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# 5(4)-CHLORO-1-(2,4-DINITROPHENYL)-PYRAZOLES FROM 2,4-DINITROPHENYL-HYDRAZONES OF CHLOROVINYL KETONES AND β,β-DICHLOROACROLEIN

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*A method has been developed for obtaining 3-alkyl(phenyl)-4(5)-chloro-1-(2,4-dinitrophenyl)pyrazoles from appropriate dinitrophenylhydrazones of 1-chloro-, 1,2-, and 2,2-dichlorovinyl ketones by heating the latter in polyphosphoric acid. The structure of the pyrazoles was studied by IR and $^1$H NMR spectroscopy.*

**Keywords:** bromoacrolein, dichloroacrolein, 2,4-dinitrophenylhydrazones, 1-(2,4-dinitrophenyl)-pyrazoles, 4(5)-chloro-1-(2,4-dinitrophenyl)pyrazoles, chlorovinyl ketones, heterocyclization.

1-Alkyl-3-alkyl(aryl)(chloroalkyl)(perfluoroalkyl)-5(4)-chloro(bromo)pyrazoles are promising for making medicinal preparations, dyestuffs, insecticides, insectoacaricides, etc. [1-8], and are formed in reactions of the corresponding 1,2-dichloro- and 2,2-dihalovinyl ketones with alkylhydrazines in the presence of base [9-12]. An extensive series of 3-alkyl-1-methylpyrazoles and 5-chloro(bromo)-1-methylpyrazoles was obtained by us using new one-stage selective heterocyclization reactions of 2-chloro- and 2,2-dichloro(bromo)vinyl ketones with unsymmetrical dimethylhydrazine [13-15].

It proved to be possible to synthesize 4(5)-chloro-1-phenylpyrazoles or 1-phenylpyrazoles unsubstituted in positions 4 and 5 by the intramolecular heterocyclization of previously obtained phenylhydrazones of 1-chlorovinylalkyl(aryl)- and 2,2-dichlorovinyl phenyl ketones [9, 16]. At the same time, only in the one example of 5-chloro-1-(2,4-dinitrophenyl)-3-phenylpyrazole [17] has the preparation been reported of 1-nitrophenyl-substituted halopyrazoles by the thermal cyclization of the corresponding arylhydrazones of 2,2-dichlorovinyl phenyl ketone. It was shown simultaneously that 2,4-dinitrophenylhydrazones (DNPH) of aliphatic 2,2-dichlorovinyl ketones are not cyclized on thermolysis into the corresponding 5-chloropyrazoles. In a systematic study of the structure of DNPH of dichlorovinyl ketones [17, 18] the determining role of the configuration of the hydrazone was established unequivocally. The DNPH of aliphatic ketones exist preferably in the *s-cis-anti* form, but the DNPH of aromatic ketones exist in the *s-trans-syn* form, capable of achieving intramolecular heterocyclization. The energy barrier for the transition of one form into the other is fairly high [17], but as was established in [18] the process of *syn-anti* conversion of geometric isomers of DNPH is catalyzed by acids.

In view of the above we have developed a convenient method of obtaining 1-(2,4-dinitrophenyl)-pyrazoles by the thermal heterocyclization of the corresponding 2,4-dinitrophenylhydrazones of 2-chlorovinyl, 1,2-, and 2,2-dichlorovinyl ketones, and of 2,2-dichloroacrolein in an acidic medium. We have established that

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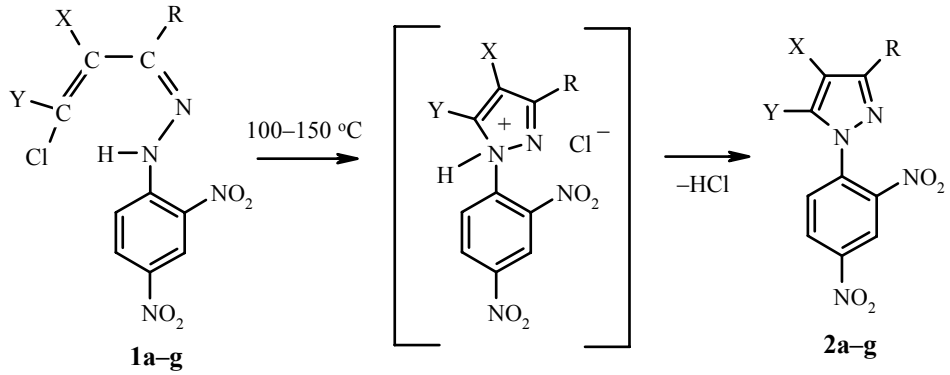
2,4-dinitrophenylhydrazones of available alkyl(phenyl) chlorovinyl ketones are cyclized into the corresponding pyrazoles on heating solutions of them in polyphosphoric acid (PPA) in 45-93% yield (Table 1).The cyclization process takes place at 100-150°C in 20-40 min. The developed method is based on available starting materials, enabling the structure of the product to be varied, including the introduction of halogen atoms at positions 4 or 5 of the heterocycle.




**1, 2 a** X = Y = H, R = Pr, **b-d** X = H, Y = Cl, **b** R = H, **c** R = Pr, **d** R = Ph, **e-g** X = Cl, Y = H, **e** R = Me, **f** R = Et, **g** R = Pr

The following compounds were obtained in high yield on carrying out the process with 2,4-dinitrophenylhydrazones **1a-g**: 1-(2,4-dinitrophenyl)-3-propylpyrazole (**2a**), 5-chloro-1-(2,4-dinitrophenyl)pyrazole (**2b**), 5-chloro-1-(2,4-dinitrophenyl)-3-propylpyrazole (**2c**), 5-chloro-1-(2,4-dinitrophenyl)-3-phenylpyrazole (**2d**), and 3-alkyl-4-chloro-1-(2,4-dinitrophenyl)pyrazoles **2e-g**.

TABLE 1. Physicochemical Characteristics of Compounds **1-3**

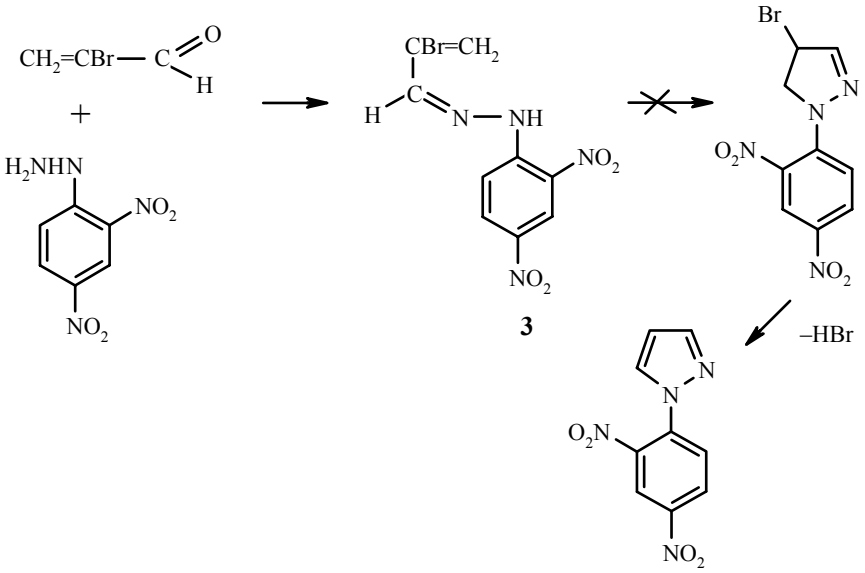
| Compound | Empirical formula | Found, % / Calculated, % | | | | mp, °C | Yield, % |
|---|---|---|---|---|---|---|---|
| | | C | H | Hal | N | | |
| **1a** | $C_{12}H_{13}ClN_4O_4$ | 46.12 / 46.09 | 4.23 / 4.19 | 11.35 / 11.34 | 17.93 / 17.92 | 130-132 | 98 |
| **1e** | $C_{10}H_8Cl_2N_4O_4$ | 37.65 / 37.64 | 2.56 / 2.53 | 22.20 / 22.22 | 17.55 / 17.56 | 205-206 | 98 |
| **1f** | $C_{11}H_{10}Cl_2N_4O_4$ | 39.64 / 39.66 | 3.07 / 3.03 | 21.26 / 21.28 | 16.80 / 16.82 | 204 | 97 |
| **1g** | $C_{12}H_{12}Cl_2N_4O_4$ | 41.53 / 41.52 | 3.46 / 3.48 | 20.43 / 20.42 | 16.13 / 16.14 | 75 | 98 |
| **2a** | $C_{12}H_{12}N_4O_4$ | 52.20 / 52.17 | 4.45 / 4.38 | — | 20.26 / 20.28 | 88-90 | 92 |
| **2b** | $C_9H_5ClN_4O_4$ | 40.22 / 40.24 | 1.89 / 1.88 | 13.25 / 13.20 | 20.79 / 20.86 | 115 | 45 |
| **2c** | $C_{12}H_{11}ClN_4O_4$ | 46.36 / 46.39 | 3.45 / 3.57 | 11.52 / 11.41 | 18.09 / 18.03 | 73-75 | 90 |
| **2d** | $C_{15}H_9ClN_4O_4$ | 52.25 / 52.27 | 2.68 / 2.63 | 10.30 / 10.28 | 16.29 / 16.25 | 136 | 78 |
| **2e** | $C_{10}H_7ClN_4O_4$ | 42.53 / 42.50 | 2.49 / 2.50 | 12.57 / 12.54 | 19.85 / 19.82 | 96 | 85 |
| **2f** | $C_{11}H_9ClN_4O_4$ | 44.55 / 44.53 | 3.09 / 3.06 | 11.97 / 11.95 | 18.85 / 18.89 | 87-89 | 87 |
| **2g** | $C_{12}H_{11}ClN_4O_4$ | 46.35 / 46.39 | 3.49 / 3.57 | 11.47 / 11.41 | 17.98 / 18.03 | 103-105 | 93 |
| **3** | $C_9H_7BrN_4O_4$ | 34.33 / 34.31 | 2.22 / 2.24 | 25.36 / 25.38 | 17.77 / 17.78 | 163 | 98 |

We have established that the action of bases (amines, alkalis, alkali metal alcoholates) on the DNPH of alkyl 2,2- and 1,2-dichlorovinyl ketones, and also heating them in various solvents (DMF, DMSO, acetonitrile, alcohols) in the presence of bases, varying the temperature from 70 to 140°C, and the process time up to 10 h, did not lead to a heterocyclization reaction with the formation of pyrazoles.

Since heating solutions of hydrazones **1a-g** in PPA leads to the formation of the corresponding pyrazoles, it may be proposed that in PPA solution the DNPH of 2,2- and 1,2-dichlorovinyl ketones undergo isomerization resulting in the *anti* form going over to the *syn* isomer which is then cyclized into a pyrazole.

The mechanism of the reaction probably includes an intramolecular nucleophilic attack by the 2,4-dinitrophenylamine fragment at the β-carbon atom of the vinyl group. The N-(2,4-dinitrophenyl)-pyrazolinium halide formed in this way is dehydrochlorinated on heating to give the aromatic pyrazole.

Nucleophilic addition of the 2,4-dinitrophenylamine fragment to the double bond, with the formation of the corresponding pyrazolines and their subsequent dehydrohalogenation with isolation of the corresponding pyrazoles, is probably not brought about. On attempting to carry out the heterocyclization of the 2,4-dinitrophenylhydrazone of α-bromoacrolein **3** in PPA neither 4-bromo-1-(2,4-dinitrophenyl)-2-pyrazoline nor 1-(2,4-dinitrophenyl)pyrazole were formed.

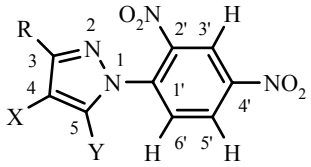



Undoubtedly the method found for obtaining 1-(2,4-dinitrophenyl)pyrazoles makes these compounds available and an interesting subject for further investigations. The use in pyrazole synthesis of alkyl(aryl) 1,2-dichloro- and alkyl(aryl) 2,2-dichloro(bromo)vinyl ketones with various groups and 2-haloacroleins enables a wide variation of both the structure of the substituent at position 3 of the heterocycle, and of the position and nature of the halogen atoms in pyrazoles.

It should be noted that previously several approaches used for the synthesis of 1-nitrophenyl-substituted pyrazoles, were limited by the poor availability of the initial compounds permitting no variation in the structure of the desired 1-(2,4-dinitrophenyl)pyrazoles, including pyrazoles with a halogen atom in the ring and with various substituents at position 3 of the pyrazole ring. The known methods of obtaining 1-nitrophenylpyrazoles include the nitration of previously obtained 1-phenylpyrazoles [19-21], the condensation of acetylacetone with nitrophenylhydrazines [22, 23], the arylation of 1-unsubstituted pyrazoles with dinitrochlorobenzene [19], or the reaction of malondialdehyde with 2,4-dinitrophenylhydrazine [24].

The synthesized 1-(2,4-dinitrophenyl)pyrazoles are promising intermediates for developing the chemistry of potential biologically active compounds of the pyrazole series.

TABLE 2. IR and $^1$H NMR Spectra of Dinitrophenylhydrazones **1a,e-g**, **3** and Pyrazoles **2a-g**




| Com-pound | IR spectrum (KBr), ν,cm$^{-1}$ | $^1$H NMR spectrum (acetone-d$_6$), δ, ppm. (*J*, Hz)* |
|---|---|---|
| **1a** | 3305 (NH); 3100, 3075 (=C–H); 1610 (C=N); 1590, 1315 ($NO_2$); 1400 (C=C) | 11.07 (1H, s, NH); 8.84 (1H, d, $^4J$ = 2.4, H-3'); 8.38 (1H, dd, $^4J$ = 2.4, $^3J$ = 9.5, H-5'); 7.88 (1H, d, $^3J$ = 9.5, H-6'); 7.34 (1H, d, $^3J$ = 13.7, =CH); 6.64 (1H, d, *J* = 13.7, =CHCl); 2.60 (2H, t, $^3J$ = 7.4, $CH_2$); 1.59 (2H, m, $CH_2$); 1.01 (3H, t, *J* = 7.4, $CH_3$) |
| **1e** | 3320 (NH); 3080 (=C–H); 1600 (C=N); 1300, 1330, 1500, 1580 ($NO_2$); 1430 (C=C) | 11.18 (1H, s, NH); 9.02 (1H, d, $^4J$ = 2.6, H-3'); 8.48 (1H, dd, $^4J$ = 2.6, $^3J$ = 9.5, H-5'); 8.13 (1H, d, $^3J$ = 9.5, H-6'); 7.53 (1H, s, =CH); 2.41 (3H, s, $CH_3$) |
| **1f** | 3300 (NH); 1620 (C=N); 1300, 1330, 1575 ($NO_2$); 1490 (C=C) | 11.15 (1H, s, NH); 8.92 (1H, d, $^4J$ = 2.6, H-3'); 8.43 (1H, dd, $^4J$ = 2.6, $^3J$ = 9.4, H-5'); 8.02 (1H, d, $^3J$ = 9.4, H-6'); 7.68 (1H, s, =CH); 2.78 (2H, q, *J* = 7.6, $CH_2$); 1.20 (3H, t, *J* = 7.6, $CH_3$) |
| **1g** | 3300 (NH); 1620 (C=N); 1300, 1330, 1575 ($NO_2$); 1490 (C=C) | 11.42 (1H, s, NH); 9.14 (1H, d, $^4J$ = 2.5, H-3'); 8.38 (1H, dd, $^4J$ = 2.5, $^3J$ = 9.5, H-5'); 8.06 (1H, d, $^3J$ = 9.5, H-6'); 7.01 (1H, s, =CH); 2.64 (2H, t, *J* = 7.8, $CH_2$); 1.70 (2H, m, $CH_2$); 1.11 (3H, t, *J* = 7.8, $CH_3$) |
| **2a** | 3145, 3120, 3090 (C=H); 1600 (C=N); 1550, 1345 ($NO_2$) | 8.79 (1H, d, $^4J$ = 2.6, H-3'); 8.56 (1H, dd, $^4J$ = 2.6, $^3J$= 9.0, H-5'); 8.39 (1H, d, *J* = 2.6, Y); 8.07 (1H, d, $^3J$= 9.0, H-6'); 6.50 (1H, d, *J* = 2.6, X); 2.53 (2H, t, *J* = 7.4, $CH_2$); 1.60 (2H, m, $CH_2$); 0.90 (3H, t, *J* = 7.4, $CH_3$) |
| **2b** | 3150, 3100, 3050 (=CH); 1600 (C=N); 1530, 1345 ($NO_2$) | 9.07 (1H, d, $^4J$ = 2.5, H-3'); 8.92 (1H, dd, $^4J$ = 2.5, $^3J$ = 8.7, H-5'); 8.29 (1H, d, $^3J$= 8.7, H-6'); 6.95 (1H, d, *J* = 1.8, H-3); 6.80 (1H, d, *J* = 1.8, X) |
| **2c** | 3150, 3105, 3090 (=CH); 1600 (C=N); 1520, 1340 ($NO_2$) | 8.86 (1H, s, H-3'); 8.70 (1H, d, $^3J$ = 8.8, H-5'); 8.06 (1H, d, $^3J$ = 8.8, H-6'); 6.43 (1H, s, X); 2.57 (2H, t, *J* = 7.3, $CH_2$); 1.66 (2H, m, *J* = 7.3, $CH_2$); 0.93 (3H, t, *J* = 7.3, $CH_3$) |
| **2d** | 3145, 3125 (=CH); 1600 (C=N); 1535, 1345 ($NO_2$) | 8.97 (1H, d, $^4J$ = 2.6, H-3'); 8.80 (1H, dd, $^4J$ = 2.6, $^3J$ = 8.7, H-5'); 8.25 (1H, d, $^3J$ = 8.7, H-6'); 7.85, 7.45 (5H, m, $C_6H_5$); 7.17 (1H, s, X) |
| **2e** | 3145 (=CH); 1600 (C=N); 1540, 1350 ($NO_2$) | 8.76 (1H, d, $^4J$ = 2.5, H-3'); 8.63 (1H, dd, $^4J$ = 2.5, $^3J$ = 8.9, H-5'); 8.43 (1H, s, Y); 8.08 (1H, d, $^3J$ = 8.9, H-6'); 2.22 (3H, s, $CH_3$) |
| **2f** | 3145, 3080 (=CH); 1600 (C=N); 1550, 1525, 1365 ($NO_2$) | 8.80 (1H, d, $^4J$ = 2.5, H-3'); 8.66 (1H, dd, $^4J$ = 2.5, $^3J$ = 8.9, H-5'); 8.47 (1H, s, Y); 8.13 (1H, d, $^3J$ = 8.9, H-6'); 2.66 (2H, κ, *J* = 7.5, $CH_2$); 1.23 (3H, t, *J* = 7.5, $CH_3$) |
| **2g** | 3145, 3075 (=CH); 1600 (C=N); 1535, 1345 ($NO_2$) | 8.77 (1H, d, $^4J$ = 2.6, H-3'); 8.63 (1H, dd, $^4J$ = 2.6, $^3J$ = 8.9, H-5'); 8.45 (1H, s, Y); 8.10 (1H, d, $^3J$ = 8.9, H-6'); 2.60 (2H, t, *J* = 7.3, $CH_2$); 1.67 (2H, m, *J* = 7.3, $CH_2$,); 0.94 (3H, t, *J* = 7.3, $CH_3$) |
| **3** | 3275 (NH); 1615 (C=N); 1510, 1320 ($NO_2$) | 11.72 (1H, s, NH); 8.84 (1H, d, $^4J_{H\text{-}3\text{-}H\text{-}5}$ = 2.5, H-3'); 8.44 (1H, s, C(O)H); 8.42 (1H, dd, $^4J$ = 2.5, $^3J$ = 9.5, H-5'); 7.91 (1H, d, $^3J$ = 9.5, H-6'); 6.49 (1H, d, $^2J$ = 1.8, =CH); 6.29 (1H, d, $^2J$ = 1.8, =CH) |

* The $^1$H NMR spectra were taken in DMSO-d$_6$ (compounds **1a**, **1f**, and **2a**) or in $CDCl_3$ (compound **1g**).

DNPH **1b-d** and pyrazole **2d** have been described previously and their physicochemical properties corresponded to the literature [17, 18]. The structures of hydrazones **1a,e-g, 3** and pyrazoles **2a-c,e-g** obtained for the first time were demonstrated by IR and NMR spectroscopic methods (Table 2), and the compositions were confirmed by elemental analysis (Table 1).

In the IR spectra of DNPH **1a,e-g, 3** absorption bands were observed for N–H, C–$H_{aryl, alkyl}$, C=N, C=C bonds, and the $NO_2$ group. In the $^1H$ NMR spectra of DNPH **1a,e-g, 3** the presence was noted of singlet signals for the protons of the NH group, the HC=C bond, and in the case of the DNPH of α-bromoacrolein (**3**) there were also two singlets for the =CH, and CH=N fragments.

Absorption bands were observed in the IR spectra of the obtained pyrazoles **2a-g** for the =C–H bond of the pyrazole ring, for aryl and hetaryl C=N, C=C bonds and for the $NO_2$ group (Table 2).

Mention should be made of the presence in the IR spectra of pyrazoles **2a-g** of bands at 3145-3150 $cm^{-1}$ characterizing the stretching vibrations of $C_{(4)}$–H and $C_{(5)}$–H bonds of the heterocycle. The absorption bands of the C=C bond of the heterocycle is displayed in the IR spectra at 1470-1575 $cm^{-1}$. The intense absorption band at 3300 $cm^{-1}$, assigned to the NH group absorption of the initial hydrazones, disappears from the IR spectra of compounds **2a-g**.

In the $^1H$ NMR spectra of pyrazoles **2a-d** the resonance signals of the $H_{(4)}$ protons are displayed at 5.9-6.5 ppm, and in pyrazoles **2e-g** the $H_{(5)}$ proton signals are found at 8.43-8.45 ppm. As was to be expected, the introduction of a dinitrophenyl group at position 1 of the heterocycle leads to a displacement of the $H_{(5)}$ signal in the $^1H$ NMR spectrum of 4-chloropyrazoles **2e-g** of 1 ppm towards low field in comparison with the $H_{(5)}$ shift in the $^1H$ NMR spectra of 1-alkyl-4-chloropyrazoles (7.23-7.49 ppm) [10]. At the same time the position of the $H_{(4)}$ signal in compounds **2b-d** is displaced towards low field to a lesser extent in comparison with its position in the $^1H$ NMR spectra of 5-chloro-1-methylpyrazoles (5.92-6.58 ppm) [15].

As a result of the investigations carried out a new simple method has been developed for obtaining 1-alkyl(aryl)-4(5)-chloro-1-(2,4-dinitrophenyl)pyrazoles from readily available starting materials.

## EXPERIMENTAL

The $^1H$ NMR spectra were obtained on Bruker DPX 400 (400 MHz) and Jeol FX 90 Q (90 MHz) instruments, internal standard was HMDS (δ 0.05 ppm for $^1H$ and 2.00 ppm for $^{13}C$ in relation to TMS). The IR spectra were taken on a Specord IR 75 spectrophotometer in KBr disks.

The previously known 2,4-dinitrophenylhydrazones **1b-d** were obtained by the usual procedure of [25], their physicochemical characteristics corresponded with the data of [26].

**2,4-Dinitrophenylhydrazones 1a,e-g (General Procedure).** The appropriate 2-chlorovinyl ketone (10 mmol) was added dropwise with stirring to a solution of 2,4-dinitrophenylhydrazine (10 mmol) in ethanol (50 ml) and 50% $H_2SO_4$ (10 ml). The product precipitating as a solid was filtered off, washed with ethanol (10 ml), and dried.

**Preparation of 1-(2,4-Dinitrophenyl)pyrazoles (General Procedure).** A solution of chlorovinyl ketone 2,4-dinitrophenylhydrazone in PPA was heated with stirring at 100-150°C for 20-40 min. The reaction mixture was cooled, and poured onto ice. The precipitated solid was filtered off, washed with water to neutral reaction, and dried over $P_2O_5$.

**1-(2,4-Dinitrophenyl)-3-propylpyrazole (2a)** was obtained from the DNPH of 2-chlorovinyl propyl ketone (2.2 g, 7 mmol) in PPA (16 g) with stirring and heating at 100-110°C for 20 min. Yield 1.78 g.

**5-Chloro-1-(2,4-dinitrophenyl)pyrazole (2b)** was obtained from the DNPH of β,β-dichloroacrolein (7.64 g, 25 mmol) and PPA (60 g) at 130-150°C, reaction time was 40 min. Yield 3.02 g.

**5-Chloro-1-(2,4-dinitrophenyl)-3-propylpyrazole (2c)** was obtained from the DNPH of 2,2-dichlorovinyl propyl ketone (2 g, 5.76 mmol) in PPA (40 g) at 130°C, reaction time was 20 min. Yield 1.59 g.

**5-Chloro-1-(2,4-dinitrophenyl)-3-phenylpyrazole (2d)** was obtained from the DNPH of 2,2-dichlorovinyl phenyl ketone (0.85 g, 2.23 mmol) in PPA (20 g) at 140-150°C, reaction time was 30 min. Yield 0.6 g.

**4-Chloro-1-(2,4-dinitrophenyl)-3-methylpyrazole (2e)** was obtained from the DNPH of 1,2-dichlorovinyl methyl ketone (1.24 g, 3.9 mmol) in PPA (20 g) at 130-150°C, reaction time was 30 min. Yield 0.93 g.

**4-Chloro-1-(2,4-dinitrophenyl)-3-ethylpyrazole (2f)** was obtained from the DNPH of 1,2-dichlorovinyl ethyl ketone (0.62 g, 1.86 mmol) in PPA (20 g) at 120-125°C, reaction time was 30 min. Yield 0.48 g.

**4-Chloro-1-(2,4-dinitrophenyl)-3-propylpyrazole (2g)** was obtained from the DNPH of 1,2-dichlorovinyl propyl ketone (0.57 g, 1.6 mmol) in PPA (20 g) at 130-140°C, reaction time was 30 min. Yield 0.46 g.

**α-Bromoacrolein 2,4-Dinitrophenylhydrazone (3)** was obtained analogously to compound **1** from dinitrophenylhydrazine (3.36 g, 17 mmol) and α-bromoacrolein (2.35 g, 17 mmol). Yield 5.24 g.

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