REACTION OF 3-HYDRAZINOACENAPHTHENO[1,2-*e*][1,2,4]TRIAZINE WITH FUNCTIONALIZED CARBONYL COMPOUNDS

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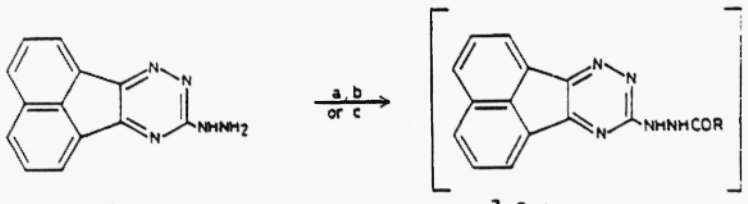
Abstract: The 10-substituted acenaphtheno[1,2-*e*][1,2,4]triazolo[4,3-*b*][1,2,4]triazines were prepared by the reaction of 3-hydrazinoacenaphtheno[1,2-*e*][1,2,4]triazine (**1**) with carboxylic acids. The respective [3,4-*c*] analogue could be prepared by the oxidative cyclization of the aldehyde derivatives of **1**. Reaction of **1** with acetylacetone and ethylacetoacetate gave the respective biheterocycle containing the pyrazole and pyrazolone rings respectively; the intermediate hydrazone could be isolated in the later case. Reactions of **1** with isatin, 5-methylisatin, acenaphthenequinone, glyoxal, ethylchloroformate, pyruvic acid, ethyloxalate as well as nitrous acid have been investigated. The regioselectivity for the reaction of hydrazine with **37** and **38** has been studied.

Acenaphthenequinone and its amine derivatives were reported to have bactericidal and fungicidal activities [1,2]. Its hydrogen sulfite inhibited the growth of transplanted tumors [3]. Condensed heterocycles with the acenaphthylene ring system provide heterocycles with various biological activities such as lowering the activity of the central nervous system [4].

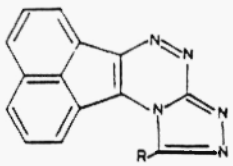
1,2,4-Triazines have various biological activities [5-10] in addition to its suitability as a carrier for moieties of particular properties. In a previous publication [11], we reported on the synthesis of the acyclic *C*-nucleoside analogues derived from 3-hydrazinoacenaphtheno[1,2-*e*][1,2,4]triazine (**1**). In the present work, the reaction of **1** with mono- and bifunctional compounds has been investigated.

The reaction of **1** with triethylorthoformate or formic acid has been anticipated to be a route to the synthesis of one or both of the isomeric ring systems **4** and/or **7**. When the hydrazine **1** was allowed to react with triethylorthoformate, the product was found to be identical with that obtained from the reaction of **1** with formic acid at room temperature or under reflux for two hours [12], and it was identified as **4**. Since, treatment of **4** by acid may cause a Dimroth type rearrangement and the condition of cyclization by triethylorthoformate did not cause such type of rearrangement, the product **4** was subjected to the action of acid or alkali. However, no such rearrangement had taken place. This means that the ring of **4** is stable towards acid or alkali and that was the reason that formic acid afforded identical product with that obtained from triethylorthoformate. Furthermore, when **1** was allowed to react with acetic anhydride or acetic acid either at room temperature or by boiling the product was found to be the same. It was identified as **5** by its identity with an authentic sample prepared by an unequivocal synthesis [11]. Surperisingly, the amides **2** or **3** could not be isolated under any of these conditions. Moreover, the isomeric structures **7** and **8** were ruled out for such products as

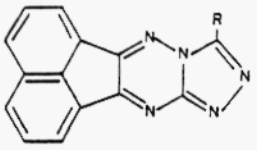


1

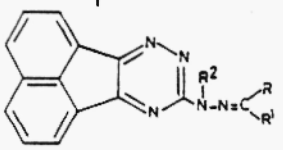
2 R = H
3 R = Me.



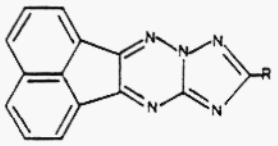
7 R = H
8 R = Me
9 R = Ph



4 R = H
5 R = Me
6 R = Ph

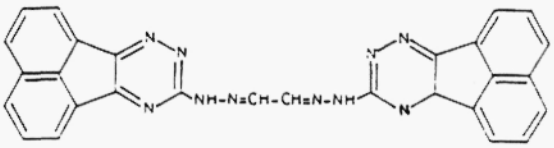


10 R = H, R¹ = Ph, R² = H
11 R = R¹ = Me, R² = H
12 R = H, R¹ = CHO, R² = H
13 R = Ph, R¹ = COPh, R² = H
14 R = H, R¹ = Ph, R² = Ac

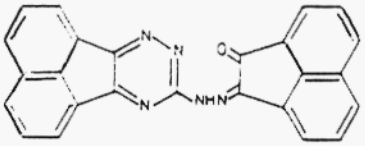


15 R = H
16 R = Me

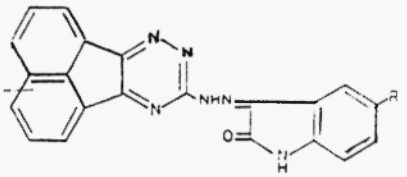
a) HCOOH; b) AcOH; c) $HC(OEt)_3$; d) heat; e) NaOH; f) $FeCl_3$



17



18



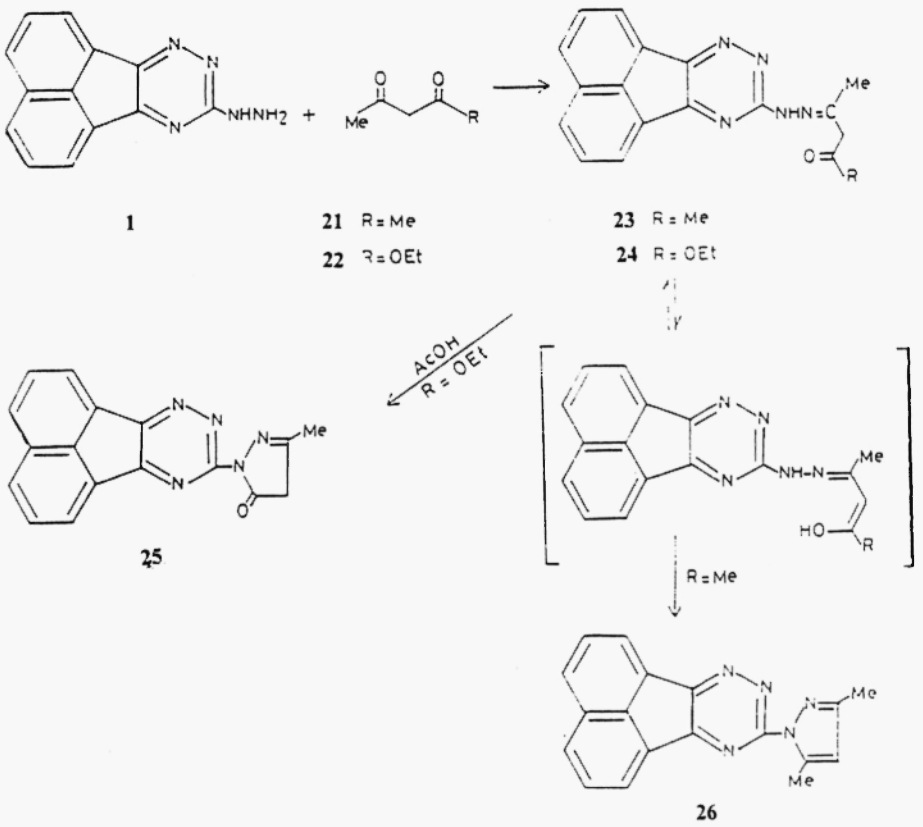
19 R = H
20 R = Me

the latter was prepared [11] by the oxidation cyclization of the respective acetaldehyde derivative of **1**. The benzaldehyde derivative **10** could be oxidatively cyclized by the action of ferric chloride to give **9**. Reaction of **1** with mono and dicarbonyl compounds, acetone, benzil, acenaphthenequinone, isatin and 5-methylisatin gave the respective monohydrazones **11**, **13**, **18**, **19** and **20**. On the other hand, glyoxal gave the *bis*(hydrazone) **17**, which it was alternatively prepared by the reaction of **1** with **12**.

Reaction of hydrazine **1** with ethylacetoacetate gave the hydrazone **24** which showed infrared absorptions characteristic for the NH and the ester carbonyl group indicating that the structure is **24** and not the reported [12] cyclized pyrazolone **25**. The ^{1}H nmr of **24** confirmed the assigned structure where signals for the ethyl ester group appeared at δ 1.30 and 4.20 as triplet and quartet respectively. Moreover, heating of **24** in presence of acetic acid caused its cyclization to give **25** whose infrared spectrum revealed the absence of the ester carbonyl amide band. Its ^{1}H nmr also confirmed the absence of resonances of the ethyl group and showed the presence of two singlets at δ 2.18 and 3.58 due to the methyl and methylene groups. The cyclization of the ester group in **24** may take place with one of the nitrogen of the triazine ring to give a seven membered heterocyclic ring [9,10]. However, the structure was readily realized by reacting 3-methylpyrazol-5-one with **38** whereby **25** was the only product formed.

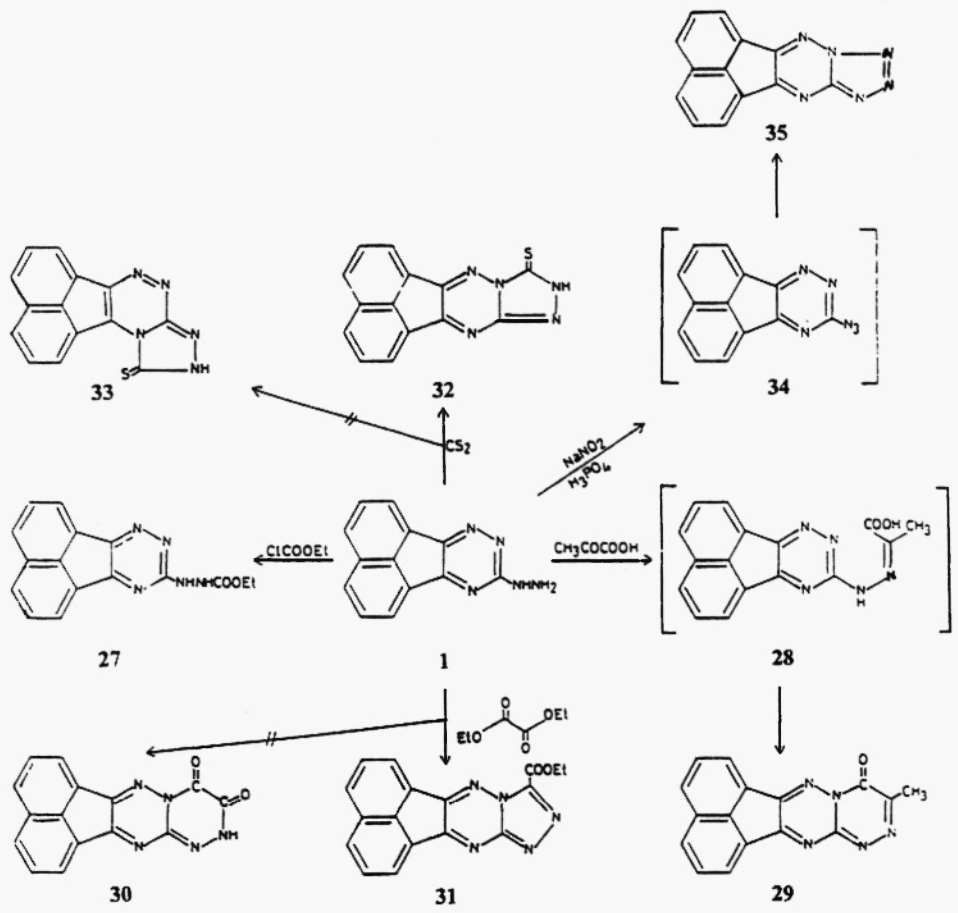
On the other hand, the reaction of **1** with acetylacetone was reinvestigated, in order to find whether the monohydrazone **23** is the structure for the reaction product as found in the case of using ethylacetoacetate or the reported cyclized product [12]. The product was found to be the cyclized one **26** and not the hydrazone **23** or its enolic form. The product did not give any color with ferric chloride and its infrared spectrum did not show any carbonyl frequency and its ^{1}H nmr spectrum agreed with the structure **26**. Heating of **1** with ethylchloroformate gave **27** whose infrared spectrum showed absorption bands in the carbonyl frequency region agreeing with the assigned structure. Its ^{1}H nmr spectrum showed the resonances of its ethyl group agreeing with the open chain structure **27**. Reaction of **1** with pyruvic acid gave the cyclized compound **29** and not the corresponding hydrazone **28**. The structure of **29** was confirmed by the absence of a carboxylic acid group and meantime the presence of a carbonyl amide absorption in the infrared spectrum. Reaction of **1** with diethyloxalate gave the cyclized product **31** and not **30**. The product showed in its infrared spectrum the presence of an absorption at 1725 cm^{-1}, which could not confirm the structure **30**, however, its ^{1}H nmr spectrum showed the presence of resonances that due to the ethyl group confirming the structure as **31**.

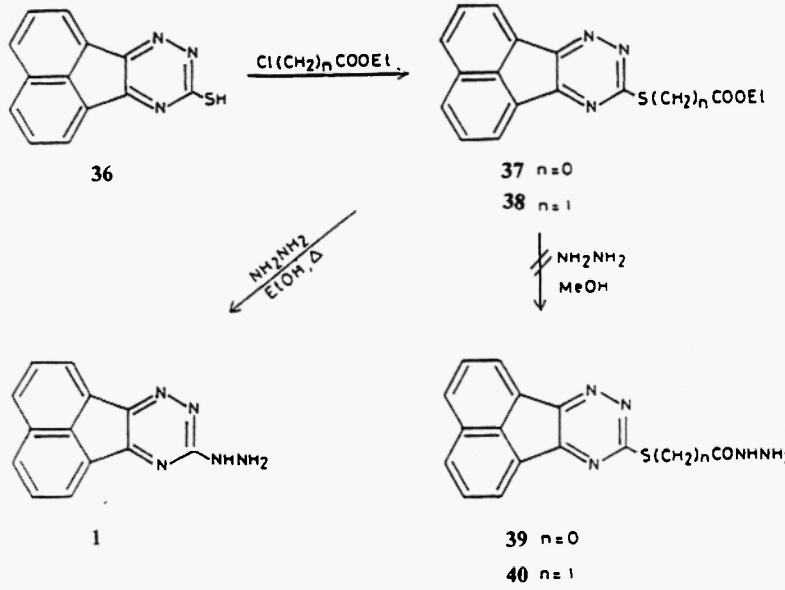
Reaction of **1** with carbon disulphide in pyridine gave the thiooxotriazolotriazine derivative **32**. The angular isomeric structure **33** was ruled out, based on the anticipated difference in nucleophilicity of N-2 and N-4 of the triazine ring



Reaction of **1** with sodium nitrite in acetic acid at 40° was reported [12] to give the tetrazole **35**. In the present study the reaction was carried out with sodium nitrite in phosphoric acid whereby other hydrazines are reported to form the respective azide. However, the product was found to be **35** and not **34** as confirmed by infrared spectroscopy which showed the absence of a band corresponding to the azide group.

The reaction of **36** with ethylchloroformate or ethyl chloroacetate afforded **37** and **38** respectively, whose reaction with hydrazine would give the corres-ponding hydrazides **39** and **40**. However, the product was found to be **1** and surprisingly **39** and **40** could not be formed even when the reaction was done at room temperature in the case of **37**. In the case of **38**, no reaction had taken place and when the reaction mixture was heated on a water-bath, it readily gave **1**. This indicates the preferential nucleophilic attack of the hydrazine on the carbon of the heterocyclic ring carrying the S-containing group rather than the carbonyl ester group.


35
34
33
32
CS_2
$NaNO_2$
H_3PO_4
ClCOOEt
$CH_3COCOOH$
27
1
28
EtO
OEt
COOEt
30
31
29


$Cl(CH_2)_nCOOEt$
36
37 n=0
38 n=1
NH_2NH_2
EtOH, Δ
NH_2NH_2
MeOH
1
39 n=0
40 n=1

EXPERIMENTAL

General methods are the same as reported in reference 11.

Acenaphtheno[1,2-*e*][1,2,4]triazolo[4,3-*b*][1,2,4]triazine (4).

a) A solution of **1** (0.10 g, 0.43 mmol) in formic acid (3.0 ml) was left overnight at room temperature. The addition of drops of petroleum ether gave a precipitate which it was crystallized from ethanol in pale yellow crystals to yield 0.08 g (77%), mp > 300°; ir (potassium bromide):1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{14}H_7N_5$: C, 68.6; H, 2.9; N, 28.6. Found: C, 68.9; H, 3.1; N, 28.5.

b) A solution of **1** (0.47 g, 2.00 mmol) in formic acid (10 ml) was heated under reflux for 10 hours. The product that separated on cooling was recrystallized from ethanol in pale yellow crystals to yield 0.4 g (82%). It was identical with the product obtained from (a).

c) A solution of **1** (0.47 g, 2.00 mmol) in triethylorthoformate (15.0 ml) was heated under reflux for 4 hours. The product that separated on cooling was filtered off, washed with ethanol. The product was crystallized from ethanol in pale yellow crystals to yield 0.40 g (82%). It was identical with the product obtained from (a).

Attempted action of acid or alkali on (4).

a) A solution of **4** (0.10 g, 0.40 mmol) in acetic acid (40 ml) and few drops of sulphuric acid was boild for 2 hours on a water bath. The product that separated on cooling was identical with the starting **4**.

b) Addition of a 1 N sodium hydroxide to **4** in acetonitrile showed no change in u.v. spectra.

10-Methylacenaphtheno[1,2-*e*][1,2,4]triazolo[4,3-*b*][1,2,4]triazine (5).

a) A solution of **1** (0.10 g, 0.43 mmol) in glacial acetic acid (3.0 ml) was left overnight at room temperature. Addition of petroleum ether gave precipitate which it was recrystallized from ethanol in pale yellow crystals to yield 0.09 g (82%), mp 236-238°; ir (potassium bromide): 1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{15}H_9N_5$: C, 69.5; H, 3.5; N, 27.0. Found: C, 69.8; H, 3.7; N, 27.0.

b) A solution of **1** (0.40 g, 1.70 mmol) in glacial acetic acid (20 ml) was heated under reflux for 10 hours. The product to yield 0.30 g (68%), was identical with the product obtained from (a).

c) A solution of **1** (0.20 g, 0.85 mmol) in acetic anhydride (5 ml) was heated under reflux for 4 hours. The product to yield 0.16 g (73%), was identical with the product obtained from (a).

3-(Benzylidenehydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (10).

A solution of **1** (1.0 g, 4.25 mmol) in ethanol (20 ml) was treated with benzaldehyde (0.45 ml) and few drops of acetic acid. The reaction mixture was heated under reflux for 1 hour. The product that separated out was recrystallized from ethanol in orange crystals to yield 1.20 g (87%), mp 262°; ir (potassium bromide): 3210 (NH) and 1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{20}H_{13}N_5$: C, 74.3; H, 4.1; N, 21.7. Found: C, 74.6; H, 4.0; N, 22.0.

3-(Isopropylidenehydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (11).

A solution of **1** (0.10 g, 0.43 mmol) in ethanol (80 ml) was treated with acetone (1.0 ml) and few drops of glacial acetic acid. The reaction mixture was processed as above. The product was crystallized from ethanol in yellow crystals to yield 0.09 g (77%), mp 212-214°; ir (potassium bromide): 3270 (NH) and 1600 (C=N) cm^{-1}.

Anal. Calcd. for $C_{16}H_{13}N_5$: C, 69.8; H, 4.7; N, 25.4. Found: C, 69.4; H, 4.5; N, 25.8.

9-(Benzilhydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (13).

A solution of **1** (0.20 g, 0.85 mmol) in methanol (60 ml) was treated with a solution of benzil (0.18 g, 0.85 mmol) in methanol (20 ml) and few drops of acetic acid. The reaction mixture was processed as above and the product was crystallized from methanol in yellow crystals to yield 0.25 g (69%), mp 131-133°; ir (potassium bromide): 3370 (NH), 1680 (C=O) and 1595 (C=N) cm^{-1}.

Anal. Calcd. for $C_{27}H_{17}N_5O$: C, 75.9; H, 4.0; N, 16.4. Found: C, 76.4; H, 4.2; N, 16.2.

Glyoxal-*bis*(acenaphtheno[1,2-*e*][1,2,4]triazin-3-yl)hydrazone (17).

a) A solution of **12** [11] (0.12 g, 0.43 mmol) in ethanol (40 ml) was treated with a solution of **1** (0.10 g, 0.43 mmol) in ethanol (20 ml) and few drops of acetic acid. The mixture was heated under reflux for 3 hours. The product was crystallized from a mixture of ethanol and N,N-dimethylformamide to give a brown crystals to yield 0.16 g (74%), mp 250-253°; ir (potassium bromide): 3385 (NH) and 1595 (C=N) cm^{-1}.

Anal. Calcd. for $C_{28}H_{16}N_{10}$: C, 68.3; H, 3.3; N, 28.4. Found: C, 68.6; H, 3.7; N, 27.9.

b) A solution of glyoxal sodium bisulphite (0.48 g, 1.70 mmol) in the least amount of water was added to a solution of **1** (0.80 g, 3.40 mmol) in ethanol (150 ml) followed by the addition of few drops of acetic acid. The product to yield 1.40 g (84%), was identical with the product obtained from method (a).

3-(2'-Oxoacenaphthenylidenehydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (18).

A solution of acenaphthenequinone (0.08 g, 0.43 mmol) in methanol (50 ml) was treated with a solution of **1** (0.10 g, 0.43 mmol) in methanol (50 ml) and few drops of glacial acetic acid. The reaction mixture was heated under reflux for 30 minutes. The product was recrystallized from ethanol in dark brown crystals to yield 0.14 g (82%), mp > 300°; ir (potassium bromide): 3230 (NH), 1725 (C=O) and 1600 (C=N) cm^{-1}.

Anal. Calcd. for $C_{25}H_{13}N_5O$: C, 75.2; H, 3.3; N, 17.5. Found: C, 75.1; H, 3.6; N, 17.8.

3-(3'-Isatinhydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (19).

A solution of isatin (0.06 g, 0.43 mmol) in methanol (10 ml) was treated with a solution of **1** (0.10 g, 0.43 mmol) in ethanol (80 ml) and few drops of glacial acetic acid. The reaction mixture was heated under reflux for 1 hour. The product was crystallized from ethanol in dark brown crystals to

yield 0.12 g (78%), mp 196° (decomp.); ir (potassium bromide): 3175 (NH), 1700 (OCN) and 1600 (C=N) cm^{-1}.

Anal. Calcd. for $C_{21}H_{12}N_6O$: C, 69.2; H, 3.3; N, 23.1. Found: C, 68.8; H, 3.5; N, 22.9.

9-(5'-Methyl-3'-isatinhydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (20).

A solution of **1** (0.10 g, 0.43 mmol) in ethanol (70 ml) was treated with a solution of 5-methylisatin (0.07 g, 0.43 mmol) in ethanol (30 ml) and few drops of glacial acetic acid. The reaction mixture was processed as above. The product was crystallized from ethanol in dark brown crystals to yield 0.13 g (81%), mp 220° (decomp.); ir (potassium bromide): 3150 (NH), 1700 (OCN) and 1600 (C=N) cm^{-1}.

Anal. Calcd for $C_{22}H_{14}N_6O$: C, 69.8; H, 3.7; N, 22.2. Found: C, 70.1; H, 4.0; N, 21.8.

1-Phenylacenaphtheno[1,2-*e*][1,2,4]triazolo[3,4-*c*][1,2,4]triazine (9).

A solution of **10** (0.32 g, 1.00 mmol) in ethanol (70 ml) was heated till boiling, and then a 2 M solution of iron(III) chloride in ethanol (20 ml) was added. The mixture was boiled for 10 minutes, and the resulting solution was left overnight at room temperature. The product that separated out was recrystallized from ethanol in pale yellow crystals to yield 0.16 g (50%), mp 295-297°; ir (potassium bromide): 1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{20}H_{11}N_5$: C, 74.8; H, 3.5; N, 21.8. Found: C, 74.3; H, 3.8; N, 22.0.

3-(N-Acetyl-N'-benzylidinehydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (14).

A solution of **10** (0.32 g, 1.00 mmol) in acetic anhydride (5 ml) was heated under reflux for 1 hour. The rection mixture was poured onto crushed ice. The product that separated out was crystallized from ethanol in colourless crystals to yield 0.19 g (53%), mp 220-222°; ir (potassium bromide): 1690 (N-Ac) and 1615 (C=N) cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.71 (s, 3 H, NAc), 7.39, 7.92, 7.98, 8.34 and 8.60 (3m, 2 dd, 12 H, aromatic and CH protons).

Anal. Calcd. for $C_{22}H_{15}N_5O$: C, 72.3; H, 4.1; N, 19.2. Found: C, 72.6; H, 3.8; N, 19.7.

3-(Carboethoxymethylethylidenehydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (24).

A solution of **1** (0.24 g, 1.00 mmol) in ethanol (25 ml) was treated with ethylacetoacetate (5.5 ml). The reaction mixture was heated under reflux for 4 hours. The product was crystallized from ethanol in yellow crystals to yield 0.23 g (65%), mp 194-196°; ir (potassium bromide): 3200 (NH) and 1725 (OCO) cm^{-1}. ^1H nmr ($CDCl_3$): δ 1.30 (t, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 3.60 (s, 2 H, CH_2), 4.20 (q, 2 H, CH_2), 7.30 (s, 1 H, NH), 7.8-8.7 (m, 6 Harom).

Anal. Calcd. for $C_{19}H_{17}N_5O_2$: C, 65.7; H, 4.9; N, 20.2. Found: C, 65.6; H, 5.0; N, 20.5.

3-(2,4-Dihydro-5-methyl-3*H*-pyrazol-3-oxo-2-yl)acenaphtheno[1,2-*e*][1,2,4]triazine (25).

(a) A solution of **24** (0.20 g, 0.58 mmol) in glacial acetic acid (30 ml) was heated under reflux for 10 hours. The reaction mixture was poured onto crushed ice. The product was recrystallized from N,N-dimethylformamide ethanol mixture in deep yellow crystals to yield 0.1 g (59%), mp 188°

(decomp.); (lit. [11] mp 183°), ir (potassium bromide): 1650 (OCN) and 1610 (C=N) cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.18 (s, 3 H, CH_3), 3.58 (s, 2 H, CH_2), 7.8-8.2 (m, 6 H, aromatic protons).

Anal. Calcd. for $C_{17}H_{11}N_5O$: C, 67.8; H, 3.7; N, 23.3. Found: C, 67.3; H, 3.4; N, 22.9.

b) A solution of **38** (0.32 g, 1.00 mmol) in ethanol (10 ml) was treated with a solution of 3-methylpyrazol-5-one (0.10 g, 1.00 mmol) in ethanol (5 ml). The reaction mixture was heated under reflux for 4 hours. The product that separated on cooling was recrystallized from ethanol in yellow crystals to yield 0.20 g (67%). It was identical with the product obtained from method (a).

3-(3',5'-Dimethylpyrazol-2-yl)acenaphtheno[1,2-*e*][1,2,4]triazine (26).

A solution of **1** (0.10 g, 0.43 mmol) in ethanol (60 ml) was treated with acetylacetone (0.1 ml) and few drops of glacial acetic acid. The reaction mixture was heated under reflux for 1 hour. The product was crystallized from ethanol in yellow crystals to yield 0.10 g (79%), mp 185-187° (lit. [12] mp 184°); ir (potassium bromide): 1615 (C=N) cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.42 and 2.81 (2s, 6 H, 2 CH_3), 6.09 (s, 1 H, CH), 7.90, 8.16, 8.28, 8.50, 8.66 (m, 4d, 6 Harom).

Anal. Calcd. for $C_{18}H_{13}N_5$: C, 72.2; H, 4.4; N, 23.4. Found: C, 72.3; H, 4.3; N, 23.6.

3-(Carboethoxyhydrazino)acenaphtheno[1,2-*e*][1,2,4]triazine (27).

A solution of **1** (0.47 g, 2.00 mmol) in ethylchloroformate (20 ml) was heated under reflux for 4 hours. The product that was crystallized from ethylacetate-petroleum ether in colorless crystals to yield 0.42 g (69%), mp 280° (decomp.); ir (potassium bromide): 1760 (COOEt) and 1610 (C=N) cm^{-1}; ^1H nmr (DMSO-d_6): δ 4.33 (t, 3 H, CH_3); 4.93 (q, 2 H, CH_2), 7.00-7.60 (m, 6 Harom) and 13.33 (brs, 2 H, 2 NH); the NH signal was exchangeable with deuterium oxide.

Anal. Calcd. for $C_{16}H_{13}N_5O_2$: C, 62.5; H, 4.3; N, 22.8. Found: C, 62.1; H, 4.6; N, 22.5.

10-Methylacenaphtheno[1,2-*e*][1,2,4]triazino[4,3-*b*][1,2,4]triazin-11-one (29).

A solution of **1** (1.00 g, 4.25 mmol) in methanol (100 ml) was treated with pyruvic acid (1.0 ml) and the reaction mixture was kept at room temperature for 72 hours. The product was crystallized from methanol in pale brown crystals to yield (0.60 g, 49%), mp 208-210°; ir (potassium bromide): 1695 (OCN) and 1605 (C=N) cm^{-1}.

Anal. Calcd. for $C_{16}H_9N_5O$: C, 66.9; H, 3.2; N, 24.4. Found: C, 66.7; H, 3.1; N, 24.5.

10-Carboethoxyacenaphtheno[1,2-*e*][1,2,4]triazolo[4,3-*b*][1,2,4]triazine (31).

A solution of **1** (0.40 g, 1.70 mmol) in diethyl oxalate (7.0 ml) was heated under reflux for 1 hour. The product was triturated with methanol, filtered, and crystallized from methanol to give pale yellow crystals to yield 0.39 g (72%), mp 265-267°; ir (potassium bromide): 1725 (COOEt) and 1610 (C=N) cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.52 (t, 3 H, CH_3), 4.62 (q, 2 H, CH_2), 8.11, 8.51 (2 m, 6 H, aromatic protons).

Anal. Calcd. for $C_{17}H_{11}N_5O_2$: C, 64.4; H, 3.5; N, 22.1. Found: C, 64.4; H, 3.8; N, 22.2.

10-Thiooxoacenaphtheno[1,2-*e*][1,2,4]triazolo[4,3-*b*][1,2,4]triazine (32).

A solution of **1** (0.20 g, 0.86 mmol) in pyridine (10 ml) was treated with carbon disulphide (0.1 ml). The reaction mixture was heated under reflux on a water-bath for 1 hour. The product was crystallized from ethanol and N,N-dimethylform-amide in yellow crystals to yield 0.18 g (76%), mp > 300°; ir (potassium bromide): 3100 (NH) and 1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{14}H_7N_5S$: C, 60.6; H, 2.6; N, 25.3. Found: C, 60.4; H, 2.9; N, 25.6.

Acenaphtheno[1,2-*e*][1,2,4]triazino[2,3-*d*]tetrazole (35).

A suspension of **1** (0.10 g, 0.43 mmol) in phosphoric acid (5 ml) was mixed with aqueous sodium nitrite (0.09 g, 1.30 mmol) with vigorous stirring. The reaction mixture was further stirred for an additional hour at 40° and the precipitate obtained was washed with water and crystallized from N,N-dimethyl-formamide-water mixture in yellow crystals to yield 0.08 g (76%), mp 282° (decomp.); [(Lit. [12] mp 286-287° (decomp.)]; ir (potassium bromide): 1610 (C=N) cm^{-1}.

Anal. Calcd. for $C_{13}H_6N_6$: C, 63.4; H, 2.5; N, 34.1. Found: C, 63.0; H, 2.7; N, 34.2.

3-(Thiocarboethoxy)acenaphtheno[1,2-*e*][1,2,4]triazine (37).

A solution of **36** (1.20 g, 5.06 mmol) in N,N-dimethylformamide (30 ml) was treated with anhydrous potassium carbonate (8.0 g, 57.9 mmol). To the reaction mixture acetone was added (40 ml), followed by the addition of ethylchloroformate (2 ml). The reaction mixture was left overnight at room temperature, then it was filtered and washed with acetone. The filterate was evaporated. The product that separated was crystallized from ethanol in pale orange crystals to yield 1.36 g (87%), mp 199- 201°; ir (potassium bromide): 1735 (COOEt) and 1610 (C=N) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.35 (t, 3 H, CH_3), 4.21 (q, 2 H, CH_2), and 7.88, 8.24, 8.52 (3 m, 6 Harom).

Anal. Calcd. for $C_{16}H_{11}N_3SO_2$: C, 62.1; H, 3.6; N, 13.6. Found: C, 62.1; H, 3.6; N, 13.7.

3-(Thiocarboethoxymethyl)acenaphtheno[1,2-*e*][1,2,4]triazine (38).

A solution of **36** (0.50 g, 2.10 mmol) in N,N-dimethylformamide (15 ml) was treated with anhydrous potassium carbonate (1.0 g, 7.20 mmol), acetone added (10 ml), and ethylchloroacetate (0.5 ml). The reaction mixture was processed as above and the product was crystallized from ethanol in pale yellow crystals to yield 0.54 g (79%), mp 160-162°; ir (potassium bromide): 1730 (COOEt) and 1610 (C=N) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.33 (t, 3 H, CH_3), 4.18 (s, 2 H, CH_2), 4.29 (q, 2 H, CH_2), 7.88, 8.21 and 8.42 (m, 2d, dd, 6 Harom).

Anal. Calcd. for $C_{17}H_{13}N_3SO_2$: C, 63.1; H, 4.1; N, 13.0. Found: C, 63.5; H, 4.1; N, 12.6.

Attempted synthesis of (39) or (40).

A solution of **37** (1.00 g, 3.23 mmol) or **38** (1.00 g, 3.10 mmol) in ethanol (150 ml) and N,N-dimethylformamide (10 ml) was treated with hydrazine hydrate (2 ml). The reaction mixture was heated under reflux for 15 minutes. The product that separated out on cooling was crystallized from ethanol in yellow crystals of **1** (80% yield); mp 220-223° (lit. [12], m.p. 226°). The IR spectrum was identical with an authentic sample.

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