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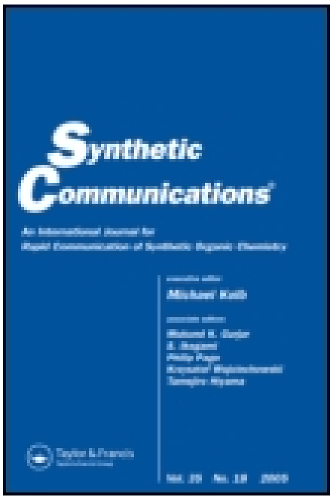

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SYNTHESIS OF CROSS-CONJUGATED HETEROCYCLIC MESOMERIC BETAINES

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SYNTHESIS OF CROSS-CONJUGATED HETEROCYCLIC MESOMERIC BETAINES

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ABSTRACT

Reaction of (chlorocarbonyl)phenyl ketene with several oximes such as *p*-chlorobenzaldehyde oxime, 2,4-dichlorobenzaldehyde oxime, *p*-N,N-dimethylbenzaldehyde oxime, 9-anthracene carboxaldehyde oxime and benzophenone oxime resulted in a series of cross-conjugated heterocyclic mesomeric betaines CCMB.

We have recently reported on the cycloaddition of (chlorocarbonyl)-phenyl ketene (1) with carbonyl compounds[1] and C = N linkages.[2,3] Reaction of thiolactam with (1) to produce a stable betaines has been reported by Padwa and his co-workers.[4] There is also a report on the reaction of pyrazoles such as 1,2,3-triazoles and 1,2,4-triazoles with (chlorocarbonyl)aryl ketenes which results in formation of a series of betaines characterized by the presence of distinct cationic and anionic segments. It has been reported that some of these betaines are unstable and immediate decomposition of product occured in solution.[5]

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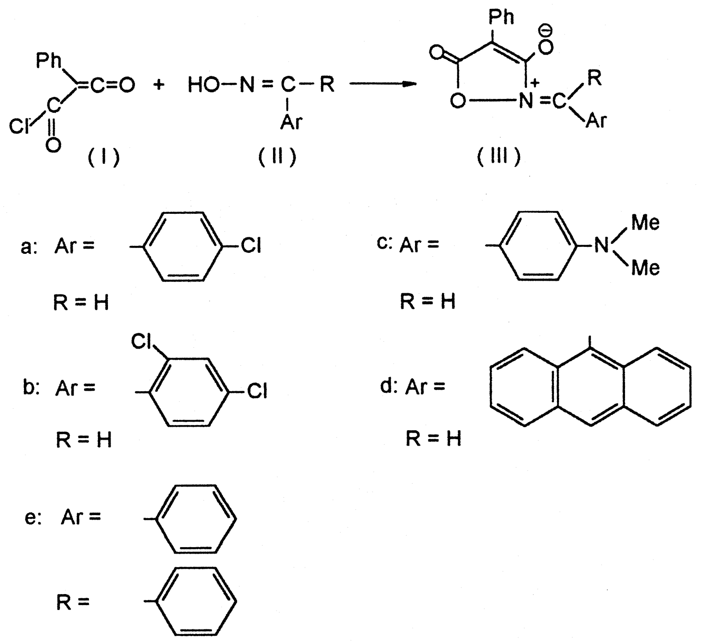
* Corresponding author.

We now wish to describe an investigation of the facile cycloaddition of this isolable and stable ketene with oximes (a 1,2-binucleophile) such as *p*-chlorobenzaldehyde oxime, 2,4-dichlorobenzaldehyde oxime, *p*-N,N-dimethylbenzaldehyde oxime, 9-anthracene carboxaldehyde oxime and benzophenone oxime to yield anhydro-2-(arylmethylene)-4-phenyl-3-hydroxy-5-oxoisoxazolium hydroxide. A series of quite stable cross-conjugated heterocyclic mesomeric betaines (CCMB) are easily prepared from these reactions in good yields. The importance of such a reaction in organic synthesis is derived from its ability to generate a five-membered heterocyclic rings, which can undergo 1,3-dipolar cycloaddition reactions.[6]

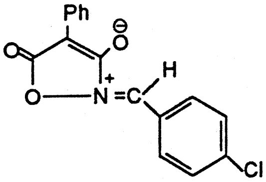
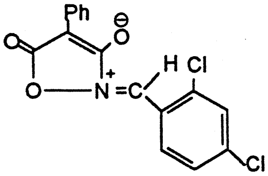
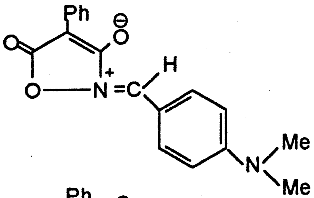
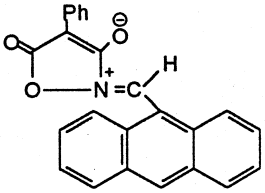
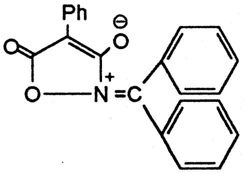
When a ketene such as (chlorocarbonyl)phenyl ketene is allowed to unite with an oxime a zwitterionic system results in which the positive and negative charges are delocalized within the π-electron system.[7]

As anticipated the addition of (1) and *P*-chlorobenzaldehyde oxime resulted in a loss of all the ketene band in IR and instant formation of a red precipitate of anhydro-2-(*P*-chlorophenylmethylene)-4-phenyl-3-hydroxy-5-oxoisoxazolium hydroxide (IIIa) which is characteristic of CCMB compounds.



The infrared spectrum of (IIIa) revealed the carbonyl bands at 1790 and 1730 cm^{-1}. The ^{1}H NMR spectrum of (IIIa) showed a singlet at δ 9.98 ppm which belongs to CH proton and phenyl protons revealed a multiplet at δ 7.11–8.01 ppm. Only one singlet is observed at 9.98 ppm. Apparently one isomer is formed, because the oxygen with a negative charge on this compound prefers cis configuration with respect to hydrogen than the larger Ar groups. The tautomer form has a s-cis configuration and in this case the Ar group also to be further away from the carbonyl oxygen (anti). Therefore it was concluded that only the Z isomer

Table 1. Yield Data for All Compounds

Entry	Products	Melting Point C°	Yield[a] (%)
a		185 (red Precipitate)	82%
b		164 (brown Precipitate)	60%
c		153 (dark red)	80%
d		155 (brown Precipitate)	89%
e		144 (black Precipitate)	73%

[a] Yield of isolated products.

is the predominant product. ^{13}C NMR spectrum is consistent with the proposed structure. The mass spectrum revealed the molecular ion peak at m/z 299 (64%) and base peak at m/z 139 (100%) which is due to $(C_7H_6ClN)^+$ fragment. It is pertinent to note that a phenyl hydrogen from ortho position shifts to the nitrogen atom giving the base peak.

This fragment along with an odd molecular weight (because it contains nitrogen) with an odd electron is a good evidence of rearrangement.

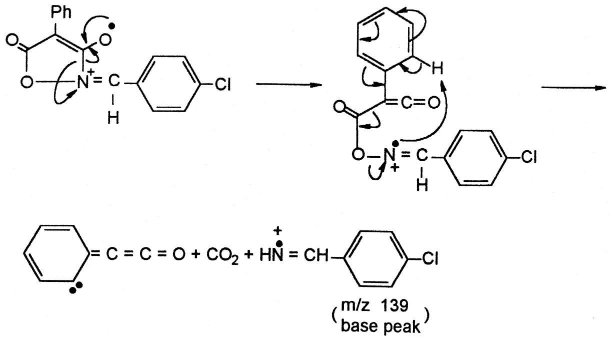


Table 2. Analytical Data

Compd. No.	Molecular Formula	Analysis (%) Calcd. (Found) C	H	N	Mass Spectrum m/z
(IIIa)	$C_{16}H_{10}ClNO_3$	64.10	3.33	4.60	molecular ion 299 (64%, M$^+$), 139 (100% base peak),
		(63.45	3.40	4.64)	118 (81%), 89 (57%)
(IIIb)	$C_{16}H_9Cl_2NO_3$	57.48	2.69	4.19	molecular ion 333 (22%, M$^+$), 173 (100% base peak), 145 (52%),
		(57.02	2.89	4.23)	118 (74%), 89 (62%)
(IIIc)	$C_{18}H_{16}N_2O_3$				molecular ion 308 (26%, M$^+$), 175 (31%), 148 (100% base peak), 118 (19%)
(IIId)	$C_{24}H_{15}NO_3$	78.90	4.11	3.84	molecular ion 365 (15%, M$^+$), 221 (38%), 203 (100% base peak)
		(77.92	4.30	3.90)	
(IIIe)	$C_{22}H_{15}NO_3$	77.41	4.40	4.11	molecular ion 341 (10%, M$^+$), 312 (50%), 249 (63%), 105
		(76.5	4.56	4.28)	(100% base peak)

Attempts to obtain satisfactory C & H analysis were unsuccessful.

Table 3. Spectral Data

Compd. No.	IR (KBr) cm^{-1} C=O	^{1}H-NMR (DMSO) TMS δ (ppm)	^{13}C-NMR (DMSO) δ (ppm)
(IIIa)	1790, 1730	9.98 [s, 1 H] 8.01–7.11 [m, 9 H]	192.5, 170.9, 170.6, 139.8, 135.3, 131.6, 129.8, 128.5, 128.1, 125.3, 125.1, 124.1
(IIIb)	1795, 1730	10.26 [s, 1 H] 7.8–6.8 [m, 8 H]	189.3, 170.9, 170.6, 140.2, 137.6, 131.54, 131.52, 131.4, 130.7, 128.7, 128.5, 125.2, 125.0
(IIIc)	1780, 1730	9.65 [s, 1 H] 8.09–6.77 [m, 9 H] 2.49 [S, 6 H]	190.3, 170.9, 170.6, 154.6, 147.9, 132.0, 131.5, 128.5, 128.1, 125.2, 125.0, 111.6, 40.15
(IIId)	1810, 1750	11.45 [s, 1 H] 9.00–7.10 [m, 14 H]	194.6, 171.1, 170.7, 135.7, 131.8, 131.7, 131.1, 129.8, 129.7, 129.2, 128.5, 126.3, 125.1, 125.0, 124.8, 123.9
(IIIe)	1795, 1730	8.35–7.10 [m, 10 H]	196.3, 171.1, 170.7, 137.4, 133.1, 131.6, 130.0, 129.0, 128.5, 125.2, 125.0

The bond cleavage occured at a similar location producing the base peaks in their respective mass spectra.

EXPERIMENTAL

Solvent was dried over sodium and distilled prior to use. Reagents were employed as purchased from Merck and Fluka. Melting points were determined on Gallkamp (UK) apparatus and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 MHz FT nuclear magnetic resonance. IR spectra were obtained using a Matson 1000 FT IR spectrometer. (Chlorocarbonyl)phenyl ketene was prepared by a procedure similar to that of Nakanishi.[8]

Typical Procedure for the Reaction of (Chlorocarbonyl)phenyl Ketene with Oximes

A 0.2 mmol (0.36 g) portion of (1) in 20 ml of dry diethyl ether was added dropwise to a stirred solution of 0.2 mmol (0.31 g) of

P-chlorobenzaldehyde oxime at 0°C under a nitrogen atmosphere. A red precipitate of anhydro-2-(*P*-chlorophenylmethylene)-4-phenyl-3-hydroxy-5-oxoisoxazolium hydroxide was formed instantly. The reaction mixture was filtered and the products were recrystalized from benzene and further characterized.

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