

Interaction of 1,5-Substituted Pyrrolin-2-ones with Dichlorocarbene under Phase Transfer Catalysis Conditions

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Abstract: Treatment of 5-alkyl(aryl)-3H-pyrrolin-2-ones with dichlorocarbene under phase transfer catalysis conditions at 20-30°C results in a cycloaddition of the carbene to the C=C bond followed by skeletal rearrangement.

Keywords: 5-alkyl(aryl)-3H-pyrrolin-2-ones, 1-alkyl-6,6-dichloro-2-azabicyclo[3.1.0]-hexan-3-ones, dichlorocarbene.

Introduction

The increasing interest in the chemistry of cyclopropanes results from the wide possibilities of their practical applications, in particular, as intermediates in organic syntheses and for obtaining biologically active compounds.

Reactions of carbenes with compounds containing multiple bonds under phase transfer catalysis (PTC) conditions is an effective method for forming cyclopropane fragments. We were interested in studying the possibility of using five-membered nonaromatic N-heterocycles containing C=C and C=O bond for the preparation of systems with cyclopropane or oxirane fragments.

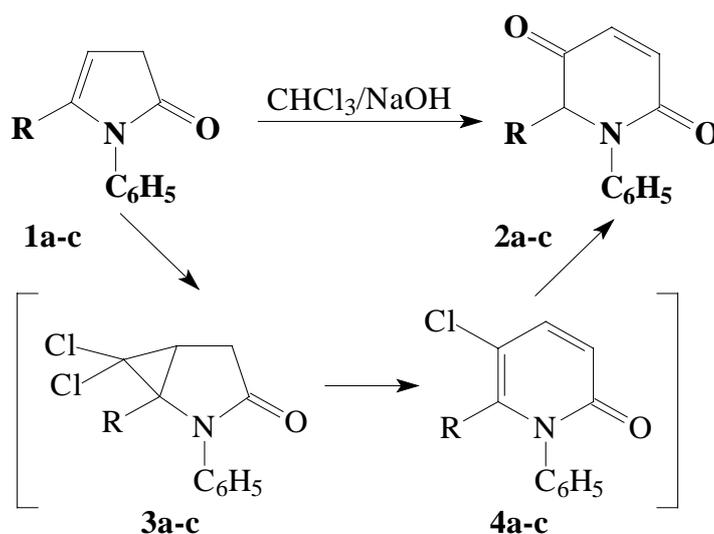
Results and Discussion

In the present work 5-alkyl(aryl)-3H-pyrrolin-2-ones **1a-c** were synthesized from 5-alkyl-3H-furan-2-ones [1]. Dichlorocarbene was used as the carbene component. It was generated by the usual method, i.e., reaction of NaOH with chloroform in a two-phase system in the presence of

benzyltriethylammonium bromide (BTEA) as the phase transfer catalyst.

The starting pyrrolin-2-ones contain several reaction centres that can react with dichlorocarbene. These are the C=C and C=O double bonds, C-H bonds and heteroatoms. It would be expected that the reaction product(s) would be determined by competing formation of the possible alternate dichlorocyclopropane structures, namely the products of nucleophilic addition of the trichloromethyl anion to the alkene or carbonyl carbon, the introduction of the dichlorocarbene into a C-H bond and the formation of ylide structures due to carbene attack on the heteroatom free electron pair.

Under mild conditions (20-30°C), [1+2]-cycloaddition at the C=C bond takes place to afford 1-alkyl-6,6-dichloro-2-azabicyclo[3.1.0]-hexan-3-ones (**3a-c**).



Scheme 1. Compounds 1-4: R = C_6H_5 (a), C_4H_9 (b), C_5H_{11} (c)

The formation of the products (**4a-c**) may occur through a skeletal rearrangement accompanied by expansion of the five-membered ring and dehydrochlorination. The net result is hydrolysis of compounds **4a-c** and formation of 6-alkyl(aryl)-1-phenyl-5-oxohydropyridin-2-ones (**2a-c**). We failed to isolate the possible intermediates.

Conclusions

The reaction of 5-alkyl(aryl)-3H-pyrrolin-2-ones with dichlorocarbene at 20-30° C involves the C=C bond and the aromatic fragment and the amide carbonyl of the substrates are not touched under the conditions investigated. When the reaction is carried out in a two-phase system, the side formation of the salts of the corresponding γ -keto-carboxylic acids was noted, due to the opening of five-membered heterocycles under the action of alkali.

Experimental

General

IR spectra were obtained on a UR-20 spectrometer. NMR spectra were recorded on a Varian FT-80A instrument (80 MHz) in CDCl₃ using SiMe₄ as the internal standard; the chemical shifts are given on the δ scale.

6-Alkyl(aryl)-1-phenyl-5-oxohydroxyridin-2-ones (**2 a-c**)

A solution of NaOH (50%, 4 mL) was added dropwise to a solution of 5-alkyl(aryl)-3H-pyrrolin-2-ones (**1a-c**) (0.08 mol) and BTEA (0.006 mol) in chloroform (25 mL). The mixture was stirred at 20–30°C for 48 h. The organic layer was separated, and dried over MgSO₄. The solvent was evaporated and the residue was recrystallized from ethanol to give compounds **2a-c**.

2a: m.p. 150–152°C, 82% yield. Anal. % Calcd. for C₁₇H₁₃O₂N: C-77.63, H-4.98, N-5.33; Found: C-78.10, H-5.05, N-5.60; ¹H-NMR: 7.05 (d, 1H), 7.50 (d, 1H, J₃₄=5.74 Hz), 2.10 (c, 1H), 7.55–7.80 (m, 10H); ¹³C-NMR: 175.20, 115.30, 140.15, 205.20, 75.80, 118.70, 119.51, 128.43, 123.31, 128.65, 119.20, 119.30, 127.81, 128.40, 124.62, 128.72, 127.50.

2b: m.p. 155–156°C, 80% yield. Anal. % Calcd. for C₁₅H₁₇O₂N: C-74.14, H-7.05, N-5.76; Found: C-74.34, H-7.30, N-5.85; ¹H-NMR: 7.10 (d, 1H), 7.60 (d, 1H, J₃₄=5.75 Hz), 1.83 (t, 1H), 0.80–1.80 (m, 9H), 7.63–7.75 (m, 5H); ¹³C-NMR: 175.40, 115.35, 140.12, 204.85, 75.90, 32.15, 20.43, 16.05, 12.10, 118.75, 120.12, 129.52, 122.31, 129.32, 119.55.

2c: m.p. 158–159°C, 75% yield. Anal. % Calcd for C₁₆H₁₉O₂N: C-74.77, H-7.45, N-5.45; Found: C-74.92, H-7.65, N-5.70; ¹H-NMR: 7.12 (d, 1H), 7.64 (d, 1H, J₃₄=5.67 Hz), 1.95 (t, 1H), 0.80–1.85 (m, 11H), 7.70–7.78 (m, 5H); ¹³C-NMR: 175.10, 115.60, 140.25, 205.62, 75.51, 32.44, 30.12, 23.25, 20.45, 11.15, 118.72, 119.65, 128.50, 122.25, 128.65, 119.85.

References

1. Morozova, N.A.; Sedavkina, A.; Egorova, A.Yu. Substituted 3H-furan-2-ones in the hydroamination and amination reactions. *Khim. Geterotsykl. Soedin.* **1994**, 349–352.

Sample Availability: Available from the authors.