

- (7) Eckstein, Z. *Rocz. Chem.* **1954**, *28*, 549-60.
 (8) Scott, A. W.; Wood, B. L. *J. Org. Chem.* **1942**, *7*, 508-16.
 (9) Harrison, D.; Smith, A. C. B. *J. Chem. Soc.* **1959**, 3157-8.
 (10) Hershenson, F. M.; Bauer, L.; King, K. F. *J. Org. Chem.* **1968**, *33*, 2543-4.
 (11) Dornow, A.; Hahmann, O. *Arch. Pharm. (Weinheim, Ger.)* **1957**, *290*, 20-31.
 (12) Koenig, W.; Geiger R. *Chem. Ber.* **1970**, *103*, 2024-33.
 (13) Flsons Pest Control Ltd., French Patent 1373 006, Oct 9, 1964; *Chem. Abstr.* **1965**, *62*, 9154d.

- (14) Junker, P.; Mees, B.; Ribka, J. German Offen. 2 131 367 Dec 28, 1972; *Chem. Abstr.* **1973**, *78*, 84413h.
 (15) Davoll, J.; Lang, D. H. *J. Chem. Soc.* **1960**, 314-8.
 (16) Clark, R. L.; Pessolano, A. A. *J. Am. Chem. Soc.* **1958**, *80*, 1657-62.
 (17) Roechling, H.; Frasca, E.; Buechel, K. H. *Z. Naturforsch. B* **1970**, *25*, 954-60.

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Studies on Nitrile Imines. Synthesis of Some Novel Five-Membered Heterocyclic Compounds

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A variety of new C-acetyl and C-ethoxycarbonyl derivatives of hydrazoneyl bromides have been prepared and reacted with a range of α,β -unsaturated carbonyl compounds, indene, isothiocyanate, and acetylacetone to afford a wide variety of novel pyrazoline, thiadiazoline, and pyrazole derivatives in excellent yields. The structural elucidation of the final products is based on spectral and analytical studies.

The synthesis of heterocyclics has held considerable attention in organic synthesis in recent years (1-6). Although a variety of five-membered heterocyclic compounds derived from α -chlorobenzylidenephénylhydrazine with various dipolarophiles have been well documented in the literature (7-9), cycloaddition reactions of C-ethoxycarbonyl and C-acetyl derivatives of hydrazoneyl bromides particularly with α,β -unsaturated carbonyl compounds have not been reported so far. In view of the ability of hydrazoneyl halides to act as good precursors for generating an active 1,3-dipolar species, i.e., nitrile imine, we have prepared some new C-ethoxycarbonyl and C-acetyl derivatives of hydrazoneyl bromides and utilized them in the cycloaddition (10, 11) with various dipolarophiles in order to prepare the heterocyclic compounds, with a view to reveal their synthetic potentialities.

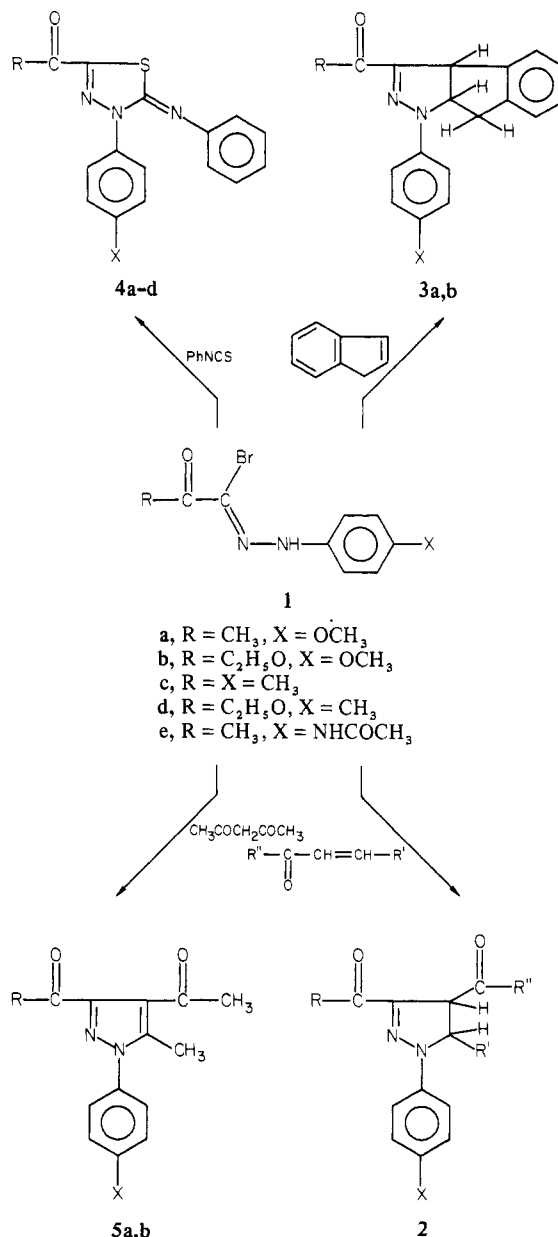
Experimental Section

All the reagents were obtained from commercial sources (BDH, E. Merck, and S. Merck). Hydrazoneyl bromides were prepared according to the method described previously (12). Melting points were determined on a Gallenkamp apparatus and are uncorrected. Products were purified by column chromatography over silica gel (60-120 mesh) and purity was checked by TLC. IR spectra were recorded on a Perkin-Elmer infracord spectrophotometer and NMR spectra were taken on a Varian A-90 spectrometer with Me₄Si as an internal standard (Table I). Unless otherwise stated, all the reactions were run under nitrogen atmosphere.

Preparation of Cycloadducts (2-4). To a solution of hydrazoneyl bromide (0.005 mol) in dried chloroform (50 mL) was added dipolarophiles in equimolar amounts. The solution was refluxed with constant stirring while triethylamine (0.005 mol) was added dropwise and the solution was allowed to reflux further for 10-12 h. After the mixture was cooled, the solid material was filtered out, washed thoroughly with water, and then dried over sodium sulfate. Chloroform was removed under pressure and the residue on purification followed by crystallization with appropriate solvents (Table II) afforded the desired cycloadducts (2-4) in excellent yields (see Scheme I).

Preparation of Pyrazoles (5a-b). To an ethanolic sodium ethoxide or methanolic sodium methoxide solution (prepared

Scheme I



- 2a(i), R' = R'' = C₆H₅
 a(ii), R' = 4-OCH₃C₆H₄, R'' = C₆H₅
 a(iii), R' = 3,4-(OCH₃)₂C₆H₃, R'' = 4-OCH₃C₆H₄
 a(iv), R' = H, R'' = NH₂
 b(i), R' = 3,4-(OCH₃)₂C₆H₃, R'' = 4-OCH₃C₆H₄
 b(ii), R' = H, R'' = NH₂
 e, R' = H, R'' = NH₂

Table I. Spectral Studies of Cycloadducts 2-5

com- pound no.	¹ H NMR		IR (Nujol)	
	δ	assignment (no. of protons)	ν , cm ⁻¹	assign- ment
2a(i)	2.35 (s)	acetyl (3)	1530	C=N
	2.51 (s)	methoxy (3)	1650	C=O
	4.50 (d, $J = 4.5$ Hz)	methine (1)	1690	C=O
	5.80 (d, $J = 4.5$ Hz)	methine (1)	1600	C=C
	7.0-8.0 (m)	aromatic (14)		
2a(ii)	2.30 (s)	acetyl (3)	1510	C=N
	2.50 (s)	methoxy (3)	1640	C=O
	3.46 (s)	methoxy (3)	1690	C=O
	6.83-7.96 (m)	aromatic (9)	1590	C=C
	4.43 (d, $J = 4.5$ Hz)	methine (1)		
2a(iv)	5.73 (d, $J = 4.5$ Hz)	methine (1)	1510	C=N
			1640	C=O
			1680	C=O
			3200,	NH ₂
			3360	
2b(i)	2.25 (s)	methoxy (3)	1590	C=N
	3.77 (s)	methoxy (3)	1680	C=O
	3.84 (s)	methoxy (6)	1720	C=O
	1.22 (t, $J = 7.5$ Hz)	methyl (3)		
	4.14 (q, $J = 7.5$ Hz)	methylene (2)		
2b(ii)	4.34 (d, $J = 4.5$ Hz)	methine (2)		
	5.67 (d, $J = 4.5$ Hz)	methine (2)		
	5.67-7.87 (m)	aromatic (11)		
	1.34 (t, $J = 7.5$ Hz)	methyl (3)	1550	C=N
	2.29 (s)	methoxy (3)	1640	C=O
2e	3.22-3.56 (q, $J = 7.5$ Hz)	methylene (2)	1700	C=O
	4.16-4.39 (d, $J = 7.5$ Hz)	methylene (2)	3180,	NH ₂
			3360	
	4.66-4.92 (q, $J = 7.5$ Hz)	methine (1)		
	6.79-7.46 (m)	aromatic (4)		
3a	7.96 (s)	amino (2)	1500	C=N
			1630	C=O
			1680	C=O
			1570	C=C
			3170,	NH ₂
3b			3360	
			1500	C=N
			1640	C=O
			1600	C=C
			1530	C=N
4a	1.35 (t, $J = 7.5$ Hz)	methyl (3)	1680	C=O
	2.33 (s)	methoxy (3)	1600	C=C
	3.45 (d, $J = 6.0$ Hz)	methylene (2)		
	4.16-4.43 (m)	methylene, methine (3)		
	6.05 (d, $J = 9$ Hz)	methine (1)		
4b	7.1-7.4 (m)	aromatic (8)	1525	C=N
			1640	C=O
			1590	C=C
			1525	C=N
			1730	C=O
4c	4.31 (q, $J = 7.5$ Hz)	methylene (2)	1590	C=C
	7.26-7.89 (m)	aromatic (9)		
	2.33 (s)	methyl (3)	1525	C=N
	2.53 (s)	acetyl (3)	1645	C=O
	7.1-7.4 (m)	aromatic (9)	1590	C=C
4d	1.30 (t, $J = 7.5$ Hz)	methyl (3)	1530	C=N
	2.50 (s)	methyl (3)	1735	C=O
	4.36 (q, $J = 7.5$ Hz)	methylene (2)	1590	C=C
	7.33-8.0	aromatic (9)		
	2.43 (s)	methyl (3)	1510	C=N
5a	2.50 (s)	acetyl (3)	1670	C=O
	2.63 (s)	acetyl (3)	1690	C=O
	2.70 (s)	methoxy (3)		
	7.33 (s)	aromatic (4)	1590	C=C
	1.45 (t, $J = 7.5$ Hz)	methyl (3)	1510	C=N
5b	2.43 (s)	methyl (3)	1650	C=O
	2.45 (s)	acetyl (3)	1750	C=O
	2.60 (s)	methoxy (3)	1610	C=C
	4.45 (q, $J =$ Hz)	methylene (2)		
	7.30 (s)	aromatic (1)		

Table II. Physical Characterization of Compounds 2-5^a

compd no.	crystallizing solvent	mp, °C	yield, %
1a	ethanol-water	130-131	85
1b	ethanol	86-89	90
1c	methanol	132-133	92
1d	methanol	90-91	89
1e	acetone	245-246	84
2a(i)	benzene-hexane	185-188	80
2a(ii)	ethanol	178-179	78
2a(iii)	chloroform-methanol	180-183	90
2a(iv)	acetone	240-270	76
2b(i)	benzene-PE	174-177	74
2b(ii)	ethanol	229	82
2e	acetone	240-245	80
3a	ethyl acetate-ethanol	167-170	80
3b	chloroform-methanol	139-141	89
4a	ethanol	207-210	86
4b	methanol	180-182	84
4c	ethanol	212-213	78
4d	ethanol	170-172	82
5a	ethanol-water	89-90	89
5b	ethanol	126-128	79

^a Satisfactory elemental analyses were obtained for all compounds.

from sodium metal (10.005 mol) and 20 mL of alcohol) was added an equimolar amount of acetylacetone, and the solution was stirred for 0.5 h. The hydrazonyl bromides (1a,b; 0.005 mol) were then added under ice-cold conditions to the above reaction mixture. Stirring was continued for 2-3 h, during which bromide went into the solution and a solid either precipitated out in the reaction mixture itself or precipitated on slight dilution with water. The solid was filtered out and further recrystallization with alcohol-water afforded the pyrazoles (5a,b) in sufficient purity.

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Registry No. 1a, 84801-68-3; 1b, 84801-69-4; 1c, 74519-39-4; 1d, 58670-19-2; 1e, 84801-70-7; 2a(I), 84801-71-8; 2a(II), 84801-72-9; 2a(III), 84801-73-0; 2a(IV), 84801-74-1; 2b(I), 84801-75-2; 2b(II), 84801-76-3; 2e, 84801-77-4; 3a, 84801-78-5; 3b, 84801-79-6; 4a, 84801-80-9; 4b, 84801-81-0; 4c, 84801-82-1; 4d, 84801-83-2; 5a, 84801-84-3; 5b, 63514-81-8; chalcone, 94-41-7; 4-methoxychalcone, 959-33-1; 3,4,4'-trimethoxychalcone, 36685-66-2; 2-propenamide, 79-06-1; indene, 95-13-6; phenyl isothiocyanate, 103-72-0; 2,4-pentanedione, 123-54-6.

Literature Cited

- (1) Katritzky, A. R.; Lagowsky, J. M. "Chemistry of the Heterocyclic N-Oxides"; Academic Press: New York, 1971.
- (2) Patai, S. "Alkenes"; Interscience: New York, 1963.
- (3) Jan Hamer, "1,4-Cycloaddition Reactions"; Academic Press: New York, 1967.
- (4) Katritzky, A. R.; Boulton, A. J. "Advances in Heterocyclic Chemistry"; Academic Press: New York; Vols. 1-24.
- (5) Wiley, H. R. "Heterocyclic Compounds"; Wiley: New York, 1967; Vol. 22.
- (6) Schofield, K. "Heterocyclic Compounds"; Butterworth: London, 1973; Vol. 4.
- (7) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.
- (8) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.
- (9) Huisgen, R.; Seldel, M.; Wallbillich, G.; Knapfer, H. *Tetrahedron* **1962**, *17*, 3.
- (10) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291.
- (11) Firestone, R. A. *J. Org. Chem.* **1968**, *33*, 2285.
- (12) Tewari, R. S.; Parihar, P. *J. Chem. Eng. Data* **1981**, *26*, 418.

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