no methyl groups.

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Registry No. 1, 87145-85-5; 2, 1081-34-1; 3, 87145-86-6; 4, 87145-87-7; 5, 87145-88-8; tridecanoic acid, 638-53-9; 1,12-dodecanedicarboxylic acid, 821-38-5.

Synthesis of 4-(Acylacetyl)-1-phenyl-2-pyrazolin-5-ones from 3-Acyl-2*H*-pyran-2,4(3*H*)-diones. Their Synthetic Applications to Functionalized 4-Oxopyrano[2,3-*c*]pyrazole Derivatives

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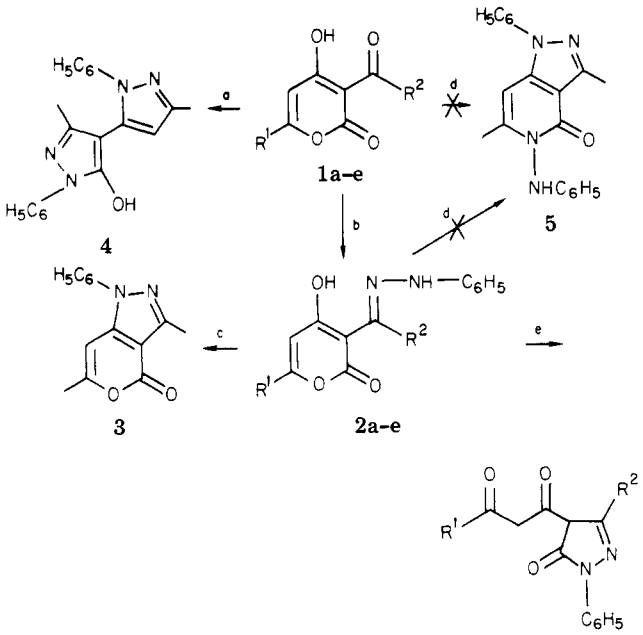
The phenylhydrazones of 3-acyl-2*H*-pyran-2,4(3*H*)-diones (**2**), in refluxing acetic acid, underwent rearrangement to 4-(acylacetyl)-1-phenyl-2-pyrazolin-5-ones (**6**), from which some functionalized 4-oxopyrano[2,3-*c*]pyrazole derivatives were synthesized. This finding showed that the phenylhydrazone of dehydroacetic acid (**2a**) gave **6a** instead of the reported pyridinopyrazole (**5**). The tautomerism of the β-tricarbonyl compounds (**6**) was studied by NMR spectroscopy.

Recent work from our laboratory has shown that the phenylhydrazones of 3-acyl-4-hydroxycoumarins were capable of cyclizing by three different processes, depending upon the conditions employed. Two of these cyclizations led to the 4-oxo-1*H*- or -2*H*-[1]benzopyrano[4,3-*c*]pyrazole derivatives[1] and the other one to the 1-aryl-4-(2-hydroxybenzoyl)pyrazol-5-ones.[2] We now wish to report on the ring transformation of the phenylhydrazones **2** of 3-acyl-2*H*-pyran-2,4(3*H*)-diones (**1**).

Some years ago, the formation of 3,6-dimethyl-1-phenyl-4-oxopyrano[4,3-*c*]pyrazole (mp 158 °C) (**3**) and 5-hydroxy-3-methyl-1-phenyl-4-(3-methyl-1-phenylpyrazol-5-yl)pyrazole (mp 260 °C) (**4**) was reported.[3,4] Surprisingly, in a more recent paper,[5] 5-anilino-3,6-dimethyl-4-oxo-1-phenylpyrazolo[4,3-*c*]pyridine (**5**) (named as pyridinopyrazole by the authors) was described from the reaction of dehydroacetic acid (**1a**) and phenylhydrazine (Scheme I). The melting point reported for this product is consistent with its formulation as **4** previously encountered by Stolle.[3] We repeated the treatment of dehydroacetic acid with phenylhydrazine following the literature method[5] and obtained the pyrazolylpyrazole (**4**) identical with the one prepared by repeating the pioneering work of Stolle. Consequently, structure **5** should be revised to **4**.

Formally, 3-acyl-2*H*-pyran-2,4(3*H*)-diones (**1**) possess four sites for nucleophilic attack.[6] As early as 1884 Perkin[7] reported that phenylhydrazine reacts readily with dehydroacetic acid, in ethanol solution, to yield 3-(1-phenylhydrazonoethyl)dehydroacetic acid (**2a**). We now report a new successful conversion of the phenylhydrazones (**2a–e**) to 3-substituted-4-(acylacetyl)-1-phenyl-2-pyrazolin-5-ones (**6a–e**) and their subsequent transformation directed toward the synthesis of 1*H*-pyrano[2,3-*c*]pyrazol-4-one derivatives, a class of compounds which has received very limited attention in the literature.[8–10]

Scheme I[a]



a, $R^1 = R^2 = Me$; b, $R^1 = Me$, $R^2 = Et$; c, $R^1 = Me$, $R^2 = Ph$; d, $R^1 = Ph$, $R^2 = Me$; e, $R^1 = Ph$, $R^2 = Ph$

[a] (a) $R^1 = R^2 = Me$, 2 $PhNHNH_2$, ref 3; (b) 1 $PhNHNH_2$; (c) $R^1 = R^2 = Me$, HCl, ref 3, 4; (d) ref 5; (e) CH_3COOH, reflux.

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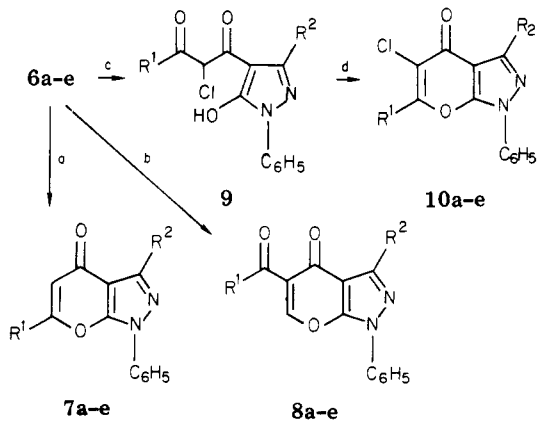
0022-3263/83/1948-4078$01.50/0

Table I. Compounds Prepared

product[a]	% yield	mp, °C	IR, $\nu_{C=O}$($CHCl_3$), cm^{-1}	UV, λ_{max} (ϵ 10^{-3}) (EtOH), nm
2a	92	211-212[b]	1705	350 (8.3), 300 (9.3)
2b	92	155	1710	340 (7.2), 308 (10.5)
2c	82	160	1710, 1735	370 (11.1), 288 (11.9)
2d	75	215	1710	350 (11.9), 286 (11.7)
2e	90	155-158	1720	336 (26.1), 304 (21.5)
6a	73	101	1720, 1620	318 (11.0), 262 (13.1)
6b	69	95	1720, 1620	318 (10.4), 260 (12.6)
6c	65	148	1720, 1620	316 (10.0), 252 (23.4)
6d	84	156	1620[c]	360 (19.8), 248 (16.7)
6e	78	177	1620	356 (22.2), 248 (26.2)
7a	82	150[d]	1660	244 (23.0)
7b	85	132	1655	244 (25.6)
7c	85	171	1660	248 (24.8)
7d	76	209-210[e]	1650	253 (25.2)
7e	90	230	1640	256 (30.8)
8a	87	178	1690, 1660	312 (12.7)
8b	82	112	1690, 1660	312 (12.6)
8c	76	173	1690, 1660	315 (13.4), 254 (23.6)
8d	76	203	1690,[c] 1665	328 (5.3), 248 (23.4)
8e	90	212	1690,[c] 1660	330 (7.6), 254 (31.8)
10a	70	140	1665	246 (25.0)
10b	72	127	1665	246 (24.9)
10c	63	208	1665	248 (25.5)
10d	50	166	1665	251 (26.2)
10e	40	221	1665	254 (30.6)

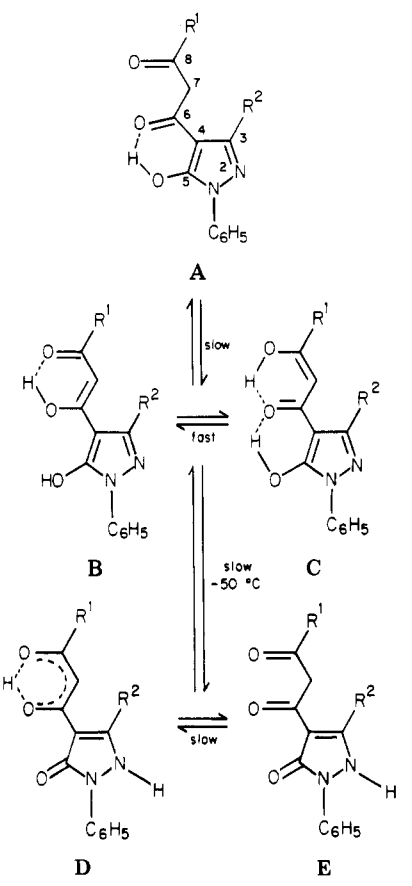
[a] Satisfactory analytical values (-0.35% for C, H, N, and Cl) were reported for all new compounds in the table, except for 2e (C; -0.56%). [b] Lit. mp 209 °C.[7] [c] Shoulder. [d] Lit. mp 152-153 °C.[8] [e] Lit. mp 210-211 °C.[8]

Scheme II[a]



[a] (a) CH_3COOH, H_2SO_4, reflux; (b) diethoxymethyl acetate; (c) sulfuryl chloride; (d) H_2SO_4.

Scheme III



When **2a-e** were refluxed in acetic acid, they underwent a rearrangement involving a nitrogen nucleophilic attack at the C-2 lactone carbonyl with ring opening to yield 3-substituted-4-(acylacetyl)-1-phenyl-2-pyrazolin-5-ones (**6a-e**) in good yields (Scheme I). This procedure did not in fact provide the compound **5** as claimed in the literature.[5] Attempts to bring about the products **6** without isolation of the phenylhydrazones **2** were unsuccessful. Structures **6** were established by analytical data and spectroscopic means, as well as by their chemical behavior. Although the compounds **6a** and **6d** have been mentioned as intermediates[8] in the synthesis of 1*H*-pyrano[2,3-*c*]-pyrazol-4-ones (**7a** and **7b**), we were unable to find a report of their physical data.

Compounds **6** are soluble in aqueous sodium carbonate. They afford a purple ferric chloride solution. The ring closure of **6a-e** to **7a-e** was easily achieved by refluxing in acetic acid in the presence of sulfuric acid as catalyst. Condensation of **6a-e** with diethoxymethyl acetate afforded 5-acyl-4-oxo-1*H*-pyrano[2,3-*c*]pyrazoles (**8a-e**). Treatment of **6a-e** with sulfuryl chloride gave the corresponding chloro derivatives **9**, which were cyclodehydrated, without purification, to 5-chloro-4-oxo-1*H*-pyrano[2,3-*c*]-pyrazoles (**10a-e**) in concentrated sulfuric acid at room

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Table II. Characteristic ^{1}H NMR Spectral Data and Tautomeric Composition of Compounds 6

product	R^1	R^2	solvent	enol (B, C forms) R^1	enol (B, C forms) R^2	enol (B, C forms) CH	enol (B, C forms) OH	keto (A form) R^1	keto (A form) R^2	keto (A form) CH$_2$	A, B, C forms OH (C-5)[a]	% enol	concn, M
6a	CH_3	CH_3	$CDCl_3$	2.13	2.47	5.72	14.8	2.35	2.47	3.87	11.8	83	0.8
			Me_2SO-d_6	2.06	2.51	6.65	12–14	2.15	2.47	3.85	12–14	50	0.8
6b	CH_3	C_2H_5	$CDCl_3$	2.10	2.80 (CH_2)	5.69	14.8	2.30	2.80 (CH_2)	3.84	12.1	80	0.8
			Me_2SO-d_6	2.07	2.95 (CH_2)	6.68	7.9–9.5	2.12	2.87 (CH_2)	3.77	7.9–9.5	41	0.8
6c	CH_3	C_6H_5	$CDCl_3$	1.87		5.42	14.6	1.96		3.56	12	81	0.8
			Me_2SO-d_6	2.00		6.10	*b*	1.85		3.10	*b*	16	0.8
6d	C_6H_5	CH_3	$CDCl_3$		2.57	6.41	*b*		2.43	4.43	11.2	93	0.2
			Me_2SO-d_6		2.57	*c*	*b*		2.47	4.57	*b*	85	0.2
6e	C_6H_5	C_6H_5	$CDCl_3$			6.10	15.0			3.95	11	94	0.2
			Me_2SO-d_6			6.87	5.9			4.42	5–9	89	0.2

[a] Broad signal. [b] The enolic proton is not observed. [c] Masked by the aromatic protons.

Table III. Concentration Effects on Enolic Hydroxyl Chemical Shifts in Deuteriochloroform

compd	R^1	R^2	concn, M	OH C-5	OH C-6 or C-8
6a	CH_3	CH_3	0.4	11.6	14.8
			0.8	11.8	14.8
			1.6	12	14.8
6b	CH_3	C_2H_5	0.4	11.8	14.8
			0.8	12.1	14.8
			1.6	12.3	14.8
6c	CH_3	C_6H_5	0.4	11.6	14.6
			0.8	12	14.6
			1.6	12	14.6

Table IV. Chemical Shifts[a] of the Enol Hydroxyl and NH Protons at Various Temperatures for 6a

t, °C	A, B, C forms OH (C_5)	B, C forms OH (C_6 or C_8)	D, E forms NH	D form OH (C_6 or C_8)	ratio A:B,C:D,E
20	11.8	14.8			20:80:0
0	11.9	14.8			13:87:0
−20	12.1	15			10:90:0
−40	12.4	15.1			10:90:0
−55	12.4	15.05	13.6	16.45	5:53:42[b]

[a] 0.8 M solution in $CDCl_3$, δ ppm. [b] Ratio (D:E) = 9:1.

temperature (Scheme II). The structure of compounds **7**, **8**, and **10** follow from their spectral data (Table I).

Compounds **6** contain a β-tricarbonyl system capable of tautomerism, and it was interesting to establish whether an equilibrium exists between the more likely species A–E, in solution by ^{1}H and ^{13}C NMR studies (Scheme III).

The tautomerism of β-diketones[11–14] and 4-acyl-2-pyrazolin-5-ones[15,16] is well documented. Much less attention has been given to β-tricarbonyl systems.[17,18] In deuteriochloroform solution, the ^{1}H NMR spectra of compounds **6** showed the presence of two low-field resonance proton signals. The ^{1}H chemical shift around δ 14.8 was concentration independent, while the one at δ 11–12 was only slightly affected (Tables II and III), suggesting that both protons are hydrogen bonded (C tautomer) as in *o*-acetylacetylphenol.[17] In addition, an equilibrium between dienol (B, C) and monoenol (A) tautomers was revealed. The ratio of these tautomers can be determined by the integration of the relative intensities of the characteristic keto and enol peaks, arising from the side chain, which exhibit a similar pattern in the chemical shifts as compared with those of related β-diketones.[11–14] The dienol content varies with the nature of the R^1 and R^2 substituents. The signal at δ ~12 is independent of such an equilibrium; thus, this signal could be attributed to the C-5 hydroxy of the B, C, and A tautomers, which are also stabilized by intramolecular hydrogen bonds. The sharp enolic peak at lower field (δ 14.6–15) fits well with the more strongly chelated OH on the side chain in tautomers B and C, while the broader one (δ 11–12) fits with the more acidic OH at C-5.[19]

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Table V. Characteristic ^{13}C NMR Chemical Shifts (δ) of Compounds 6

compd	solvent	tautomers	C-3	C-4	C-5	C-6	C-7	C-8	R^1	R^2
6a	$CDCl_3$	A	*a*	*a*	*a*	189.57	54.63	*a*	30.58	15.04
		B, C	146.78	100.37	158.46	188.07	96.59	180.93	22.29	15.44
6a	Me_2SO-d_6	A	151.09	105.12	161.51	189.51	55.68	187.97	31.40	14.77
		B, C	151.38	101.48	160.48	184.53	98.28	*a*	25.03	15.10
6b	$CDCl_3$	A	*a*	*a*	*a*	189.34	54.38	*a*	30.54	22.77 (CH_2), 11.93 (CH_3)
		B, C	151.84	99.58	158.71	187.94	96.68	180.90	22.35	22.59 (CH_2), 12.15 (CH_3)
6c	$CDCl_3$	A	*a*	*a*	*a*	188.58	53.85	*a*	30.39	*b*
		B, C	150.45	99.85	158.46	188.48	97.22	180.64	22.19	*b*
6d	$CDCl_3$	B, C	146.85	101.19	158.38	188.37	93.62	175.55	*b*	15.74
6e	$CDCl_3$	B, C	150.55	100.83	158.23	188.59	94.30	174.58	*b*	*b*

[a] Resonance could not be distinguished with base line noise in available spectra. [b] No attempt was made to assign the resonance to a specific carbon atom of the phenyl group.

The monoenol ratio increased when the temperature was lowered until −30 °C, whereas the position of the broadening resonance lines is almost unaffected. At −50 °C, four signals appear at low field which could be due to an equilibrium between the OH (A, B, C) and NH (D, E) forms, as observed in the case of 4-acyl-1-phenyl-2-pyrazolin-5-ones[15,16] (Table IV). The diketo form on the side chain is favored in Me_2SO-d_6 solution as compared to a chloroform solution.

The ^{13}C NMR chemical shifts of compounds **6** are summarized in Table V. The straightforward assignment is based on off-resonance decoupling, examination of the coupled spectra, and analogy to literature assignments for acetylacetone, benzoylacetone, and dibenzoylmethane,[20-22] and 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones.[15-16] In chloroform solution, the magnitude of the C-5 carbon atom δ 158–159 is quite close to the C-5 hydroxy tautomer.[15,16,23,24] The C-5 carbonyl would be expected at lower field (δ 168.8).[15] Consequently, the NH forms (D and E) are ruled out at 25 °C. A good estimate can be made of the population of the tautomers from the observed ^{13}C chemical values. The equilibria between A and B, C are expected to be slow with regard to spectra averaging and the equilibrium between B and C fast. The recorded spectrum should show a weighted average of the B and C tautomers. The relative populations are difficult to obtain, since the chemical shifts of the individual tautomers are unknown. However, it is known that a hydrogen-bonded carbonyl resonates at lower field than a corresponding free carbonyl and that an enolic carbon atom resonates at higher field than a corresponding keto carbon atom.[20] The C-6 resonance of the C form should be at a lower field than the C-8 carbon atom. From the chemical values, respectively at δ 188 and 174–180, it can be reasonably concluded that the C tautomer contributes mainly to the tautomeric population of the dienol, in deuteriochloroform solution. In Me_2SO-d_6 solution, the ^{13}C NMR spectrum of **6a** gives rise to two resonances for all the carbon atoms corresponding to the mono- and dienol tautomers. The resonances from C-5 are in accord with the C-5 hydroxy structures. The C-6 carbonyl signal is displaced to higher field in the dienol forms, as compared to chloroform. This result suggests that there is an appreciable change in the position of the B ⇌ C equilibrium. The amount of the B form should be greater.

Experimental Section

All melting points were determined on a Kofler block. Infrared and ultraviolet spectra were obtained with Beckman Model Acculab 2 and DB spectrometers. NMR spectra were recorded on a Brucker WP 80 and on a Varian XL 100 12FT spectrometers and are expressed in parts per million from Me_4Si as internal standard. Elemental analyses were performed by Microanalytical laboratory, Centre National de la Recherche Scientifique, 69390 Vernaison, France.

Compounds **1a**,[25] **1b-d**,[26] **1e**,[25] and **2a**[7] were prepared by literature methods. Compound **2b** was synthesized according to the procedure described for **2a**.

Preparation of Phenylhydrazones (2c–e). To a solution of **1c–e** (10 mmol) in 20 mL of benzene was added phenylhydrazine (1.08 g, 10 mmol). The mixture was refluxed for 5 min and allowed to stand at room temperature for 2 h; after the mixture cooled, the phenylhydrazone was collected as yellow crystals and recrystallized from ethanol.

(Acylacetyl)-1-phenyl-2-pyrazolin-5-ones (6a–e). A solution of **2a–e** (10 mmol) in acetic acid (20 mL) was refluxed for 1 h. After evaporation of the solvent, the residue was recrystallized from acetonitrile, yielding **6a–c**. In the case of **2d–e** the acetic acid solution was cooled to give a precipitate which was recrystallized from acetonitrile.

4-Oxo-1*H*-pyrano[2,3-*c*]pyrazoles (7a–e). To a solution of **6** (10 mmol) in acetic acid (20 mL) was added dropwise concentrated sulfuric acid (1 mL). The mixture was poured into cold water (150 mL). The precipitate was filtered, washed with 5% aqueous Na_2CO_3 solution and water, and dried to furnish the title compounds, which were recrystallized from acetonitrile.

5-Acyl-4-oxo-1*H*-pyrano[2,3-*c*]pyrazoles (8a–e). A mixture of **6** (10 mmol) and diethoxymethyl acetate (20 mL) was heated at 130–140 °C for 15 min. The reaction mixture was cooled and filtered to give the crude products **8**, which were recrystallized from acetonitrile or ethyl acetate.

5-Chloro-4-oxo-1*H*-pyrano[2,3-*c*]pyrazoles (10a–e). To a solution of **6** (10 mmol) in dry methylene chloride (20 mL for **6a–c**; 100 mL for **6d,e**) was added dropwise sulfuryl chloride (1.35 g, 10 mmol). The mixture was allowed to stand at room temperature for 2 h and then poured into 10% aqueous K_2CO_3 solution (50 mL) with stirring for 5 min. The aqueous layer was acidified with 10% hydrochloric acid and extracted with chloroform. The combined organic extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave compounds **9** in a crude state. Concentrated sulfuric acid (50 mL) was added. After 4 h at room temperature, the mixture was poured into 200 mL of ice water. The precipitate was extracted with chloroform. The chloroform solution was washed with 5% aqueous K_2CO_3 solution,

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dried, and evaporated to give products **10**, which were recrystallized from acetonitrile.

Registry No. **1c**, 17965-42-3; **1d**, 17313-50-7; **1e**, 14895-21-7; **2a**, 54107-17-4; **2b**, 87100-57-0; **2c**, 87100-58-1; **2d**, 87100-59-2; **2e**, 87100-60-5; **6aA**, 87100-61-6; **6aB**, 87100-62-7; **6aC**, 87100-63-8; **6aD** (isomer 1), 87114-10-1; **6aD** (isomer 2), 87114-11-2; **6aE**, 87100-64-9; **6bA**, 87100-65-0; **6bB**, 87100-66-1; **6bC**, 87100-67-2; **6bD** (isomer 1), 87100-68-3; **6bD** (isomer 2), 87100-69-4; **6bE**, 87100-70-7; **6cA**, 87100-71-8; **6cB**, 87100-72-9; **6cC**, 87100-73-0; **6cD** (isomer 1), 87100-74-1; **6cD** (isomer 2), 87100-75-2; **6cE**, 87100-76-3; **6dA**, 87100-77-4; **6dB**, 87100-78-5; **6dC**, 87100-79-6; **6dD** (isomer 1), 87100-80-9; **6dD** (isomer 2), 87100-81-0; **6dE**, 87100-82-1; **6eA**, 87100-83-2; **6eB**, 87100-84-3; **6eC**, 87114-12-3; **6eD** (isomer 1), 87100-85-4; **6eD** (isomer 2), 87100-86-5; **6eE**, 87100-87-6; **7a**, 64360-24-3; **7b**, 87100-88-7; **7c**, 87100-89-8; **7d**, 64360-25-4; **7e**, 87100-90-1; **8a**, 87100-91-2; **8b**, 87100-92-3; **8c**, 87100-93-4; **8d**, 87114-13-4; **8e**, 87100-94-5; **9a**, 87100-95-6; **9b**, 87100-96-7; **9c**, 87100-97-8; **9d**, 87114-14-5; **9e**, 87100-98-9; **10a**, 87100-99-0; **10b**, 87101-00-6; **10c**, 87101-01-7; **10d**, 87101-02-8; **10e**, 87101-03-9; phenylhydrazine, 100-63-0.

Supplementary Material Available: Microanalytical and ^{1}H NMR data for all the compounds **2**, **6**, **7**, **8** and **10** (2 pages). Ordering information is given on any current masthead page.

Eliminative Ring Fission of 4-Acyl-2,3-dihydro-4*H*-1,4-benzothiazines

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The behavior of 4-acyl-2,3-dihydro-1,4-benzothiazines **1–11** upon treatment with lithium diisopropylamide (LDA) in THF at −78 °C has been examined. Very marked differences have been observed. Whereas unsubstituted and monosubstituted derivatives (**1–4**) readily undergo "eliminative ring fission", providing 2-(alkylthio)phenyl enamides **12**, 2-aminophenyl vinyl sulfides **16**, and 3-acylbenzothiazolines **13**, 2,3-disubstituted derivatives (**5–7**) do not react at all. The relationship between structural features of the above-mentioned dihydrobenzothiazines and their reactivity is considered. Lithium ion plays a fundamental role in providing activation for the ring-opening reaction.

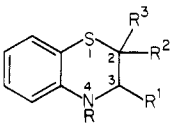
A number of reactions of dihydrobenzo-1,4-thiazines, compounds of considerable pharmacological interest,[1] which lead to heterocyclic ring cleavage have been described. Ring opening of the thiazino moiety may involve S–C_2 or C_3–N bond cleavage. The S–C_2 bond breaking has been reported for dihydro-1,4-thiazinones by reaction with sodium in liquid ammonia[2] and with Raney nickel.[3] The C_3–N bond of dihydrobenzothiazinones can be reductively cleaved[4] under certain circumstances, such as where aromatic stabilization is gained by the ring-opened product.

"Eliminative ring fission" reactions of dihydrothiazines and dihydrobenzothiazines are quite rare. The only known example of eliminative ring fission is that reported by Stoodley[5] for a few dihydrothiazines bearing an acidic hydrogen atom at the 3-position.

The present paper deals with a new dipole-stabilized-carbanion promoted "eliminative ring fission" reaction of some 2,3-dihydro-4*H*-1,4-benzothiazines. Attention will be focused upon the relationship between structure and reactivity in this type of reaction.

Results and Discussion

Following our studies[6] directed toward the synthesis of new dihydrobenzothiazine derivatives by metalation of simpler available precursors, we reasoned that 4-acyl-2,3-dihydro-4*H*-1,4-benzothiazines **1–10** bearing hydrogens on



1, R = COPh; R^1 = R^2 = R^3 = H
2, R = COPh; R^1 = Me; R^2 = R^3 = H
3, R = COPh; R^1 = R^3 = H; R^2 = Me
4, R = COPh; R^1 = R^3 = H; R^2 = Ph
5, R = COPh; R^1 = Me; R^2 = Ph; R^3 = H
6, R = COPh; R^1,R^2 = $(CH_2)_3$; R^3 = H
7, R = COPh; R^1,R^2 = $(CH_2)_5$; R^3 = H
8, R = COPh; R^1 = H; R^2 = R^3 = Cl
9, R = $COCF_3$; R^1 = R^2 = R^3 = H
10, R = CHO; R^1 = R^2 = R^3 = H
11, R = Me; R^1 = R^2 = R^3 = H

the carbon close to the nitrogen might be metalated at that position and that the resulting "dipole-stabilized carbanions" would undergo either alkylation or an "eliminative ring fission" reaction due to the presence of the sulfur, a good leaving group, in the 1-position of the heterocyclic ring. It has been established that base-promoted alkene-forming elimination can be greatly accelerated by insertion, β to the leaving group, of groups capable of stabilizing a carbanion.[7] Such a stabilization may also be provided in the form of a "dipole stabilization" by a heteroatom bonded to a carbonyl function.[8,9]

Treatment of 4-benzoyl-2,3-dihydro-1,4-benzothiazine (**1**) with lithium diisopropylamide (LDA) at −78 °C in tetrahydrofuran (THF) or *sec*-BuLi in hexane/THF and

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