Table II. *N*-(1-Aryl-4-phenyl-1,6-dihydro-1,3,5-triazinyl)-*N'*-arylthiourea[a]

Ar	R'	mp, °C	yield, %
C_6H_5	CH_3	157	92
C_6H_5	C_2H_5	182	85
C_6H_5	n-C_4H_9	239	63
C_6H_5	C_6H_5	241	80
C_6H_5	o-$CH_3C_6H_4$	213	85
C_6H_5	p-$CH_3C_6H_4$	246	90
C_6H_5	o-$CH_3OC_6H_4$	219	80
C_6H_5	p-$CH_3OC_6H_4$	251	86
C_6H_5	p-$C_2H_5OC_6H_4$	197	65
C_6H_5	o-ClC_6H_4	224	88
p-ClC_6H_4	CH_3	162	95
p-ClC_6H_4	C_2H_5	229	85
p-ClC_6H_4	n-C_4H_9	239	75
p-ClC_6H_4	C_6H_5	234	85
p-ClC_6H_4	o-$CH_3C_6H_4$	237	80
p-ClC_6H_4	p-$CH_3C_6H_4$	232	84
p-ClC_6H_4	o-$CH_3OC_6H_4$	236	75
p-ClC_6H_4	o-$C_2H_5OC_6H_4$	243	65
p-ClC_6H_4	p-$C_2H_5OC_6H_4$	241	68
p-ClC_6H_4	o-ClC_6H_4	231	85

[a] All of these compounds gave elemental analysis (C, H, N, S) within ±0.30 of the calculated values. These compounds are submitted for review.

details are recorded in Table II.

Acknowledgment

We are thankful to Prof. B. M. Shukla, Head, Department of Chemistry, Banaras Hindu University, for providing necessary laboratory facilities.

Registry No. I(Ar = Ph), 39543-11-8; I(Ar = C_6H_4-*p*-Cl), 15998-34-2; II(Ar = Ph, R = H), 84119-18-6; II(Ar = R = Ph), 83490-26-0; II(Ar = Ph, R = C_6H_4-*o*-Me), 84119-19-7; II(Ar = Ph, R = C_6H_4-*m*-Me), 84119-20-0; II(Ar = Ph, R' = C_6H_4-*p*-Me), 84119-21-1; II (Ar = Ph, R = C_6H_4-*o*-OMe), 84119-22-2; II(Ar = Ph, R = C_6H_4-*p*-OMe), 84119-23-3; II(Ar = Ph, R = C_6H_4-*p*-Cl), 84119-24-4; II(Ar = Ph, R = CH_2-Ph), 84119-25-5; II(Ar = Ph, R = Bu), 84119-26-6; II(Ar = C_6H_4-*p*-Cl, R = H), 84119-27-7; II(Ar = C_6H_4-*p*-Cl, R = Ph), 84119-28-8; II(Ar = C_6H_4-*p*-Cl, R = C_6H_4-*m*-Me), 84119-29-9; II(Ar = C_6H_4-*p*-Cl, R = C_6H_4-*p*-Me), 84119-30-2; II(Ar = C_6H_4-*p*-Cl, R = C_6H_4-*o*-OMe), 84119-31-3; II(Ar = C_6H_4-*p*-Cl, R = C_6H_4-*p*-OMe), 84119-32-4; II(Ar = C_6H_4-*p*-Cl, R = C_6H_4-*m*-Cl), 84119-33-5; II(Ar = R = C_6H_4-*p*-Cl), 84119-34-6; II(Ar = C_6H_4-*p*-Cl, R = CH_2-Ph), 84119-35-7; II(Ar = C_6H_4-*p*-Cl, R = Bu), 84119-36-8; III(Ar = Ph, R' = Me), 84119-37-9; III(Ar = Ph, R' = Et), 84119-38-0; III(Ar = Ph, R' = Bu), 84119-39-1; III(Ar = R' = Ph), 84119-40-4; III(Ar = Ph, R' = C_6H_4-*o*-Me), 84119-41-5; III(Ar = Ph, R' = C_6H_4-*p*-Me), 84119-42-6; III(Ar = Ph, R' = C_6H_4-*o*-OMe), 84130-11-0; III(Ar = Ph, R' = C_6H_4-*p*-OMe), 84119-43-7; III(Ar = Ph, R' = C_6H_4-*p*-OEt), 84119-44-8; III(Ar = Ph, R' = C_6H_4-*o*-Cl), 84119-45-9; III(Ar = C_6H_4-*p*-Cl, R' = Me), 84119-46-0; III(Ar = C_6H_4-*p*-Cl, R' = Et), 84119-47-1; III(Ar = C_6H_4-*p*-Cl, R' = Bu), 84119-48-2; III(Ar = C_6H_4-*p*-Cl, R' = Ph), 84119-49-3; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*o*-Me), 84119-50-6; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*p*-Me), 84119-51-7; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*o*-OMe), 84119-52-8; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*o*-OEt), 84119-53-9; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*p*-OEt), 84119-54-0; III(Ar = C_6H_4-*p*-Cl, R' = C_6H_4-*o*-Cl), 84119-55-1; benzoyl isothiocyanate, 532-55-8; *S*-benzyl-*N*-phenylisothiourea, 28269-82-1; *S*-benzyl-*N*-(*p*-chlorophenyl)isothiourea, 39536-26-0; aniline, 62-53-3; *o*-methylaniline, 95-53-4; *m*-methylaniline, 108-44-1; *p*-methylaniline, 106-49-0; *o*-methoxyaniline, 90-04-0; *p*-methoxyaniline, 104-94-9; *p*-chloroaniline, 106-47-8; benzylamine, 100-46-9; butylamine, 109-73-9; methyl isothiocyanate, 556-61-6; ethyl isothiocyanate, 542-85-8; butyl isothiocyanate, 592-82-5; phenyl isothiocyanate, 103-72-0; *o*-methylphenyl isothiocyanate, 614-69-7; *p*-methylphenyl isothiocyanate, 622-59-3; *o*-methoxyphenyl isothiocyanate, 3288-04-8; *p*-methoxyphenyl isothiocyanate, 2284-20-0; *p*-ethoxyphenyl isothiocyanate, 3460-49-9; *o*-chlorophenyl isothiocyanate, 2740-81-0.

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Facile Synthesis of Benzimidazol-2-one Derivatives by Modified Lossen Rearrangement

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A "formamide modification" has been applied to the Lossen rearrangement of several biologically important anthranilohydroxamic acids, some of them prepared for the first time. It has been found that a short heating at temperatures in the range 130–140 °C converts these compounds into corresponding benzimidazol-2-ones with excellent yields.

Unlike the Curtius and Hofmann rearrangements, the Lossen rearrangement (*1*) has not found wide applications in organic synthesis. The reason is that two preceding steps are usually essential to this reaction: an acylation of hydroxamic acid and then conversion to a salt, which can undergo rearrangement. In the past 20 years several modifications of the Lossen rearrangement have been reported, all of them attempts, more or less successful, to improve it (*2*, *3*). We should like to report the results of our recent attempt of an "amide modification" of this reaction as applied to the rearrangement of anthranilohydroxamic acids, known for their biological activities (*4*–*6*).

Results and Discussion

Eckstein noticed (*7*) that hydroxamic acids when heated in formamide underwent Lossen rearrangement without any previous treatment. On the basis of this observation we have examined the rearrangement of anthranilohydroxamic acids

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Table I. Anthranilohydroxamic Acids 1a-h

compd	R	X	Y	yields, %	mp,[a] °C	IR (KBr), cm^{-1}	^{1}H NMR,[b] ppm
1a	H	H	H	52	144-145, 144-145 (*10*)	1640 (CO), 3390-3290 (NH, OH)	7.0 (s, 4 H, aromatic protons)
1b	CH_3	H	H	61	117-118, 111-112 (*6*)	1625 (CO), 3420-3000 (NH, OH)	6.9 (s, 4 H, aromatic protons), 2.8 (s, 3 H, CH_3)
1c	C_2H_5	H	H	50	115-116, 100-101 (*6*)	1620 (CO), 3440-3000 (NH, OH)	6.9 (s, 4 H, aromatic protons), 3.2 (q, J = 7.2 Hz, 2 H, CH_2), 1.3 (t, J = 7.2 Hz, 3 H, CH_3)
1d	H	H	Br	64	162-164, 162-165 (*12*)	1630 (CO), 3420-3280 (NH, OH)	7.5 (m, 4 H, aromatic protons)
1e	CH_3	H	Br	53	138-139	1650 (CO), 3350-3330 (NH, OH)	7.4 (m, 4 H, aromatic protons), 2.9 (s, 3 H, CH_3)
1f	H	Br	Br	68	208-209	1640 (CO), 3450-3300 (NH, OH)	7.2 (q, J = 2.4 Hz, 2 H, aromatic protons)
1g	H	H	Cl	59	148-149	1615 (CO), 3400-3300 (NH, OH)	7.3 (m, 4 H, aromatic protons)
1h	H	Cl	Cl	67	189, 190 (*13*)	1640 (CO), 3420-3300	7.4 (q, J = 2.4 Hz, 2 H, aromatic protons)

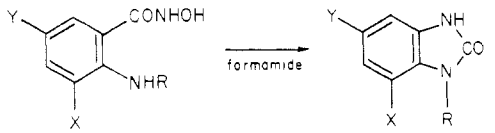
[a] Literature values in parentheses. [b] In CD_3OD.

Table II. Benzimidazol-2-ones 2a-h

compd	R	X	Y	yields, %	mp,[a] °C	IR (KBr), cm^{-1}	^{1}H NMR,[b] ppm
2a	H	H	H	99	309-310, 309-310 (*10*)	1725 (CO), 3120 (NH)	7.01 (s, 4 H, aromatic protons)
2b	CH_3	H	H	82.3	189-190, 190-191 (*14*)	1720 (CO), 3180 (NH)	7.09 (s, 4 H, aromatic protons), 3.37 (s, 3 H, CH_3)
2c	C_2H_5	H	H	81.5	117-118, 118-120 (*15*)	1715 (CO), 3150 (NH)	7.08 (s, 4 H, aromatic protons), 3.88 (q, J = 7.3 Hz, 2 H, CH_2), 1.27 (t, J = 7.3 Hz, 3 H, CH_3)
2d	H	H	Br	98.5	336-337, 336-337 (*16*)	1740 (CO), 3180-3140 (NH)	6.96 (m, 3 H, aromatic protons)
2e	CH_3	H	Br	98.5	263-264	1720 (CO), 3140 (NH)	6.96 (m, 4 H, aromatic protons), 3.25 (s, 3 H, CH_3)
2f	H	Br	Br	71.4	340	1745 (CO), 3170-3120 (NH)	7.12 (q, J = 2.1 Hz, 2 H, aromatic protons)
2g	H	H	Cl	94.2	306-307, 305 (*17*)	1735 (CO), 3180-3150 (NH)	6.96 (m, 3 H, aromatic protons)
2h	H	Cl	Cl	95.6	340, 340 (*14, 16*)	1745 (CO), 3190-3160 (NH)	7.2 (q, J = 2.1 Hz, 2 H, aromatic protons)

[a] Literature values in parentheses. [b] Compounds **2a-f** were examined in CD_3OD, and compounds **2g** and **2h** in Me_2SO-d_6.

1a-h, some of them (**1e-g**) prepared for the first time. We find that a short heating in formamide converts these compounds into the corresponding benzimidazol-2-ones (**2a-h**) almost quantitatively:



1 2

It should be noted here that in a previous report of the Lossen rearrangement of *O*-benzoylanthranilohydroxamate (*8*) the yield was unspecified and also that pyrolysis of either anthranilohydroxamic acid (*9*) or sodium anthranilohydroxamate (*8*) produces benzimidazol-2-one with a negligible yield. Among the attempts of benzimidazol-2-one synthesis by the Lossen rearrangement reported so far only one successful modification of this reaction, via *O*-sulfonyl derivatives (*10*), has been described.

It should also be mentioned that the yields of benzimidazol-2-one in the Hofmann rearrangement of anthranilamide and Curtius rearrangement of anthraniloyl azide were only 34% (*11*) and 45% (*9*), respectively.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Satisfactory elemental analyses for all examined compounds were obtained with a Perkin-Elmer 240 B analyzer. Infrared spectra were recorded as KBr pellets with a Perkin-Elmer 377 spectrophotometer. ^{1}H NMR spectra were run on a Varian A-60 spectrophotometer with Me_4Si as an internal standard. Chemical shifts are expressed in δ values.

Anthranilohydroxamic Acids 1a-h. All anthranilohydroxamic acids were prepared by the reaction of hydroxylamine chloride with the corresponding methyl or ethyl anthranilate.

Sodium methoxide, prepared from 6.9 g (0.3 g-atom) of sodium in 150 mL of methanol, was mixed with a solution of hydroxylamine hydrochloride (14.0 g, 0.2 mol) in methanol (140 mL). After 15 min the solution was filtered, 0.1 mol of the corresponding anthranilate added to the filtrate, and the mixture set aside at room temperature for 4 days. Then, when methanol had been removed under reduced pressure, the solid was dissolved in a minimum amount of water, filtered, and acidified cautiously with acetic acid. The hydroxamic acid so obtained was crystallized from water or ethanol (cf. Table I).

Rearrangement of the Anthranilohydroxamic Acids 1a-h. A sample (0.01 mol) of the chosen anthranilohydroxamic acid was heated in 20 mL of formamide to 100 °C. At this temperature the solid was all dissolved and evolution of basic gases commenced; with further heating an exothermic effect (until ca. 130 °C) was usually observed. Heating at ca. 130 °C was continued for about 20 min, until the presence of the hydroxamic acid group could not be detected by means of the ferric chloride test. The solution was cooled and the benzimidazol-2-one filtered and washed with water. Dilution of the formamide filtrate with water precipitated a small amount of benzimidazol-2-one. The precipitated solids were then recrystallized from ethanol (cf. Table II).

Registry No. **1a**, 5623-04-1; **1b**, 20885-65-8; **1c**, 20885-66-9; **1d**, 28230-35-5; **1e**, 84712-05-0; **1f**, 84712-06-1; **1g**, 84712-07-2; **1h**, 1130-71-8; **2a**, 615-16-7; **2b**, 1849-01-0; **2c**, 10045-45-1; **2d**, 39513-26-3; **2e**, 84712-08-3; **2f**, 84712-09-4; **2g**, 2034-23-3; **2h**, 39513-29-6; hydroxylamine hydrochloride, 5470-11-1.

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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 hydrazonyl 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-chlorobenzylidenephenylhydrazine with various dipolarophiles have been well documented in the literature (*7-9*), cycloaddition reactions of *C*-ethoxycarbonyl and *C*-acetyl derivatives of hydrazonyl bromides particularly with α,β-unsaturated carbonyl compounds have not been reported so far. In view of the ability of hydrazonyl 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 hydrazonyl 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.

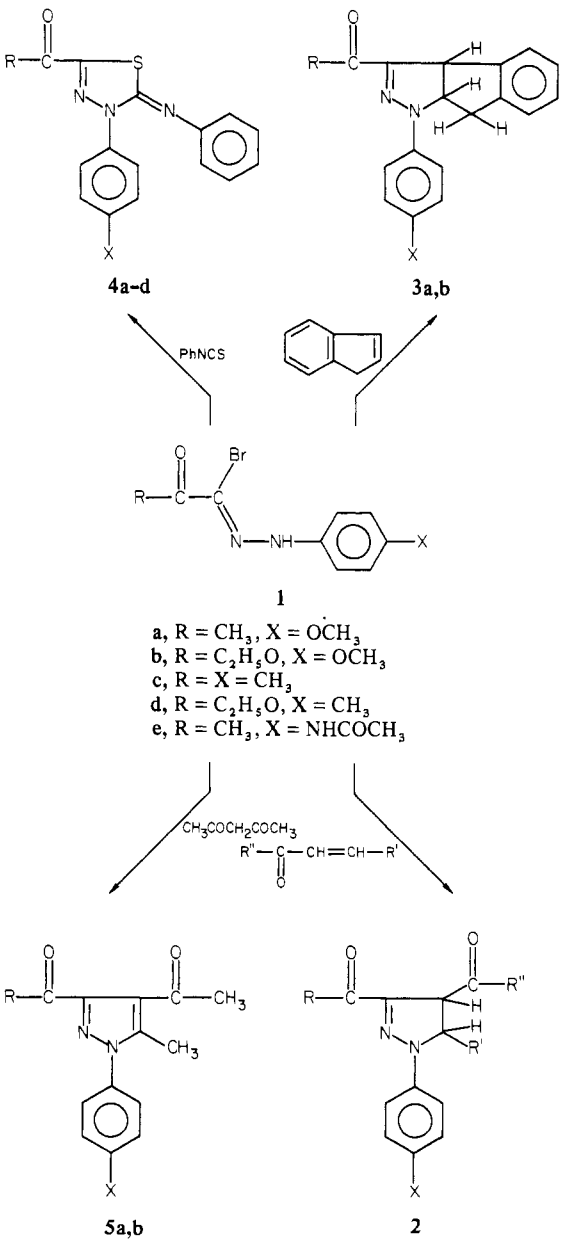
Experimental Section

All the reagents were obtained from commercial sources (BDH, E. Merck, and S. Merck). Hydrazonyl 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 Me_4Si 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 hydrazonyl 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



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