine atom is *trans* related to the aryl substituent in the pyrazoline ring.

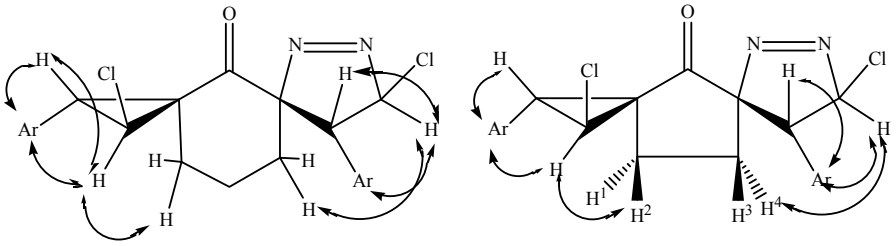


Fig. 1. Main proton interaction obtained from the ^1H–^1H NOESY spectra of compound **8b** (a) and **9a** (b).

From consideration of the intensity of the cross peaks in the ^1H–^1H NOESY spectra of compound **9a** we can deduce that the H-1 and H-2 protons can be assigned to one carbon and protons H-3 and H-4 to the other carbon atom in the cyclopentane ring while the H-1 proton occurs close to proton H-4 and proton H-2 near to proton H-3. The structure shown in the Figure is chosen because the hydrogen atom shifted to lower field is situated close to the aryl substituent (in this case H-1 and H-3).

Further heating of compounds **8a,b** and **9a,b** gave the substituted 1,6-dichlorodispiro[2.1.2.3]decan-4-ones **10a,b** and 1,6-dichlorodispiro[2.1.2.2]nonan-4-ones **11a,b** in 86-91% yield. The spectra of the reaction mixtures point to the presence of signals for only one isomer.

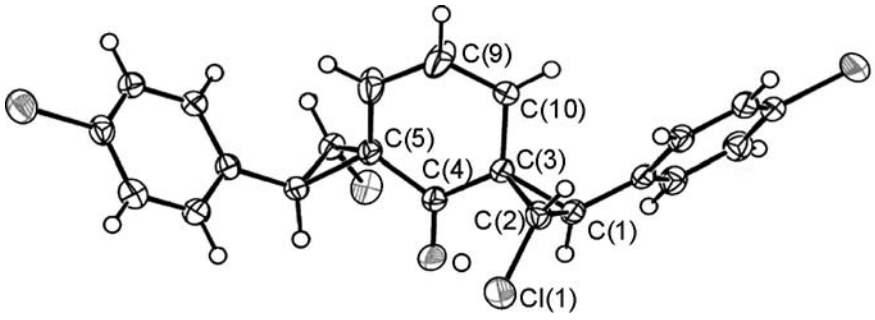


Fig. 2. X-ray structure of compound **10b.**

The composition and structure of the compounds are based on their spectroscopic and elemental analytical data. The ^1H NMR spectra show signals for the protons of the tricyclic ring as a CHCl group at 3.26-3.31 and CHAr at 3.70-3.75 ppm and also for the aromatic protons and the protons of the cyclohexane or cyclopentane ring. The ^{13}C NMR spectra of compounds **10a,b** show signals for the carbon atom of the cyclohexane ring at 20.2-20.3 and 26.7-26.8 ppm, the CH groups of the cyclopropane ring at 37.5-38.2 and 44.3-44.4 ppm, the quaternary carbon atoms (41 ppm), and also signals for the aromatic ring atoms and carbonyl

group (199 ppm). The carbon atoms of the cyclopropane ring are shifted to higher field when compared with the signals of the pyrazoline ring carbon atoms. The IR spectrum of compound **10b** shows carbonyl group stretching absorption at 1675 cm^{-1}.

The structure of compound **10b** was proved by X-ray structural analysis (Fig. 2).

Hence we can deduce that the reaction of diazomethane with 2,6-bis(arylmethylidene)cyclohexanones and 2,5-bis(arylmethylidene)cyclopentanones occurs regioselectively with the principal formation of the stereoisomer arising from *syn*,*anti* attack of two diazomethane molecules. Chlorination of the pyrazolines formed and subsequent extrusion of nitrogen occurs regio- and stereospecifically to give chlorocyclopropane-spirocycloalkane-spirochlorocyclopropane systems with (*RS*, *RS*)-configured spiroatoms.

EXPERIMENTAL

IR spectra were obtained on a Specord 75 IR spectrophotometer using KBr. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (300 and 75 MHz) instrument for compounds solutions in DMSO-d_6 or $CDCl_3$ (compounds **1, 2, 5-7, 9-11**). Chemical shifts are quoted relative to the residual signals of deuterochloroform or DMSO-d_6 (7.26 and 2.50 ppm respectively for ^{1}H NMR). Checking of the purity of the products and analysis of the reaction mixtures was carried out TLC using Silufol UV-254 plates.

Elemental analysis of compounds **1a-c, 2a-c, 5a-c, 6b, 7** and **9b** did not prove possible because they are thermally unstable.

Preparation of Pyrazolines 1a-c, 2a-c (General Method). An ether solution of diazomethane prepared from N-nitrosomethylurea (10 g, 0.1 mol) was added to a cold solution of the corresponding diene **3a-c, 4a-c** (4 mmol) in chloroform (15 ml). The reaction mixture was left overnight, solvent was evaporated, and the residue was recrystallized from ethanol.

4,11-Diphenyl-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (1a). Yield 80%; mp 114-115ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.77 (2H, m, CH_2); 1.88 (2H, m, CH_2); 2.19 (2H, m, CH_2); 3.90 (2H, dd, *J* = 8.7, *J* = 2.9, H-3(10)); 4.69 (2H, dd, *J* = 18.2, *J* = 8.7, H-10(3)); 5.05 (2H, dd, *J* = 18.2, *J* = 2.9, H-4(11)); 7.01 (4H, d, *J* = 6.5, ArH); 7.20-7.38 (6H, d, ArH). ^{13}C NMR spectrum, δ, ppm: 18.9 (CH_2); 31.8 (CH_2); 43.4 (CH); 84.5 (CH_2); 104.2 (C), 127.9 (CH); 129.0 (CH); 129.1 (CH); 138.3 (C); 198.7 (CO).

4,11-Bis(4-chlorophenyl)-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (1b). Yield 82%; mp 137-138ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.77 (2H, m, CH_2); 1.88 (2H, m, CH_2); 2.20 (2H, m, CH_2); 3.87 (2H, dd, *J* = 8.3, *J* = 3.0, H-3(10)); 4.68 (2H, dd, *J* = 18.1, *J* = 8.4, H-10(3)); 4.98 (2H, dd, *J* = 18.1, *J* = 3.0, H-4(11)); 6.94 (4H, d, *J* = 8.2, ArH); 7.29 (4H, d, *J* = 8.2, ArH). ^{13}C NMR spectrum, δ, ppm: 18.9 (CH_2); 31.9 (CH_2); 42.7(CH); 84.3 (CH_2); 104.1 (C); 129.3 (CH); 130.3 (CH); 133.9 (C); 136.6 (C); 198.3 (CO).

4,11-Bis(4-methoxyphenyl)-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (1c). Yield 79%; mp 143-145ºC (decomp). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.76 (2H, m, CH_2); 1.88 (2H, m, CH_2); 2.19 (2H, m, CH_2); 3.80 (6H, s, OCH_3); 3.84 (2H, dd, *J* = 8.4, *J* = 3.0, H-3(10)); 4.65 (2H, dd, *J* = 18.0, *J* = 8.4, H-10(3)); 4.98 (2H, dd, *J* = 18.0, *J* = 3.0, H-4(11)); 6.82 (4H, d, *J* = 7.5, ArH); 6.92 (4H, d, *J* = 7.5, ArH). ^{13}C NMR spectrum, δ, ppm: 18.7 (CH_2); 31.5 (CH_2); 42.4 (CH); 55.4 (CH_3); 84.2 (CH_2); 103.9 (C); 114.1 (CH); 129.7 (CH); 129.8 (C); 158.9 (C); 198.5 (CO).

4,11-Diphenyl-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-one (2a). Yield 85; mp 117-119ºC (decomp). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 (4H, m, CH_2CH_2); 3.49 (2H, dd, *J* = 8.4, *J* = 3.4, H-3(10)); 4.99 (2H, dd, *J* = 18.1, *J* = 8.4, H-10(3)); 5.13 (2H, dd, *J* = 18.1, *J* = 3.4, H-4(11)); 6.91 (4H, d, *J* = 7.5, ArH); 7.22-7.31 (6H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 28.4 (CH_2); 44.0 (CH); 85.8 (CH_2); 105.5 (C); 127.6 (CH); 127.8 (CH); 128.9 (CH); 138.8 (C); 206.3 (CO).

4,11-Bis(4-chlorophenyl)-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-one (2b). Yield 81%; mp 126-128ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 (4H, m, CH_2CH_2); 3.46 (2H, dd, *J* = 8.2, *J* = 3.4, H-3(10)); 4.95 (2H, dd, *J* = 18.1, *J* = 8.4, H-10(3)); 5.06 (2H, dd, *J* = 18.1, *J* = 3.4, H-4(11)); 6.83 (4H, d, *J* = 8.5, ArH); 7.24 (4H, d, *J* = 8.5, ArH). ^{13}C NMR spectrum, δ, ppm: 28.9 (CH_2); 43.8 (CH); 86.3 (CH_2); 105.9 (C); 129.6 (CH); 130.0 (CH); 134.0 (C); 137.8 (C); 206.2 (CO).

4,11-Bis(4-methoxyphenyl)-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-one (2c). Yield 76%; mp 129-132ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.19 (4H, m, CH_2CH_2); 3.45 (2H, dd, *J* = 8.2, *J* = 3.5, H-3(10)); 4.99 (2H, dd, *J* = 18.0, *J* = 8.2, H-10(3)); 5.06 (2H, dd, *J* = 18.0, *J* = 3.5, H-4(11)); 6.75-6.87 (8H, m, ArH).

Preparation of the Chloropyrazolines 5a-c, 6a-c (General Method). A solution of the pyrazoline **1a-c** or **2a-c** (5 mmol) in chloroform (20 ml) was cooled to -10ºC and a stream of chlorine was passed through and monitored by TLC to the disappearance of the starting pyrazoline. The mixture was warmed to room temperature and separated from an admixture on a column eluting with a 6:1 mixture of hexane and ethyl acetate. Solvent was evaporated off and the precipitate was recrystallized from alcohol.

3,10-Dichloro-4,11-diphenyl-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (5a). Yield 84%; mp 115-117ºC (decomp.). IR spectrum, ν, cm^{-1}: 835 s, 1090 s, 1190, 1320, 1360, 1505 s, 1685, 1700, 2950. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.68 (2H, m, CH_2); 1.82 (2H, m, CH_2); 2.15 (2H, m, CH_2); 4.23 (2H, d, *J* = 5.0, H-4(11)); 6.37 (2H, d, *J* = 5.0, CHCl); 7.12 (4H, d, *J* = 7.7, ArH); 7.30-7.45 (6H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 18.3 (CH_2); 33.5 ($2CH_2$); 51.3 (CH), 96.5 (CH); 104.3 (C); 128.7 (CH); 129.1 (CH); 129.4 (CH); 134.5 (C); 197.8 (CO).

3,10-Dichloro-4,11-bis(4-chlorophenyl)-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (5b). Yield 84%; mp 123-125ºC (decomp.). IR spectrum, ν, cm^{-1}: 825 s, 1010, 1090 s, 1490 s, 1710 s, 2960. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.70 (2H, m, CH_2); 1.82 (2H, m, CH_2); 2.15 (2H, m, CH_2); 4.18 (2H, d, *J* = 5.1, H-4(11)); 6.31 (2H, d, *J* = 5.1, CHCl); 7.07 (4H, d, *J* = 7.8, ArH); 7.35 (4H, d, *J* = 7.8, ArH). ^{13}C NMR spectrum, δ, ppm: 17.9 (CH_2); 33.0 ($2CH_2$); 50.4 (CH); 95.9 (CH); 103.7 (C); 129.3 (CH); 130.0 (CH); 132.4 (C); 134.4 (C); 197.1 (CO).

3,10-Dichloro-4,11-bis(3-chloro-4-methoxyphenyl)-1,2,8,9-tetraazadispiro[4.1.4.3]tetradeca-1,8-dien-6-one (5c). Yield 75%; mp 133-135ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.72 (2H, m, CH_2); 1.85 (2H, m, CH_2); 2.19 (2H, m, CH_2); 3.91 (6H, s, OCH_3); 4.14 (2H, d, *J* = 5.1, H-4(11)); 6.28 (2H, d, *J* = 5.1, CHCl); 6.91 (2H, d, *J* = 8.7, ArH); 7.00 (2H, dd, *J* = 8.7, *J* = 2.2, ArH); 7.12 (2H, d, *J* = 2.2, ArH). ^{13}C NMR spectrum, δ, ppm: 18.0 (CH_2); 33.1 ($2CH_2$); 50.1 (CH); 56.2 (CH_3); 95.9 (CH); 103.6 (C); 112.4 (CH); 123.1 (C); 126.7 (C); 128.4 (CH); 130.0 (CH); 155.9 (C); 197.2 (CO).

3,10-Dichloro-4,11-diphenyl-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-one (6a). Yield 78%; mp 129-131ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 (2H, m, CH_2); 2.18 (2H, m, CH_2); 3.76 (2H, d, *J* = 6.2, H-4(11)); 6.38 (2H, d, *J* = 6.2, CHCl); 7.00 (4H, dd, *J* = 7.6, *J* = 1.7, ArH); 7.29-7.34 (6H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 28.9 (CH_2), 52.7 (CH), 98.0 (CH), 104.5 (C), 128.1 (CH), 128.4 (CH), 129.3 (CH), 134.4 (C), 203.2 (CO). Found, %: C 61.04; H 4.36; N 13.45. $C_{21}H_{18}Cl_2N_4O$. Calculated, %: C 61.04; H 4.39; N 13.56.

3,10-Dichloro-4,11-bis(4-chlorophenyl)-1,2,8,9-tetraazadispiro[4.1.4.2]trideca-1,8-dien-6-one (6b). Yield 72%; mp 135-137ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 (2H, m, CH_2); 2.19 (2H, m, CH_2); 3.73 (2H, d, *J* = 6.2, H-4(11)); 6.32 (2H, d, *J* = 6.2, CHCl); 6.95 (4H, d, *J* = 8.5, ArH); 7.37 (4H, d, *J* = 8.5, ArH). ^{13}C NMR spectrum, δ, ppm: 28.8 (CH_2), 52.1 (CH), 97.7 (CH), 104.1 (C), 129.3 (CH), 129.5 (CH), 131.0 (C), 134.5 (C), 202.8 (CO).

1,1,6,6-Tetrachloro-2,7-bis(4-chlorophenyl)dispiro[2.1.2.2]nonan-4-one (7). A stream of chlorine was passed through a solution of the pyrazoline **2b** (5 mmol) in chloroform (20 ml) at 0ºC and monitored by TLC to the disappearance of starting material. The mixture was warmed to room temperature, chloroform was evaporated, and the product **7** was separated on a silica gel column using a 6:1 mixture of hexane and ethyl

acetate as eluent. Yield 12%; mp 151-153ºC (alcohol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (4H, s, CH_2CH_2); 3.56 (2H, s, H-2(7)); 7.23 (4H, d, *J* = 8.1, ArH); 7.38 (4H, d, *J* = 8.1, ArH). ^{13}C NMR spectrum, δ, ppm: 26.5 (2 CH_2), 41.7 (CH), 48.0 (C), 67.1 (C), 128.9 (CH), 129.9 (C), 131.0 (CH), 134.2 (C), 200.6 (CO).

Preparation of Compounds 8a,b and 9a,b (General Method). A solution of the corresponding chloropyrazoline (4 mmol) in ethanol (60 ml) was refluxed for 30 min and monitored by TLC. The solvent was partially distilled off, cooled, and the precipitate formed was filtered off.

2,8-Dichloro-1,9-diphenyl-6,7-diazadispiro[2.1.4.3]dodecan-4-one (8a). Yield 92%; mp 135-136ºC (decomp.). IR spectrum, ν, cm^{-1}: 930, 1085 s, 1250, 1290, 1440, 1490, 1710 s, 2965. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.32 (1H, m, CH_2); 1.68 (1H, m, CH_2); 1.72 (1H, m, CH_2); 1.78 (1H, m, CH_2); 1.96 (1H, m, CH_2); 2.10 (1H, m, CH_2); 3.65 (2H, s, CHAr, CHCl); 4.00 (1H, d, *J* = 6.6, CHAr); 6.33 (1H, d, *J* = 6.6, CHCl); 7.14 (2H, d, *J* = 6.0, ArH); 7.24-7.39 (8H, m, ArH). ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.69 (1H, m, CH_2); 0.98 (1H, m, CH_2); 1.32 (1H, m, CH_2); 1.46 (1H, m, CH_2); 1.67 (2H, m, CH_2); 3.14 (1H, d, *J* = 5.8, CH); 3.73 (1H, d, *J* = 5.8, CH); 4.36 (1H, d, *J* = 7.5, CH); 6.09 (1H, d, *J* = 7.5, CHCl); 6.85 (2H, m, ArH); 6.96 (2H, m, ArH); 7.11 (6H, m, ArH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 18.5 (CH_2); 27.6 (CH_2); 29.6 (CH_2); 37.6 (CH); 40.7 (C); 44.4 (CH); 51.2 (CH); 96.8 (CH); 101.7 (C); 127.5 (CH); 128.0 (CH); 128.6 (CH); 128.7 (CH); 128.8 (CH); 128.9 (CH); 133.4 (C); 133.9 (C); 197.5 (CO). Found, %: C 65.65; H 5.19; N 6.92. $C_{22}H_{20}Cl_2N_2O$. Calculated, %: C 65.84; H 5.53; N 6.98.

1,8-Dichloro-2,9-bis(4-chlorophenyl)-6,7-diazadispiro[2.1.4.3]dodecan-4-one (8b). Yield 89%; mp 139-140ºC (decomp.). IR spectrum, ν, cm^{-1}: 820,1010 s, 1230, 1375, 1480 s 1690 s, 2950. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.25 (1H, m, CH_2); 1.39 (1H, m, CH_2); 1.71 (2H, m, CH_2); 2.00 (2H, m, CH_2); 3.57 (1H, d, *J* = 5.8, CH); 3.59 (1H, d, *J* = 5.8, CH); 4.00 (1H, d, *J* = 7.3, CH); 6.25 (1H, d, *J* = 7.3, CHCl); 7.08 (2H, d, *J* = 7.8, ArH); 7.19 (2H, d, *J* = 7.8, ArH); 7.30-7.40 (6H, m, ArH). ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.59 (1H, m, CH_2); 0.93 (2H, m, CH_2); 1.35 (2H, m, CH_2); 1.71 (1H, m, CH_2); 2.95 (1H, d, *J* = 5.8, CH); 3.50 (1H, d, *J* = 5.8, CH); 4.24 (1H, d, *J* = 8.0, CH); 5.87 (1H, d, *J* = 8.0, CHCl); 6.52 (2H, d, *J* = 8.7, ArH); 6.65 (2H, d, *J* = 8.7, ArH); 7.05-7.13 (4H, m, ArH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 18.2 (CH_2); 27.0 (CH_2); 29.3 (CH_2); 37.0 (CH); 40.3 (C); 44.1 (CH); 50.5 (CH); 96.0 (CH); 101.5 (C); 128.6 (CH); 128.9 (CH); 129.7 (CH); 129.8 (CH); 131.7 (C); 131.8 (C); 133.4 (C); 134.0 (C); 197.1 (CO). Found, %: C 56.12; H 4.09; N 5.82. $C_{22}H_{18}Cl_4N_2O$. Calculated, %: C 56.19; H 4.29; N 5.96.

2,8-Dichloro-1,9-diphenyl-6,7-diazadispiro[2.1.4.2]undecan-4-one (9a). Yield 94%; mp 143-144ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.60 (1H, m, CH_2); 1.77 (1H, m, CH_2); 1.96 (1H, m, CH_2); 2.33 (1H, m, CH_2); 3.37 (1H, d, *J* = 5.6, CH); 3.75 (1H, d, *J* = 5.6, CH); 3.78 (1H, d, *J* = 7.5, CH); 6.28 (1H, d, *J* = 7.5, CHCl); 7.03 (2H, d, *J* = 7.5, ArH); 7.19 (2H, d, *J* = 7.5, ArH); 7.29-7.35 (6H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 26.3 (CH_2); 29.2 (CH_2); 41.4 (CH); 42.1 (C); 45.8 (CH); 52.2 (CH); 96.8 (CH); 105.2 (C); 127.8 (2CH); 128.1 (CH); 128.2 (CH); 128.8 (CH); 129.2 (CH); 133.5 (C); 134.1 (C); 203.6 (CO). Found, %: C 65.40; H 4.81; N 7.22. $C_{21}H_{18}Cl_2N_4O$. Calculated, %: C 65.46; H 4.71; N 7.27.

1,8-Dichloro-2,9-di(4-chlorophenyl)-6,7-diazadispiro[2.1.4.2]undecan-4-one (9b). Yield 91%; mp 157-159ºC (decomp.). IR spectrum, ν, cm^{-1}: 825, 850, 1010 s, 1090, 1220, 1490 s, 1730 s, 2950. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.61 (1H, m, CH_2); 1.76 (1H, m, CH_2); 1.94 (1H, m, CH_2); 2.33 (1H, m, CH_2); 3.33 (1H, d, *J* = 5.6, CH); 3.73 (2H, m, CH); 6.21 (1H, d, *J* = 7.5, CHCl); 6.97 (2H, d, *J* = 7.5, ArH); 7.14 (2H, d, *J* = 7.5, ArH); 7.24-7.41 (4H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 26.4 (CH_2); 29.2 (CH_2); 40.6 (CH); 42.0 (C); 45.7 (CH); 51.7 (CH); 96.6 (CH); 104.9 (C); 129.1 (CH); 129.4 (CH); 129.5 (2CH); 131.9 (C); 132.3 (C); 133.8 (C); 134.3 (C); 203.2 (CO).

Preparation of Compounds 10a,b and 11a,b (General Method). A solution of compound **8a,b, 9a,b** (4 mmol) in ethanol (60 ml) was refluxed for about 40 min with monitoring by TLC, the solvent was partially evaporated, and the precipitate was filtered off.

2,7-Dichloro-1,6-diphenyldispiro[2.1.2.3]decan-4-one (10a). Yield 85%; mp 213-214ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (2H, m, CH_2); 1.71-1.76 (4H, m, CH_2); 3.61 (4H, s, CHCHCl); 7.22-7.39 (10H,

m, ArH). ^{13}C NMR spectrum, δ, ppm: 19.8 (CH_2); 26.3 (CH_2); 37.7 (CH); 41.1 (C); 43.9 (CH); 127.3 (CH); 128.4 (CH); 128.7 (CH); 134.3 (C); 199.1 (CO). Found, %: C 70.60; H 5.47. $C_{22}H_{20}Cl_2O$. Calculated, %: C 71.17; H 5.43.

1,6-Dichloro-2,7-di(4-chlorophenyl)dispiro[2.1.2.3]decan-4-one (10b). Yield 87%; mp 223-225ºC. IR spectrum, ν, cm^{-1}: 820, 1010, 1075 s, 1175, 1315, 1375, 1490 s, 1675 s, 2960. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (2H, m, CH_2); 1.70-1.80 (4H, m, CH_2); 3.56 (4H, s, CHCHCl); 7.16 (4H, d, *J* = 8.4, ArH); 7.33 (4H, d, *J* = 8.4, ArH). ^{13}C NMR spectrum, δ, ppm: 19.8 (CH_2); 26.3 (CH_2); 37.1 (CH); 41.2 (C); 43.9 (CH); 128.8 (CH); 130.1 (CH); 132.9 (C); 133.4 (C); 199.2 (CO). Found, %: C 60.14; H 4.21. $C_{22}H_{18}Cl_4O$. Calculated, %: C 60.03; H 4.12.

1,6-Dichlo-2,7-diphenylrodispiro[2.1.2.2]nonan-4-one (11a). Yield 91%; mp 210-212ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.76 (2H, m, CH_2); 2.07 (2H, m, CH_2); 3.31 (2H, d, *J* = 5.8, CHCl), 3.75 (2H, d, *J* = 5.8, CH); 7.16 (4H, d, *J* = 8.2, ArH); 7.27-7.40 (6H, m, ArH). ^{13}C NMR spectrum, δ, ppm: 26.8 (CH_2); 39.1 (CH); 43.5 (C); 44.9 (CH); 127.4 (CH); 127.9 (CH); 128.7 (CH); 134.2 (C); 203.5 (CO). Found, %: C 70.09; H 5.48. $C_{21}H_{18}Cl_2O$. Calculated, %: C 70.60; H 5.08.

1,6-Dichloro-2,7-bis(4-chlorophenyl)dispiro[2.1.2.2]nonan-4-one (11b). Yield 86%; mp 219-221ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.75 (2H, m, CH_2); 2.05 (2H, m, CH_2); 3.26 (2H, d, *J* = 5.7, CHCl); 3.70 (2H, d, *J* = 5.7, CH); 7.09 (4H, d, *J* = 8.4, ArH); 7.33 (4H, d, *J* = 8.4, ArH). ^{13}C NMR spectrum, δ, ppm: 26.9 (CH_2); 38.3 (CH); 43.5 (C); 44.7 (CH); 129.0 (CH); 129.4 (CH); 132.7 (C); 133.5 (C); 202.9 (CO). Found, %: C 70.09; H 5.48. $C_{21}H_{18}Cl_2O$. Calculated, %: C 70.60; H 5.08.

X-ray Analysis of Compound 10b. $C_{22}H_{18}Cl_4O$. M 437.14, monoclinic: space group *C*2/*c* (No. 15); *a* = 19.9398(18), *b* = 11.4991(11), *c* = 9.5915(9) Å, β = 116.44(0)º, *V* = 1969.16(30) Å^3, *Z* = 4, d_c = 1.474 g/cm^3, R_{all} = 0.047, radiation source MoKα, λ = 0.71073 Å, graphite monochromator. Selected bond lengths: C(1)–C(2) 1.762(2), O–C(4) 1.222(3), C(1)–C(2) 1.478(3), C(1)–C(3) 1.550(3), C(2)–C(3) 1.518(3), C(3)–C(4) 1.502(2), C(1)–C(10) 1.522(3) Å. Selected valence angles: C(4)–C(3)–C(2) 116.83(16), C(1)–C(3)–C(2) 57.60(12), C(2)–C(4)–C(3) 60.12(12), C(1)–C(2)–C(3) 62.29(12)º. The full crystallographic data for compound **10b** has been placed in the Cambridge Crystallographic Centre Database (reference CCDC 657427).

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