Preparation of 5,5-Dicyano- and 5-Cyano-5-ethoxycarbonyl-5,6-dihydro-3,7-diphenyl-4*H*-1,2-diazepines and Their Halogenations

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5,5-Dicyano- and 5-cyano-5-ethoxycarbonyl-5,6-dihydro-3,7-diphenyl-4*H*-1,2-diazepines were prepared by the condensation of α-bromoacetophenone azine with malononitrile and ethyl cyanoacetate in the presence of sodium ethoxide, respectively. Halogenations of the dihydrodiazepines gave pyridazines, diazanorcaradienes, 4,4,6,6-tetrachlorodihydrodiazepines, and/or a 4-chloropyrazole whose relative yields strongly depended upon the nature of 5-substituents of the dihydrodiazepines as well as the reaction conditions.

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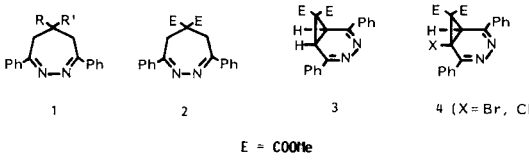
In contrast with easy ring contraction to pyridazines *via* 3,4-diazanorcaradienes in halogenations of 5,6-dihydro-3,7-diphenyl-4*H*-1,2-diazepines **1** (R = H, R' = H, Me, Ph) having no electron-withdrawing groups [1-3], it has been found that halogenations of 5,5-bis(ethoxycarbonyl)dihydrodiazepine (**2**) bearing two electron-withdrawing groups afforded stable 7,7-bis(ethoxycarbonyl)-3,4-diazanorcaradiene (**3**), its halogenated derivative **4**, or halogenated dihydrodiazepines in good yields, respectively, under controlled conditions [4].

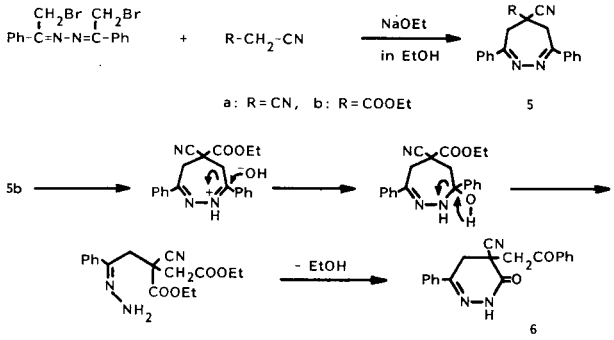


Thus, it appeared of interest to investigate the effects of nature of substituents (R,R') of the dihydrodiazepine system **1** on the modes of halogenations and on the stability of intermediary 3,4-diazanorcaradienes formed from a halogenation-dehydrohalogenation process. As part of the investigation along this line, our attention was directed to the halogenation of a dihydrodiazepine, other than **2**, bearing two electron-withdrawing groups at the 5-position: it may be expected to form a stable 3,4-diazanorcaradiene. In this paper we wish to report the preparation of 5,5-dicyano- (**5a**) and 5-cyano-5-ethoxycarbonyl-5,6-dihydro-3,7-diphenyl-4*H*-1, 2-diazepine (**5b**), and their halogenations.

Preparation.

The dihydrodiazepines **5a** and **5b** were prepared according to the reported method for the synthesis of **2** [4]. α-Bromoacetophenone azine [5] was allowed to react with malononitrile or ethyl cyanoacetate in the presence of sodium ethoxide in ethanol to give **5a** or **5b** in 70 or 75% yield, respectively. Structural elucidation of **5** was accomplished on the basis of spectral data.

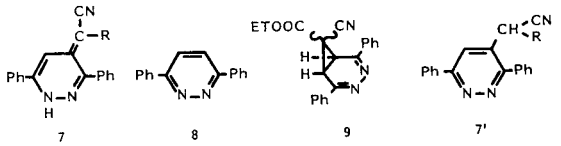
Scheme 1



Hydrolysis of the dihydrodiazepine **5b** with hydrochloric acid in ethanol afforded 4,5-dihydro-4-cyano-4-phenacyl-6-phenyl-3(2*H*)-pyridazinone (**6**) in 87% yield. The formation of **6** is illustrated by hydrolytic ring cleavage followed by cyclization with the elimination of ethanol as shown in Scheme I.

Bromination.

When **5a** was treated with an equivalent of bromine in methanol at room temperature, 4-dicyanomethylene-3,6-diphenyl-1*H*-pyridazine (**7a**, R = CN) and 3,6-diphenylpydazine (**8**) were obtained in 49 and 41% yields, respectively. The same reaction in dichloromethane afforded again a mixture of **7a**(29%) and **8** (60%). In the reaction with two equivalents of bromine in methanol at room temperature or *N*-bromosuccinimide (NBS) in carbon tetrachloride under reflux, **7a** was obtained in 82 or 74% yield, accompanied with small amounts of **8**, respectively. In all cases no deazanorcaradienes like **3** and **4** were isolated. These results are great contrast to those of the bromination of **2**, since under the former and latter conditions **2** gave the diazanoradienes, **3** and **4** (X = Br), in excellent yields, respectively.



7 8 9 7'

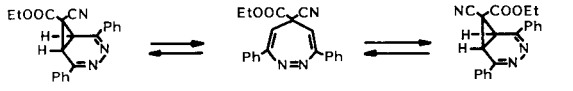
On the other hand, the bromination of **5b** in methanol afforded a mixture of two stereoisomeric 3,4-diazanorcaradienes **9** in 85% yield, accompanied with small amounts of 4-cyano(ethoxycarbonyl)methylene-3,6-diphenyl-1*H*-pyridazine (**7b**, R = COOEt) and **8**. However, **5b** reacted with bromine in dichloromethane or with NBS in carbon tetrachloride to give **7b** and **8** in 55 and 35% or 13 and 81% yields, respectively.

It was proved on the basis of spectral data that the ring-contracted pyridazines exist as 1*H*-pyridazine forms **7** rather than normal pyridazine forms **7'**.

Although one of the isomers **9** could be purely isolated by recrystallization, the other was rather less stable and thermally transformed into the stable one as will be described later. The methyl protons of the ethoxycarbonyl group in less stable isomer appear at a higher field (δ 0.93) than those (δ 1.40) in the stable one in ^{1}H-nmr spectra. Thus, it was concluded that the stable isomer is 7-endo-cyano-7-exo-ethoxycarbonyl- (**9-1**) and the less stable one 7-endo-ethoxycarbonyl-7-exo-cyanodiazanorcaradiene (**9-2**), respectively.

It has been found on the basis of ^{1}H-nmr data that a mixture of isomers **9** isolated by chromatography on silica gel consisted of about 2.7/1 ratio of **9-1** to **9-2**. A mixture of isomers **9** (2,7/1) was completely transformed into a single isomer **9-1** when heated in benzene or ethanol under reflux for 30 minutes or 5 hours, respectively. It has also been observed that the less stable isomer **9-2** was gradually converted into the stable one **9-1** even in deuteriochloroform at room temperature: the initial ratio (2.7/1) was changed to the ratio 6/1 after 2 weeks.

Scheme II

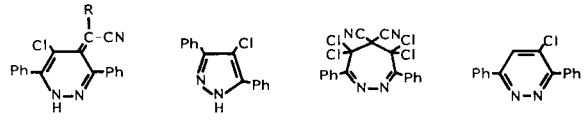


9-1 A 9-2

It has been reported that the isomerization between two stereoisomeric diazanorcaradienes proceeds *via* an intermediary valence isomer, diazacycloheptatriene [6]. Thus, it can be thought that the diazanorcaradiene **9-2** is transformed *via* a diazacycloheptatriene **A** into the thermodynamically stable one **9-1** (Scheme II).

Chlorination.

Somewhat complicating features were observed in the chlorination of **5a**. The treatment of **5a** with an equivalent of sulfuryl chloride in dichloromethane at room temperature afforded the 1*H*-pyridazine **7a** (46%) as the main product, together with small amounts of new products, 5-chloro derivative **10a** of **7a** and 4-chloro-3,5-diphenylpyrazole (**11**). On the other hand, **5a** reacted with *N*-chlorosuccinimide (NCS) in carbon tetrachloride under reflux to give **7a** or **10a** in an excellent yield depending upon the amounts of NCS employed. In the reaction with excess chlorine gas in dichloromethane at room temperature, however, **5a** gave the 4,4,6,6-tetrachlorodihydrodiazepine (**12a**) in a good yield.



10a (R=CN) 10b (R=COOEt) 11 12a (R=CN) 12b (R=COOEt) 13

The reaction of **5b** with a slight excess of sulfuryl chloride in dichloromethane at room temperature afforded the diazanorcaradiene **9-1** (71%) as the main product, accompanied with the 1*H*-pyridazine **7b** and 4-chloro-3,6-diphenylpyridazine (**13**). Although **5b** reacted with NCS in carbon tetrachloride to give a mixture of four products, **7b**, **8**, 4,4,6,6-tetrachlorodihydrodiazepine (**12b**), and **13**, in which the major product was **7b**, the chlorination with excess chlorine gas gave the tetrachloride **12b** in a good yield.

Futher chlorination of the 1*H*-pyridazine **7a** with an equivalent of sulfuryl chloride in dichloromethane afforded the 5-chloro-1*H*-pyridazine **10a** in a quantitative yield. The compound **10a** was also formed by the treatment of the tetrachloride **12a** with sodium iodide in ethanol under reflux. On the treatment of the tetrachloride **12b** with sodium iodide under similar conditions, however, pure 5-chloro-1*H*-pyridazine **10b** was not isolated.

Structural elucidation of the products, **10-13**, was accomplished on the basis of spectral data.

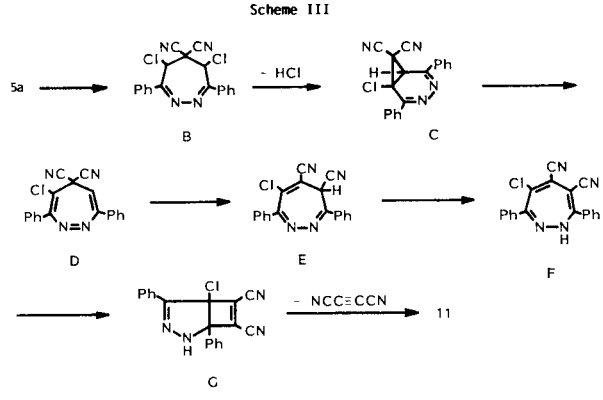
Pathways for the Formation of the Products.

As described above, the products obtained from halogenations of dihydrodiazepines **5** were somewhat different from those in the case of **2**. These facts, however, may be attributed to the difference of stability of intermediary diazanorcaradienes formed *via* a halogenation-dehydrohalogenation process. It is clear that the 1*H*-pyridazines **7** are formed *via* pyridazines **7'** produced from a ring opening of diazanorcaradienes like **9** by the reaction of hydrogen halide. The formation of the pyridazine **8** is anomalous, however, the similar contraction to **8** with the fragmentation was observed in the bromination of 5-benzyl-4,6-dihydro-3,7-diphenyl-1,2,5-triazepine [7]. Although

7-cyano-7-ethoxycarbonyldiazanorcaradienes **9** could be isolated, the lability of 7,7-dicyanonorcaradiene having two strong electron-withdrawing groups formed from **5a** is particularly surprising in view of the thermal stability of 7,7-dicyanonorcaradiene systems [8].

The pyrazole **11** obtained as a minor product in the chlorination of **5a** is a new type product of ring contraction in the halogenation of the dihydrodiazepine system **1**. The probable pathway for the novel ring contraction is depicted in Scheme III. A chlorodiazanorcaradiene **C** like **3** forms from a dichloride **B** *via* a dehydrochlorination. A 1,7-migration of cyano group in a diazacycloheptatriene **D**, a valence isomer of **C**, to **E**, followed by a 1,3-migration of hydrogen atom yields **F**. A subsequent ring contraction of **F** to a bicyclic intermediate **G**, and then the elimination of dicyanoacetylene from **G** gives a stable pyrazole **11**.

Scheme III



EXPERIMENTAL

The ir spectra were obtained on a JASCO A-702 spectrometer. The ^{1}H-nmr spectra were recorded on a Hitachi R-40 or a JEOL FX-100 instrument, and ^{13}C-nmr spectra were measured on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were taken with a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV. Elemental analyses were performed on a Hitachi 026 CHN micro analyzer. Melting points are uncorrected.

5,5-Dicyano-5,6-dihydro-3,7-diphenyl-4*H*-1,2-diazepine (**5a**).

A solution of 2-α-bromoacetophenone azine (3.94 g, 0.01 mole) in benzene (100 ml) was added to a solution of malononitrile (1.32 g, 0.02 mole) and sodium ethoxide (1.4 g, 0.02 mole) in ethanol (25 ml), and then the reaction mixture was stirred below 35° for 10 minutes. The mixture was poured into water (200 ml) and the benzene layer was washed with water, dried over magnesium sulfate, and then evaporated in vacuo to leave crystals. Recrystallization from benzene gave 2.09 g (70%) of the dihydrodiazepine **5a** as colorless prisms, mp 186-187°; ir (potassium bromide): 2250 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 3.35 (4H, s, CH_2),7.3-7.7 (6H, m, Ar*H*), 7.8-8.2 (4H, m, Ar*H*); ^{13}C-nmr (DMSO-d_6): δ 32.4 (t, 4- and 6-*C*), 40.4 (s, 5-*C*), 115.1 (s, *C*≡N), 126.8, 128.6, 130.8 (each d), 134.4 (s), 152.5 (s, 3- and 7-*C*); ms: m/z 298 (M$^+$).

Anal. Calcd. for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.56; H, 4.71; N, 18.79.

5-Cyano-5-ethoxycarbonyl-5,6-dihydro-3,7-diphenyl-4*H*-1,2-diazepine (5b).

A solution of α-bromoacetophenone azine (3.94 g, 0.01 mole) in benzene (50 ml) was added to a solution of ethyl cyanoacetate (2.26 g, 0.02 mole) and sodium ethoxide (1.4 g, 0.02 mole) in ethanol (25 ml), and then the reaction mixture was stirred at 50° for 30 minutes. The mixture was poured into water (200 ml), and the benzene layer was worked up in a similar manner as above. Recrystallization of crystals from ethanol gave 2.59 g (75%) og **5b** as colorless prisms, mp 107-108°; ir (potassium bromide): 2240, 1730 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.18 (3H, t, CH_2CH_3), 3.12, 3.48 (each 2H, d, CH_2, J = 14.4 Hz), 4.18 (2H, q, CH_2CH_3), 7.2-7.7 (6H, m Ar*H*), 7.7-8.2 (4H, m, Ar*H*); ^{13}C-nmr (deuteriochloroform): δ 13.7 (q, CH_2CH_3), 32.3 (t, 4- and 6-*C*), 53.8 (s, 5-C), 64.1 (t, CH_2CH_3), 118.3 (s, *C*≡N), 126.8, 128.7, 130.7 (each d), 135.1 (s), 153.9 (s, 3- and 7-*C*), 166.1 (s, C=O); ms: m/z 345 (M$^+$).

Anal. Calcd. for $C_{21}H_{19}N_3O_2$: C, 73.03; H, 5.55; N, 12.17. Found: C, 72.97; H, 5.56; N, 12.19.

Hydrolysis of the Dihydrodiazepine **5b**.

A solution of **5b** (1.73 g, 5 mmoles) in ethanol (30 ml) was refluxed with concentrated hydrochloric acid (2 ml) for 15 minutes during which time crystals separated out. The crystals were filtered off, and recrystallized from ethanol to give 1.38 g (87%) of 4,5-dihydro-4-cyano-4-phenacyl-6-phenyl-3(2*H*)-pyridazinone (**6**) as colorless needles, mp 202-203°; ir (potassium bromide): 3310, 1710, 1680 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 3.46, 3.82 (each 1H, d, CH_2, J = 17.1 Hz), 3.83, 4.06 (each 1H, d, CH_2, J = 18.6 Hz), 7.3-8.2 (10*H*, m, Ar*H*), 11.75 (1H, s, N*H*); ^{13}C-nmr (DMSO-d_6): δ 31.0, 37.9 (each t, CH_2), 35.9 (s, 4-*C*), 118.0 (s, *C*≡N), 125.8, 128.0, 128.8, 130.0, 133.8 (each d), 135.0, 135.8 (each s), 149.2 (s, 6-*C*), 160.9 (s, 3-*C*), 195.1 (s, *C*OPh); ms: m/z 317 (M$^+$).

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.83; H, 4.72; N, 13.11.

Bromination of the Dihydrodiazepines **5**.

i) A solution of bromine (1.6 g, 10 mmoles) in methanol (30 ml) was added, drop by drop, over a period of 30 minutes to a suspension of the dihydrodiazepine **5a** (2.98 g, 10 mmoles) in methanol (30 ml), and the reaction mixture was stirred at room temperature for 30 minutes. The mixture changed to a solution and then yellow crystals separated out. Filtration gave crystals which on recrystallization from ethanol afforded 1.44 g (49%) of 4-dicyanomethylene-3,6-diphenyl-1*H*-pyridazine (**7a**) as yellow prisms, mp 273-275° dec; ir (potassium bromide): 3240, 2200, 2170 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.17 (1H, s, 5-*H*), 7.3-8.0 (10H, m, Ar*H*), 13.0-16.0 (1H, br, N*H*, exchanged with deuterinm oxide); ^{13}C-nmr (DMSO-d_6): δ 48.3 (s, =*C*(CN)$_2$), 115.5 (d, 5-*C*), 117.8 (s, *C*≡N), 127.4, 128.1, 128.8, 129.3, 129.6, 131.6 (each d), 131.3, 146.4, 148.1, 150.7 (each s); ms: m/z 296 (M$^+$), 295.

Anal. Calcd. for $C_{19}H_{12}N_4$: C, 77.01; H, 4.08; N, 18.91. Found: C, 76.95; H, 4.06; N, 18.83.

The filtrate was concentrated *in vacuo*, and the residue was washed with aqueous ammonia. Recrystallization from ethanol gave 0.95 g (41%) of 3,6-diphenylpyridazine (**8**), mp 223° (lit [9] mp 222°), as colorless prisms.

The reaction of **5a** with bromine in dichloromethane under the same conditions afforded 0.87 g (29%) of **7a** and 1.39 g (60%) of **8**. Similarly, **5a** (2.98 g, 10 mmoles) reacted with bromine (3.2 g, 20 mmoles) in methanol (60 ml) at room temperature for 30 minutes gave 2.43 g (82%) of **7a**, together with a trace amount of **8**.

ii) A mixture of **5a** (1.49 g, 5 mmoles) and NBS (1.78 g, 10 mmoles) in carbon tetrachloride (30 ml) was refluxed for 2 hours. The reaction mixture was evaporated *in vacuo* to leave a residue which was washed with hot water. Recrystallization of the residue gave 1.09 g (74%) of **7a**. The filtrate was concentrated to give 40 mg (3.4%) of **8**.

iii) A solution of bromine (0.88 g, 5.5 mmoles) in methanol (15 ml) was added, drop by drop, over a period of 30 minutes to a suspension of the dihydrodiazepine **5b** (1.73 g. 5 mmoles) in methanol (15 ml), and then the reaction mixture was stirred at room temperature for 15 minutes. The mixture was poured into a saturated aqueous sodium hydrogencarbonate solution (100 ml), and extracted with chloroform (40 ml x 2). The chloroform extract was washed with water, dried over magnesium sulfate, and then evaporated *in vacuo* to leave a residue. Chromatography of the residue on silica gel using chloroform as the eluent to give 1.46 g (85%) of a mixture of 7-cyano-7-ethoxycarbonyl-2,5-diphenyl-3,4-diaza-2,4-norcaradienes (**9**), 56 mg (3.3%) of 4-cyano(ethoxycarbonyl)methylene-3,6-diphenyl-1*H*-pyridazine (**7b**), and 50 mg of the pyridazine **8**.

The following ^{1}H-nmr data (deuteriochloroform) indicated that the mixture of isomers **9** consisted of about 2.7/1 ratio of **9-1** to **9-2**: δ 0.93 (0.8H, t, CH_2CH_3 in **9-2**), 1.40 (2.2H, t, CH_2CH_3 in **9-1**), 3.50 (0.54H, s, ≡C*H* in **9-2**), 3.66 (1.46H, s, ≡CH in **9-1**), 7.4-7.7 (6H, m, Ar*H*), 7.9-8.3 (4H, m, Ar*H*).

The 1*H*-pyridazine **7b** was obtained as yellow prisms, mp 186-187°; ir (potassium bromide): 3220, 2180, 1665 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 1.17 (3H, t, CH_2CH_3), 4.09 (2H, q, CH_2CH_3), 7.3-8.0 (10H, m, Ar*H*), 8.83 (1H, s, 5-*H*), 14.5 (1H, br, N*H*); ^{13}C-nmr (DMSO-d_6): δ 14.3 (q, CH_2CH_3), 59.2 (t, CH_2CH_3), 70.6 (s. =*C*CN(COOEt)), 112.8 (d, 5-*C*), 118.2 (s, *C*≡N),127.2 128.0, 128.4, 128.9, 129.3, 131.3 (each d), 130.4, 136.4, 145.4, 147.1, 151.4 (each s), 166.7 (s, *C*=O); ms m/z 343 (M$^+$).

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.45; H, 4.95; N, 12.05.

The reaction of **5b** with bromine in dichloromethane under the same conditions afforded 0.94 g (55%) of **7b** and 0.41 g (35%) of **8**, while **5b** (1.73 g, 5 mmoles) reacted with NBS (0.98 g, 5.5 mmoles) in carbon tetrachloride (30 ml) under reflux for 30 minutes to give 0.22 g (13%) of **7b** and 0.94 g (81%) of **8**.

7-*endo*-Cyano-7-exo-ethoxycarbonyl-2,5-diphenyl-3,4-diaza-2,4-norcaradiene (**9-1**).

When a solution of the mixture of isomeric diazanorcaradienes (**9-1**/**9-2** = 2.7/1) was heated in ethanol or benzene under reflux for 5 hours or 30 minutes, respectively, pure diazanorcaradiene **9-1** was obtained in a quantitative yield, yellow prisms, mp 160-161°; ir (potassium bromide): 2240, 1740 cm^{-1}; ^{13}C-nmr (deuteriochloroform): δ14.0 (q, CH_2CH_3), 15.4 (s, 7-*C*), 31.1 (d, 1- and 6-*C*), 64.7 (t, CH_2CH_3), 110.7 (s, *C*≡N), 127.4, 128.8, 132.0 (each d), 134.7 (s), 152.5 (s, 2- and 5-*C*), 166.3 (s, *C*=O); ms: m/z 343 (M$^+$).

Anal. Calcd. for $_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.32; H, 4.99; N, 12.24.

Chlorination of the Dihydrodiazepines **5**.

i) A solution of the dihydrodiazepine **5a** (2.98 g, 10 mmoles) and sulfuryl chloride (1.35 g, 10 mmoles) in dichloromethane (80 ml) was stirred at room temperature for 30 minutes. Filtration of the separated crystals gave 1.35 g (46%) of the 1*H*-pyridazine **7a**. The filtrate was evaporated *in vacuo* and the residue was chromatographed on silica gel using chloroform as the eluent to give 86 mg (2.6%) of 5-chloro-4-dicyanomethylene-3,6-diphenyl-1*H*-pyridazine (**10a**) and 0.15 g (6%) of 4-chloro-3,5-diphenylpyrazole (**11**).

5-Chloro-4-dicyanomethylene-3,6-diphenyl-1*H*-pyridazine (**10a**).

This compound was obtained as yellow prisms, mp 283-284° dec; ir (potassium bromide): 3200, 2200, 2180 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.4-7.8 (10H, m, Ar*H*), 10-16 (1H, br, N*H*); ^{13}C-nmr (DMSO-d_6): δ 50.0 (s, =*C*(CN)$_2$), 117.5 (s, *C*≡N), 118.7 (s, 5-C), 128.3, 128.7, 129.0, 129.3, 129.7, 131.0 (each d), 135.2, 143.4, 148.7, 151.0 (each s); ms m/s 330, 332 (M$^+$).

Anal. Calcd. for $C_{19}H_{11}ClN_4$: C, 68.99; H, 3.35; N, 16.93. Found: C, 69.15; H, 3.32; N, 16.96.

4-Chloro-3,5-diphenylpyrazole (**11**).

This compound was obtained as colorless prisms, mp 203-204°; ir (potassium bromide): 3200 cm^{-1} (br); ^{1}H-nmr (DMSO-d_6): δ 7.3-8.1 (10H, m, Ar*H*), *ca.* 13.8 (1H, br, N*H*); ms: m/z 254, 256 (M$^+$).

Anal. Calcd. for $C_{15}H_{11}ClN_2$: C, 70.81; H, 4.34; N, 11.07. Found: C, 70.73; H, 4.35; N, 11.00.

ii) A mixture of **5a** (1.49 g, 5 mmoles) and NCS (0.67 g, 5 mmoles) was heated in cabon tetrachloride (30 ml) under reflux for 2 hours. The reaction mixture was evaporated *in vacuo* to leave a residue which was washed with hot water. Recrystallization of the residue from ethanol gave 1.37 g (93%) of **7a**.

The reaction of **5a** (1.49 g, 5 mmoles) with NCS (1.34 g, 10 mmoles) under similar conditions afforded 1.64 g (99%) of **10a**.

iii) After chlorine gas was vigorously bubbled into a solution of **5a** (2.98 g, 10 mmoles) in dichloromethane (40 ml) at room temperature for 30 minutes, the reaction mixture was evaporated *in vacuo* to leave a residue which on recrystallization from ethanol gave 3.36 g (77%) of 5,5-dicyano-5,6-dihydro-3,7-diphenyl-4,4,6,6-tetrachloro-4*H*-1,2-diazepine (**12a**) as colorless prisms, mp 152-153°; ir (potassium bromide): 2240 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 7.3-7.9 (m, Ar*H*); ^{13}C-nmr (deuteriochloroform): δ 43.3 (s, 5-*C*), 79.1 (s, 4- and 6-*C*), 108.8 (s, *C*≡N), 128.4, 129.1, 130.9 (each d), 133.3 (s), 148.4 (s, 3- and 7-*C*); ms: m/z 434, 436, 438, 440, 442 (M$^+$).

Anal. Calcd. for $C_{19}H_{10}Cl_4N_4$: C, 52.33; H, 2.31; N, 12.85. Found: C, 52.20; H, 2.26; N, 12.74.

iv) A solution of the dihydrodiazepine **5b** (1.73 g, 5 mmoles) and sulfuryl chloride (1.01 g, 7.5 mmoles) in dichloromethane (30 ml) was stirred at room temperature for 30 minutes. The reaction mixture was poured into a saturated aqueous sodium hydrogencarbonate solution (100 ml), and the organic layer was washed with water, dried over magnesium sulfate, and then evaporated *in vacuo*. The chromatography of the residue on silica gel using chloroform as the eluent gave 1.22 g (71%) of the diazanorcaradiene **9-1**, 102 mg (5.9%) of the 1*H*-pyridazine **7b**, and 83 mg (6.2%) of 4-chloro-3,6-diphenylpyridazine (**13**).

4-Chloro-3,6-diphenylpyridazine (**13**).

This compound was obtained as colorless prisms, mp 133-134°; ^{1}H-nmr (deuteriochloroform): δ 7.4-8.3 (10H, m, Ar*H*), 7.98 (1H, s, 5-*H*); ms: m/z 266, 268 (M$^+$).

Anal. Calcd. for $C_{16}H_{11}ClN_2$: C, 72.05; H, 4.16; N, 10.50. Found: C, 71.83; H, 4.43; N, 10.24.

v) After chlorine gas was vigorously bubbled into a solution of **5b** (1.73 g, 5 mmoles) in dichloromethane (30 ml) at room temperature for 30 minutes, the reaction mixture was evaporated *in vacuo* to leave a residue. Recrystallization of the residue from ethanol gave 1.96 g (81%) of 5-cyano-5-ethoxycarbonyl-5,6-dihydro-3,7-diphenyl-4,4,6,6-tetrachloro-4*H*-1,2-diazepine (**12b**) as colorless prisms, mp 169-170°; ir (potassium bromide); 1765 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.32 (3H, t, CH_2CH_3), 4.44 (2H, q, CH_2CH_3), 7.3-8.0 (10H, m, Ar*H*); ^{13}C-nmr (deuteriochloroform): δ 13.7 (q, CH_2CH_3), 65.3 (t, CH_2CH_3), 79.7 (s, 4- and 6-*C*), 87.6 (s, 5-*C*), 112.1 (s, *C*≡N), 127.9, 129.3, 130.2 (each d), 134.4 (s), 149.8 (s, 3- and 7-*C*), 159.6 (s, *C*=O); ms: m/z 481, 483, 485, 487, 489 (M$^+$).

Anal. Calcd. for $C_{21}H_{15}Cl_4N_3O_2$: C, 52.09; H, 3.10; N, 8.76. Found: C, 52.20; H, 3.13; N, 8.70.

vi) A mixture of **5b** (1.73 g, 5 mmoles) and NCS (1.0 g, 7.5 mmoles) was heated in carbon tetrachloride (30 ml) under reflux for 30 minutes. The reaction mixture was evaporated *in vacuo* to leave a residue which on chromatography on silica gel using chloroform as the eluent to give 0.65 g (38%) of the 1*H*-pyridazine **7b**,0.2 g (18%) of the pyridazine **8**, 26 mg (2%) of chloropyridazine **13**, and 44 mg of the tetrachloride **12b**.

Chlorination of the 1*H*-Pyridazine **7a**.

When a solution of **7a** (592 mg, 2 mmoles) and sulfuryl chloride (270 mg, 2 mmoles) in dichloromethane (30 ml) was stirred at room temperature for 15 minutes, the chloro-1*H*-pyridazine **10a** was spearated out, yield, 661 mg (100%).

Dechlorination of the Tetrachloride **12a**

A mixture of **12a** (872 mg, 2 mmoles) and sodium iodide (1.5 g, 10 mmoles) was heated in ethanol (30 ml) under reflux for 2 hours. The reaction mixture was poured into water (200 ml) to give 645 mg (88%) of the chloro-1H-pyridazine **10a**.

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