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# Reactions of tosylhydrazones of benzaldehyde and benzophenone with cyanoalkenes in a basic two-phase system

Andrzej Jończyk,[a,*] Joanna Włostowska[b] and Mieczysław Mąkosza[a]

[a]*Faculty of Chemistry, Warsaw University of Technology, Koszykowa 75, PL00-662 Warsaw, Poland*
[b]*Institute of Chemistry, Agriculture University, Rakowiecka 26/30, 02-528 Warsaw, Poland*

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**Abstract**—Reaction of tosylhydrazones **1a**,**b** with cyanoalkenes **3a**,**b**, carried out in the presence of concentrated aq. sodium hydroxide in dioxane, afforded either cyanocyclopropanes **5**, **9** or pyrazoles **13**, **14** and **16**, **17**. The process takes place via generation of diazocompounds **2a**,**b** from **1a**,**b** their [3+2] cycloaddition to **3a**,**b** with the formation of unstable pyrazolines **4**, further fate of which depends on the structure of $R^1$ and $R^2$ substituents. © 2001 Elsevier Science Ltd. All rights reserved.

We have previously[1,2] found that treatment of tosylhydrazones dissolved in dioxane or diglyme with concentrated aqueous sodium hydroxide solution (two-phase system) is a convenient way of preparation of diazocompounds in the Bamford–Stevens reaction,[3] or products of their further transformations.

Now, we would like to report that action of 50% aq. sodium hydroxide solution on the tosylhydrazones **1a**,**b** in dioxane, followed by addition of an excess of cyanoalkenes **3a**,**b** results in a series of multistep reactions giving a variety of products shown in Scheme 1.

These products are obviously formed via 1,3-dipolar cycloaddition[4] of diazocompounds **2**, generated in the Bamford–Stevens reaction, and subsequent base catalyzed transformation of the pyrazoline derivatives **4**. The fate of pyrazolines **4** depends on the structure of substituents $R^1$ and $R^2$. Thus, if there are no hydrogen atoms at C-3 and C-5 of **4** ($R^1$,$R^2 \neq H$, like in **4aa**) extrusion of nitrogen results in formation of cyclopropane **5**. This is an analogous reaction to the thermal, photochemical or metal assisted[5] transformations of $\Delta^1$-pyrazolines, used in the preparation of cyclopropanes.

On the other hand, when pyrazoline **4** posesses a hydrogen atom at the α position to the cyano group (as in the case of pyrazoline **4ab**, formed in the reaction of **2a** with **3b**), it tautomerizes[6] easily into $\Delta^2$-pyrazoline **7** via ambident anion **6a**$^-$. Anion **6a**$^-$ also reacts with **3b**, when the latter is used in excess. This Michael type reaction leads to unstable $\Delta^1$-pyrazoline **8a** which upon extrusion of nitrogen forms cyclopropane **9**. The alternative reaction pathway, i.e. cyanoethylation of the eventually produced intermediate 1-cyano-2,2-diphenylcyclopropane (**10**) was excluded, because when separately prepared,[1,8] cyanoethylation did not take place under the same conditions.

To confirm the reaction pathway according to which cyanocyclopropane derivative **9** is formed, we synthesized pyrazoline **7** and allowed it to react with **3b** in the presence of a base. However, this pyrazoline prepared essentially as described in the literature for similar compounds,[7] slowly eliminated hydrogen cyanide (even when stored in a refrigerator) with formation of a gummy product. Nevertheless, freshly prepared **7** reacted with the excess of nitrile **3b** in the presence of 50% aq. NaOH and tetrabutylammonium bromide (TBAB) as a catalyst, in dioxane (phase transfer catalysis, PTC conditions[9]) to give cyanocyclopropane derivative **9** in 46% yield (without TBAB **9** is formed in lower yield).

It appears that the formation of cyanoethyl derivatives substituted at nitrogen **11** (not identified among the products) or at carbon **8a**, are reversible processes, yet the latter product is irreversibly transformed into cyclopropane **9**, by fast extrusion of nitrogen. On the other hand, the reported reaction of substituted 3-benzoylpyrazoline[10] with **3b** carried out in the presence of pyridine, yielded *N*-substituted product. These and our results indicate that the kind of products formed from reaction of pyrazolines with electrophilic alkenes depends on the structure of the former as well as on the reaction conditions, and cannot be easily predicted.

Furthermore, we found that reaction of **7** with benzyl chloride, carried out under PTC conditions, resulted in the

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* Corresponding author. Tel.: +48-22-621-42-30; fax: +48-22-628-27-41; e-mail: anjon@ch.pw.edu.pl


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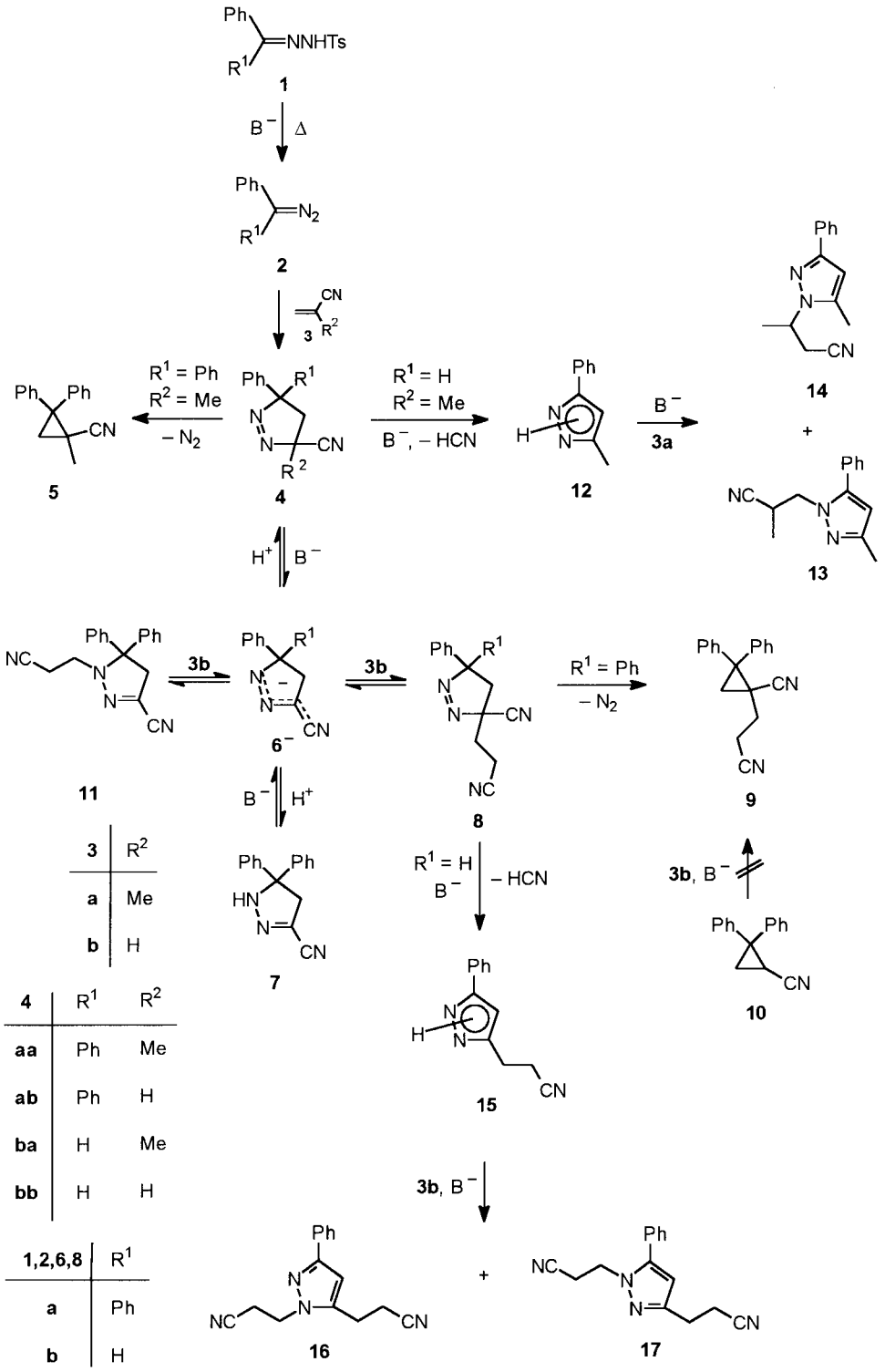
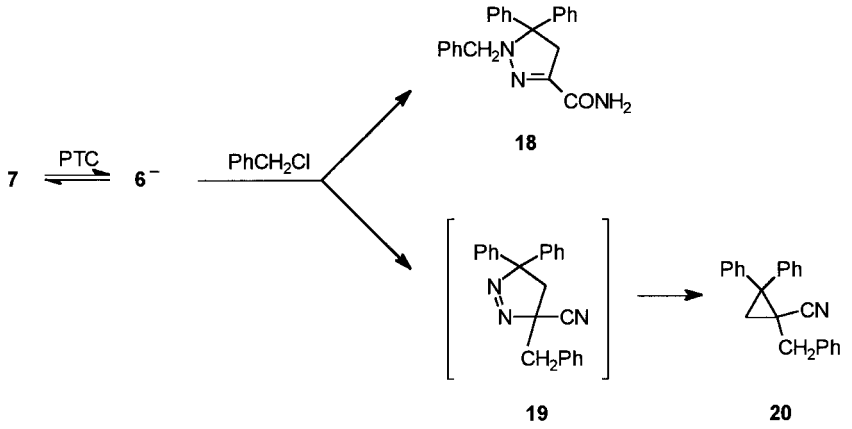



**Scheme 1.**

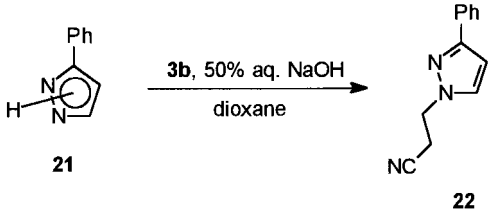
formation of a mixture of stable *N*-benzyl substituted pyrazoline **18** and cyclopropane **20**, via unstable C-substituted pyrazoline **19**, apart from other unidentified products. Evidently, under these conditions the cyano group in **18** has been hydrated to give amide functionality (Scheme 2).

Thus, ambident anion **6a**$^-$ can react with electrophilic compounds on both nucleophilic centers. This result is without a precedent: 3-triphenylphosphonium 5,5-diphenyl substituted pyrazoline was alkylated under basic conditions exclusively at nitrogen.[11] Finally, it is worth mentioning that alkylation of ketone and aldehyde phenylhydrazones (chain analogues of $\Delta^2$-pyrazolines) under PTC conditions, resulted in the formation of *N*-substituted derivatives.[12]

Other base mediated processes were observed in the case of




**Scheme 2.**




**Scheme 3.**

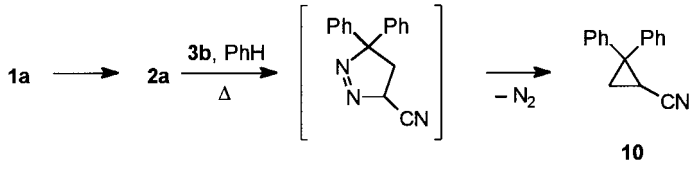
3,3,5-trisubstituted **4ba** and 3,5-disubstituted **4bb** pyrazolines which were formed in the reaction of diazocompound **2b** with cyanoalkene **3a** or **3b**, respectively (Scheme 1). Elimination of hydrogen cyanide from pyrazoline **4ba** produces pyrazole **12** which was deprotonated, and the generated anion reacted further with **3a** to give two isomeric *N*-substituted pyrazoles **13** and **14**. Elimination of hydrogen cyanide from pyrazolines under treatment with a base to give pyrazoles is a known process.[10] Independently sythesised pyrazole **12** indeed formed under similar conditions a mixture of pyrazoles **13** and **14**.

A similar reaction sequence was observed in the case of pyrazoline **4bb** (Scheme 1) however, this process led to formation of complex products mixture. Ambident pyrazoline anion **6b**$^-$ was C-cyanoethylated to give **8b** which was somewhat similar to **4ba**. In the basic medium elimination of hydrogen cyanide proceeds faster than extrusion of nitrogen to give C-cyanoethyl substituted pyrazole **15**, which has been isolated in a low yield. This pyrazole is readily deprotonated, and the resulting anion reacts smoothly with **3b** to afford two isomeric bis-cyanoethyl substituted pyrazoles **16** and **17**. It should be stressed that inverse order of reactions, i.e. first elimination of hydrogen cyanide from **4bb** to give phenylpyrazole (**21**) and then its reaction with **3b** in two-phase system did not account for the formation of **16** and **17**, since this process afforded mono-*N*-cyanoethylated product **22** (Scheme 3) which has been isolated in moderate yield.

The products presented in Scheme 1 were usually accompanied by small amount of the corresponding azines. To avoid the formation of undesired arylazines, it has been recommended that Bamford–Stevens reactions be carried out in the two-phase system, in the presence of 14% aq. NaOH and benzyltriethylammonium chloride (TEBAC) as a catalyst.[13] We generated diazocompound **2b** from **1b** under these conditions and allowed it to react with methacrylonitrile (**3a**). The main product of this reaction was pyrazole **12**. Evidently, diluted aq. NaOH solution is unable to deprotonate **12** which was thus the final product.

The role of a base in transformations visualized in Scheme 1 is evident from the experiment described below. If crude diazoalkane **2a** was separated from aq. alkaline phase and neutralized, then allowed to react with **3b**, the corresponding cyclopropane **10**[1,8] was formed in moderate yield (Scheme 4). Evidently, the lack of base did not allow the tautomerization of $\Delta^1$- into stable $\Delta^2$-pyrazoline. Such a conclusion is well documented in the literature.[7]

The above reactions of in situ generated diazocompounds **2** with cyanoalkenes **3**, carried out in the presence of concentrated aq. NaOH solution, constitute a useful shortcut approach for synthesis of some cyclopropanes and pyrazoles. They also open up an interesting problem of reactivity of ambident pyrazoline anions which is currently the subject of further research of the authors.




**Scheme 4.**

## 1. Experimental

### 1.1. General

Melting points (determined in open capillary tube apparatus) are uncorrected. $^1$H NMR spectra were measured on a Bruker WP 100 SY,Varian Gemini 200 or Varian XL-VXR 300 (at 100, 200 and 300 MHz, respectively), $^{13}$C NMR spectra on a Varian Gemini 200 (at 50 MHz) or Mercury 400BB (at 100 MHz). Unless otherwise indicated all NMR spectra were measured in $CDCl_3$ solutions. Chemical shifts ($\delta$) are given in ppm relative to TMS and coupling constants ($J$) in Hz. Gas chromatography (GC) analysis were performed with a Hewlett–Packard 5890 Series II chromatograph equipped with HP50+ capillary column (30 m). GC/MS spectra were determined on a Hewlett–Packard 5791spectrometer. IR spectra were recorded on Perkin–Elmer 577 as solutions in $CHCl_3$ and $CCl_4$ or on Specord M 80 spectrometer in KBr pellets. Elemental analyses were performed with a Perkin–Elmer CHNO/S Series II, 2400 microanalyzer. Column chromatography (CC) was carried out on Merck Kieselgel 60 (230–400 mesh) with hexane-ethyl acetate (gradient) as eluent. Tosylhydrazones **1a** and **1b** were prepared as described in the literature.[14]

### 1.2. Reactions of tosylhydrazones 1a,b with cyanoalkenes 3a,b. General procedure

Tosylhydrazone **1** (0.02 mol), dioxane (20 mL) and 50% aq. NaOH (30 g, 20 mL, 0.375 mol) were stirred at 80–90°C for 1 h (pink colour), then cyanoalkene **3** (0.12 mol) was added dropwise. The mixture was stirred at 80–90°C for 0.25 h (colour faded), cooled, diluted with water (ca. 100 mL), extracted with $CHCl_3$ (2×ca. 50 mL), the organic extracts were washed with water, dried ($MgSO_4$), the solvent was evaporated, the residue was separated by CC and the solid products were crystallised. The results for each reaction are given below.

**1.2.1. Reaction of 1a with 3a.** Benzophenone azine (0.30 g, 8%) as a yellow solid and cyclopropane **5** (1.60 g, 34%) as a white solid.

Benzophenone azine: mp 160–162°C (MeOH), lit.[14] mp 164°C; $\delta_H$ (100 MHz) 7.75–7.18 (m, ArH).

Cyclopropane **5**: mp 142–144°C (MeOH), lit.[8] mp 141–142°C; $\nu_{max}$ ($CHCl_3$) 2220 cm$^{-1}$; $\delta_H$ (100 MHz) 7.70–7.05 (10H, m, Ph), 2.01 (1H, d, $J$=5.6 Hz, CH), 1.55 (1H, d, $J$=5.6 Hz, CH), 1.29 (3H, s, Me).

**1.2.2. Reaction of 1a with 3b.** Benzophenone azine (0.35 g, 10%) and cyclopropane **9** (2.22 g, 41%) as a white solid.

Cyclopropane **9**: mp 135–137°C (MeOH); (Found: C, 83.9; H, 5.9; N, 10.3; $C_{19}H_{16}N_2$ requires C, 83.79; H, 5.92; N, 10.29%); $\nu_{max}$ (KBr) 3064, 3028, 2232, 1600, 1496, 1448, 708 cm$^{-1}$; $\delta_H$ (300 MHz) 7.56–7.53 (2H, m, Ph), 7.43–7.25 (8H, m, Ph), 2.62 (2H, part $A_2$ of $A_2MX$, $^3J$=6.6 Hz, $^3J$=8.3 Hz, $CH_2CN$), 2.17 (1H, part M of $A_2MX$, $^2J$=14.4 Hz, $^2J$=6.6 Hz, CH), 2.14 and 1.93 (2H, AB, $^2J$=5.8 Hz, $CH_2$ cycloprop.), 1.25 (1H, part X of $A_2MX$, $^2J$=14.4 Hz, $^3J$=8.3 Hz, CH); $\delta_C$ (100 MHz) 140.4, 138.1, 129.0, 128.9, 128.8, 128.75, 127.85, 127.8, 42.9, 29.0, 25.0, 21.1, 15.3.

**1.2.3. Reaction of 1b with 3a.** Benzaldehyde azine (0.06 g, 3%) as a yellowish solid and mixture of pyrazoles **13** and **14** (4.1 g, 91%, slowly crystallizing colourless oil) of ratio ca. 17:3 (from GC).

Benzaldehyde azine: mp 90–92°C (MeOH), lit.[15] mp 92–93°C; $\delta_H$ (100 MHz) 8.66 (2H, s, HC=N), 8.10–7.78 (4H, m, Ph), 7.72–7.39 (6H, m, Ph).

Pyrazoles **13**+**14**: (Found: C, 74.6; H, 6.6; N, 18.6. $C_{14}H_{15}N_3$ requires C, 74.64; H, 6.71; N, 18.65%). 13: *m/z* 225 (31, M$^+$), 171 (100), 158 (14), 130 (29), 77 (34), 51 (14), 39 (14%); 14: *m/z* 225 (27, M$^+$), 171 (100), 158 (12), 130 (23), 77 (22), 42 (17%).

Pyrazole **14**: $\delta_H$ read from $^1$H NMR spectrum of **13**+**14** (300 MHz) 7.47–7.25 (m, overlapped with Ph of **13**), 6.08 (1H, s, HC=C), 4.27 and 4.07 (2H, part AB of ABX, $J_{AB}$=13.5 Hz, $J_{AX}$=8.1 Hz, $J_{BX}$=7.25 Hz, $CH_2$), 2.39 (1H, m, CHCN), 2.30 (3H, s, MeC=N), 1.16 (3H, d, $J$=7.2 Hz, Me).

This mixture was separated by CC and recrystallised (MeOH) to give a sample of pure **13** (1.6 g, 35.5%) as a white solid, mp 53–55°C; (Found: C, 74.4; H, 6.7; N, 18.7; $C_{14}H_{15}N_3$ requires: C, 74.64; H, 6.71; N, 18.65%); $\nu_{max}$ (KBr) 3060, 2988, 2932, 2244, 1556, 1444, 1336, 764, 692 cm$^{-1}$; $\delta_H$ (300 MHz) 7.79–7.75 (2H, m, *ortho*-Ph), 7.42–7.28 (3H, m, *meta*+*para*-Ph), 6.33 (1H, s, HC=C), 4.28 and 4.15 (2H, part AB of ABX, $J_{AB}$=13.8 Hz, $J_{AX}$=7.9 Hz, $J_{BX}$=6.6 Hz, $CH_2$), 3.41 (1H, m, CHCN), 2.36 (3H, s, Me), 1.37 (3H, d, $J$=7.1 Hz, C**H**$_3$CH); $\delta_C$ (100 MHz) 151.1, 140.6, 132.8, 128.5, 127.8, 125.5, 120.7, 103.0, 50.5, 27.1, 15.2, 11.1.

**1.2.4. Reaction of 1b with 3b.** Benzaldehyde azine (0.18 g, 9%), mixture of pyrazoles **16** and **17** (0.70 g, 12%) of ratio ca. 16:9 (from $^1$H NMR spectrum) as a white solid and isomeric pyrazoles **15** (0.6 g, 15%) as a white solid.

Pyrazoles **16**+**17**: (Found: C, 72.1; H, 5.5; N, 22.4. $C_{15}H_{14}N_4$ requires C, 71.98; 5.64; N, 22.38%); $\delta_H$ (100 MHz) 7.79–7.73 and 7.56–7.30 (5H, two m, Ph), 6.52 and 6.21 (1H, two s, HC=C), 4.58–4.20 (2H, two overlapping t, $NCH_2$), 3.32–2.56 (6H, m, $CH_2CN$ and $CH_2CH_2CN$); *m/z* (one signal on GC) 250 (78, M$^+$), 222 (34), 210 (100), 197 (86), 162 (62), 156 (68), 128 (25), 102 (18), 77 (29%).

Crystallisation of this mixture (from $CCl_4$ then $Et_2O$) afforded **17** (0.15 g, 3%) as a white solid, mp 107–109°C (Found: C, 72.1; H, 5.8; N, 22.3; $C_{15}H_{14}N_4$ requires C, 71.98; H, 5.64; N, 22.38%); $\nu_{max}$ (KBr) 2968, 2248, 1548, 1492, 1456, 1412, 1392, 1276, 1000, 768 cm$^{-1}$; $\delta_H$ (300 MHz) 7.50–7.36 (5H, m, Ph), 6.21 (1H, s, HC=C), 4.31 and 2.92 (4H, two t, $J$=6.85 Hz, $NCH_2CH_2CN$), 3.02 and 2.75 (4H, two t, $J$=7.4 Hz, $CH_2CH_2CN$); $\delta_C$ (100 MHz) 149.2, 145.5, 129.3, 129.1, 128.9, 128.8, 119.3, 116.9, 105.5, 44.3, 24.3, 18.6, 16.9.

Isomeric pyrazoles **15** mp 124–126°C, one signal on GC; (Found: C, 73.3; H, 5.4; N, 21.4; $C_{12}H_{11}N_3$ requires C, 73.07; H, 5.62; N, 21.30%); $\nu_{max}$ (KBr) 3132, 3104, 3016, 2936, 2876, 2248, 1572, 1496, 1004, 828, 764, 684 $cm^{-1}$; $\delta_H$ (200 MHz) 12.65 (1H, br s, NH), 7.90–7.38 (5H, m, Ph), 6.84 and 6.72 (1H, two s, HC═C), 3.39–2.75 (4H, four overlapping t, $CH_2CH_2CN$); $\delta_C$ (100 MHz) 147.3, 146.9, 146.0, 131.0, 129.5, 129.4, 129.0, 128.8, 126.5, 125.9, 118.9, 118.4, 102.2, 77.2, 23.4, 17.3, 17.1; *m/z* 197 (89, $M^+$), 170 (33), 157 (100), 128 (34), 102 (8), 77 (12), 52 (4%).

**1.2.5. Preparation of pyrazoline 7.** A solution of diazocompound **2a** (2.50 g, 12.9 mmol) and triethylamine (1.44 g, 14.2 mmol) in hexane (55 mL) was added dropwise to a solution of nitrile **3b** (0.76 g, 14.3 mmol) in hexane (55 mL), and the mixture was stirred with magnetic stirrer for 48 h. The solid was filtered off and crystallised (EtOH) to give 1.46 g (46%) of **7**, mp 108–113°C (dec.). (Found: C, 77.7; H, 5.3; N, 16.65; $C_{16}H_{13}N_3$ requires: C, 77.71; H, 5.30; N, 16.99%); $\nu_{max}$ (KBr) 3316, 3276, 2216, 1544, 1492, 1444, 1420, 1312, 760, 700, 612 $cm^{-1}$; $\delta_H$ (200 MHz) 7.42–7.15 (10H, m, Ph), 6.86 (1H, s, NH), 3.51 (2H, s, $CH_2$); $\delta_C$ (50 MHz) 143.7, 128.8, 128.0, 126.1, 121.7, 114.5, 75.9, 46.8.

**1.2.6. Preparation of cyclopropane 9 from reaction of pyrazoline 7 with acrylonitrile (3b).** Pyrazoline **7** (0.50 g, 2 mmol), dioxane (2 mL), 50% aq. NaOH (2 mL) and TBABr (0.06 g, 0.19 mmol) were stirred (the mixture thickened and the solid separated), then **3b** (0.64 g, 12 mmol) was added dropwise (the solid dissolved), and the temperature raised from 25 to ca. 42°C. The stirring was continued for 20 min, the mixture was diluted with water (ca. 50 mL), extracted with $CHCl_3$ (3×20 mL), the organic extracts were washed with water (50 mL), dried ($MgSO_4$), the solvent was evaporated, and the residue was crystallised (MeOH) to give **9** (0.25 g, 46%), mp 136–138°C, identified by comparison (mixed mp, TLC, GC, $^1H$ NMR) with that obtained from **1a** and **3b**.

**1.2.7. Reaction of pyrazoline 7 with benzyl chloride.** Pyrazoline **7** (2.47 g, 10 mmol), benzyl chloride (1.53 g, 20 mmole), dioxane (3 mL), 50% aq. NaOH (15 mL) and TBAB (0.3 g, 0.9 mmol) were stirred at ca. 60°C for 6 h (the solid that was formed at the beginning, dissolved later). The mixture was diluted with water, extracted with benzene (3×20 mL), the organic extracts were washed with water, dried ($MgSO_4$), and the solvent was evaporated. The semi-solid orange residue (3.8 g) was analyzed by $^1H$ NMR to show largely the signals of **18** and **20**, partially overlapped with the signals of impurities. This mixture was twice crystallized (MeOH) to give **20** (0.62 g, 20%), mp 171–173°C; (Found: C, 89.1; H, 6.1, N, 4.4; $C_{23}H_{19}N$ requires: C, 89.28; H, 6.19; N, 4.53%); $\nu_{max}$ (KBr) 3064, 3028, 2232, 1596, 1496, 1448, 1080, 704 $cm^{-1}$; $\delta_H$ (200 MHz) 7.59–7.14 (15H, m, Ph), 3.15 (1H, d, *J*=5.4 Hz, CH**H**), 2.18 (1H, d, *J*=5.4 Hz, C**H**H), 2.04 and 1.92 (each 1H, AB q, *J*=5.4 Hz, $CH_2$ cycloprop.); $\delta_C$ (100 MHz) 141.2, 139.1, 137.1, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 127.7, 127.6, 127.1, 121.6, 43.6, 38.7, 25.1, 23.4.

The filtrate after first crystallisation was evaporated, dissolved in $CHCl_3$, passed through short column with Kieselgel (eluent: ethyl acetate/hexane 5:1), the eluate was evaporated and the residue was crystallized from acetone, to give **18** (0.25 g, 8%), mp 216–218°C; (Found: C 77.6, H 5.9, N 11.8. $C_{23}H_{21}N_3O$ requires C, 77.72; H, 5.96; N, 11.82%); $\nu_{max}$ (KBr) 3436, 3276, 3208, 3164, 1676, 1596, 1560, 1444, 1276, 1252, 767, 740, 700 $cm^{-1}$; $\delta_H$ (200 MHz) 7.40–7.23 (15H, m, Ph), 6.40 (1H, br s, CONH), 5.14 (1H, br s, CONH), 3.95 (2H, s, $CH_2$), 3.74 (2H, s, $CH_2$); $\delta_C$ (100 MHz) 164.2, 143.1, 143.6, 137.9, 128.4, 128.3, 127.7, 127.6, 127.1, 80.1, 77.2, 53.5, 48.0.

**1.2.8. Reaction of 3-phenylpyrazole (21) with acrylonitrile (3b).** Pyrazole **21** (1.44 g, 10 mmol), 50% aq. NaOH (5 mL), dioxane (10 mL) and nitrile **3b** (1.00 g, 19 mmol) were stirred at 80°C for 0.5 h. The mixture was cooled, diluted with water, extracted with $Et_2O$ (2× 20 mL), the organic extracts were washed with water, dried ($MgSO_4$), and the solvent was evaporated. The residue was crystallized ($Et_2O$/light petroleum (ca. 3:1) mixture) to give **22** (1.01 g, 51%), mp 50–52°C, lit.[16] mp 51–53°C; (Found: C; 72.85; H, 5.6; N, 21.0; $C_{12}H_{11}N_3$ requires C, 73.07; H, 5.62; N, 21.30%); $\nu_{max}$ ($CCl_4$) 2260 $cm^{-1}$; $\delta_H$ ($CCl_4$, 100 MHz) 7.74–7.64 (2H, m, Ph), 7.39–7.19 (4H, m with overlapped d, *J*=2.6 Hz, Ph and HC═C), 6.44 (1H, d, *J*=2.6 Hz, HC═C), 4.24 (2H, t, *J*=6.8 Hz, $NCH_2$), 2.81 (2H, t, *J*=6.8 Hz, $CH_2CN$).

**1.2.9. Reaction of tosylhydrazone 1b with 3a in the presence of 14% aq. NaOH.** Tosylhydrazone **1b** (0.55 g, 2 mmol), benzene (50 mL), TEBAC (0.1 g, 0.4 mmol) and 14% aq. NaOH (50 mL) were stirred at 65–70°C for 2 h. Then, nitrile **3a** (0.8 g, 12 mmol) was added and the reaction continued at 65–70°C for 45 min (after 15 min pink colour faded). The mixture was cooled, diluted with water (50 mL), the phases were separated, the water phase was extracted with benzene (2×20 mL), the combined organic extracts were washed with water, dried ($MgSO_4$) and the solvent was evaporated. The yellowish solid (0.4 g) was refluxed with hexane (ca. 20 mL) and filtered to give colourless crystals of pyrazole **12** (0.2 g, 68%), mp 124–126°C.

Analytical sample of **12** was crystallized from EtOH, mp 127°C (lit.[17] mp 128°C); $\nu_{max}$ ($HCCl_3$) 3440 $cm^{-1}$; $\delta_H$ (100 MHz) 7.73–7.63 (2H, m, Ph), 7.41–7.04 (3H, m, Ph), 6.28 (1H, s, HC═C), 2.21 (3H, s, $CH_3$).

**1.2.10. Reaction of diazoalkane 2a with acrylonitrile (3b).** Diazoalkane **2a** prepared[2] from tosylhydrazone **1a** (10 mmol) was refluxed with **3b** (1.1 g, 20 mmol) in benzene (25 mL) until the red colour faded, the solvent was evaporated and the solid was crystallized (EtOH) to give **10** (1.14 g, 52%), mp 107°C, lit.[8] mp 107–108°C. The product was compared (mixed mp, $^1H$ NMR) with that obtained according to lit.[1,8]

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