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Ultrasound-accelerated aromatisation of *trans*- and *cis*-pyrazolines under heterogeneous conditions using claycop

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Abstract—A simple, efficient and eco-friendly procedure has been developed for the aromatisation of various pyrazolines in heterogeneous media using clay-supported copper(II) nitrate (claycop) under ultrasound activation. The reaction rate enhancement and the sonication effect are discussed.

1. Introduction

The aromatisation process is an interesting transformation in organic synthesis and few methods have been explored to accomplish this conversion of pyrazolines to pyrazoles compounds.[1] The pyrazole compounds are important systems that often exist in biologically active natural products and synthetic derivatives.[2] Among the literature methods, the most widely used procedure for the preparation of pyrazoles is the aromatisation of 1,3,4- and 1,3,5- trisubstituted pyrazolines and also the 1,3,4,5-tetrasubstituted *cis*-pyrazolines.[3] However, this process requires drastic reaction conditions and the use of toxic heavy metals or reagents such as *p*-chloranil,[3a,b] DDQ,[3c] lead tetraacetate,[3d,e] copper chloride,[3f] manganese dioxide,[3g,h] mercury oxide,[3i] potassium permanganate,[3j] iodobenzene diacetate,[3k] and silver nitrate.[3l] Recently, Nakamishi et al. reported the conversion of 1,3,5-trisubstituted pyrazolines to pyrazoles using Pd/C catalyst.[3m] However, such reagents were found to be inefficient for the conversion of tetrasubstituted *trans*-pyrazoline isomers and, two steps are usually required for this transformation.[4] Consequently, there is a need for the development of newer methods, which proceed under mild and environmentally benign conditions. In this context, the use of inexpensive supported reagents has attracted much attention because of their increased chemoselectivity and their simple manipulation.[5] Precisely, clay-supported reagents have found widespread utility in a variety of heterogeneous reactions and synthetic transformations.[5f,g,6,7]

Furthermore, sonochemistry has become increasingly popular to improve the yield and shorten reaction times in various organic reactions.[8–10] Most of the observed effects are due to cavitation related to the formation, growth and collapse of bubbles in an irradiated liquid. Indeed, cavitation induces very high local temperatures and pressures inside the bubbles, which enhanced mass transfer and turbulent flow in the liquid.

In continuation of our studies using supported reagents in organic transformation,[7a,11] herein we report a convenient and eco-friendly procedure for the preparation of pyrazoles by simple oxidation of both *cis*- and *trans*-pyrazolines[7a,12] using K10 clay-supported copper nitrate (claycop),[13] under ultrasound activation (Scheme 1). The sonication effect on the rate enhancement is also reported.

2. Results and discussion

Our investigation began with the aromatisation reaction on 1,3-diphenyl-indano[3,2-*d*] pyrazoline **1** (Scheme 1). First, the effect of the solvent, catalyst and temperature

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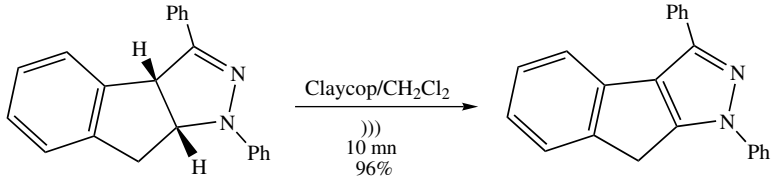


1 **1a**

Scheme 1. Aromatisation of 1,3-diphenyl-indano[3,2-*d*] pyrazoline.

on conversion rates was examined. Accordingly, the reaction was carried out in various solvents such as ether, cyclohexane, toluene and THF and gave only the best results with CH_2Cl_2. The relative proportion of the reactants and the reaction time were also tested and the best result was obtained by using 2 equiv of $Cu(NO_3)_2{\cdot}3H_2O$ (claycop) for 1 equiv of pyrazoline **1**. Under these mild conditions, the reaction was very rapid (10 min) and compound **1a** was obtained in high yield (96%). A larger excess of claycop was not required and did not change the results.

The temperature was varied using the experimental conditions determined above (2 equiv claycop, sonication for 10 min) and the results are listed in Table 1. The best yield was obtained at room temperature and lowering or increasing the reaction temperature only induced yield decrease. This is a well-known result for the reactions under sonication for which an optimum range of temperature exists.[10c] At low temperature, the ultrasonic irradiation is not totally efficient whereas at higher temperature, the cavitation is less efficient. Indeed, in this case, the presence of relatively large amounts of vaporised liquid in the bubbles of cavitation makes the collapse less energetic.

In order to check the usefulness of the sonication, a silent reaction with only a magnetically stirring was performed: the reaction rate was reduced and the yield was very low (<10%).

We have also examined the effect of oxidising agent. Indeed, association of the reagent with the clay support provides a favourable reaction microenvironment, with strong reactivity enhancement as demonstrated by control experiments (Table 2).

Once suitable conditions have been determined, we extended this reaction to other *cis*-pyrazolines (**1**–**5**) and *trans*-pyrazolines (**6**–**10**). Compounds **6**–**10** were used as mixture of two regioisomers **a/b** (Table 3).

Table 1. Temperature effect in the reaction of Scheme 1

Entry	Temperature (°C)[a]	Yield (%)[b]
1	10	38
2	25	96
3	35	79
4	45[c]	70
5	65[c]	65

[a] Temperature of ultrasonic bath.
[b] Isolated yield.
[c] Refluxed and sonicated reaction.

Table 2. Control experiments with pyrazoline **1**[a]

Oxidizing agent	Amount	Conversion rate (%)[b]
Claycop	2.42 g	100
$Cu(NO_3)_2{\cdot}3H_2O$	1 g	10
$Cu(NO_3)_2{\cdot}3H_2O$/water	1 g/5 mL	0
K10 clay	2 g	0

[a] All reactions were carried out by using **1** (2 mmol) in CH_2Cl_2 (15 mL) under sonication (10 min).
[b] On the basis of ^1H NMR.

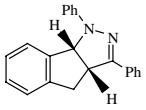
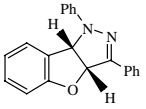
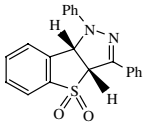
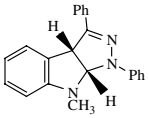
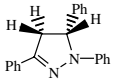
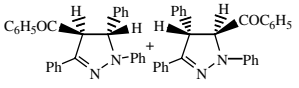
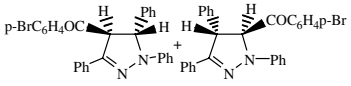
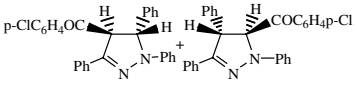
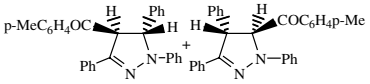
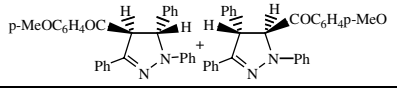
Reactions were monitored by TLC, the end of the reaction is indicated by the disappearance of the pyrazoline identified by its intense fluorescence to $\lambda = 365$ nm. Inspection of the table reveals that claycop is an efficient reagent for the aromatisation of *cis*- and *trans*-pyrazolines, that is, reactions are extremely accelerated under sonication. Ultrasound does not modify the nature of the oxidised adduct but rates are significantly enhanced. Reactions are generally complete within a few minutes (10–15 min) whereas hours (1–5.5 h) are required under magnetical stirring. Irradiation of the heterogeneous medium by ultrasonic waves reduces the reaction time in any cases. This result is in line with our previously proposed mechanism involving the *1H*-pyrazole radical as intermediate (Scheme 2).[7a] Thus, the process probably involved as key steps (i) formation of nitrogen dioxide radical $NO_2{\cdot}$ from claycop reagent (initiation step), then (ii) electron transfer and C–H bond cleavage to give the radical intermediate (**I**) and finally (iii) C–C bond formation and hydrogen abstraction on **I** to afford the stable pyrazole. An other process, which may also be taken into account is the one that involves a single electron transfer between pyrazoline and copper, with a radical cation **II** as intermediate.

A catalytic effect of the metal and/ or air oxidation could also play a role in the dehydrogenation of the pyrazolines. However, the role of the metal remains enigmatic. In this study, our choice was based on the change of colouration observed in the clay supported from blue to green during the reaction.

3. Conclusion

This ultrasound-accelerated oxidation reaction of *cis*- and *trans*-pyrazolines with claycop is a simple and facile method to produce pyrazoles in high yields that uses relatively much reduced amount of the oxidant. The operational simplicity, the use of inexpensive oxidizing agent, rapid reaction rates and high yields of pure

Table 3. Aromatisation of pyrazolines **1**–**10** to pyrazoles **1a**–**10a** produced via Scheme 1

Substrate		Regioisomers, ratio, respectively	Products **1a**–**10a**, magnetical stirring, time (h), yield (%)	Products **1a**–**10a**, sonochemical, time (min), yield (%)
1		100	1 (98)	10 (96)
2		100	1 (98)	10 (98)
3		100	1 (95)	10 (98)
4		100	1 (96)	10 (97)
5		100	3 (96)	15 (96)
6		90/10	3 (64)	15 (93)
7		90/10	6 (65)	15 (91)
8		95/5	5 (73)	15 (93)
9		88/12	4 (78)	15 (93)
10		95/5	5.5 (79)	15 (94)

[a]The regioisomers ratios were evaluated either by ^{1}H NMR or GC.
[b]Isolated yields.

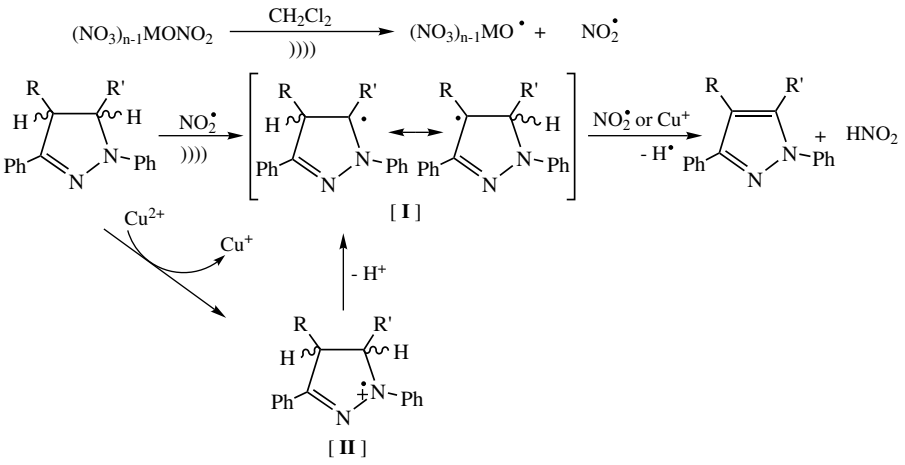
product formation when compared to existing protocols makes this a useful procedure and an attractive alternative to the currently available methods. Further studies extending this approach to the aromatisation of other heterocyclic systems are currently in progress.

4. Experimental

4.1. General procedure for aromatisation of *cis* and *trans*-pyrazolines

The pyrazoline derivative **1**–**10** (1.0 mmol) and the 'claycop' 1.21 g (2 mmol de $Cu(NO_3)_2{\cdot}3H_2O$), were introduced in 10 mL CH_2Cl_2 under atmosphere pressure or dry nitrogen. The reaction medium was sonicated for 10–15 min at room temperature. Completion of the reaction was generally revealed by TLC or by the colour conversion of blue to green. The reaction medium was then filtered and washed with 3×10 mL of dichloromethane. The resulting residue was purified by small column chromatography on silica gel (eluted with CH_2Cl_2).

4.1.1. 1,3-Diphenyl-1,4-dihydroindeno[1,2-*c*]pyrazole (1a). Mp 172–174 °C (EtOH) (lit.[3a] 171–172 °C). IR (KBr): 1620, 1597, 1506, 1491 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.74 (2H, s), 7.75–7.04 (14H, m). ^{13}C NMR ($CDCl_3$): δ 143.70, 139.49, 137.60, 136.41, 130.81, 129.26, 129.40, 128.30, 127.63, 127.43, 126.81, 125.97, 124.62, 124.58, 121.57, 119.47, 117.99, 33.94. CIMS (isobutane, reagent gas): m/z 309 $[M+H]^+$. Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found C, 85.82; H, 5.18; N, 9.01.



Scheme 2. Proposed mechanism for aromatisation of pyrazolines to pyrazoles.

4.1.2. 1,3-Diphenyl-1*H*-[1]benzofuro[3,2-*c*]pyrazole (2a). Mp 218–220 °C (EtOH). IR (KBr): 1659, 1593, 1513, 1495, 1481 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.10–7.20 (14H, m). ^{13}C NMR ($CDCl_3$): δ 152.40, 144.64, 139.12, 129.30, 129.15, 128.65, 127.83, 127.90, 127.39, 125.67, 124.58, 124.47, 121.60, 118.75, 118.47, 111.13, 110.09. CIMS (isobutane, reagent gas): m/z 311 $[M+H]^+$. Anal. Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03. Found C, 81.21; H, 4.50; N, 9.09.

4.1.3. 1,3-Diphenyl-4,4(1*H*)-dione-benzothieno[3,2-*c*]pyrazole (3a). Mp 210–212 °C (EtOH). IR (KBr): 1623, 1594, 1513, 1496, 1480 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.66–6.91 (14H, m). ^{13}C NMR ($CDCl_3$): δ 144.93, 141.19, 140.48, 134.80, 134.60, 131.82, 130.60, 129.57, 128.57, 128.41, 126.56, 126.48, 124.58, 124.38, 121.50, 119.69, 108.88. CIMS (isobutane, reagent gas): m/z 359 $[M+H]^+$. Anal. Calcd for $C_{21}H_{14}N_2O_2S$: C, 70.37; H, 3.94; N, 7.82. Found C, 70.31; H, 3.96; N, 7.79.

4.1.4. 8-Methyl-1,3-diphenyl-1,8-dihydropyrazolo[3,4-*b*]-indole (4a). Mp 184–186 °C (EtOH) (lit.[11d] 182–184 °C). IR (KBr): 1645, 1595, 1524, 1510 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.25 (3H, s), 8.01–7.20 (14H, m). ^{13}C NMR ($CDCl_3$): δ 153.01, 144.02, 138.08, 131.90, 129.94, 129.22, 129.13, 128.03, 126.41, 126.29, 123.34, 122.23, 121.82, 121.55, 120.77, 115.57, 103.88. CIMS (isobutane, reagent gas): m/z 324 $[M+H]^+$. Anal. Calcd for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99. Found C, 81.68; H, 5.37; N, 13.01.

4.1.5. 1,3,5-Triphenyl-pyrazole (5a). Mp 136–138 °C (EtOH) (lit.[3m] 138–139 °C). IR (KBr): 1610, 1596, 1547, 1488, 1462 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.94–6.82 (16H, m). ^{13}C NMR ($CDCl_3$): δ 151.10, 144.30, 140.10, 132.97, 130.14, 129.20, 128.99, 128.66, 128.54, 128.37, 128.19, 125.73, 125.21, 119.39, 105.10 ($'H$ and $'^3C$ NMR spectra consistent with values reported in the lit.[13]). CIMS (isobutane, reagent gas): m/z 297 $[M+H]^+$. Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found C, 85.18; H, 5.38; N, 9.51.

4.1.6. 1,3,5-Triphenyl-4-benzoylpyrazole (6a) and 1,3,4-triphenyl-5-benzoylpyrazole (6b). Mp 118–120 °C (EtOH) (lit.[7a] 119–120 °C). Data for **6a**: IR (KBr): 1736, 1659, 1596, 1580, 1523, 1500 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.02–7.13 (20H, m). ^{13}C NMR ($CDCl_3$): δ 197.40, 147.05, 144.56, 140.00, 139.05, 132.58, 131.44, 130.35, 129.62, 129.27, 129.20, 128.77, 128.79, 128.70, 128.38, 127.52, 126.39, 124.57, 118.48, 115.01. CIMS (isobutane, reagent gas): m/z 401 $[M+H]^+$. Data for **6b**: IR (KBr): 1736, 1659, 1596, 1580, 1523, 1500 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.02–7.13 (20H, m). ^{13}C NMR ($CDCl_3$): δ 197.40, 144.56, 140.00, 139.05, 134.41, 132.58, 131.44, 130.35, 129.62, 129.27, 129.20, 128.77, 128.79, 128.70, 128.38, 127.52, 126.39, 124.57, 122.33, 118.48. CIMS (isobutane, reagent gas): m/z 401$[M+H]^+$.

4.1.7. 1,3,5-Triphenyl-4-parabromobenzoylpyrazole (7a) and 1,3,4-triphenyl-5-parabromobenzoylpyrazole (7b). Mp 138–140 °C (EtOH) (lit.[7a] 139–140 °C). Data for **7a**: IR (KBr) 1730, 1675, 1595, 1591, 1529, 1511 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.00–7.26 (19H, m). ^{13}C NMR ($CDCl_3$): δ 199.40, 148.15, 147.45, 140.05, 139.09, 134.78, 132.93, 130.36, 129.92, 129.87, 129.80, 129.77, 129.65, 128.76, 128.99, 127.53, 127.40, 124.97, 119.08, 117.22. CIMS (isobutane, reagent gas): m/z 479 $[M+H]^+$. Data for **7b**: IR (KBr) 1730, 1675, 1595, 1591, 1529, 1511 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.00–7.26 (20H, m). ^{13}C NMR ($CDCl_3$): 199.40, 147.45, 140.05, 139.09, 137. 61, 134.78, 132.93, 130.36, 129.92, 129.87, 129.80, 129.77, 129.65, 128.76, 128.99, 127.53, 127.40, 125.03, 124.97, 119.08. CIMS (isobutane, reagent gas): m/z 479 $[M+H]^+$.

4.1.8. 1,3,5-Triphenyl-4-parachlorobenzoylpyrazole (8a) and 1,3,4-triphenyl-5-parachlorobenzoylpyrazole (8b). Mp 124–126 °C (EtOH) (lit.[7a] 125–126 °C). Data for

8a: IR (KBr) 1735, 1685, 1559, 1531, 1529, 1523 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01–7.29 (19H, m). ^{13}C NMR ($CDCl_3$): δ 200.01, 149.05, 148.56, 140.01, 139.99, 134.88, 133.33, 130.35, 129.99, 129.89, 129.89, 129.87, 129.68, 128.98, 128.01, 127.86, 127.68, 125.00, 119.18, 118.23. CIMS (isobutane, reagent gas): m/z 435 $[M+H]^+$. Data for **8b**: IR (KBr) 1735, 1685, 1559, 1531, 1529, 1523 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01–7.29 (19H, m). ^{13}C NMR ($CDCl_3$): δ 200.01, 148.56, 140.01, 139.99, 137.62, 136.43, 134.88, 133.33, 130.35, 129.99, 129.89, 129.89, 129.87, 129.68, 128.98, 128.01, 127.86, 127.68, 125.00, 119.18. CIMS (isobutane, reagent gas): m/z 435 $[M+H]^+$.

4.1.9. 1,3,5-Triphenyl-4-paramethylbenzoylpyrazole (9a) and 1,3,4-triphenyl-5-paramethylbenzoylpyrazole (9b). Mp 132–134 °C (EtOH) (lit.[7a] 133–134 °C). Data for **9a**: IR (KBr) 1660, 1610, 1598, 1576, 1518, 1499 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.16–7.00 (19H, m), 2.41 (3H, s). ^{13}C NMR ($CDCl_3$): δ 197.94, 148.15, 145.57, 140.01, 139.95, 132.78, 131.49, 130.38, 129.66, 129.28, 129.21, 128.79, 128.80, 128.71, 128.38, 127.51, 126.88, 124.58, 118.99, 117.26, 21.80. CIMS (isobutane, reagent gas): m/z 415 $[M+H]^+$. Data for **9b**: IR (KBr) 1660, 1610, 1598, 1576, 1518, 1499 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.16–7.00 (19H, m), 2.52 (3H, s). ^{13}C NMR ($CDCl_3$): δ 197.94, 145.57, 140.01, 139.95, 135.42, 132.78, 131.49, 130.38, 129.66, 129.28, 129.21, 128.79, 128.80, 128.71, 128.38, 127.51, 126.88, 125.66, 124.58, 118.99, 21.90. CIMS (isobutane, reagent gas): m/z 415 $[M+H]^+$.

4.1.10. 1,3,5-Triphenyl-4-paramethoxybenzoylpyrazole (10a) and 1,3,4-triphenyl-5-paramethoxybenzoyl pyrazole (10b). Mp 112–114 °C (EtOH) (lit.[7a] 112–113 °C). Data for **10a**: IR (KBr) 1647, 1600, 1597, 1575, 1521, 1497 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01–6.95 (19H, m), 4.01 (3H, s). ^{13}C NMR ($CDCl_3$): δ 199.33, 148.00, 147.25, 140.12, 138.89, 134.55, 132.73, 130.36, 129.82, 129.37, 129.60, 129.67, 129.00, 128.66, 128.56, 127.44, 127.34, 124.67, 119.00, 117.99, 56.13. CIMS (isobutane, reagent gas): m/z 431 $[M+H]^+$. Data for **10b**: IR (KBr) 1647, 1600, 1597, 1575, 1521, 1497 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01–6.95 (19H, m), 4.11 (3H, s). ^{13}C NMR ($CDCl_3$): δ 199.33, 147.25, 140.12, 138.89, 136.44, 134.55, 132.73, 130.36, 129.82, 129.37, 129.60, 129.67, 129.00, 128.66, 128.56, 127.44, 127.34, 125.02, 124.67, 119.00, 56.33. CIMS (isobutane, reagent gas): m/z 431 $[M+H]^+$.

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