extracted with a mixture of ether–benzene. The extract was evaporated and a red residue was crystallized; 1.1 g of product was obtained.

***Dimethyl 2-[(Methoxycarbonyl)amino]-2,3-dihydrobenzimidazole-1,3-dicarboxylate* (5‴).** A 5-g sample of **4** was added to 50 cm^3 of methyl chloroformate. The reagents were boiled at 69 °C for 5 h. A brown precipitate was filtered, the methyl chloroformate was evaporated, and 5.4 g of a dry residue was obtained.

***2-[(Phenylthiocarbamoyl)amino]-2,3-dihydrobenzimidazole-1,3-dicarbothioamide* (6).** A 8.35-g sample of **1** and 15 g of potassium phthalimide were mixed in a porcelain mortar. The reagents were heated at 200 °C for 2 h. The product was cooled and dissolved in 100 cm^3 of methanol, and 10 cm^3 of 80% aqueous hydrazine was added. The reagents were stirred under reflux for 3 h. The precipitate was filtered and the filtrate was neutralized with KOH. The filtrate was extracted with a mixture of ether–benzene and reextracted with water. The water solution was treated with 10 g of phenyl thioisocyanate and heated and intensively stirred. After 2 h a few drops of emulsion were transferred into green solid product.

Registry No. **1**, 85354-90-1; **2**, 85355-01-7; **3**, 85354-91-2; **4**, 85354-92-3; **5**, 85354-93-4; **5′**, 86834-46-0; **5‴**, 85354-94-5; **6**, 85354-95-6; NH_3, 7664-41-7; *o*-phenylenediamine, 95-54-5; chloroform, 67-66-3; *o*-phenylenediamine dihydrochloride, 615-28-1; potassium phthalimide, 1074-82-4; hydrazine, 302-01-2; methyl chloroformate, 79-22-1; phenyl isothiocyanate, 103-72-0.

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Reaction of 4,6-Diarylhexahydro-1,3,5-triazine-2-thiones with α-Haloketones. 3

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4,6-Diarylhexahydro-*s*-triazine-2-thiones reacted with α-haloketones to give the S-substituted derivatives, which were cyclized to substituted thiazolo[3,2-*a*]-*s*-triazines. 7-(3-Aryl-2-propenoyl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-*a*]-*s*-triazines were prepared and their behavior toward amine derivatives and benzamidine was investigated.

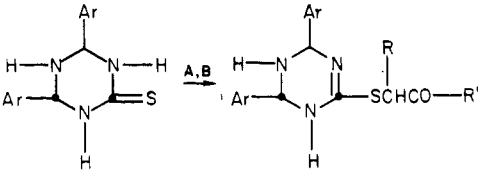
In continuation of my previous work on the reaction of triazinethiones (*1*, *2*), I report here on the reaction of triazinethiones with α-haloketones.

Experimental Section

Satisfactory elemental analyses were found.

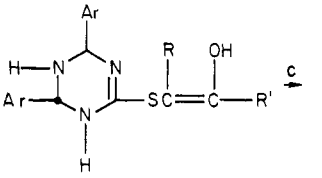
***4,6-Diaryl-3,4,5,6-tetrahydro-2-(phenacylthio)-1,3,5-triazines* (*IIa,b,d,e,g,h*).** A solution of about 1 g of Ia–c in 25 mL of ethanol, to which 3 mL of 10% sodium hydroxide solution had been added, was treated with an equimolecular quantity of the phenacyl bromide, refluxed for 2 h, and left overnight. The precipitate was collected and crystallized (see Table I).

***4,6-Diaryl-3,4,5,6-tetrahydro-2-(2,4-dioxopent-3-ylthio)-1,3,5-triazines* (*IIc,f,i*).** A mixture of 0.1 mol of I in 200 mL of ethanol and 5.6 g (0.1 mol) of 85% potassium hydroxide was heated at 70–80 °C for 10 min. After the resulting solution was cooled to 30 °C, 13.45 g (0.1 mol) of α-chloroacetylacetone was added in one portion. An exothermic reaction set in causing a temperature rise from 30 to 40 °C. The reaction mixture was stirred at room temperature for 18 h and added to 200 g of ice water. The precipitates which formed by stirring were collected by filtration, washed with water, and crystallized (see Table I). The IR spectrum of IIc shows an absorption band at 1705 cm^{-1} (CO) and a broad band at 3100 cm^{-1} (NH and OH) while the IR spectrum of IIa shows only a broad band at 3050 cm^{-1} (NH and OH). Compounds II give a deep color with ferric chloride solution. Compounds II exist in the enolic form II′.

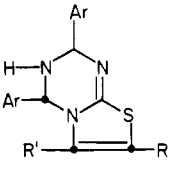


Ia, Ar = C_6H_5
b, Ar = $C_6H_4OCH_3$-*p*
c, Ar = C_6H_4Cl-*p*

II



II′



III

II, IIIa, Ar = C_6H_5; R = H; R′ = C_6H_5
b, Ar = C_6H_5; R = H; R′ = $C_6H_4CH_3$-*p*
c, Ar = C_6H_5; R = $COCH_3$; R′ = CH_3
d, Ar = $C_6H_4OCH_3$-*p*; R = H; R′ = C_6H_5
e, Ar = $C_6H_4OCH_3$-*p*; R = H; R′ = $C_6H_4CH_3$-*p*
f, Ar = $C_6H_4OCH_3$-*p*; R = $COCH_3$; R′ = CH_3
g, Ar = C_6H_4Cl-*p*; R = H; R′ = C_6H_5
h, Ar = C_6H_4Cl-*p*; R = H; R′ = $C_6H_4CH_3$-*p*
i, Ar = C_6H_4Cl-*p*; R = $COCH_3$; R′ = CH_3

A = phenacyl bromides
B = α-chloroacetylacetone
C = polyphosphoric acid

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Table I. (Phenacylthio)triazines and (Dioxopentylthio)triazines (II)

compd	mp, °C	solvent[a]	yield, %
IIa	165	E	73
b	142	E	76
c	126	dil E	70
d	157	A	82
e	121	A	68
f	118	E	65
g	167	dil A	77
h	151	E	69
i	133	E	61

[a] E = ethanol; A = acetic acid.

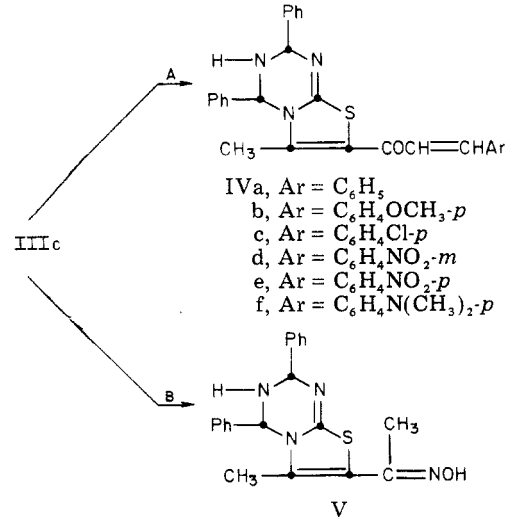
Table II. Thiazolo[3,2-*a*]-*s*-triazines (III)[a]

compd	mp, °C	solvent[b]	yield, %
IIIa	245	A	74
b	234	E	67
c	205	A	60
d	226	A	78
e	220	A	82
f	201	E	57
g	238	dil A	64
h	229	E	66
i	212	dil A	52

[a] Satisfactory elemental analyses were found. [b] E = ethanol; A = acetic acid.

Thiazolo[3,2-a]-s-triazines (III). A suspension of 2 g of II and 10 g of polyphosphoric acid (prepared by dissolving 5 g of phosphorus pentoxide in 5 mL of orthophosphoric acid) was heated at 100 °C for 1 h and then at 120 °C for 15 min. The solution was left to cool, poured into ice water, and stirred. The solids that separated were collected and crystallized from the proper solvent (see Table II). The IR spectrum of IIIc shows an absorption band at 1680 cm^{-1} (=CH—CO). The ^1H NMR of IIIa (in trifluoroacetic acid (TFA)) showed the two CH protons as a singlet at δ 4.2 (2 H), the =CH proton as a singlet at δ 6.15 (1 H), the NH proton as a singlet at δ 9.45 (1 H), and the aromatic protons as a multiplet in the δ 7.45–8.25 region.

7-(3-Aryl-2-propenoyl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-a]-s-triazines (IV). A mixture of 3.5 g (0.01 mol) of IIIc and the appropriate amount of aldehyde (0.015 mol) in the presence of catalytic piperidine was heated at 160 °C for 30 min, cooled, and triturated with ethanol. The precipitate obtained was filtered and crystallized (see Table III). The IR spectrum of compound IVa shows absorption at 1680 cm^{-1} (C=O). The ^1H NMR of IVa (in TFA) showed the two CH protons as a singlet at δ 4.1 (2 H), the CH_3 protons as a singlet at δ 2.15, the CH=CH protons as a multiplet at δ 5.07 and 6.1, and the aromatic protons as a multiplet in the δ 7.5–8.25 region.



IVa, Ar = C_6H_5
b, Ar = $C_6H_4OCH_3$-*p*
c, Ar = C_6H_4Cl-*p*
d, Ar = $C_6H_4NO_2$-*m*
e, Ar = $C_6H_4NO_2$-*p*
f, Ar = $C_6H_4N(CH_3)_2$-*p*

V

A = aldehydes
B = hydroxylamine hydrochloride

Table III. 7-(Arylpropenoyl)thiazolo[3,2-*a*]-*s*-triazines (IV)[a]

compd	mp, °C	solvent[b]	yield, %
IVa	250	A	70
b	244	A	72
c	239	E	66
d	262	D	67
e	253	D	73
f	225	E	62

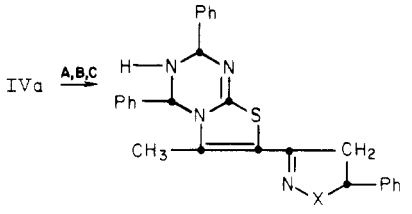
[a] Satisfactory elemental analyses were found. [b] A = acetic acid; E = ethanol; D = dioxane.

7-Acetyl-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo-[3,2-a]-1,3,5-triazine Oxime (V). A solution of 1.75 g (0.005 mol) of IIIc and 0.35 g (0.005 mol) of hydroxylamine hydrochloride in 25 mL of glacial acetic acid was refluxed for 30 min. The solid formed by cooling was collected and crystallized from nitrobenzene to give V: mp 210 °C; yield 58%. The ^1H NMR of V (in TFA) showed the two methyl groups as two singlets at δ 2.15 (3 H) and δ 2.82 (3 H), the two CH protons as a singlet at δ 4.15, the OH proton at δ 2.45, and the aromatic protons as a multiplet in the δ 7.45–8.15 region (10 H).

7-(5-Phenyl-Δ²pyrazolin-3-yl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-a]-1,3,5-triazine (VIa). A mixture of 2.18 g (0.005 mol) of IVa and 0.5 mL of hydrazine hydrate (98%) in 20 mL of dioxane was heated to boiling and left overnight. The pale yellow precipitate formed was collected and crystallized from ethanol: mp 227 °C; yield 67%.

7-(1,5-Diphenyl-Δ²-pyrazolin-3-yl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-a]-1,3,5-triazine (VIb). This compound was prepared as above by replacing the hydrazine hydrate with phenylhydrazine and crystallizing from acetic acid: mp 215 °C; yield 70%.

7-(5-Phenyl-Δ²-isoxazolin-3-yl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-a]-s-triazine (VIc). A mixture of 0.005 mol of IVa and 0.005 mol of hydroxylamine hydrochloride in 20 mL of dioxane containing about 0.4 g of sodium hydroxide was refluxed for 6 h and left overnight. The separated product was filtered off and crystallized from dimethylformamide: mp 230 °C; yield 72%. Structures VI are established on the basis



VIa, X = NH
b, X = NNH-C_6H_5
c, X = O

A = hydrazine hydrate
B = phenylhydrazine
C = hydroxylamine hydrochloride

of the following facts: (a) correct values in elemental analysis, (b) the absence of any absorption in the carbonyl region in the IR spectra of VIa–c, (c) compounds VIa,b giving a color test characteristic of arylpyrazolines (*3*, *4*). The ^1H NMR of VIa (in TFA) showed the CH_3 protons as a singlet at δ 2.15 (3 H), the CH_2 protons as a singlet at δ 5.25 (2 H), the three CH protons as a singlet at δ 4.2 (3 H), the two NH protons as a singlet at δ 9.45 (2 H), and the aromatic protons as a multiplet

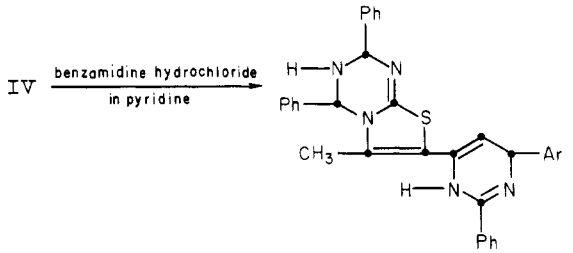
Table IV. 7-(4-Aryl-2-phenylpyrimidinyl)thiazolo-*s*-triazines (VII)

compd	mp, °C	solvent[a]	yield, %
VIIa	232	A	73
b	219	N	65
c	224	A	68
d	237	D	61
e	213	E	77

[a] A = acetic acid; N = nitrobenzene; D = dioxane; E = ethanol.

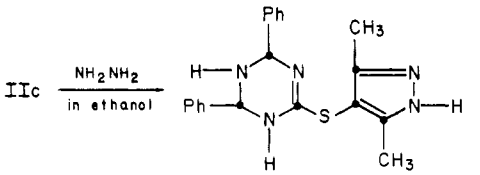
in the δ 7.5–8.25 region (15 H).

7-(4-Aryl-4,5-dihydro-2-phenylpyrimidin-6-yl)-6-methyl-2,4-diphenyl-2,3,4-trihydrothiazolo[3,2-a]-1,3,5-triazines (VII). A solution of IV (0.01 mol) and benzamidine hydrochloride (0.01 mol) in pyridine (20 mL) was heated under reflux for 6 h and left overnight. The separated substances were filtered and crystallized (see Table IV). The IR spectrum of VII shows an absorption band at 3200 cm^{-1} (NH).



VIIa, Ar = C_6H_5
b, Ar = $C_6H_4OCH_3$-*p*
c, Ar = C_6H_4Cl-*p*
d, Ar = $C_6H_4NO_2$-*m*
e, Ar = $C_6H_4N(CH_3)_2$-*p*

2-(3,5-Dimethylpyrazol-4-ylthio)-4,6-diphenyl-3,4,5,6-tetrahydro-1,3,5-triazine (VIII). To a solution of IIc (0.005 mol) in ethanol (20 mL), hydrazine hydrate (98%, 0.5 mL) was added and the reaction mixture was refluxed for 3 h and left to cool; compound VIII was separated, filtered off, and crystallized from acetic acid: mp 206 °C; yield 65%. The IR spectrum of VIII shows a broad band at 3200 cm^{-1} (3 NH). The ^1H NMR of compound VIII showed the methyl groups as two singlets at δ 2.35 (3 H) and δ 2.85 (3 H), the =CH proton at δ 6.15 (1 H), the two CH protons as a singlet at δ 4.2 (2 H), the three NH protons at δ 9.5 (3 H), and the aromatic protons as a multiplet in the δ 7.45–8.15 region (10 H).



VIII

Registry No. Ia, 61582-10-3; Ib, 61582-11-4; Ic, 87102-21-4; II'a, 87102-22-5; II'b, 87102-23-6; II'c, 87102-24-7; II'd, 87102-25-8; II'e, 87102-26-9; II'f, 87102-27-0; II'g, 87102-28-1; II'h, 87102-29-2; II'i, 87102-30-5; IIIa, 87102-31-6; IIIb, 87102-32-7; IIIc, 87102-33-8; IIId, 87102-34-9; IIIe, 87102-35-0; IIIf, 87102-36-1; IIIg, 87114-29-2; IIIh, 87102-37-2; IIIi, 87102-38-3; IVa, 87102-39-4; IVb, 87102-40-7; IVc, 87102-41-8; IVd, 87102-42-9; IVe, 87102-43-0; IVf, 87102-44-1; V, 87102-45-2; VIa, 87102-46-3; VIb, 87102-47-4; VIc, 87102-48-5; VIIa, 87114-30-5; VIIb, 87114-31-6; VIIc, 87135-99-7; VIId, 87114-32-7; VIIe, 87114-33-8; VIII, 87102-49-6; C_6H_5CHO, 100-52-7; *p*-$CH_3OC_6H_4CHO$, 123-11-5; *p*-ClC_6H_4CHO, 104-88-1; *m*-$NO_2C_6H_4CHO$, 99-61-6; *p*-$NO_2C_6H_4CHO$, 555-16-8; *p*-$(CH_3)_2NC_6H_4CHO$, 100-10-7; H_2NNH_2, 302-01-2; phenacyl bromide, 70-11-1; *p*-methylphenacyl bromide, 619-41-0; α-chloroacetylacetone, 1694-29-7; phenylhydrazine, 100-63-0; hydroxylamine hydrochloride, 5470-11-1; benzamidine hydrochloride, 1670-14-0.

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Activated Nitriles in Heterocyclic Synthesis. Synthesis of Several New Pyrimidine and Pyridazine Derivatives

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Several new pyrimidine, pyridazine, and pyridine derivatives were obtained from 2-(ethoxycarbonyl)-3-aminopentenedinitrile (I) as starting component.

Malononitrile, ethyl cyanoacetate, and their derivatives are among the most commonly utilized intermediates in heterocyclic synthesis (*1*, *2*). Recently, Junek et al., (*3*) have reported the formation of 2-(ethoxycarbonyl)-3-aminopentenedinitrile (I) via simple addition of ethyl cyanoacetate to malononitrile. This product seemed to be an excellent candidate for utility in heterocyclic synthesis. In conjunction with our interest in the utility of activated nitriles in heterocyclic synthesis (*4*, *5*) we report here the utility of I for preparation of a variety of polyfunctionally substituted heterocyclic derivatives of potential synthetic and biological importance. Thus, it has been found that I coupled with benzenediazonium chloride to yield the hydrazone II. Compound II, cyclized into the diacetyl derivative III on refluxing with acetic anhydride. Compound IV was obtained on refluxing II in acetic acid.

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