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SYNTHESIS OF HETEROCYCLES USING THE PRODUCTS OF THE ADDITION OF POLYHALOALKANES TO UNSATURATED SYSTEMS.

7.* REACTIONS OF 5-ARYL-1,1-DICHLORO-1,3-PENTADIEN-5-ONES AND 6-ARYL-2-PYRONES WITH HYDRAZINES

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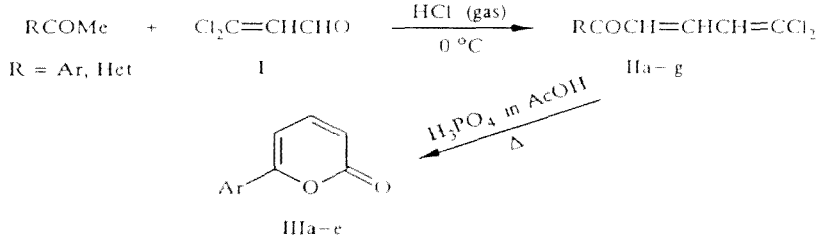
Substituted Δ^2-pyrazolines were synthesized from 5-aryl-1,1-dichloro-1,3-pentadien-5-ones and 6-aryl-2-pyrones. A detailed analysis of the ^1H and ^{13}C NMR spectra of the starting compounds and final products was carried out.

3,3-Dichloropropenal (I), which is formed from the products of the addition of CCl_4 to vinyl alkyl ethers [2], is a convenient starting compound for the synthesis of various types of heterocycles. Either both the aldehyde and dichlorovinyl functions or only the aldehyde function may be used. Thus, we synthesized 1-aryl-5-chloropyrazoles by the cyclization of arylhydrazones of 3,3-dichloropropenal using both these functions [3]. Only the aldehyde function was used in the synthesis of 3-dichlorovinylisoxazoles by the 1,3-dipolar cycloaddition of the dichlorovinylnitroxide, obtained from the oxime of aldehyde I, to unsaturated systems [4].

Dichloropropenal I undergoes the Knoevenagel condensation with various aryl methyl ketones. The condensation products, namely, 5-aryl-1,1-dichloro-1,3-pentadien-5-ones (II), readily cyclize to give the corresponding 6-aryl-2-pyrones (III) [5]. We note that only the CHO group participates in the preparation of II, while both the aldehyde and dichlorovinyl functions participate in the preparation of III.



II, III a Ar = C_6H_4Me-*p*; b Ar = $C_6H_4NO_2$-*m*, c Ar = Ph, d Ar = C_6H_4Br-*p*, e Ar = C_6H_4Cl-*p*, f Het = 5-methyl-2-furyl-2, g Het = 2-thienyl

In the present work, we synthesized nitrogen heterocycles from readily available ketones II and their cyclization products, namely, pyrones III.

*Communication [6], see ref. [1].

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TABLE 1. ^1H NMR Spectra of the Products of the Knoevenagel Condensation of Dichloroacrolein with Ketones in $CDCl_3$, Chemical Shifts, δ, ppm, Coupling Constants (J), Hz

Compound	Side chain $Cl_2C^1=C^2H-C^3H=C^4H-C^5O$			Ar, Het or fragment $C_6H_4CH_2CH_2$
	2-H	3-H	4-H	
IIa	6,70 d J_{23} = 11,0	7,57 d.d J_{34} = 15,1	7,08 d	7,88 m (2- and 6-H), 7,30 m (3- and 5-H); 2,44 s (4-CH_3)
IIb	6,75 d J_{23} = 11,0	7,65 d.d J_{34} = 15,1	7,10 d	8,76 d.d (2-H), 8,45 d.d d (4-H), 7,72 t (5-H), 8,29 d (6-H), J_{24} = 2,1; J_{46} = 1,0, J_{45} = 8,0; J_{56} = 8,0
IIc	6,69 d.d J_{23} = 11,1	7,53 d.d J_{34} = 15,1	7,07 d.d J_{24} = 0,8	7,92 m (2- and 6-H); 7,47 m (3-, 4- and 5-H)
IId	6,67 d J_{23} = 11,1	7,53 d.d J_{34} = 15,1	6,99 d	7,78 m (2-and 6-H), 7,59 m (3- and 5-H)
IIe	6,66 d J_{23} = 11,1	7,53 d.d J_{34} = 15,1	7,00 d	7,86 m (2- and 6-H) 7,43 m (3- and 5-H)
IIf	6,61 d.d J_{23} = 11,1	7,49 d.d J_{34} = 15,2	6,86 d.d J_{24} = 0,7	7,15 d.q (3-H); 6,15 d.q (4-H), 2,36 d.d (5-CH_3) J_{34} = 3,5; J_{4Me} = 0,9, J_{3Me} = 0,5
IIg	6,69 d J_{23} = 11,0	7,58 d.d J_{34} = 14,8	6,96 d	7,77 d.d (3-H), 7,17 d.d (4-H), 7,69 d.d (5-H) J_{34} = 3,7, J_{45} = 4,7, J_{35} = 1,3
VIII	6,77 d J_{23} = 11,6	7,45 d J_{23} = 11,6	—	7,46 m (3-H); 7,28 m (4- and 5-H), 8,05 d (6-H), 2,90 m (CH_2CH_2), J_{56} = 7,7

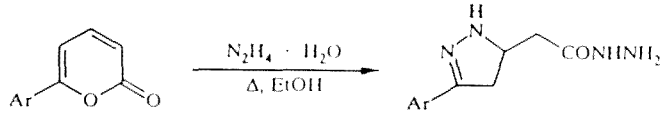
TABLE 2. ^{13}C NMR Spectra of the Products of the Knoevenagel Condensation of Dichloroacrolein with Ketones in $CDCl_3$, Chemical Shifts, δ, Coupling Constants (J), Hz

Compound	Side chain $Cl_2C^1=C^2H-C^3H=C^4H-C^5O$					Ar, Het or fragment 
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	
IIa	130,24	127,73	136,71	127,59	189,20	135,10 ($C_{(1)}$); 144,06 ($C_{(4)}$), 128,63 ($C_{(2)}$ and $C_{(6)}$); 129,44 ($C_{(3)}$ and $C_{(5)}$); 21,70 (CH_3)
IIb*	132,36	127,36	138,93	125,93	187,44	138,88 ($C_{(1)}$); 123,30 ($C_{(2)}$), 148,47 ($C_{(3)}$), 127,40 ($C_{(4)}$), 130,10 ($C_{(5)}$), 134,00 ($C_{(6)}$)
IIc*	130,39 ^3J = 4,6	127,58 ^1J = 163,4	136,94 ^1J = 160,6	127,32 ^1J = 157,9	189,53	137,41 ($C_{(1)}$, ^3J = 7,2), 128,34 ($C_{(2)}$ and $C_{(6)}$), 128,61 ($C_{(3)}$ and $C_{(5)}$), 133,04 ($C_{(4)}$, ^1J = 161,2)
IId	130,87	127,26	137,33	126,54	188,30	136,00 ($C_{(1)}$); 127,18 ($C_{(4)}$), 129,68 ($C_{(2)}$ and $C_{(6)}$), 131,79 ($C_{(3)}$ and $C_{(5)}$)
IIf*	130,04 ^3J = 6,3	127,47 ^1J = 163,2, ^3J = 7,5	135,46 ^1J = 160,2	126,97 ^1J = 158,5, ^3J = 4,3	176,27	152,02 ($C_{(1)}$, ^3J = 8,9), 120,09 ($C_{(2)}$, ^1J = 175,8), 109,44 ($C_{(3)}$, ^1J = 176,2), 158,55 ($C_{(4)}$), 14,00 (CH_3)
IIg	130,99	127,57	136,82	127,28	181,68	145,20 ($C_{(1)}$), 128,53 ($C_{(3)}$), 132,23 ($C_{(2)}$), 134,58 ($C_{(4)}$)
VIII	129,49	126,87	133,19	133,07	186,38	136,91 ($C_{(1)}$), 143,00 ($C_{(2)}$), 127,94, 128,07, 124,16, 128,22 ($C_{(3)}$), ($C_{(4)}$), ($C_{(5)}$), ($C_{(6)}$), 26,32 and 28,28 (CH_2 CH_2)

*Selective heteronuclear double resonance was used for the precise assignment of the signals.

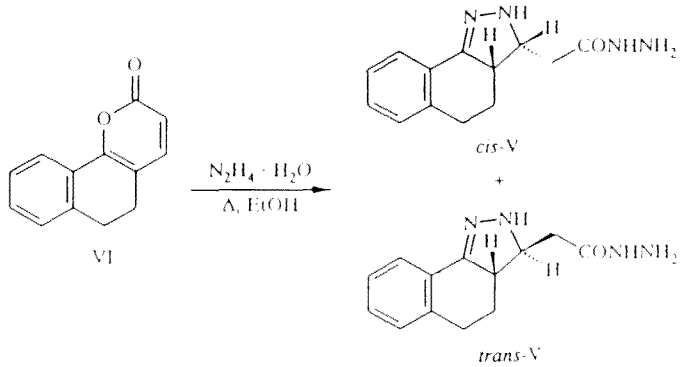
The reaction of 2-pyrones with hydrazine yields various nitrogen heterocycles. For example, syntheses have been reported for diazepinones [6, 7] and N-aminopyridones [8] from 2-pyrones and hydrazine. Substituted pyrazoles or pyrazolines were obtained in the case of dehydracetic acid [9]. The reaction of 6-aryl-2-pyrones III with hydrazines had not been studied.

We have shown that pyrones IIIa-IIId are converted upon heating at reflux with excess hydrazine hydrate in ethanol into hydrazides of 3-aryl-Δ^2-pyrazolin-5-ylacetic acids (IVa-IVd) in 67-95% yields.



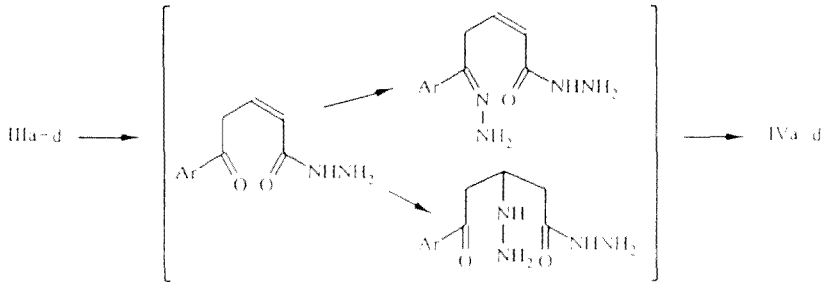
IIIa–d IVa–d

The analogous reaction but leading to a mixture of stereoisomers (as indicated by NMR spectroscopy, see below) of the hydrazide of 3,3*a*,4,5-tetrahydro-(2H)-benzo[*g*]indazol-3-ylacetic acid (V) occurs in the case of 5,6-dihydro-(2H)-naphtho-[1,2-*b*]pyran-2-one (VI) obtained from α-tetralone and aldehyde I.



6-Aryl-2-pyrones III may be seen as convenient intermediates in the transformation of dienones II. The COCH=CH fragment is used in this transformation for heterocycle formation, while the dichlorovinyl group is used for construction of the acetic acid residue in the pyrazolinylacetic acid hydrazides IV.

The first step in the recyclization is probably attack of the hydrazine at $C_{(2)}$ of the pyrone by analogy with hydrazinolysis of carboxylic acid esters [10], which leads to opening of the pyrone ring. A second hydrazine molecule then adds at the carbonyl group or at the double bond followed by cyclization to give 3-aryl-Δ^2-pyrazolines:



The proposed mechanism for the recyclization of the α-pyrones found some support in the work of Chiodoni [11], who showed that the hydrazide of β-hydrazino-*o*-hydroxydihydrocinnamic acid is formed upon the treatment of coumarin with excess hydrazine hydrate at 30°C.

Intermediates could not be identified in the reaction mixture by thin-layer chromatography upon carrying out the reaction of starting pyrones III with equimolar amounts of hydrazine hydrate. Only spots for the starting pyrones III and pyrazolines IV were found on the chromatograms. The reaction step with the second hydrazine molecule is clearly more rapid than the hydrolysis of α-pyrones III.

TABLE 3. ^{1}H NMR Spectra of 6-Aryl-2-pyrones IIIa-IIIe and VI in $CDCl_3$, Chemical Shifts, δ, ppm, Coupling Constants (*J*), Hz*

Compound	Protons of α-pyrone ring			Ar or $C_6H_4CH_2CH_2$
	3-H	4-H	5-H	
IIIa	6,11 d J_{34} = 9,3	7,29 d.d J_{45} = 6,9	6,49 d	7,55 m (2- and 6-H), 7,09 m (3-H and 5-H), 2,25 s (CH_3)
IIIb	6,38 d J_{34} = 9,3	7,50 d.d J_{45} = 6,8	6,81 d	8,63 d.d (2-H); 8,29 d.d.d (4-H); 8,16 d.d.d (6-H), 7,67 t (5-H), J_{24} = 2,1, J_{26} = 1,4; J_{46} = 0,9; J_{45} = = J_{56} = 8,0
IIIc	6,20 d.d J_{34} = 9,3	7,36 d.d J_{45} = 6,8	6,60 d.d J_{35} = 0,8	7,73 m (2- and 6-H), 7,37 m (3-, 4- and 5-H)
IIId	6,21 d J_{34} = 9,3	7,35 d.d J_{45} = 6,8	6,58 d	7,56 m (2- and 6-H), 7,46 m (3- and 5-H)
IIIe	6,28 d J_{34} = 9,3	7,40 d.d J_{45} = 6,8	6,64 d	7,72 m (2- and 6-H), 7,37 m (3- and 5-H)
VI	6,13 d J_{34} = 9,1	7,22 d.d J_{34} = 9,1	—	7,71 m (6-H), 7,10 7,30 m (3-, 4- and 5-H), 2,85 m and 2,62 m (CH_2CH_2)

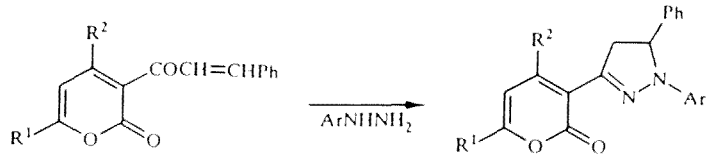
*The ^{1}H NMR spectrum of unsubstituted 2-pyrone [17]: 7.77 d.d.d for 6-H, 7.56 d.d.d for 4-H, 6.43 d.d.d for 5-H, 6.38 d.d.d for 3-H, J_{34} = 9.4, J_{35} = 1.5, J_{36} = 1.3, J_{45} = 6.3, J_{46} = 2.4, J_{56} = 5.0.

TABLE 4. ^{13}C NMR Spectra of 6-Aryl-2-pyrones IIIa-IIIe and VI in $CDCl_3$, Chemical Shifts, δ, Coupling Constants ($J_{C-\{H\}}$), Hz*

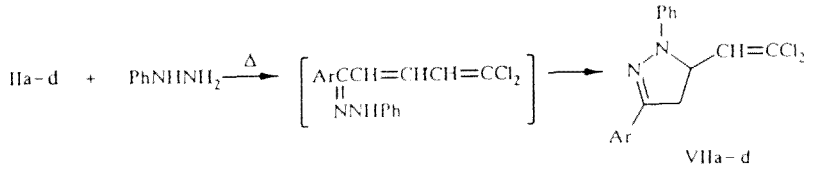
Compound	Carbon atoms of α-pyrone ring					Ar or fragment $C_6H_4CH_2CH_2$
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	
IIIa	161,69 ^2J = 5,3, ^3J = 11,7	112,90	143,75	100,17	160,80	140,90 ($C_{(4)}$), 129,25 ($C_{(3)}$ and $C_{(5)}$), 128,10 ($C_{(1)}$); 125,08 ($C_{(2)}$ and $C_{(6)}$); 21,04 (CH_3)
IIIb	160,99	115,80	143,31	102,51	158,18	148,90 ($C_{(3)}$); 133,00 ($C_{(1)}$); 131,10 ($C_{(6)}$), 130,25 ($C_{(5)}$); 125,10 ($C_{(4)}$), 120,45 ($C_{(2)}$)
IIIc	161,98	113,90	143,96	101,14	160,95	131,26 ($C_{(1)}$), 130,86 ($C_{(4)}$); 128,92 ($C_{(3)}$ and $C_{(5)}$), 125,52 ($C_{(2)}$ and $C_{(6)}$)
IIId	161,32 ^2J = 4,8, ^3J = 11,5	114,16 ^1J = 173,0, ^3J = 6,6	143,54 ^1J = 164,0	101,13 ^1J = 169,0, ^3J = 7,5	159,57	129,90 ($C_{(1)}$); 125,13 ($C_{(4)}$), 126,74 ($C_{(2)}$ and $C_{(6)}$, ^1J = 164,0); 131,94 ($C_{(3)}$ and $C_{(5)}$, ^1J = 168,0, ^2J = 5,2)
IIIe	161,55	114,27	143,65	101,19	159,76	136,90 ($C_{(4)}$); 129,67 ($C_{(1)}$), 129,17 ($C_{(3)}$ and $C_{(5)}$), 126,75 ($C_{(2)}$ and $C_{(6)}$)
VI	161,80	113,49	145,61	111,87	154,75	127,62 ($C_{(1)}$), 136,90 ($C_{(2)}$), 122,80, 126,83, 127,70, 130,00 ($C_{(3)}$, $C_{(4)}$, $C_{(5)}$ and $C_{(6)}$), 24,05 and 27,11 (CH_2-CH_2)

*The ^{13}C NMR spectrum of unsubstituted 2-pyrone [17]: 161.6 ($C_{(2)}$), 117.0 ($C_{(3)}$), 142.9 ($C_{(4)}$), 106.0 ($C_{(5)}$), and 152.1 ($C_{(6)}$).

Pyrones III do not react with phenylhydrazine and other arylhydrazines in ethanol. Phenylhydrazine, which is a weaker nucleophile than hydrazine, presumably is incapable of opening the pyrone ring. The inactivity of α-pyrones relative to phenylhydrazine was demonstrated by Manesh et al. [12], who showed that compounds containing both pyrone and chalcone fragments react with arylhydrazines exclusively at the chalcone fragment to give N-aryl-Δ^2-pyrazolines:



Dienones II, in our view, are rather close analogs to chalcones and reactions characteristic for chalcones, in particular, the formation of pyrazolines upon the action of hydrazine or substituted hydrazines [12, 13] should be expected for II. This hypothesis was supported by the results of our study of the reaction of equimolar amounts of IIa-IId and phenylhydrazine hydrochloride in ethanol at reflux, which gave 3-aryl-1-phenyl-5-dichlorovinyl-Δ^2-pyrazolines (VIIa-VIId) in 60-70% yield. Since dienones II readily form hydrazones [5], pyrazolines VII are most likely products of their subsequent cyclization:



Tetralone derivative VIII gives a mixture of stereoisomers of 2-phenyl-3-(2,2-dichlorovinyl)-3,3*a*,4,5-tetrahydro-(2H)-benzo[*g*]indazole (IX), which may be resolved using ^{1}H and ^{13}C NMR spectroscopy (see below).

The reaction of pentadienones II with hydrazine hydrate, which is a stronger nucleophile, gives considerable tar formation due perhaps to the conjugated terminal dichlorovinyl group in II.

The structures of all previously unreported compounds are in good accord with their ^{1}H and ^{13}C NMR spectra (see Tables 1-8) and elemental analysis (Table 9).

There have been only relatively few studies, in which the ^{1}H and ^{13}C NMR spectral data of 6-substituted 2-pyrones have been analyzed [14, 15], while there is no information available at all on the spectra of ketones II, 3-aryl-1-phenyl-5-(2,2-dichlorovinyl)-Δ^2-pyrazolines VII, and hydrazides of Δ^2-pyrazolinylacetic acids IV. In the present communication, the first detailed analysis is given for the ^{1}H and ^{13}C NMR spectra of II-IX in Tables 1-8.

The ^{1}H NMR spectra of all the synthesized products IIa-IIg in $CDCl_3$ (see Table 1) show AMX signals for the 2-H protons at 6.61-6.75 ppm (d or d.d), for the 3-H protons at 7.45-7.65 ppm (d.d), and for 4-H at 6.86-7.10 ppm (d or d.d) with the following coupling constants: J_{23} = 11.0-11.1, J_{24} = 0.7-0.8 ppm, J_{34}-14.8-15.2 Hz. The assignment made for the AMX system is readily carried out by comparison of the spectra of ketones IIa-IIg with the spectrum of analogous ketone VIII, which lacks a proton corresponding to 4-H. Furthermore, J_{23} is always less than J_{34}, which also unequivocally confirms the assignment made for 2-H and 4-H. The values of J_{23} and J_{34} indicate *trans* arrangement of 2-H and 3-H and of 3-H and 4-H. This is also indicated by the value of J_{24} in the spectra of IIc and IIf.

In examining the ^{13}C NMR spectra of IIa-IIg and VIII, which are close chalcone analogs, we should note that the signal for $C_{(3)}$ is always at lower field than for the signals of $C_{(1)}$, $C_{(2)}$, and $C_{(4)}$ (see Table 2). This feature of the spectra rather convincingly supports our proposal that $C_{(3)}$ in II is the most suitable electrophilic site for nucleophilic attack, in particular, in Michael additions. The chemical shifts of $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ undergo only slight change relative to the nature of the aryl or hetaryl substituent and vary in the following ranges: 130.04-132.36 for $C_{(1)}$, 127.26-127.73 for $C_{(2)}$, 135.46-138.93 for $C_{(3)}$, and 125.93-127.59 ppm for $C_{(4)}$. A rather narrow range of chemical shifts is also characteristic for the carbonyl group carbon atom: 186.38-189.53 ppm. Exceptions are found only for the chemical shifts of $C_{(5)}$ in the spectra of IIf (176.27 ppm) and IIg (181.68 ppm), which may be attributed to the specific electron donor effect of the hetaryl substituent. The ^{13}C NMR

TABLE 5. ^{1}H NMR Spectra of Hydrazides IVa-IVd and V in DMSO-d_6, Chemical Shifts, δ, Coupling Constants (J), Hz

Compound	Fragment* 1 2 3 4 5 6 HN—N=C—C—C—C			NH signal		Ar or fragment α β $C_6H_4CH_2CH_2$
	4-H (H_A, H_B for IV)	5-H (H_X)	6-H (H_M, H_N for IV)	-N=NH / CONH	NH_2	
IVa	2,65; 3,01 J_{AB} = 16,4; J_{AX} = 7,7; J_{BX} = 10,0	4,01 J_{MX} = 7,1; J_{NX} = 6,8	2,22; 2,31 J_{MN} = 14,1	4,61 br.s 9,08 br.s	4,0 5,2 br.s	7,48 m (2- and 6-H); 7,16 m (3- and 5-H); 2,30 s (CH_3)
IVb	2,75; 3,10 J_{AB} = 16,5; J_{AX} = 7,8; J_{BX} = 10,3	4,10 J_{MX} = 7,2; J_{NX} = 6,7	2,25; 2,34 J_{MN} = 14,1	7,28 s 9,05 s	3,2 4,4 br.s	8,27 d.d (2-H), 8,08 d.d† (4-H), 7,94 t (5-H), 7,63 d (6-H)
IVc	2,68; 3,04 J_{AB} = 16,4; J_{AX} = 7,6; J_{BX} = 10,0	4,03 J_{MX} = 7,1; J_{NX} = 6,7	2,22; 2,32 J_{MN} = 14,0	6,94 s 9,05 s	4,23 b.s	7,60 m (2- and 6-H), 7,34 m (3-, 4- and 5-H)
IVd	2,67; 3,03 J_{AB} = 16,4; J_{AX} = 7,8; J_{BX} = 10,1	4,04 J_{MX} = 7,2, J_{NX} = 6,7	2,21; 2,32 J_{MN} = 14,1	7,65 br.s 9,06 br.s	4,40 b.s	7,53 m (2-, 3-, 5- and 6-H)
V‡	3,11 J_{AP} = 13,3; J_{BP} = 4,7; J_{PX} = 9,3	4,07 J_{PX} = 13,3	2,04 J_{MX} = 6,0; J_{NX} = 8,3	5,01 br.s 9,05 br.s	4,5 5,5 br.s	7,74 m (6-H); 7,18 m (3-, 4- and 5-H)
	2,75 J_{AP} = 13,0; J_{BP} = 4,8; J_{PX} = 13,3	3,66 J_{PX} = 13,3	2,49 J_{MX} = 6,6; J_{NX} = 6,7			2,84 m (α-CH_2), 2,04 m and 1,58 m (β-CH_2)

*ABX and MNX systems with a common X part for IIa-IIe and ABPX and MNPX systems with common P and X parts for V.

†The coupling constants are identical to those for the aromatic protons in IIb (see Table 1).

‡Data are given for a ~1:1 mixture of two stereoisomers without complete assignment of the signals of each isomer. The chemical shifts for 4-H, 5-H, and 6-H and the corresponding coupling constants are given consecutively for the *cis* and *trans* isomers.

spectral data for II indicate an electron-withdrawing effect for the COCH=CHCH=CH=CCl_2 group bound to the phenyl, aryl, or hetaryl ring, which is similar in magnitude to the COR group in acetophenone or benzophenone [16].

The ^{1}H NMR data of 6-aryl-2-pyrones IIIa-IIIe (Table 3) are in good accord with the sparse data available for unsubstituted 2-pyrone [17], 6-methoxycarbonyl-2-pyrone [15], and 6-formyl-2-pyrone [14] and show a three-spin AMX system (3-H, 4-H, and 5-H) with coupling constants J_{34} = 9.3, J_{45} = 6.8-6.9, and J_{35} = 0.8 Hz.

We should note that there are certain difficulties in a precise assignment of the signals for 3-H and 5-H, whose chemical shifts are rather similar. These difficulties are likely responsible for the incorrect interpretation of the signals of these protons in the spectrum of 6-phenyl-2-pyrone IIIc [18]. However, comparison of the chemical shifts and coupling constants of 3-H and 5-H in unsubstituted 2-pyrone [17] and 6-formyl- and 6-methoxycarbonyl-2-pyrones [14, 15] with the observed chemical shifts (6.13 ppm) and coupling constant (J_{34} = 9.1 Hz) for 3-H in the spectrum of VI permits the reliable assignment of the signals of 3-H and 5-H of arylpyrones IIIa-IIIe.

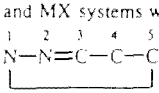
Detailed ^{13}C NMR spectral data are given for 6-aryl-2-pyrones IIIa-IIIe and 2-pyrone derivative VI for the first time in Table 4. These results indicate a somewhat greater downfield shift for $C_{(2)}$ (160.99-161.98 ppm) than for $C_{(6)}$ (158.18-160.80 ppm), which is indirect evidence for preferred attack of hydrazine on the electrophilic site at $C_{(2)}$ rather than $C_{(6)}$.

TABLE 6. ^{13}C NMR Spectra of Hydrazides IVa-IVd and V in DMSO-d_6 (δ 39.5 ppm), Chemical Shifts, δ, Coupling Constants ($J_{C-\{H\}}$), Hz

Compound	Pyrazoline ring			Fragment $C^6H_2C^7ONHNH_2$		Ar or fragment $C_6H_4CH_2CH_2$
	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	
IVa	149.46	37.23 ^1J = 132.0	56.96 ^1J = 144.7	38.51 ^1J = 128.0, ^3J = 6.0	169.59	137.46 ($C_{(4)}$); 130.60 ($C_{(1)}$); 125.35 ($C_{(2)}$ and $C_{(6)}$, ^1J = 158.0); 128.97 ($C_{(3)}$ and $C_{(5)}$, ^1J = 157.0); 20.80 (CH_3)
IVb	147.04	36.61 ^1J = 134.8	57.52 ^1J = 146.0	38.41	169.34	147.99 ($C_{(3)}$, ^3J = 10.0); 135.01 ($C_{(1)}$, ^3J = 7.9); 131.20 ($C_{(6)}$, ^1J = 163.0); 129.95 ($C_{(5)}$, ^1J = 165.0), 122.02 ($C_{(4)}$, ^1J = 169.0), 119.15 ($C_{(2)}$, ^1J = 167.0)
IVc	149.19	37.05 ^1J = 132.0	57.02 ^1J = 144.0	38.47 ^1J = 128.0, ^3J = 6.3	169.47	133.28 ($C_{(1)}$, ^3J = 6.8); 128.34 ($C_{(3)}$ and $C_{(5)}$, ^1J = 168.0), 127.92 ($C_{(4)}$, ^1J = 161.0); 125.30 ($C_{(2)}$ and $C_{(6)}$, ^1J = 160.0)
IVd	148.15	36.84 ^1J = 131.0	57.24 ^1J = 144.0	38.44 ^1J = 128.0, ^3J = 6.3	169.45	132.52 ($C_{(1)}$); 131.30 ($C_{(3)}$ and $C_{(5)}$, ^1J = 168.0); 127.20 ($C_{(2)}$ and $C_{(6)}$, ^1J = 163.0); 120.95 ($C_{(4)}$, ^1J = 7.6)
V*	149.42	46.18	59.24	33.18	170.01	137.70 128.69 137.60 ($C_{(2)}$); 128.52 ($C_{(1)}$);
	152.35	48.87	64.19	37.43	169.39	128.60 128.20 123.10 128.20 128.00 122.90 ($C_{(3)}$, $C_{(4)}$, $C_{(5)}$); 126.07 ($C_{(6)}$);
						29.09 21.31 28.72 26.50 (CH_2CH_2)

*Chemical shifts given for the carbon atoms of both stereoisomers.

TABLE 7. ^1H NMR Spectra of 1-Phenyl-3-aryl-5-dichlorovinyl-Δ^2-pyrazolines VIIa-VIId and IX in $CDCl_3$, Chemical Shifts, δ, ppm, Coupling Constants ($J_{C-\{H\}}$), Hz

Compound	ABM (AM) and MX systems with common M part 				3-Ar or α β $C_6H_4CH_2CH_2$	1-Ph
	4-H_A	4-H_B	5-H_M	6-H_X		
VIIa	3,07 ABM J_{AB} = 16,9, J_{AM} = 6,4	3,62 ABM J_{BM} = 11,5	5,07 ABMX J_{MX} = 8,4	6,04 MX	7,62 m (2- and 6-H); 7,22 m (3-5-H); 2,41 s (CH_3)	7,32 m (2H, *m*-H); 7,16 m (2H, *o*-H); 6,91 m (1H, *n*-H)
VIIb	3,10 ABM J_{AB} = 17,0, J_{AM} = 6,4	3,65 ABM J_{BM} = 11,8	5,17 ABMX J_{MX} = 8,4	6,02 MX	8,42 d.d* (2-H); 8,15 d.d.d (4-H); 8,02 d.d.d (6-H); 7,55 t (5-H)	7,33 m (2H, *m*-H); 7,15 m (2H, *o*-H); 6,95 m (1H, *n*-H)
VIIc	3,09 ABM J_{AB} = 17,0, J_{AM} = 6,3	3,63 ABM J_{BM} = 11,6	5,10 ABMX J_{MX} = 8,4	6,05 MX	7,74 m (2- and 6-H); 7,36...7,48 m (3-, 4- and 5-H)	7,35 m (2H, *m*-H); 7,19 m (2H, *o*-H); 6,94 m (1H, *n*-H)
VIId	3,03 ABM J_{AB} = 17,0, J_{AM} = 6,4	3,58 ABM J_{BM} = 11,7	5,09 ABMX J_{MX} = 8,4	6,02 MX	7,45 m (2-, 3-, 5- and 6-H, AA'BB')	7,32 m (2H, *m*-H); 7,15 m (2H, *o*-H); 6,93 m (1H, *n*-H)
IX†	3,28 AM J_{AM} = 11,9, 3,60 AM J_{AM} = 10,5		4,57 AMX J_{MX} = 8,4, 5,30 AMX J_{MX} = 9,4	6,26 MX 5,74 MX	7,97...8,16 m (6-H) 7,12...7,38 m (3-, 4- and 5-H); 2,92...3,06 m (α-CH_2), 1,76...2,50 m (β-CH_2)	7,12...7,38 m (4H, *o*- and *m*-H); 6,89 and 6,97 m (for 0,5H, *n*-H)

*The coupling constants are identical to those for IIb and IIIb (see Tables 1 and 3).

†Data given for two stereoisomers in ~1:1 ratio.

TABLE 8. ^{13}C NMR Spectra of 1-Phenyl-3-aryl-5-dichlorovinyl-Δ^2-pyrazolines VII and IX in $CDCl_3$, Chemical Shifts, δ, ppm, Coupling Constants ($J_{C-\{H\}}$), Hz

Compound	Pyrazoline ring and dichlorovinyl group $N^1-N^2=C^3-C^4-C^5-C^6=CCl_2^7$					3-Ar or $C_6H_4CH_2CH_2$	1-Ph
	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$		
VIIa	148,10	39,43	59,86	130,66	122,90	129,68 ($C_{(1)}$); 125,83 ($C_{(2)}$, $C_{(6)}$); 129,37 ($C_{(3)}$, $C_{(5)}$); 139,09 ($C_{(4)}$); 21,42 (CH_3)	144,82 (C_i), 113,74 (C_o); 129,22 (C_m), 119,88 (C_p)
VIIb	145,20	38,98	60,09	129,90	123,70	134,24 ($C_{(1)}$); 120,73 ($C_{(2)}$); 148,70 ($C_{(3)}$); 123,66 ($C_{(4)}$); 129,60 ($C_{(5)}$), 131,03 ($C_{(6)}$)	143,75 (C_i); 113,88 (C_o), 129,37 (C_m), 120,27 (C_p)
VIIc	147,90	39,36	59,92	130,59	123,00	132,46 ($C_{(1)}$), 125,88 ($C_{(2)}$, $C_{(6)}$), 128,71 ($C_{(3)}$, $C_{(5)}$), 128,99 ($C_{(4)}$)	144,67 (C_i), 113,81 (C_o), 129,30 (C_m), 120,06 (C_p)
VIId	146,70	39,12	59,97	130,33	122,90	131,40 ($C_{(1)}$), 127,20 ($C_{(2)}$, $C_{(6)}$), 131,84 ($C_{(3)}$, $C_{(5)}$), 123,24 ($C_{(4)}$)	144,32 (C_i), 113,79 (C_o), 129,30 (C_m), 120,28 (C_p)
IX*	150,10	48,40	63,13	129,42	123,20	127,96 128,30 ($C_{(1)}$), 138,05 ($C_{(2)}$); 128,98, 129,18 ($C_{(3)}$ and $C_{(4)}$); 124,46 124,57 ($C_{(5)}$), 126,80 ($C_{(6)}$)	144,39 146,89 (C_i); 113,93 114,96 (C_o); 129,25 (C_m); 119,62 121,02 (C_p)
	151,10	52,53	68,30	130,61	123,40		

*Chemical shifts given for the two stereoisomers: the signals for the CH_2CH_2 fragment are found at 23.24, 27.41, 28.41, and 29.57 ppm.

The ^1H NMR spectra of hydrazides of Δ^2-pyrazolin-5-ylacetic acids IVa-IVd in DMSO-d_6 (Table 5) show two three-spin systems: ABX (4-H_A, 4-H_B, and 5-H) and MNX (6-H_M, 6-H_N, and 5-H) with a common X part (5-H). Depending on the nature of aryl substituents, the parameters of these systems vary in the following narrow ranges: (δ, ppm) 2.65-2.75 (4-H_A), 3.01-3.10 (4-H_B), 4.01-4.10 (5-H), J_{AB} = 16.4-16.5, J_{AX} = 7.6-7.8, J_{BX} = 10.0-10.3 Hz, 2.21-2.25 (6-H_M), 2.31-2.34 (H-H_N), J_{MN} = 14.0-14.1, J_{MX} = 7.0-7.2, J_{NX} = 6.6-6.8 Hz. The chemical shifts of the proton of the CONH group for all these hydrazides are virtually the same (9.05-9.08 ppm). On the other hand, the chemical shifts of the proton of the =N−NH− fragment differ markedly: 6.94-7.65 ppm for IVb-IVd. The signal for this proton is displaced markedly upfield in the case of hydrazide IVa (4.61 ppm) and overlaps the signals of the NH_2 group protons (4.0-5.2 ppm). The ^1H NMR spectrum of hydrazide V shows doubled signals for 4-H, 5-H, and 6-H (1:1 intensity ratio). The coupling constants (J_{45} = 9.3 and 13.3 Hz) suggest that this compound is a mixture of *cis* and *trans* isomers.

^{13}C NMR spectral data are given for hydrazides of Δ^2-pyrazolin-5-ylacetic acids IVa-IVd and their analog, hydrazide V, for the first time in Table 6. These data clearly indicate pyrazoline structure for these compounds formed upon the recyclization of 6-aryl-2-pyrazones III and naphthopyrone VI, which is characterized by the following signals: 147.04-149.46 ($C_{(3)}$), 36.61-37.23 ($C_{(4)}$), and 56.96-57.52 ppm ($C_{(5)}$). The signal for $C_{(7)}$ in the $CONHNH_2$ group in these hydrazides is found at 169.34-170.34 ppm, while the chemical shifts for $C_{(6)}$ of the methylene group vary in an even narrower range: 38.41-38.51 ppm (with the exception of the chemical shifts for $C_{(6)}$ of the isomers of hydrazide VI at 33.18 and 37.43 ppm). We should note several characteristic heteronuclear coupling constants found for $C_{(4)}$ and $C_{(6)}$: $^1J_{4\text{-}CH}$ = 131.2-132, $^1J_{6\text{-}CH}$ = 128, $^3J_{6\text{-}CH}$ = 6.3, and $^1J_{5\text{-}CH}$ = 144.1-144.7 Hz. The use of selective heteronuclear double resonance for the precise assignment of the signals for $C_{(4)}$ and $C_{(6)}$ in hydrazide IVc permit a reliable distinction of the signals in IVa-IVd, whose chemical shifts are very close to the signals of analogous atoms. We should note the possibility of the complete assignment of the signals for each of the two abovementioned stereoisomers of hydrazide V.

The ^1H NMR spectra of 1-phenyl-3-aryl-(2,2-dichlorovinyl)-Δ^2- pyrazolines VIIa-VIId in $CDCl_3$ (Table 7) show a two-spin MX system (5-H, 6-H) and three-spin ABM system (4-H_A, 4-H_B, 5-H) with a common M part. The parameters of

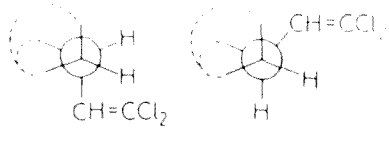
TABLE 9. Physical Indices of IIf, IVa-IVd, and IX

Compound	Chemical formula	Found, % / Calculated, %				T_{mp}, °C	Yield, %
		C	H	Cl	N		
IIf	$C_{10}H_8Cl_2O_2$	52.12 51,98	3.67 3,49	30.67 30,69	—	111...113	53
IVa	$C_{12}H_{16}N_4O$	62.08 62,05	7.09 6,94	—	23.75 24,12	146...147	67
IVb	$C_{11}H_{13}N_5O_3$	50.32 50,18	5.27 4,97	—	—	136	92
IVc	$C_{11}H_{14}N_4O$	60.66 60,53	6.69 6,46	—	25.47 25,67	137...138	95
IVd*	$C_{11}H_{13}BrN_4O$	44.33 44,45	4.56 4,41	—	18.84 18,86	159...160	92
V	$C_{13}H_{16}N_4O$	63.93 63,91	6.92 6,60	—	22.99 22,94	125	69
VIIa	$C_{18}H_{16}Cl_2N_2$	65.92 65,27	4.88 4,87	21.33 21,41	—	146	82
VIIb	$C_{17}H_{13}Cl_2N_3O_2$	56.49 56,37	3.80 3,62	19.57 19,58	10.73 11,60	148	63
VIIc	$C_{17}H_{14}Cl_2N_2$	64.42 64,37	4.52 4,45	21.66 22,35	9.33 8,83	125	71
VIId†	$C_{17}H_{13}BrCl_2N_2$	51.88 51,55	3.52 3,31	18.12 17,90	6.95 7,07	115	74
IX	$C_{10}H_{16}Cl_2N_2$	66.77 66,48	4.85 4,70	20.66 20,66	8.03 8,16	140...141	87

*Br, %, Found: 26.48%. Calculated: 26.89%.

†Br, %, Found: 20.42%. Calculated: 20.17%.

the ABM system are extremely characteristic for the Δ^2-pyrazoline ring and are in good accord with the data given above for the ABX system of hydrazides IVa-IVd (Table 5). Thus, the chemical shifts of 4-H_A and 4-H_B are found at 3.03-3.10 and 3.58-3.65 ppm, respectively, while the coupling constants of the ABM system also have very similar values: J_{AB} = 16.9-17.0, J_{AM} = 6.3-6.4, J_{BM} = 11.5-11.8 Hz. The signals for 5-H (M) are found at 5.07-5.17 ppm, i.e., about 1 ppm downfield relative to the signals of the analogous protons in the related Δ^2-pyrazoline structure of IVa-IVd (4.01-4.10 ppm). Such a downfield shift of the signal for 5-H may readily be attributed to the electron-withdrawing effect of both the dichlorovinyl group and the phenyl substituent at $N_{(1)}$ in the pyrazoline ring. The electron donor effect of the heterocycle causes a marked upfield shift of the signal for the dichlorovinyl group proton (6.02-6.05 ppm) in comparison with the chemical shift of the proton of the same group in dienones IIa-IIg and VII (6.61-6.77 ppm). The spectrum of IX consists of signals of the protons of two stereoisomers in 1:1 ratio. A complete assignment of the signals for 4-H, 5-H, and 6-H was carried out using double homonuclear resonance 1H-{^{1}H}. The spectra of both isomers show a two-spin PX system, three-spin MPX system, and four-spin ABMX system. The following parameters are found for one of the isomers: 3.28 ppm (4-H, ABMX, M part), $J_{MX} = J_{45}$ = 11.9 Hz, 4.57 ppm (5-H, MPX, X part), $J_{56} = J_{PX}$ = 8.4, 6.26 ppm (6-H, PX, P part). These values are in good accord with the corresponding data found for pyrazolines VIIa-VIId (Table 7). The PMR spectrum of the other isomer has the following parameters for these spin systems: 3.60 ppm (4-H, ABMX, M part), $J_{MX} = J_{45}$ = 10.5 Hz, 5.30 ppm (5-H, MPX, X part), $J_{PX} = J_{56}$ = 9.4 Hz, 5.74 ppm (6-H, PX, P part). The slight differences in the J_{45} values given above may be attributed to the similarity of the $HC_{(4)}C_{(5)}H$ dihedral angles for the *cis* and *trans* isomers in condensed system IX.



Examination of the ^{13}C NMR data for Δ^2-pyrazolines VIIa-VIId (Table 8) as in the case of hydrazides IVa-IVd reveals characteristic chemical shifts for $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ of the heterocycle found in the following narrow ranges: 145.22-148.19, 38.98-39.43, and 59.86-60.09 ppm, respectively. The chemical shifts of the carbon atoms of the dichlorovinyl group are also

characteristic: 129.90-130.66 ppm ($C_{(6)}$) and 122.91-123.66 ppm ($C_{(7)}Cl_2$). Comparison of these data with the chemical shifts of the analogous atoms of the dichlorovinyl group ($C_{(2)}$ and $C_{(1)}$) of ketones IIa-IIg (Table 2) clearly reveals a shift of the signals for $C_{(6)}$ downfield by up to 3 ppm and for $C_{(7)}$ upfield by up to 7-8 ppm in the spectra of pyrazolines VIIa-VIId. We also note that the chemical shifts of the phenyl group carbon atoms at $N_{(1)}$ in Δ^2-pyrazoline vary in very narrow ranges, which permits the facile identification of the signals of these atoms in the spectra of VII and IX. Table 8 also gives the spectral data for the mixture of two stereoisomers of IX, for which a complete signal assignment was not carried out. We should note the rather considerable difference (4-5 ppm) in the chemical shifts of $C_{(4)}$ and $C_{(5)}$ in each isomer.

Thus, our analysis of the ^1H and ^{13}C NMR spectra of II-IX permits the assignments of ^1H and ^{13}C NMR signals in the spectra of close analogs. Furthermore, the ^{13}C NMR spectral data for ketones IIa-IIg and 2-pyrones III permit us to evaluate the enhanced electrophilicity of the sites at $C_{(3)}$ and $C_{(2)}$, respectively and, thus, predict the preferred attack of these sites by nucleophiles. Our complete assignment of the signals in the ^1H and ^{13}C NMR spectra of IIc, IIIc, IVc, and VIIa-VIId permits us to evaluate the electronic effects of the corresponding substituents and determine their increments for the corresponding monosubstituted benzenes.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on Bruker AC200P, WM-50, and AM-300 spectrometers in DMSO-d_6 and $CDCl_3$. The quaternary carbon atoms in the ^{13}C NMR spectra were identified using the standard JMOD HX.AO technique for spectral editing. Selective heteronuclear double resonance was used for the precise assignment of the ^{13}C NMR signals of IIb, IIc, IIf, IIIa, IIIb, IIId, and IVc.

The melting points were determined on a Boetius microscope block and were not corrected. The reactions were monitored by thin-layer chromatography on Silufol UV-254 using 4:1 – 1:1 hexane – ethyl acetate as the eluent.

5-Aryl- and 5-hetaryl-1,1-dichloro-1,3-pentadien-5-ones (IIa-IIg) and 2-(3,3-dichloroallylidene)-1-tetralone (VIII) were prepared by a reported method [5] by the condensation of the corresponding aryl methyl ketones, hetaryl methyl ketones, or α-tetralone with 3,3-dichloropropenal I.

5-(*p*-Tolyl)-1,1-dichloro-1,3-pentadien-5-one (IIa) was obtained in 63% yield, mp 97-98°C (98-99°C [19]).

5-(*m*-Nitrophenyl)-1,1-dichloro-1,3-pentadien-5-one (IIb) was obtained in 64% yield, mp 147-148.5°C (148-150°C [20]).

5-Phenyl-1,1-dichloro-1,3-pentadien-5-one (IIc) was obtained in 62% yield, mp 76-77.5°C (76-77°C [3]).

5-(*p*-Bromophenyl)-1,1-dichloro-1,3-pentadien-5-one (IId) was obtained in 76% yield, mp 130-132°C (130.5-131.5°C [18]).

5-(*p*-Chlorophenyl)-1,1-dichloro-1,3-pentadien-5-one (IIe) was obtained in 70% yield, mp 122-123°C (122°C [5]).

5-(2-Thienyl)-1,1-dichloro-1,3-pentadien-5-one (IIg) was obtained in 54% yield, mp 114-116°C (114.5-115.5°C [20]).

5-(5-Methyl-2-furyl)-1,1-dichloro-1,3-pentadien-5-one (IIf) was synthesized for the first time. The physical indices for this compound are given in Table 9.

2-(3,3-Dichloroallylidene)-1-tetralone (VIII) was obtained in 84% yield, mp 95-96°C (94.5-95.5°C [21]).

The spectral data for IIa-IIg and VIII are given in Tables 1 and 2.

6-Aryl-2-pyrones (IIIa-IIIe) and 5,6-dihydro(2H)naphtho[1,2-*b*]-2-pyranone (VI) were obtained by the method of Zakharkin and Sorokina [5] by the cyclization of ketones IIa-IIe or substituted tetralone VIII.

6-(*p*-Tolyl)-2-pyrone (IIIa) was obtained in 74% yield, mp 105-106°C (104.5-106°C [19]).

6-(*m*-Nitrophenyl)-2-pyrone (IIIa) was obtained in 82% yield, mp 160-162°C (161-161.5°C [20]).

6-Phenyl-2-pyrone (IIIc) was obtained in 60% yield, mp 67°C (67°C [5]).

6-(*p*-Bromophenyl)-2-pyrone (IIId) was obtained in 71% yield, mp 87.5-87°C (87-88°C [19]).

6-(*p*-Chlorophenyl)-2-pyrone (IIIe) was obtained in 81% yield, mp 93.-93.5°C (93-94°C [19]).

5,6-Dihydro(2H)naphtho[1,2-*b*]-2-pyranone (VI) was obtained in 63.5% yield, mp 96.5-97.5°C (96-98°C [21]).

The spectral indices for IIIa-IIIe and VI are given in Tables 3 and 4.

Hydrazides of 3-aryl-Δ^2-pyrazolin-5-ylacetic acids (IVa-IVd) and hydrazide of 3,3*a*,4,5-tetrahydro-(2H)benzo[*g*]-indazol-3-ylacetic acid (V). A sample of 0.01 mole arylpyrone IIIa-IIId was dissolved in a minimal amount of hot ethanol (15-25 ml) and 0.01 mole hydrazine hydrate was added. The mixture obtained was heated at reflux for 5 h and cooled. The precipitate formed was filtered off and crystallized from ethanol or aqueous ethanol to give the corresponding hydrazide IV.

Analogously, 5,6-dihydro(2H)naphtho[1,2-*b*]-2-pyranone VI gave hydrazide V as a mixture of stereoisomers. The physical indices of these compounds are given in Table 9 and their spectral data are given in Tables 5 and 6.

3-Aryl-5-(2,2-dichlorovinyl)-Δ^2-pyrazolines (VIIa-VIId) and 2-phenyl-3-(2,2-dichlorovinyl)-3,3*a*,4,5-tetrahydro-(2H)benzo[*g*]indazole (IX). A solution of 0.01 mole ketone IIa-IId and 0.011 mole phenylhydrazine hydrochloride in 15-20 ml ethanol was heated at reflux for 4 h and then maintained for ~10 h at ~20°C. The precipitate formed was filtered off and crystallized from ethanol or aqueous ethanol to give the corresponding pyrazoline VII. Analogously, VIII gave IX as a mixture of stereoisomers. The physical indices of these products are given in Table 9, while their spectral data are given in Tables 7 and 8.

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