Phase-transfer catalysis in reactions of 5-alkyl-3*H*-furan-2-ones with dichlorocarbene

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Treatment of 5-alkyl-3*H*-furan-2-ones and 5-alkyl-3*H*-thiophen-2-ones with dichlorocarbene under conditions of phase-transfer catalysis at 20—90 °C results in insertion of the carbene at the C=C bond followed by skeletal rearrangement.

Key words: 5-alkyl-3*H*-furan-2-ones, 5-alkyl-3*H*-thiophen-2-ones, 6-alkyl-5-chloropyran-2-ones, 6-alkyl-5-oxohydropyran-2-ones, 1-alkyl-6,6-dichloro-2-oxabicyclo[3.1.0]hexan-3-ones, dichlorocarbene, phase-transfer catalysis.

The increasing interest in the chemistry of cyclopropanes results from the wide possibilities of their practical application, in particular, as intermediates in organic syntheses and for obtaining biologically active compounds.[1]

Reactions of carbenes with compounds containing multiple bonds under conditions of phase-transfer catalysis (PTC) is an effective method for forming cyclopropane fragments.

It was of interest to study the possibility of using five-membered nonaromatic *O,S*-heterocycles containing C=C and C=O bonds for the preparation of systems with cyclopropane or oxirane fragments.

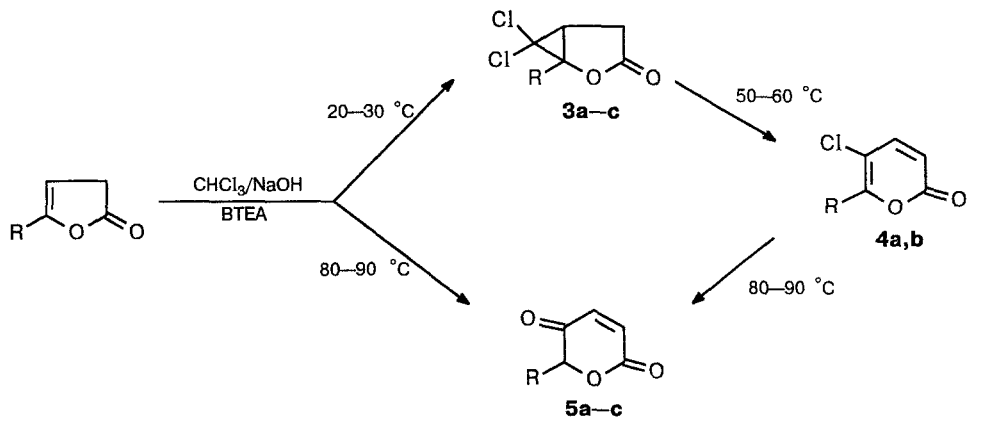
In the present work, 5-alkyl-3*H*-furan-2-ones (**1a—c**), synthesized from γ-ketocarboxylic acids,[2] and 5-alkyl-3*H*-thiophen-2-ones (**2b,c**), prepared according to the previously developed method,[3] were studied. Dichlorocarbene was used as the carbene component. It was generated by a usual method, *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 insertion of dichlorocarbene into C=C bonds of heterocycles **1a—c** and **2b,c** (Schemes 1 and 2) was found to occur at 20—90 °C.

Temperature is the factor determining the nature of the products formed. Varying the temperature with a constant reaction time and reagent ratio resulted in a series of products (**3a—c**, **4a,b**, **5a—c**), whose structures were confirmed by independent syntheses and IR and ^1H and ^{13}C NMR spectroscopy (Tables 1, 2).

Under mild conditions (20—30 °C), [1+2]-cycloaddition at one C=C bond takes place to afford 1-alkyl-6,6-dichloro-2-oxabicyclo[3.1.0]hexan-3-ones (**3a—c**). The band at 1640 cm^{-1} (C=C) disappears in the IR spectra of compounds **3a—c**, while the absorption

Scheme 1



1—5: R = C_4H_9 (**a**), C_5H_{11} (**b**), C_6H_{13}-*i* (**c**)

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Scheme 2

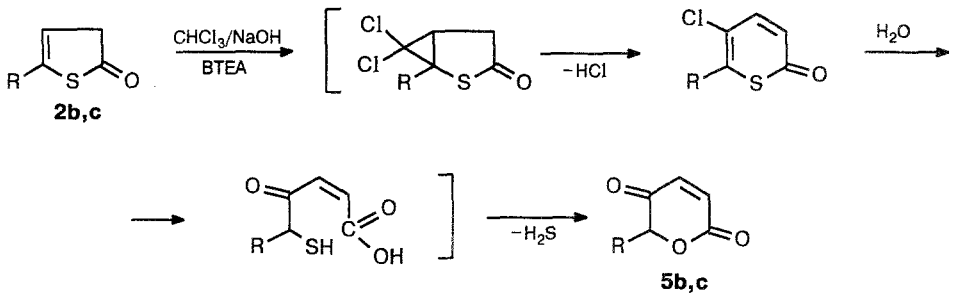


Table 1. Characteristics of synthesized compounds **3—5**

Compound	M.p./°C (*p*/Torr)	n_D^{20}	Found / Calculated (%)			Molecular formula	Yield (%)
			C	H	Cl		
3a	133 —135(10)	1.4400	48.65 48.43	5.40 5.38	31.53 31.84	$C_9H_{12}O_2Cl_2$	53
3b	138 —140(10)	1.4420	50.42 50.63	5.88 5.91	29.72 29.96	$C_{10}H_{14}O_2Cl_2$	55
3c	144 —150(10)	1.4490	53.40 52.59	6.77 6.37	28.41 28.06	$C_{11}H_{16}O_2Cl_2$	48
4a	125 —130(4)	1.4480	58.00 57.80	6.00 5.93	18.80 18.96	$C_9H_{11}O_2Cl$	47
4b	132 —134(4)	1.4619	59.00 58.87	6.05 5.93	17.55 17.38	$C_{10}H_{12}O_2Cl$	50
5a	110 —111(3)	1.4770	65.00 64.72	6.94 6.64	— —	$C_9H_{11}O_3$	68
5b	113 —116(3)	1.4730	66.10 66.63	7.22 7.18	— —	$C_{10}H_{13}O_3$	72
5c	115 —116(3)	1.4750	67.80 67.69	7.85 7.69	— —	$C_{11}H_{15}O_3$	70

band of the lactone carbonyl is observed at 1770—1760 cm^{-1}.

When the temperature was increased to 50—60 °C, 6-alkyl-5-chloropyran-2-ones (**4a,b**) were obtained in satisfactory yields. The formation of the latter may occur through a skeleton rearrangement accompanied by expansion of the five-membered ring and dehydrochlorination.

The structure of compounds **4a,b** is confirmed by the existence of signals of vinyl protons of C(3) and C(4) at 7.14—7.17 and 7.55—7.60 ppm, respectively, in the ^1H NMR spectrum, as well as absorption bands at 1710—1700 cm^{-1} typical of six-membered unsaturated lactones with conjugated bonds and a band at 1570—1550 cm^{-1} (C=C—C(1)) in the IR spectrum.

An increase in temperature to 80—90 °C results in hydrolysis of compounds **4a,b** and formation of 6-alkyl-5-oxohydropyran-2-ones (**5a—c**) (Tables 1, 2).

The reaction of 5-alkyl-3*H*-thiophen-2-ones (**2b,c**) with dichlorocarbene at 20—30 °C, similarly to that of compounds **1**, proceeds at the C=C bond but is accompanied by elimination of H_2S from the unstable mercaptoacid formed during the hydrolysis. This yields compounds **5b,c**. We failed to isolate the intermediates.

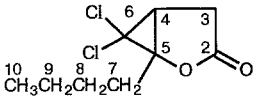
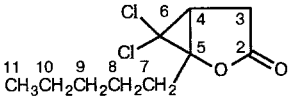
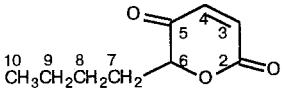
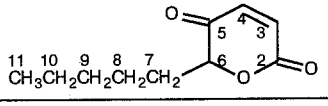
Hence, the reaction of 5-alkyl-3*H*-furan-2-ones and thiophen-2-ones with dichlorocarbene at 20—90 °C involves the C=C bond.

When the reaction is carried out in a two-phase system, the side formation of the salts of γ-ketocarboxylic acids due to opening of five-membered heterocycles under the action of alkali can be avoided.

Experimental

IR spectra were obtained on a UR-20 spectrometer (in thin films). NMR spectra were recorded on a Varian FT-80A

Table 2. ^{13}C NMR spectra of synthesized compounds **3—5**

Compounds	(CDCl$_3$) δ									
	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
	172.03	31.73	29.57	100.58	74.81	33.48	21.82	15.80	12.03	
	175.04	31.40	29.30	100.41	74.85	35.42	30.64	22.33	21.32	12.71
	172.51	100.21	145.89	208.96	80.46	34.60	22.05	15.93	12.20	
	172.54	100.34	145.72	208.60	80.52	35.95	30.75	22.42	21.45	12.85

instrument (working frequency 80 MHz) in $CDCl_3$ using $SiMe_4$ as the internal standard; the chemical shifts are given on the δ scale. Elemental analysis data, yields, and spectral characteristics of the compounds synthesized are given in Tables 1 and 2.

1-Alkyl-6,6-dichloro-2-oxabicyclo[3.1.0]hexan-3-ones (3a—c). A solution of NaOH (50 %, 4 mL) was added dropwise to a solution of 5-alkyl-3*H*-furan-2-one (0.08 mol) in chloroform (25 mL) and benzyltriethylammonium bromide (BTEA) (0.006 mol). The mixture was stirred at 20—30 °C for 48 h. The combined organic layer was separated, washed with water, extracted with chloroform, and dried with $MgSO_4$. The solvent was evaporated, and the residue was distilled *in vacuo*.

6-Alkyl-5-chloropyran-2-ones (4a,b). A solution of NaOH (50 %, 5 mL) was added dropwise to a solution of 5-alkyl-3*H*-furan-2-one (0.04 mol) in chloroform (20 mL) and BTEA (0.003 mol). The reaction mixture was heated to 50—60 °C. The reaction mixture was treated as described above.

6-Alkyl-5-oxohydropyran-2-ones (5a—c). A solution of NaOH (50 %) was added dropwise to a solution of 5-alkyl-3*H*-furan-2-one (0.04 mol) in chloroform (20 mL) and BTEA (0.003 mol) maintaining the temperature at 80—90 °C. The reaction mixture was treated as described above.

6-Alkyl-5-oxohydropyran-2-ones (5b,c) were prepared from 5-alkyl-3*H*-thiophen-2-one (0.03 mol), chloroform (15 mL), NaOH (50 %, 5 mL), and BTEA (0.003 mol) similarly to compounds **3a—c**.

References

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