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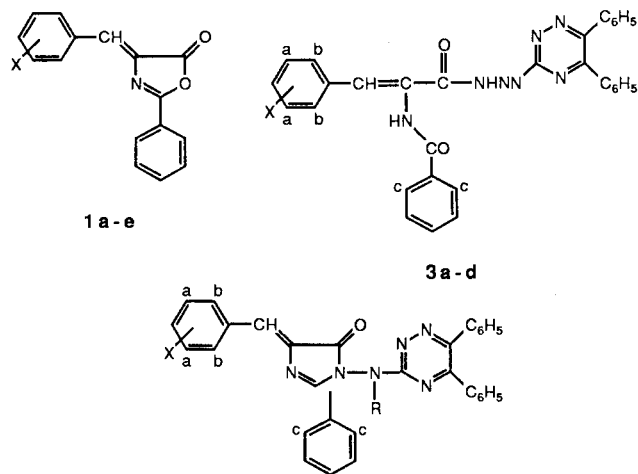
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3-Hydrazino-5,6-diphenyl-1,2,4-triazine reacts with 4-arylidene-2-phenyl-5(4*H*)-oxazolones in toluene to give substituted acrylic acid hydrazides, and in glacial acetic acid to give substituted imidazolones. On the other hand the hydrazinotriazine reacts with 4-benzylidene-3-methyl-5(4*H*)-isoxazolone, probably *via* a 1,4 addition reaction followed by an elimination reaction, to give benzaldehyde 5,6-diphenyl-1,2,4-triazin-3-ylhydrazone and 3-methyl-5(4*H*)-isoxazolone.

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Studies on 1,2,4-triazines reveal that some of these compounds are biologically active [1-10]. In continuation of our previous work in this field, now we have synthesized some new acrylic acid and imidazolone derivatives containing a 1,2,4-triazine moiety. Thus, 4-arylidene-2-phenyl-5(4*H*)-oxazolones **1a-e** were treated with 3-hydrazino-5,6-diphenyl-1,2,4-triazine (**2**) in toluene to give the hydrazides **3a-d** and the imidazolone **4e** respectively. When the reaction was conducted in glacial acetic acid the imidazolones **4a-e** were obtained, presumably *via* the intermediate hydrazides **3a-c**. This presumption was confirmed by the ready conversion of compounds **3a-c** to **4a-c** when the former compounds were heated either in glacial acetic acid or hydrochloric acid. Heating compound **4a** with acetic anhydride and anhydrous sodium acetate gave the *N*-acetyl derivative **4f**. Attempts to affect cyclization and concurrent acetylation of compound **3a** to **4f** failed; instead, the oxazolone **1a** was obtained. Heating compound **3a** with acetic anhydride alone gave, also, the same oxazolone **1a**.



**4a-e**; R = H; **f**, X = H; R = COCH<sub>3</sub>  
**a**, X = H; **b**, X = OCH<sub>3</sub>-*p*; **c**, X = OCH<sub>3</sub>-*o*;  
**d**, X = (OCH<sub>3</sub>)<sub>2</sub>-3,4; **e**, X = Cl-*p*

The structures of the hydrazides **3a-d** and the imidazolones **4a-f** are proposed from the following facts: (1) The compounds give the corresponding correct analytical values. (2) Treatment of each of compounds **3a,b** in glacial acetic acid with sodium nitrite affords the oxazolones **1a,b** respectively. (3) The infrared absorption spectra of the hydrazides **3a-d** show NH and amide C=O absorption bands; the imidazolones **4a-e** show NH absorption bands and C=O absorption of a five-membered lactam ring. Compound **4f** shows no absorption band in the NH region, meanwhile a broad C=O absorption band is clear (Table). (4) The <sup>1</sup>H nmr spectra of compounds **3b**, **4a**, **4b** and **4f** are in good agreement with the assigned structures:

**Compound 3b.**

This compound had <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): δ 3.75 (s, 3H, OCH<sub>3</sub>), 6.9 (d, 2H, H<sub>a</sub>), 7.3-7.7 (m, 14H, 13 arom and 1 vinylic), 7.95-8.1 (m, 4H, H<sub>b</sub>, H<sub>c</sub>) and 9.7-10.4 (br m, 3H, NH's) ppm.

**Compound 4a.**

This compound had <sup>1</sup>H nmr (deuteriochloroform): δ 7.25-7.5 (m, 17H, 16 arom and 1 vinylic), 8.1-8.35 (m, 5H, 1H, NH, 2H<sub>b</sub> and 2H<sub>c</sub>) ppm.

**Compound 4b.**

This compound had <sup>1</sup>H nmr (deuteriochloroform): δ 3.9 (s, 3H, OCH<sub>3</sub>), 7 (d, 2H, H<sub>a</sub>), 7.3-7.5 (m, 14H, 13 arom and 1 vinylic), 7.95 (s, 1H, NH), 8.2-8.3 (d, 2H, H<sub>b</sub> and 2H, H<sub>c</sub>) ppm.

**Compound 4f.**

This compound had <sup>1</sup>H nmr (deuteriochloroform): δ 2.8 (s, 3H, COCH<sub>3</sub>), 7.35 (m, 17H, 16 arom and 1 vinylic), 7.85-8.2 (m, 2H, H<sub>a</sub>, m, 2H, H<sub>c</sub>) ppm.

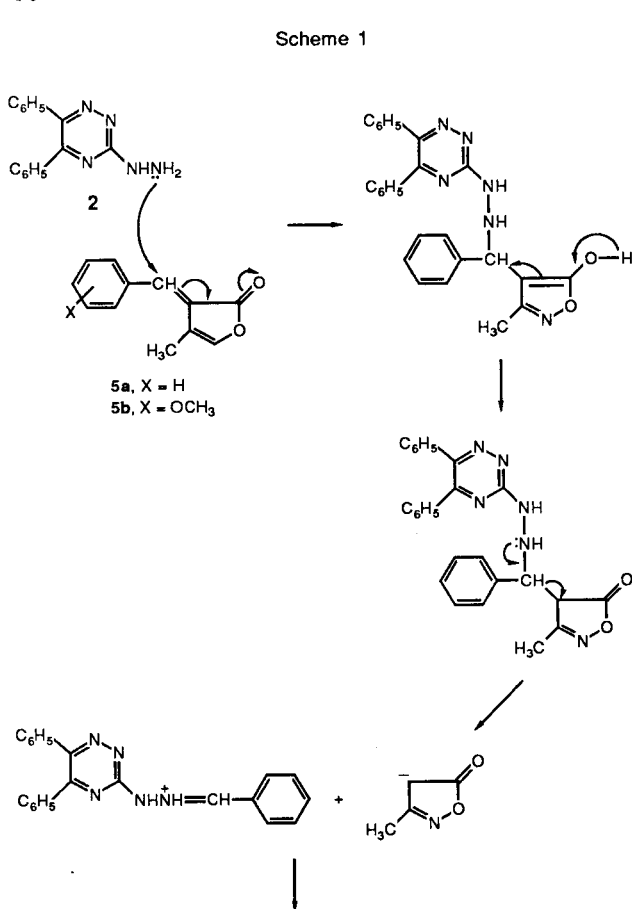
In contrast to the behavior of the oxazolones **1a-d** towards the action of compound **2** which affects ring opening to give the hydrazides **3a-d**, we found that compound **2** reacts with 4-benzylidene-3-methyl-5(4*H*)-isoxazolone (**5a**) [11] in toluene, under the same conditions, to give the

Table

Compound	Mp °C	Yield %	Formula (MW)	Analysis %			ir (potassium bromide) cm <sup>-1</sup>	
				Calcd./Found C	H	N	NH	C=O
<b>3a</b>	215	60	C <sub>31</sub> H <sub>24</sub> N <sub>6</sub> O <sub>2</sub> (512.57)	72.64	4.72	16.40	3220 (br)	1660, 1690
				72.49	4.71	16.12		
<b>3b</b>	235	63	C <sub>32</sub> H <sub>26</sub> N <sub>6</sub> O <sub>3</sub> (542.59)	70.83	4.83	15.49	3300, 3380	1655, 1675
				70.61	5.12	15.64		
<b>3c</b>	218	71	C <sub>32</sub> H <sub>26</sub> N <sub>6</sub> O <sub>3</sub> (542.59)	70.83	4.83	15.49	3260 (br)	1660, 1680
				70.50	4.87	15.72		
<b>3d</b>	239	77	C <sub>33</sub> H <sub>28</sub> N <sub>6</sub> O <sub>4</sub> (572.62)	69.21	4.92	14.67	3310, 3360	1650, 1675
				69.20	4.67	14.92		
<b>4a</b>	267-268	66	C <sub>31</sub> H <sub>22</sub> N <sub>6</sub> O (494.55)	75.28	4.48	16.99	3220 (br)	1700, 1725
				75.54	4.72	16.76		
<b>4b</b>	247	71	C <sub>32</sub> H <sub>24</sub> N <sub>6</sub> O <sub>2</sub> (524.58)	73.26	4.61	16.02	3200 (br)	1710
				73.55	4.91	16.22		
<b>4c</b>	275	82	C <sub>32</sub> H <sub>24</sub> N <sub>6</sub> O <sub>2</sub> (524.58)	73.26	4.61	16.02	3200 (br)	1710 (br)
				73.52	4.93	16.13		
<b>4d</b>	245	79	C <sub>33</sub> H <sub>26</sub> N <sub>6</sub> O <sub>3</sub> (554.61)	71.46	4.72	15.15	3200 (br)	1710
				71.56	4.89	14.92		
<b>4e [a]</b>	256	69	C <sub>31</sub> H <sub>21</sub> N <sub>6</sub> OCl (529.00)	70.38	4.00	15.88	3200 (br)	1710, 1730
				70.08	4.01	15.65		
<b>4f</b>	188	81	C <sub>33</sub> H <sub>24</sub> N <sub>6</sub> O <sub>2</sub> (536.59)	73.86	4.51	15.66	—	1730 (br)
				73.55	4.75	15.35		

[a] Cl, Calcd: 6.70. Found: 6.42%.

Scheme 1



hydrazone **6** and 3-methyl-5(4H)-isoxazolone (**7**) identified as its 4-*p*-methoxybenzylidene derivative **5b** [11]. This suggests that the reaction takes place by 1,4 addition followed by elimination according to Scheme 1.

#### EXPERIMENTAL

All melting points are uncorrected. The ir spectra (potassium bromide) were recorded with a Unicam SP 1200 infrared spectrophotometer. The <sup>1</sup>H nmr spectra were recorded with a Varian EM 360 A spectrometer or a Varian A 60 spectrometer.

2-(5,6-Diphenyl-1,2,4-triazin-3-yl)- $\alpha$ -benzoylamino- $\beta$ -arylacrylhydrazides **1a-d**.

A mixture of each of the 4-arylidene-2-phenyl-5(4H)-oxazolones **1a-d** (0.004 mole) and 3-hydrazino-5,6-diphenyl-1,2,4-triazine (**2**) (0.004 mole) in toluene (25 ml) was heated under reflux for 2½ hours. After cooling, the precipitates formed were collected and crystallized from ethanol into colorless crystals of **2a-d** (Table).

1-(5,6-Diphenyl-1,2,4-triazinyl-3-amino)-4-arylidene-2-phenylimidazolin-5-ones **4a-e**.

A mixture of the oxazolones **1a-e** (0.004 mole) and the hydrazinotriazine **2** (0.004 mole) in glacial acetic acid (20 ml) was heated under reflux for 1 hour. After cooling, the precipitates formed were collected and recrystallized from glacial acetic acid into yellow crystals of **4a-e** (Table). Compound **4e** was also obtained when the oxazolone **1e** (0.004 mole) and compound **2** (0.004 mole) in toluene (25 ml) was heated under reflux for

2½ hours. The precipitate formed after cooling was crystallized from acetic acid into yellow crystals of **4e**, mp 256°, yield ca. 61%, mixed mp with **4e** obtained before showed no depression.

Cyclization of the Hydrazides **3a-c** to the Imidazolones **4a-c**.

Method (i).

Each of the hydrazides **1a-c** (0.005 mole) in glacial acetic acid (10 ml), was heated under reflux for 4 hours. The precipitates formed after cooling were collected and crystallized from acetic acid into yellow crystals of the imidazolones **4a-c** identical with compounds **4a-c** obtained before (mps and mixed mps showed no depression), yields ca. 35, 60, and 75% respectively.

Method (ii).

The hydrazide **3a** (0.0005 mole) was heated with hydrochloric acid (10 ml concentrated hydrochloric and 15 ml water) under reflux for 45 minutes. After cooling, the yellow precipitate obtained was crystallized from ethanol into yellow crystals of **4a**, mp 268°, yield ca. 82%. Mixed mp with compound **4a** obtained before showed no depression.

Action of Acetic Anhydride on the Hydrazide **3a**.

Acetic anhydride (5 ml) was added to compound **3a** (0.0004 mole) and the reaction mixture was boiled under reflux for 2 hours. It was, then poured into cold water and allowed to stand for 2 hours. The precipitate formed was collected and crystallized from ethanol into pale yellow crystals of **1a**, mp 165-166°. Mixed mp with an authentic sample showed no depression.

Action of Acetic Anhydride and Anhydrous Sodium Acetate on the Hydrazides **3a-c**.

A mixture of each of the hydrazides **3a-c** (0.002 mole), anhydrous sodium acetate (0.1 g) and acetic anhydride (4 ml) was heated under reflux for 5 minutes. The reaction mixture which darkened on boiling, soon became clear and colorless. It was then poured into water to give the oxazolones **1a-c**, identified by mps and mixed mps with authentic samples, yields ca. 54, 56, and 58% respectively.

Action of Nitrous Acid on the Hydrazides **3a-c**.

A suspension of each of compounds **3a-c** (0.002 mole) in glacial acetic acid (10 ml) was treated with sodium nitrite (0.2 g) portionwise, at room temperature. The reaction mixture was allowed to stand at room temperature overnight. The oxazolones which separated were collected and identified as before, yields ca. 30, 27 and 32% respectively.

Acetylation of Compound **4a**.

A mixture of compound **4a** (0.2 g), anhydrous sodium acetate (0.2 g) and acetic anhydride (5 ml) was heated under reflux for 2 hours. It was then cooled and poured into water. The precipitate formed was collected and crystallized from ethanol into yellow crystals of compound **4f** (Table).

Action of Compound **2** on 4-Benzylidene-3-methyl-5(4*H*)-isoxazolone (**5a**) [11].

A mixture of compound **2** (0.001 mole) and the isoxazolone **5a** (0.001 mole) in toluene (15 ml), was heated under reflux for 15 minutes. The yellow solid obtained was identified as benzaldehyde (5,6-diphenyl-1,2,4-triazin-3-yl)hydrazone **6**, mp 256°, yield ca. 64%. Mixed mp with an authentic sample showed no depression [12]. The filtrate was treated with *p*-methoxybenzaldehyde (0.13 g), heated under reflux for 20 minutes and concentrated to a sticky residue which solidified on cooling. This was crystallized from ethanol and identified as 4-(*p*-methoxybenzylidene)-2-methyl-5(4*H*)-isoxazolone (**5b**), mp 174°. Mixed mp with an authentic sample showed no depression [11].

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