erhitzt. Das Gemisch erstarrte nach dem Erkalten. Farblose, rötlichviolett schimmernde*) Kristalle, Schmp. 149° (Ethanol), Ausb.: 1.39 g (76 %). – IR (KBr): 3430 (NH), 1655 cm^{-1} (C=O). – ^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.70 (s; Alkyl-CH_3), 2.23 (s; Aryl-CH_3), 3.00 [m; $N(CH_2)_2$], 3.65 (s; Alkylester-CH_3), 3.80 [m; $O(CH_2)_2$], 3.96 (s; Arylester-CH_3), 4.72 (s; =CH), 6.36 (m; 1 aromat. H), 9.5 (bs; NH), 11.3 (s; OH). $C_{18}H_{24}N_2O_6$ (364.4) Ber. C 59.3 H 6.63 N 7.7; Gef. C 59.4 H 6.60 N 7.7.

3-(4'-Hydroxy-3'-methoxycarbonyl-6'-methyl-2'-morpholino)anilino-2-butensäuremethylester **(5)**

Analog **3** ausgehend von **1e.** Hellrötlich schimmernde*) Kristalle, Schmp. 189–191° (Ethanol), Ausb.: 80 %. – IR (KBr): 3288 (NH), 1730, 1650 cm^{-1} (C=O). – ^{1}H-NMR ($CDCl_3$): δ(ppm) = 1.59 (s; Alkyl-CH_3), 2.20 (s; Aryl-CH_3), 3.09 [m; $N(CH_2)_2$], 3.67 [m; $O(CH_2)_2$], 3.72 (s; Alkylester-CH_3), 4.00 (s; Arylester-CH_3), 4.72 (s; =CH), 6.65 (m; 1 aromat. H), 9.6 (bs; NH), 9.7 (s; OH). $C_{18}H_{24}N_2O_6$ (364.4) Ber. C 59.3 H 6.63 N 7.7; Gef. C 59.1 H 6.73 N 7.6.

* Vermutlich auf geringfügige Oberflächenoxidation zurückzuführen.

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Arch. Pharm. (Weinheim) *313*, 465–471 (1980)

Condensed 1,2,4-Triazines, III**

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Eingegangen am 16. August 1979

Alkylation of 3-mercaptophenanthreno[9,10-*e*]-1,2,4-triazine **(1b)** yielded the *S*-alkyl derivatives **2 a-d.** Amination of **1a** afforded the 3-amino derivatives **3a-h.** Reaction of **1a** with hydrazine hydrate gave 3-hydrazinophenanthreno[9,10-*e*]-1,2,4-triazine **(4)** which underwent cyclisation with nitrous, formic or acetic acids giving the phenanthreno[9,10-*e*]-1,2,4-triazino[2,3-d]-1,2,3,4-tetrazole **(5)** and the phenanthreno[9,10-*e*]-1,2,4-triazino[2,3-*d*]-3*H*-methyl-1,2,4-triazoles **6, 7.** Compound **4** also reacted with methyl [bis(dimethylmercapto)methylene]cyanoacetate, ethyl acetoacetate, ethoxymethylenemalononitrile, ethyl ethoxymethylencyanoacetate or acetyl acetone to yield the 3-(pyrazol-1-yl)-phenanthreno[9,10-*e*]-1,2,4-triazines **8–12.**

0365–6233/80/0505–0465 $ 02.50/0

Kondensierte 1,2,4-Triazine, 3. Mitt.

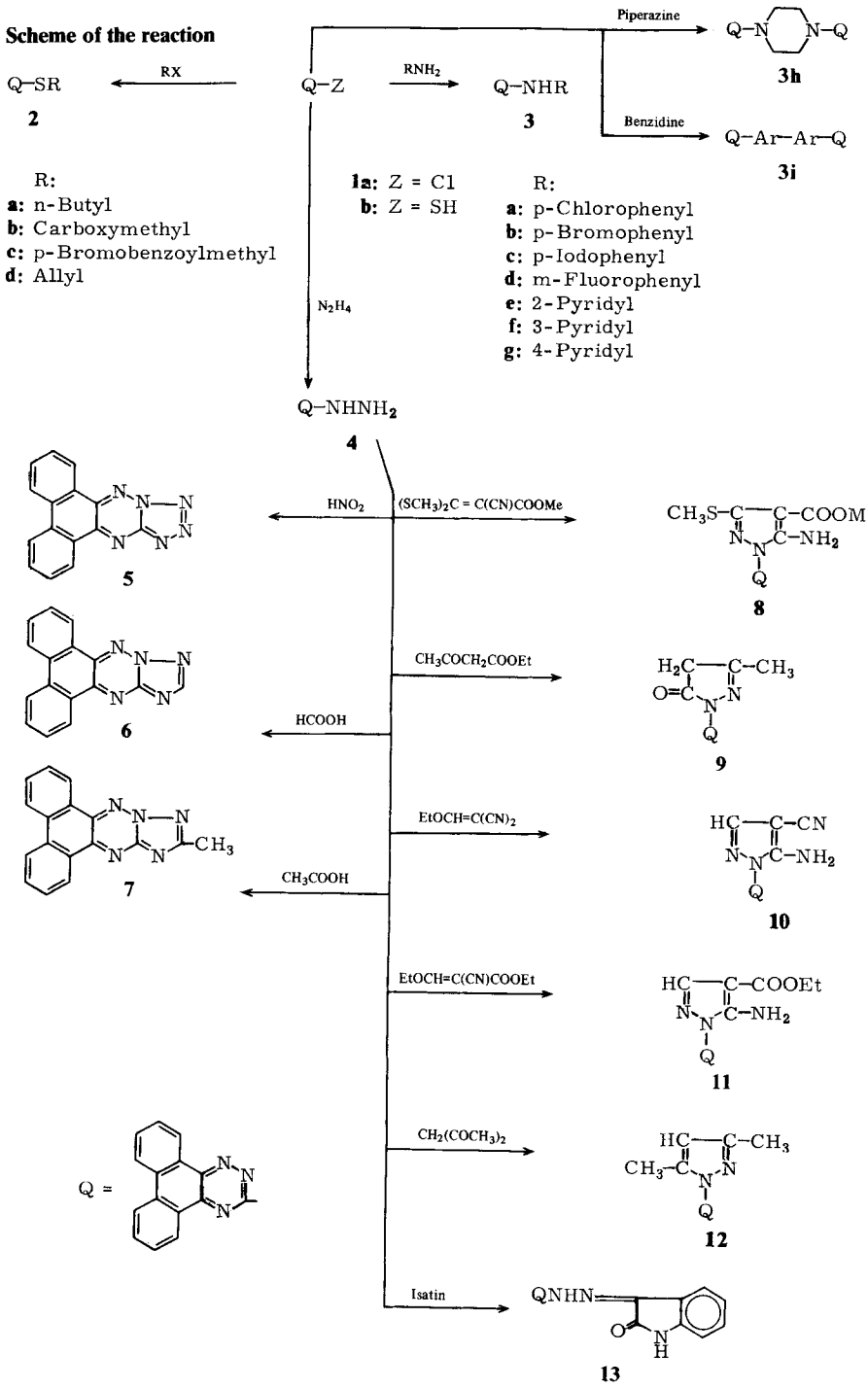
Die Alkylierung von 3-Mercapto-phenanthreno[9,10-e]-1,2,4-triazin **(1b)** ergab die S-Alkylderivate **2a-d.** Aus **1a** wurden die 3-Aminoverbindungen **3a–h** hergestellt. Die Reaktion von **1a** mit Hydrazinhydrat führte zum 3-Hydrazin-phenanthreno[9,10-e]-1,2,4-triazin **(4),** das durch Behandlung mit Säuren zu Phenanthreno[9,10-e]-1,2,4-triazino[2,3-d]-1,2,3,4-tetrazol **(5)** und den Phenanthreno[9,10-e]-1,2,4-triazino[2,3-d]3*H*-methyl-1,2,4-triazolen **6** und **7** zyklisierte. Durch Umsetzung von **4** mit 2-Cyan-3-dimethylmercaptoacrylsäuremethylester, Acetessigsäureethylester, Ethoxymethylenmalonitril, 2-Cyan-3-ethoxy-acrylsäureethylester und Acetylaceton wurden die entsprechenden 3-Pyrazolyl-phenanthreno[9,10-e]-1,2,4-triazine **8–12** synthetisiert.

The therapeutic importance of several 1,2,4-triazines[1,2,3] led us synthesise various triazine derivatives with the highly biologically active heterocyclic moietis: pyridine, piperazine, indole and pyrazole. *Saikawa* et al.[4] have recently reported bactericidal and fungicidal properties of 1,2,4-triazine derivatives. Although the chemical behaviour of uncondensed analogues has been extensively studied[5], the reactivity of such condensed systems is so far not investigated in detail.

The intermediate compounds 3-mercapto-[2] and 3-chloro-phenanthreno-[9,10-e]-1,2,4-triazines were prepared by the method of *Laakso* et al.[6]. The behaviour of the mercapto compound towards alkylating agents and hydrazine was of interest. The reaction of alkyl halides on **1b** produced the S-alkyl derivatives **(2a-d)** in good yield. Their structures were assigned on the basis of analytical and spectroscopical data. Both, compounds **1a,b** on reaction with hydrazine hydrate (80 %) yielded 3-hydrazino-phenanthreno[9,10-e]-1,2,4-triazine **(4),** which on condensation with aromatic and heterocyclic amines afforded a yellowish crystalline solid of the corresponding 3-amino derivatives **3a-g.** Due to the increased aromaticity of this condensed 1,2,4-triazine **1a,** the formation of amino derivatives necessiates longer heating and higher temperatures than in case of uncondensed analogue. Bis(phenanthreno[9,10-e]-1,2,4-triazine-3 yl)piperazine/benzidine **(3h, i)** were prepared by the reaction of **1a** with piperazine and benzidine resp. and their structures were confirmed by mass spectra and elemental analyses. On reaction with nitrous acid **4** underwent cyclisation to the tetrazolotriazine **(5)** while with formic and acetic acid the phenanthreno[9,10-e]-1,2,4-triazino-[2,3-d]-3H/methyl-1,2,4-triazoles **6, 7** were formed in good yield. Condensation-cyclisation of **4** with methyldimethylmercaptomethylenecyanoacetate, ethylacetoacetate, ethoxymethylenemalononitrile, ethoxymethyleneethylcyanoacetate and acetyl acetone gave the corresponding 3-(pyrazol-1 yl)phenanthreno[9,10-e]-1,2,4-triazines **8–12.** In order to introduce the indole nucleus in the phenanthreno[9,10-e]-1,2,4-triazine, **4** was condensed with isatin to yield the hydrazone **13.**

The authors are thankful to departmental colleagues and Prof. *R. P. Rastogi,* Head, Chemistry Dept., University of Gorakhpur, for his encouragements. One of us (VJR) is grateful to CSIR, New Delhi, for financial support of the research scheme.

Scheme of the reaction



Experimental

All the m. ps. are uncorrected.

3-Chloro-phenanthreno[9,10-e]-1,2,4-triazine ***(1a)***

It was synthesised by the method reported earlier[6] in 60 % yield.

3-Mercapto-phenanthreno[9,10-e]-1,2,4-triazine ***(1b)***

It was prepared by the method of *Sallam* et al.[2] in 85 % yield.

3-Butylmercapto-phenanthreno[9,10-e]-1,2,4-triazine ***(2a)***

To a solution of 0.2 g **1b** in aqueous KOH (5 %) 0.2 ml. n-butyl chloride was added. The mixture was stirred for 3 h and then poured into water. The precipitate was washed with water and crystallised from ethanol-water mixture, yield 0.18 g (75 %), m. p. 80°C. $C_{19}H_{17}N_3S$ (319) Calcd.: C 71.4 H 5.3 N 13,1; Found: C 71.6 H 5.6 N 13.2.

3-Carboxymethylmercapto-phenanthreno[9,10-e]-1,2,4-triazine ***(2b)***

A mixture of 0.2 g **1b** and 0.07 g chloroacetic acid in aqueous KOH (5 %) was stirred for 4 h. The reaction mixture was poured into water and neutralized with dilute hydrochloric acid. The precipitate was washed with water and crystallised from ethanol-water mixture, yield 0.16 g (65 %), m. p. 214°C. $C_{17}H_{11}N_3O_2S$ (321) Calcd.: C 63.5 H 3.4 N 13.1; Found: C 63.2 H 3.3 N 13.3.

3-(p)Bromobenzoyl-methylmercapto-phenanthreno[9,10-e]-1,2,4-triazine ***(2c)***

To a solution of 0.2 g **1b** in aqueous KOH (5 %) an ethanolic solution of 1.2 g- p-bromo-ω-bromoacetophenone was added and the mixture was refluxed for 30 min. After cooling the precipitate was washed with water and finally crystallised from DMF, yield 0.14 g (40 %), m. p. 185°C. $C_{23}H_{14}BrN_3OS$ (460) Calcd.: C 60.0 H 3.0 N 9,1; Found: C 60.3 H 3.1 N 9.4.

3-Allylmercapto-phenanthreno[9,10-e]-1,2,4-triazine ***(2d)***

2d was prepared from 0.2 g **1b** and 0.2 ml allylbromide as described in the preceding experiment. The crude product was crystallised from ethanol, yield 0.14 g (60 %), m. p. 122°C. $C_{18}H_{13}N_3S$ (303) Calcd.: C 71.2 H 4.2 N 13.8; Found: C 71.3 H 4.0 N 14.1.

3-(p)-Chloroanilino-phenanthreno[9,10-e]-1,2,4-triazine ***(3a)***

To a solution of 0.2 g **1a** in little dimethylformamide 0.14 g p-chloro-aniline were added and the reaction mixture was refluxed for 4.5 h, and cooled. The precipitate was washed with water-ethanol and crystallised from DMF, yield 0.15 g (55 %), m. p. > 300°C. $C_{21}H_{13}N_4Cl$ (356.5) Calcd.: C 70.6 H 3.6 N 15.7; Found: C 70.4 H 3.8 N 15.4. Other compounds in this series are prepared similarly and are listed in Table 1 along with their relevant data.

Table 1: *3-Aryl/pyridylamino-phenanthreno[9,10-e]-1,2,4-triazines* **3**

3	Ar.	Yield %	M.P. °C	M^+	Molecular formula
a	p-Bromophenyl-	45	> 300	401	$C_{21}H_{13}N_4Br$
b	p-Iodophenyl-	55	> 300	448	$C_{21}H_{13}N_4I$
c	m-Fluorophenyl-	50	173	339	$C_{21}H_{13}N_4F$
d	2-Pyridyl-	52	> 300	323	$C_{20}H_{13}N_5$
e	3-Pyridyl-	56	> 300	323	$C_{20}H_{13}N_5$
f	4-Pyridyl-	50	> 300	323	$C_{20}H_{13}N_5$
g	p-Carbethoxyphenyl-	30	> 300	394	$C_{24}H_{18}N_4O_2$

All the compounds were analysed for C, H and N satisfactorily and crystallised from DMF.

Bis(phenanthreno[9,10-e]-1,2,4-triazin-3-yl)-piperazine ***(3h)***

A solution of 0.1 g **1b** in little dimethylformamide was refluxed with 0.05 g piperazine for 2 h. The precipitate obtained was crystallised from DMF-water mixture, yield 0.11 g (50 %), m. p. > 300°C. $C_{34}H_{24}N_8$ (544) Calcd.: C 75.0 H 4.4 N 20.5; Found: C 75.3 H 4.2 N 20.2.

4,4'-Bis(phenanthreno[9,10-e]-1,2,4-triazin-3 yl)benzidine ***(3i)***

It was prepared from 0.1 g **1a** and 0.07 g benzidine as described in the previous experiment. The crude product was crystallised from DMF, yield 0.12 g (43 %), m. p. 300°C. $C_{42}H_{26}N_8$ (702) Calcd.: C 78.5 H 4.0 N 17.4; Found: C 78.6 H 4.1 N 17.2.

3-Hydrazinophenanthreno[9,10-e]-1,2,4-triazine ***(4)***

It was prepared by refluxing 1.0 g **1a** with 2 ml hydrazine hydrate (80 %) for 4 h. After cooling the precipitate was crystallised from DMF, yield 0.9 g (90 %), m. p. 231°C. $C_{15}H_{11}N_5$ (261) Calcd.: C 68.9 H 4.1; Found: C 69.1 H 4.3.

Phenanthreno[9,10-e]-1,2,4-triazino[2,3-d]-1,2,3,4-tetrazole ***(5)***

To a solution of 0.1 g **4** in minimum amount of acetic acid (50 %) an aqueous solution of 100 mg sodium nitrite was added dropwise with constant stirring at 5–12°C. After complete addition the resulting mixture was maintained at 40°C for 1 h and the precipitate thus obtained was washed with water and crystallised from DMF, yield 0.1 g (90 %), m. p. 218°C. $C_{15}H_8N_6$ (272) Calcd.: C 66.1 H 2.9 N 30.8; Found: C 66.3 H 3.1 N 30.6.

Phenanthreno[9,10-e]-1,2,4-triazino[2,3-d]-1,2,4-triazole ***(6)***

0.1 g **4** in 2 ml formic acid was refluxed for 3 h and the excess of acid was removed under reduced pressure. The solution was cooled overnight and the precipitate was washed with ethanol and crystallised from DMF, yield 0.1 g (90 %), m. p. 293°C. $C_{16}H_9N_5$ (271) Calcd.: C 70.8 H 3.3 N 25.8; Found: C 71.1 H 3.5 N 26.1.

Phenanthreno[9,10-e]-1,2,4-triazino[2,3-d]-3-methyl-1,2,4-triazole **(7)**

0.1 g **4** was refluxed in 2 ml acetic acid for 3 h and the desired product was isolated as described in the preceding experiment. The crude product was crystallised from DMF, yield 0.07 g (75 %), m. p. 282°C. $C_{17}H_{11}N_5$ (285) Calcd.: C 71.5 H 3.8 N 24.5; Found: C 71.6 H 3.5 N 24.1.

3-(5'-Amino-4'-carbomethoxy-3'-methylmercaptopyrazolo-1'yl)phenanthreno[9,10-e]-1,2,4-triazine **(8)**

To a solution of 0.1 g **4** in little dimethylformamide 0.07 g methyldimethylmercapto-methylene-cyanoacetate were added and refluxed for 2 h in the presence of a few drops of acetic acid. After cooling the precipitate was washed with ethanol and crystallised from DMF, yield 0.09 g (62 %), m. p. 293°C. $C_{21}H_{16}N_6O_2S$ (416) Calcd.: C 60.5 H 3.8 N 20.1; Found: C 60.7 H 3.4 N 20.3.

3-(3'-Methyl-5'-pyrazolon-1'-yl)-phenanthreno[9,10-e]-1,2,4-triazine **(9)**

It was prepared by refluxing a mixture of 0.1 g **4** and 0.2 ml ethylacetoacetate in dimethylformamide in presence of a few drops of acetic acid and isolated as described in the preceding experiment. The crude product was crystallised from DMF, yield 0.1 g (82 %), m. p. 208°C. $C_{19}H_{13}N_5O$ (327) Calcd.: C 69.7 H 3.9 N 21.4; Found: C 69.5 H 4.1 N 21.6.

3-(5'-Amino-4'-cyano-pyrazolo-1'-yl)-phenanthreno[9,10-e]-1,2,4-triazine **(10)**

A mixture of 0.1 g **4** and 0.05 g ethoxymethylenemalononitrile in little dimethylformamide was refluxed for 2 h in presence of a few drops of acetic acid. The product was isolated as stated earlier and crystallised from DMF, yield 0.1 g (76 %), m. p. 295°C. $C_{19}H_{11}N_7$ (337) Calcd.: C 67.6 H 3.2 N 29.1; Found: C 67.4 H 3.5 N 29.2.

3-(5'-Amino-4'-carbethoxypyrazolo-1'yl)phenanthreno[9,10-e]-1,2,4-triazine **(11)**

A solution of 0.1 g **4** and 0.07 g ethoxymethyleneethylcyanoacetate in dimethylformamide was refluxed for 2 h in presence of a few drops of acetic acid. Precipitate obtained was crystallised from DMF, yield 0.1 g (70 %), m. p. 270°C. $C_{21}H_{16}N_6O_2$ (384) Calcd.: C 65.6 H 4.1 N 21.8; Found: C 67.0 H 4.2 N 21.6.

3-(3',5'-Dimethylpyrazolo-1'yl)phenanthreno[9,10-e]-1,2,4-triazine **(12)**

To a mixture of 0.1 g **4** and 0.1 ml acetyl acetone in ethanol, 2 drops of acetic acid were added. The reaction mixture was refluxed for 2 h and cooled. Addition of a few drops of water to the content gave a precipitate which was crystallised from DMF-water mixture, yield 0.08 g (66 %), m. p. 225°C. $C_{20}H_{15}N_5$ (325) Calcd.: C 73.8 H 4.5 N 21.5; Found: C 73.5 H 4.4 N 21.6.

3-Hydrazono-(indolin-2-one)phenanthreno[9,10-e]-1,2,4-triazine **(13)**

A mixture of 0.1 g **4** and 0.06 g isatin in dimethylformamide was heated under reflux for 2 h. The precipitate thus obtained was crystallised from DMF, yield 0.09 g (60 %), m. p. > 300°C. $C_{23}H_{14}N_6O$ (390) Calcd.: C 70.7 H 3.5 N 21.5; Found: C 70.3 H 3.2 N 21.6.

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Organosulfur Compounds as Potential Pesticides

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Eingegangen am 21. August 1979

Condensation of 1-nitro-2,2-bis(methylmercapto)ethylene with aralkylamines gave the 1-nitro-2,2-bis-(aralkylamino)ethylenes **1** while its reaction with aromatic amines gave the 1-nitro-2-arylamino-2-methylmercaptoethylenes **2** under similar conditions. Reactions of methyl 1-cyano-2,2-bis(methylmercapto)acrylate with aromatic amines and hydrazine gave the methyl 1-cyano-2-arylamino-2--methylmercaptoacrylate **3** and the 1-substituted 3-methylmercapto-4-methoxycarbonyl-5-aminopyrazoles **4**, respectively. All the compounds except **4** were screened for their pesticidal activities but only five of them were found to be active.

Organo-Schwefelverbindungen als potentielle Pestizide

Die Kondensation von 1-Nitro-2,2-dimethylmercapto-ethylen mit Aralkylaminen gab die 1-Nitro-2,2-diaralkylamino-ethylene **1,** während die Reaktion mit aromatischen Aminen unter ähnlichen Bedingungen die 1-Nitro-2-arylamino-2-methyl-mercapto-ethylene **2** ergab. Die Reaktion von 1-Cyan-2,2-dimethylmercapto-acrylsäuremethylester mit aromatischen Aminen und Hydrazin gab die 1-Cyan-2-arylamino-2-methylmercapto-acrylsäuremethylester **3** und die 1-substituierten 3-Methyl-mercapto-4-carbmethoxy-5-aminopyrazole **4.** Alle Verbindungen außer **4** wurden auf ihre pestizide Aktivität untersucht, aber nur fünf davon waren wirksam.

0365–6233/80/0505–0471 $ 02.50/0