

The effect of pressurized carbon dioxide on the cyclocondensation reaction between 4-alkoxy-1,1,1-trifluoro-3-alken-2-ones and hydrazines

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This article is dedicated to Prof. Rosa Maria Claramunt on the occasion of her 65th anniversary

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Abstract

The synthesis of 1-unsubstituted and 1-phenyl-5-trifluoromethylpyrazoles from the reaction of 4-alkoxy-1,1,1-trifluoro-3-alken-2-ones [CF₃C(O)CH=C(R¹)OR, where R = Me, Et and R¹ = H, Me, Ph] with hydrazines [NH₂NHR², where R² = H, Ph] in pressurized carbon dioxide is reported for the first time. Reaction conditions such as pressure, temperature and time were evaluated. The methodology developed herein was suitable to synthesize products in moderate to excellent yields (60 % - 96 %) and short reaction times (15 - 45 min).

Keywords: Pressurized carbon dioxide, trifluoromethylpyrazole, enone, cyclocondensation

Introduction

Supercritical fluids (SCF) are becoming increasingly important solvent systems for organic chemistry and engineering.^{1,2} Supercritical fluids, which are pure compounds or mixtures heated and pressurized beyond their critical points,¹ have several advantages as solvents for

homogeneous catalysis. Some of these advantages are true for all SCF solvents and essentially all reactions: mass transfer is very rapid, the solvent is completely miscible with gaseous reactants, and the solvent is easy to remove from the product. Among the SCF, supercritical carbon dioxide (sc-CO₂) is the most popular.³ sc-CO₂ has received special attention since it is readily accessible, has a low critical temperature ($T_c = 31\text{ }^\circ\text{C}$) and moderate critical pressure ($P_c = 75.8\text{ bar}$), conditions that are easily achieved in the laboratory.⁴ The advantages related to the use of sc-CO₂ are so numerous that they have prompted intense research to develop its potential as a solvent for synthesis.^{5,6} Some advantages, such as it being non-toxic, non-flammable, and non-polluting,⁷⁻⁹ are specific to sc-CO₂, and it does not cause cancer or other long-term health problems.

Over the past few years, the investigation of reactions in SCF has become an important research area for modern synthetic chemistry and has included studies of enzymatic reactions, stereoselective syntheses, polymer processing,¹⁰⁻¹³ and homogeneously catalyzed reactions such as Baylis–Hillman coupling, and cycloaddition reactions.^{14,15} The study of model reactions is an efficient strategy for acquiring knowledge of the chemical reactivity in sc-CO₂, as is the case for the cyclocondensation reaction, which is an important and general route to the construction of five-membered heterocyclic ring systems. There are few examples devoted to cyclocondensation reactions using SCF as the reaction media;¹⁶ the synthesis of pyrazoles, for example, has not yet been reported. These heterocyclic systems have many derivatives with a wide range of interesting properties. Additionally, the presence of trifluoromethyl substituents in heterocyclic rings is of importance, since physiological activity is in part promoted by the increased lipophilicity of these molecules, resulting in greater cell permeability.¹⁷

We have used β -alkoxyvinyl trihalomethyl ketones (enones) to build five-, six-, and seven-membered trihalomethylated heterocyclic compounds.¹⁸⁻²¹ Also, our research group is continuously interested in a more environmentally benign synthesis, demonstrated by our recent papers that focus on solvent-free synthesis²² and the use of ionic liquids as reaction media,²³ something that is associated with efficient techniques such as microwave^{20,21} and ultrasound irradiation.²⁴ Due to our sustained interest in the study of heterocyclic synthesis and the lack of cyclocondensation reactions under pressurized CO₂ in the literature, herein, we wish to report a mild and efficient method for the preparation of *NH*- and phenyl-pyrazoles under pressurized CO₂ conditions.

Results and Discussion

Enones **1a-c** were synthesized from the reaction of trifluoroacetic anhydride with enol ether or acetal, in accordance with the methodology developed in our laboratory.²⁵ Hydrazine monohydrate and phenylhydrazine were obtained commercially and used without further purification.

Initially, two sets of experiments were programmed in order to evaluate the effect of pressurized CO₂ on cyclocondensation reactions. For this purpose we chose three enones (**1a-c**) and two different hydrazines (hydrazine monohydrate (**2**) and phenylhydrazine (**4**) which were studied under different reaction conditions and with variations in pressure, temperature, and time. These substrates were screened in order to evaluate the substituent effect, where hydrogen had no electronic effects on the structure, methyl was electron-donating, and Phenyl was electron-donating or electron-withdrawing. Similarly, these effects were considered in the choice of hydrazines, where the hydrazine monohydrate there is no substituent and phenyl hydrazine where phenyl reduced the electronic density of nitrogen of hydrazine.

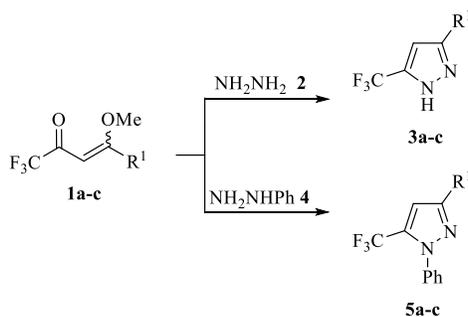
The effect of pressurized CO₂ was primarily evaluated for the reaction of hydrazine monohydrate with enones **1a-c**, as depicted in **Table 1**. From this data it can be seen that the substrate **1a** suffers a strong influence from the applied pressure, which is reflected in the product yield. Indeed, as the pressure was increased two-fold (entries 1 and 2), the product yield increased by more than 40 % and the *NH*-pyrazole **3a** was furnished at 95 % yield. On the other hand, an increase in the temperature from 65 °C to 80 °C at 60 bar (entry 1 and 3) did not lead to a considerable increase in the product yield, showing that 65 °C is a suitable temperature to perform this reaction. The same set of experiments was applied for enone **1b**. A pressure of 60 bar and temperature of 65 °C furnished the *NH*-pyrazole **3b** at 77 % yield in only 15 min. The use of a longer reaction time did not lead to an improvement in the yield. Comparing this result with what was previously observed for **3a**, it can be seen that enone **1b** performs better in relation to **1a** in terms of both reaction time as well as product yield. In the next test, we decided to maintain the temperature of 65 °C and double the pressure (entries 4 and 5). Surprisingly, this reaction condition was not as effective as expected (based on the results for enone **1a**) as there was a yield decrease of 6 % (entries 4 and 5). Finally, the temperature was increased to 80 °C, which resulted in the product yield decreasing (entries 3 and 6). The last evaluated substrate, enone **1c**, was strongly affected by the increase in the temperature and in the pressure. The mild condition (entry 7) led to the product being obtained at a moderate yield. However, maintaining the temperature at 65 °C and using a pressure of 120 bar (entry 8) led to the desired product **3c** at an excellent yield (96 %). Although the temperature increase to 80 °C also raises the product yield (entry 7 and 9), the two-fold increase in the pressure is a prevalent factor. Thus, this methodology has been successful for the three enones studied which were obtained in good to excellent yields. In spite of pressurized CO₂ being a nonpolar and aprotic solvent, it acts as a Lewis acid¹⁶ which favors the desired pyrazole formation.

With these results in hand, we decided to investigate the reaction of phenylhydrazine **4** with enones **1a-c**. Sets of experimental tests similar to that for hydrazine **2** were applied to phenylhydrazine **4**. The results obtained are shown in **Table 2**. A condition of 65 °C and 60 bar (entry 1) led to the desired product **5a** at a moderate yield (65 %). Subsequently, a two-fold increase in the pressure (entry 2) raised the product yield to 87 %, following the same behavior already found for the reaction with hydrazine **2**. The last attempt involved an increase in the temperature (entry 3), however it led to a lower product yield (50 %). An interesting find was

observed from the reaction between enone **1a** and hydrazine **4**, as the use of pressurized CO₂ led to the attainment of product **5a** with high regioselectivity. In previous works, using other methodologies as microwave irradiation and/or ionic liquids, this product was obtained as a mixture of 1-phenylpyrazole and the 4,5-dihydropyrazole derivative.^{26,27} Analyzing enone **1b**, we can see that at 65 °C and 60 bar (entry 4) product **5b** was obtained in 60 % yield. In an attempt to improve this result, pressure and temperature were evaluated. However, a two-fold increase in pressure (entry 5) resulted in a similar yield, demonstrating that the pressure has no influence on enone **1b**, as already seen with hydrazine **2**. Likewise, the increase in the temperature (entry 6) led to a lower product yield (45 %), as already observed with this enone and hydrazine **2**. As expected, enone **1c** resulted in a high product yield (89 %) at 65 °C and 60 bar (entry 7). A two-fold increase in pressure (entry 8) resulted in the yield decreasing to 57 % and a temperature increase (entry 9) led to a 78 % yield. Of all the cases, this is the only one where an increase in the temperature favors the product yield when compared with an increase in the pressure.

In a general analysis of the two evaluated hydrazines, it can be seen that a pressure increase is preponderant to good product yield. When a two-fold increase in the pressure was applied, product reaction with hydrazine **2** was obtained at better yields for enone **1a** and **1c**, but was invariable to reaction with **1b**. When the same variation was applied to reactions with hydrazine **4**, the best yield was observed in enone **1a**, while the product yield for reaction with enone **1c** was small and product yields from enone **1b** were not affected by an increase in pressure. The reaction was also sensitive to the resultant temperature increase in products formed at small yields. In general, the effect of the temperature was less significant than the pressure and it had an inverse effect, in other words, the yields were better or invariable with an increase in the pressure and were smaller with a temperature increase. Taking into account the electronic effects of enone substituents, it can be seen that enones **1a** and **1b** led to product formation at excellent yields, while enone **1b** furnished the product at a good yield, independent of hydrazine. Additionally, the CO₂ pressurization is expected to have physical and/or chemical effects. The volume of a liquid phase may expand by dissolution of CO₂ molecules, causing a dilution of reacting species in the liquid phase.²⁸ Pressurization of CO₂ has not only the physical effect of enhancing the dissolution of gaseous reactants but also a chemical effect as it changes polarity.

From the results described here, it is evident that there is an sc-CO₂ effect in the solvent reaction, with differential solvation occurring. The solvation effect of sc-CO₂ in this reaction, which is similar to ionic liquid effects,²³ can be attributed to the interaction with Lewis acid or the well-known role of sc-CO₂ as Lewis acid.²⁹ Additionally, in the case of the reaction presented in this work, the CO₂ probably participates in hydrogen bonds with carbonyl compounds,²⁹ enhancing the solvation effects in the activated complex of the reaction.

Table 1. Influence of the temperature and pressurized CO₂ on the synthesis of **3a-c** and **5a-c**

Entry	Enone	R ¹	R	Temp. (°C)	Pressure (Bar)	Time (min) ^a	Yield (%) ^b 3	Yield (%) ^b 5
1	1a	H	Et	65	60	45	51	65
2	1a	H	Et	65	120	45	95	87
3	1a	H	Et	80	60	45	54	50
4	1b	Me	Me	65	60	15	77	60
5	1b	Me	Me	65	120	15	71	59
6	1b	Me	Me	80	60	15	55	45
7	1c	Ph	Me	65	60	45	72	89
8	1c	Ph	Me	65	120	45	96	57
9	1c	Ph	Me	80	60	45	81	78

^a Reaction time for all conditions to product **5 a-c** was 45 min. ^b Isolated product.

Conclusions

In conclusion, we have developed a simple and efficient method for the synthesis of *NH*- and *N*-phenyl-pyrazoles by applying a cyclocondensation reaction between different enones and hydrazines under pressurized CO₂ conditions. The notable features of this procedure are mild and green reaction conditions, good yields and reaction rates, and cleaner reaction profiles. At present, further investigations are in progress in order to find additional synthetic applications for obtaining other heterocyclic compounds under pressurized CO₂ conditions.

Experimental Section

General. Unless otherwise indicated, all common reactants were used as obtained from commercial suppliers without further purification. ¹H and ¹³C NMR spectra were acquired on a Bruker DPX 200 or Bruker DPX 400 spectrometer (¹H at 200.13 MHz or 400.13 MHz, and ¹³C

at 50.32 MHz or 100.13 MHz, respectively) at 300 K, using 5 mm sample tubes, and with digital resolution of ± 0.01 ppm. CDCl_3 , or DMSO-d_6 were used as solvents containing TMS as internal standard. GC-MS EI was registered in an Agilent 6890N series connected to an Agilent G1530CN GC and interfaced by a Pentium PC. The GC was equipped with a split-splitless injector, autosampler, cross-linked HP-5 capillary column (30 m, 0.32 mm i.d.), and He was used as the carrier gas. A Teledyne Isco syringe pump (series D, model 256D) equipped with a pump controller, a Parr Instrument Co. model 4592 micro reactor (50 mL vessel) equipped with a temperature and pressure controller (Parr instrument Co., model 4843), and a thermal bath (Nova Ética, model 521/3D, CO_2 gas, cooling 5 - 7 °C) were used during the experiments.

General procedures for the cyclocondensation reactions under pressurized carbon dioxide.

Preparation of pyrazoles: Firstly, the ultrathermostat bath coupled to the CO_2 pump was adjusted to 5 °C. Subsequently, the enone **1a-c** (1 mmol) and the hydrazine (1 mmol) were placed in the Parr reactor cell which is coupled to a pressure and temperature controller. Carbon dioxide was then introduced into the mixture directly from the cylinder at 1.8 MPa pressure at room temperature. The mixture was stirred for the appropriate time and at the appropriate temperature, as described in Tables 1 and 2. After the reaction time, the system was slowly depressurized and the products were obtained in their pure forms.

Spectroscopic data of Compounds 3 and 5

The spectroscopic data found for these compounds are in accordance with reference 26.

5-Trifluoromethyl-1H-pyrazole (3a). Oil. ^1H NMR (CDCl_3) δ 6.60 (d, 1H, 3J 2 Hz, H4), 7.86 (d, 1H, 3J 2 Hz, H3), 13.57 (s, 1H, NH). ^{13}C NMR (CDCl_3) δ 103.2 (C4), 122.1 (q, 1J 267 Hz, CF_3), 130.5 (C3), 141.3 (q, 2J 36 Hz, C5). GC/MS (EI, 70 eV) m/z 136 (M^+ , 100%), 117 (49), 69 (65).

5-Trifluoromethyl-3-methyl-1H-pyrazole (3b). Mp 84-85°C. ^1H NMR (CDCl_3) δ 2.30 (s, 3H, CH_3), 6.40 (s, 1H, H4), 13.29 (s, 1H, NH). ^{13}C NMR (CDCl_3) δ 10.1 (CH_3), 102.1 (C4), 122.0 (q, 1J 267 Hz, CF_3), 140.6 (C3), 141.2 (q, 2J 36 Hz, C5). GC/MS (EI, 70 eV) m/z 150 (M^+ , 100%), 131(17), 81 (18).

5-Trifluoromethyl-3-phenyl-1H-pyrazole (3c). Oil. ^1H NMR (CDCl_3) δ 6.80 (s, 1H, H4), 7.26-7.59 (m, 5H, Ph). ^{13}C NMR (CDCl_3) δ 100.9 (C4), 125.6, 127.9, 129.1, 129.3 (Ph), 121.1 (q, 1J 268 Hz, CF_3), 143.5 (q, 2J 38 Hz, C5), 145.1 (C3). GC/MS (EI, 70 eV) m/z 212 (M^+ , 100%), 193 (9), 143 (25), 77 (27).

5-Trifluoromethyl-1-phenyl-1H-pyrazole (5a). ^1H NMR (CDCl_3) δ 6.82 (d, 1H, H4), 7.90 (d, 1H, H3), 7.73 (m, 5H, Ph). ^{13}C NMR (CDCl_3) δ 109.2 (C4), 120.2 (q, 1J = 269 Hz, CF_3), 125.6, 129.0, 129.2, 138.0 (Ph), 132.9 (q, 2J = 39 Hz, C5), 139.9 (C3).

5-Trifluoromethyl-3-methyl-1-phenyl-1H-pyrazole (5b). ^1H NMR (CDCl_3) δ 2.29 (s, 3H, CH_3), 6.52 (s, 1H, H4) 7.5 (m, 5H, Ph). ^{13}C NMR (CDCl_3) δ 13.2 (CH_3), 108.5 (C4), 120.1 (q, 1J = 267 Hz, CF_3), 125.0-139.0 (Ph), 132.9 (q, 2J = 39 Hz, C5), 149.0 (C3). GC/MS (EI, 70 eV) m/z 226 (M^+ , 100%), 77 (70).

5-Trifluoromethyl-1,3-diphenyl-1H-pyrazole (5c). Mp 54-56°C. ¹H NMR (CDCl₃) δ 7.11 (s, 1H, H4), 7.3-7.88 (m, 10H, 2Ph). ¹³C NMR (CDCl₃) d 106.0 (C4), 121.1 (q, ¹J 269 Hz CF₃), 125.6, 125.8, 128.6, 128.7, 129.0, 129.2, 131.7, 139.1 (Ph), 133.8 (q, ²J 38 Hz, C5), 151.6 (C3). GC/MS (EI, 70 eV) m/z 288 (M⁺, 100%), 219 (13), 77 (88).

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