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Received for review October 22, 1984. Accepted January 22, 1985.

A Synthetic Approach toward the Synthesis of Indolizines via 1,3-Dipolar Cycloaddition Reactions of Cycloimmonium Ylide

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Dehydrohalogenation of *N*-(2-aroylmethyl)-2-picolinium and -4-picolinium bromide, prepared by the quanternization of corresponding bromide salt with triethylamine, afforded a highly reactive cycloimmonium ylide. Its 1,3-dipolar cycloaddition reactions with various dipolarophiles have been investigated. These reactions ultimately result in the formation of novel heterocyclic compounds. The structural assignment of the products were made on the basis of elemental analyses and spectroscopic data.

Introduction

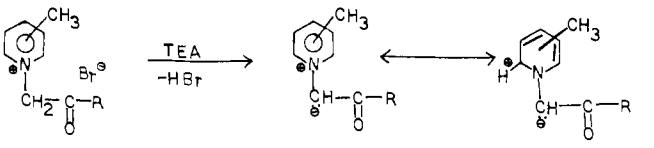
The chemistry of cycloimmonium ylide has engaged the attention of chemists because of their importance as useful intermediates in the synthesis of novel heterocyclics. Despite the wide applicability of cycloimmonium ylide (*1*–*11*) in synthetic studies, no information is available concerning the 1,3-dipolar cycloaddition reactions of methyl-substituted pyridinium ylide.

In the course of our investigations on the preparative utility of cycloimmonium ylide, we wish to report the syntheses and physical and spectral properties of indolizines having biological activities.

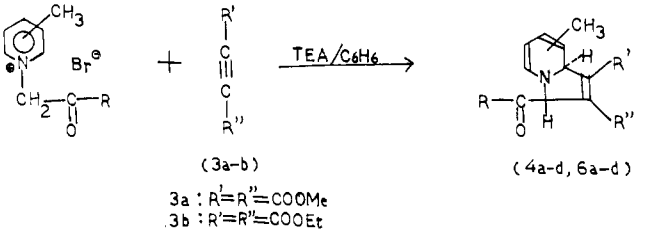
Results and Discussion

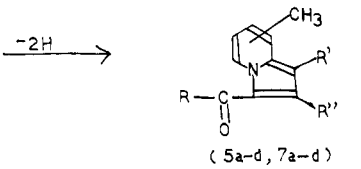
Treatment of ω-bromo ketones with picolines in anhydrous benzene at reflux temperature lead to the quarternization of picolines giving *N*-(2-aroylmethyl)picolinium bromides (Scheme I), in excellent yield. The bromide salts when treated with triethylamine in dry benzene immediately generated a dark red coloration due to the formation of corresponding ylide, which on subsequent reaction with various dipolarophiles (acetylenic esters) gave five-membered heterocyclic derivatives (**5a–d**, **7a–d**).

Scheme I



Scheme II





The reaction of picolinium ylides with the acetylenic triple bond of acetylenic ester such as dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate appears to proceed by the nucleophilic attack of the carbanion similar to the first step of Michael type of addition. The stabilization of this zwitterion presumably takes place by internal nucleophilic attack of the carbanion on the α-position of the picoline ring

0021-9568/85/1730-0505$01.50/0

Table I. Physical and Spectral Data of the Indolizine Derivatives 5a-d, 7a-d

compd no.	R	R′	mp, °C	%, yield	recrystn solvent	spectral data	no. of protons	assign.
5a	4-Cl·C_6H_4	COOMe	168–70	56	$CHCl_3$/MeOH	IR[a]		
						1740		C=O ester
						1710		C=O
						1630		C=C
						1510		C-N
						2980		C-H
5b	C_4H_3S	COOEt	112–15	54	$CHCl_3$/MeOH	IR[a]		
						1720		C=O ester
						1700		C=O
						1600		C=C
						1490		C-N
						2980		C-H
5c	4-Cl·C_6H_4	COOEt	102–3	58	$CHCl_3$/MeOH	IR[a]		
						1740		C=O ester
						1710		C=O
						1630		C=C
						1510		C-N
						2980		C-H
						^{1}H NMR[b]		
						6.65–8.85 m	7	aromatic
						1.00 t J = 8 H	3	methyl
						1.23 t J = 8 Hz	3	methyl
						2.30 s	3	methyl
						3.62 q J = 8 Hz	2	methylene
						4.20 q J = 8 Hz	2	methylene
5d	2-$C_{10}H_7$	COOMe	141–43	58	$CHCl_3$/MeOH	IR[a]		
						1720		C=O ester
						1690		C=O
						1620		C=C
						1490		C-N
						2980		C-H
7a	C_4H_3S	COOMe	210–12	61	$CHCl_3$/MeOH	IR[a]		
						1720		C=O ester
						1690		C=O
						1590		C=C
						1490		C-N
						2980		C-H
						^{1}H NMR[b]		
						6.65–935 m	6	aromatic
						3.35 s	3	methyl
						3.65 s	3	methyl
						2.35 s	3	methyl
7b	4-Cl·C_6H_4	COOEt	118–20	53	$CHCl_3$/MeOH	IR[a]		
						1730		C=O ester
						1700		C=O
						1610		C=C
						1500		C-N
						2980		C-H
						^{1}H NMR[b]		
						6.70–9.50 m	7	aromatic
						1.00 t J = 8 Hz	3	methyl
						1.23 t J = 8 Hz	3	methyl
						2.35 s	3	methyl
						3.50 q J = 8 Hz	2	methylene
						4.20 q J = 8 Hz	2	methylene
7c	4-Cl·C_6H_4	COOMe	145–47	51	$CHCl_3$/MeOH	IR[a]		
						1720		C=O ester
						1690		C=O
						1580		C=C
						1490		C-N
						2980		C-H
7d	2-$C_{10}H_7$	COOMe	176–78	56	$CHCl_3$/MeOH	IR[a]		
						1740		C=O ester
						1700		C=C
						1600		C=C
						1490		C-N
						2980		C-H
						^{1}H NMR[b]		
						6.65–9.65 m	10	aromatic
						3.78 s	3	methyl
						2.85 s	3	methyl
						2.35 s	3	methyl

[a] cm^{-1} (Nujol). [b] δ, ppm ($CDCl_3$).

and closing of five-membered ring. The same on dehydrogenation gave rise to the formation of aromatized indolizine derivatives (**5a-d**, **7a-d**) (Scheme II). The yield of the products ranged between 50 and 61%.

The structures of the compounds were established by microanalysis, physical, and spectra data (Table I).

Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. A Perkin-Elmer infra cord spectrophotometer was used to record the IR spectra. The nuclear magnetic resonance spectra ($CDCl_3$) were run using a Varian A-60 spectrometer with Me_4Si as the internal standard, and chemical shifts are expressed in δ ppm values (Table I). Products were purified by column chromatography over silica gel (60-120 mesh), and then crystallized by appropriate solvents. The purity was checked by TLC.

Preparation of N-(2-Aroylmethyl)picolinium Bromide. Aroylmethyl bromide (0.1 mol) was digested in 20 mL of anhydrous benzene, and 0.1 mol of picoline was added dropwise with constant stirring. After the addition of picoline was complete, the reaction mixture was kept on reflux for about 2 h on a water bath; a pale yellow solid deposited on the inner surface of the flask, and the crude product was recrystallized by methanol/water, to yield a crystalline solid.

Preparation of 1,2-Dicarbomethoxy-3-aroylindolizine and 1,2-Dicarbomethoxy-3-aroylindolizine via 2-Picolinium Ylide and 4-Picolinium Ylide. To the stirred suspension of *N*-(2-aroylmethyl)picolinium bromide (5 mmol) and acetylenic dipolarophile (5 mmol) in anhydrous benzene was added dropwise a solution of 0.7 mL of triethylamine in 10 mL of benzene. After it was stirred for 1 h the whole mass was refluxed on a water bath for 4-6 h. After completion of reaction the resulting mixture was concentrated to 1/10 of its original volume and kept overnight at room temperature. On the next day triethylamine hydrobromide was filtered off and the filtrate was concentrated under reduced pressure to give the reddish brown mass. This product was chromatographed on silica gel with benzene as eluant to give crude product (**5a-d**, **7a-d**) as colored powder and recrystallized from appropriate solvents to obtain the product in pure and crystalline form.

Acknowledgment

We express our thanks to Director, H.B.T.I., Kanpur for providing research facilities.

Registry No. **3a**, 762-42-5; **3b**, 762-21-0; **5a**, 96844-93-8; **5b**, 96844-99-4; **5c**, 96844-94-9; **5d**, 96844-95-0; **7a**, 96826-76-5; **7b**, 96844-96-1; **7c**, 96844-97-2; **7d**, 96844-98-3; *p*-$ClC_6H_4COCH_2Br$, 536-38-9; $C_4H_3SCOCH_2Br$, 63511-54-6; 2-methylpyridine, 109-06-8; 4-methylpyridine, 108-89-4; 2-(bromoacetyl)naphthalene, 613-54-7; (*p*-chlorobenzoylmethyl)-2-picolinium bromide, 82746-43-8; (thienylcarbonylmethyl)-2-picolinium bromide, 96826-74-3; (2-naphthoylmethyl)-2-picolinium bromide, 6276-80-8; (*p*-chlorobenzoylmethyl)-4-picolinium bromide, 25357-43-1; (thienylcarbonylmethyl)-4-picolinium bromide, 96826-75-4; (2-naphthaloylmethyl)-4-picolinium bromide, 6277-78-7.

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Received for review October 12, 1984. Revised manuscript received December 12, 1984. Accepted February 12, 1985. The award of SRF to A.B. by CSIR (New Delhi) is gratefully acknowledged.

Syntheses and Characterization of Some Carbobutoxythio Compounds and Substituted Oxathiazolones

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Eight new carbobutoxythio compounds have been synthesized by reacting *n*-butoxycarbonylsulfenyl chloride with appropriate compounds to test their use as herbicides, fungicides, and insecticides. Three new oxathiazolone derivatives were also synthesized by reacting chlorocarbonylsulfenyl chloride with amides.

A series of carbobutoxythio compounds (**1-8**) was synthesized by reacting *n*-butoxycarbonylsulfenyl chloride (*1*) with substituted amines, bicycloheptanol, and cyclohexene. Table I lists the melting points, the yields, and the proton NMR data of these new compounds. The IR spectra of these compounds have a very strong carbonyl band at 1720-1727 cm^{-1}, characteristic of thiocarbonates.

Three new 5-substituted-1,3,4-oxathiazol-2-ones (**9-11**) were obtained by reaction of chlorocarbonylsulfenyl chloride (*1*) with the appropriate amides according to the literature procedure (*2*, *3*). The physical data of these compounds are listed in Table II.

Experimental Section

All melting points are uncorrected. The proton NMR spectra were recorded on a Perkin-Elmer R-12B spectrometer with

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0021-9568/85/1730-0507$01.50/0