0° with stirring. To this a solution of 0.77 g (1.0 mmol) of 90% nitric acid in 5 ml of acetic anhydride was added during 30 min. The reaction mixture was then stored at 0° for 24 hr and then poured into 50 g of ice and set aside at 0° for 24 hr. The solution was extracted with ether (two 25-ml portions) and the combined dried (Na_2SO_4) extracts were stripped of solvent. The residue was distilled at 80° (15 Torr) to give 0.72 g (4.9 mmol, 87%) of product: pmr τ 2.40 (t, J = 4.6, 4.6 Hz, H^3), 3.47 (d of d, J = 4.6. 2.0 Hz, H^4).

Anal. Calcd for $C_4H_2FNO_2S$: C, 32.63; H, 1.37; N, 9.52; S, 21.80. Found: C, 32.90; H, 1.61; N, 9.55; S, 22.01.

Registry No.—**2**, 29669-44-1; 2 2,4-DNP, 29669-45-2; **3**, 4377-58-6; **4**, 29669-47-4; **5**, 29669-48-5; **6**, 29669-49-6; 6 2,4-DNP, 29669-50-9.

Condensed 1,3-Benzothiazines. A Facile Rearrangement of 3-Alkyl-8-nitro-*s*-triazolo-[3,4-*b*](1,3,4)benzothiadiazepine

T. GEORGE* AND R. TAHILRAMANI

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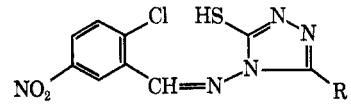
The fission of an N–N or of an N–O bond with formation of a cyano group under the influence of nucleophilic agents is well documented in five- and six-membered systems.[1] This note describes a novel example of a rearrangement in a seven-membered heterocyclic system involving fission of an N–N bond.

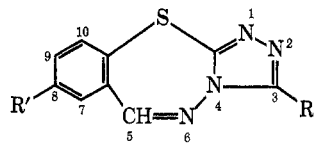
In connection with the synthesis of condensed *s*-triazole heterocycles described earlier,[2] 3-alkyl-4-(2-chloro-5-nitro)benzalamino-5-mercapto-*s*-triazoles were prepared by condensation of 3-alkyl-4-amino-5-mercapto-*s*-triazoles[3] with 2-chloro-5-nitrobenzaldehyde. It was reported earlier[2] that refluxing the sodium salt of the ethyl analog **1a** in dioxane gave 3-ethyl-8-nitro-*s*-triazolo[3,4-*b*](1,3,4)benzothiadiazepine (**2a**) as a yellow compound which showed in the nmr spectrum in DMSO-d_6 the azomethine proton as a singlet at δ 8.86. **2a** was also obtained by refluxing **1a** with 1 equiv of sodium ethoxide in ethanol.

In the presence of 1.3–2.0 equiv of sodium ethoxide, **1a** gave a new product isomeric with **2a** as shown by analytical values and spectral data. The nmr spectrum showed no signal at δ 8.86 corresponding to the azomethine proton of **2a**; the ir spectrum contained an NH band at 3350 and 3260 cm^{-1} but no nitrile band. From these data, the product can be formulated as 3-ethyl-5-imino-7-nitro-5*H*-*s*-triazolo[3,4-*b*]-1,3-benzothiazine (**3a**). The course of the reaction from **1a** can be envisaged as involving the formation of **2a** which in the presence of base undergoes scission of the N–N bond to form the nitrile **2'a** which undergoes facile intramolecular ring closure to form **3a**. An alternative structure, 3-ethyl-5-imino-7-nitro-5*H*-*s*-triazolo[5,1-*b*]-1,3-benzothiazine (**3'a**) cannot be ruled out. Treatment of **2a** in presence of 0.3–1 equiv of sodium ethoxide in ethanol gave **3a** in 68% yield, showing that the reaction from **1a** proceeds through **2a** as an intermediate.

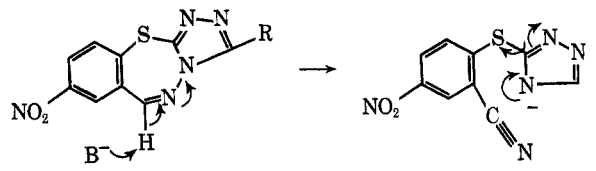
Confirmation of the product as **3a** or **3'a** was obtained by establishing its identity with the condensation product of 2-chloro-5-nitrobenzonitrile[4] (**4a**) and 3-ethyl-5-mercapto-*s*-triazole[3] (**5**) in presence of sodium ethoxide. Under carefully controlled conditions of hydrolysis, **3a** gave **3d**, the corresponding oxo compound which showed the carbonyl band at 1710 cm^{-1} in the ir spectrum. This is in agreement with the reported values for fused cyclic lactams.[5] The chloroacetyl derivative **3c** and the oxo compound **3d** can have the alternative structures **3'c** and **3'd**.



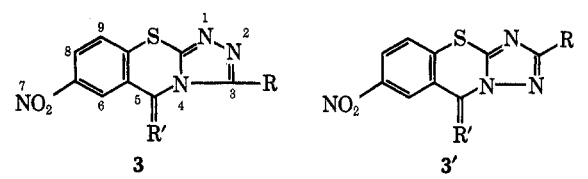
1a, R = C_2H_5
b, R = CH_3



2a, R = C_2H_5; R' = NO_2
b, R = CH_3; R' = NO_2
c, R = C_2H_5; R' = NH_2

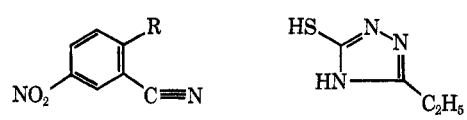


2 **2'a**, R = C_2H_5 **2'**
b, R = CH_3

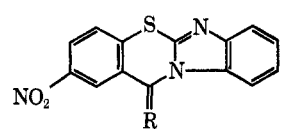


3 **3'**

3a, 3'a; R = C_2H_5; R' = NH
3b, 3'b; R = CH_3; R' = NH
3c, 3'c; R = C_2H_5; R' = NC(=O)CH_2Cl
3d, 3'd; R = C_2H_5; R' = O



4a, R = Cl **5**
b, R = OC_2H_5



6a, R = NH
b, R = O

(1) Yu. A. Naumov and I. I. Grandberg, *Russ. Chem. Rev.*, **35**, 9 (1966).
(2) T. George, R. Tahilramani, and D. A. Dabholkar, *Indian J. Chem.*, **7**, 959 (1969).
(3) H. Beyer and C. F. Kroger, *Justus Liebigs Ann. Chem.*, **637**, 135 (1960).
(4) J. J. Blanksma and P. G. Fohr, *Recl. Trav. Chim. Pays-Bas*, **65**, 706 (1946).
(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1957, p 205.

The methyl analog **1b** gave **2b** on refluxing with 1.1 equiv of sodium ethoxide in ethanol. Treatment of **2b** with 1 equiv of sodium ethoxide gave **3b** as the main product along with a low yield of 2-ethoxy-5-nitrobenzonitrile (**4b**) which was obviously formed by the action of sodium ethoxide on the intermediate nitrile **2'b**. Reduction of **2a** with Raney nickel gave **2c** which failed to undergo base-catalyzed rearrangement to a condensed 1,3-benzothiazine system, showing that the nitro group is essential for the rearrangement to occur.

As intramolecular amidine formation to give rise to condensed 1,3-benzothiazine system occurs in a facile way in the case of 4-amino-5-mercapto-*s*-triazoles, it was of interest to use other heterocyclic substrates containing the -NHC(SH)=N- system. 2-Mercaptobenzimidazole was treated with 2-chloro-5-nitrobenzonitrile (**4a**) in presence of sodium ethoxide to give in good yield 6-imino-8-nitro-6*H*-benzimidazolo[2,3-*b*]-1,3-benzothiazine (**6a**). On treatment with ethanolic hydrochloric acid, the corresponding oxo compound **6b** was obtained, the carbonyl band of which appeared at 1702 cm^{-1} in the ir spectrum.

Experimental Section

Melting points are uncorrected. The ir spectra were examined as Nujol mulls on a Perkin-Elmer Model 421 spectrophotometer. The uv spectra in 95% ethanol were recorded on a Beckman DK-2A Model spectrophotometer and the nmr spectra were recorded on a Varian Associates A-60 spectrometer with TMS as internal standard.

3-Alkyl-4-(2-chloro-5-nitro)benzalamino-5-mercapto-*s*-triazoles.—The above compounds were prepared by refluxing together 1 equiv of 3-alkyl-4-amino-5-mercapto-*s*-triazole with 1.1 equiv of 2-chloro-5-nitrobenzaldehyde in 2-propanol containing 5 drops of concentrated HCl. The product was separated by filtration, washed with dilute sodium bicarbonate solution and water, and recrystallized from methanol.

4-(2-Chloro-5-nitro)benzalamino-3-ethyl-5-mercapto-*s*-triazole (**1a**) was obtained as yellow crystals in 80% yield: mp 236°; ir 1605 and 1588 cm^{-1}; uv max 250 nm (log ϵ 4.43) and 350 (3.62); nmr (CF_3COOH) 1.62 (t, 3 H, CH_2CH_3), 3.3 (q, 2 H, CH_2CH_3), 7.81 (d, 1 H, J = 9 Hz, aromatic), 8.40 (q, 1 H, J = 2.5 and 9 Hz, aromatic), 8.77 (d, 1 H, J = 2.5 Hz, aromatic), and 8.81 (s, 1 H, CH=N).

Anal. Calcd for $C_{11}H_{10}ClN_5O_2S$: C, 42.38; H, 3.23; N, 22.47; S, 10.55. Found: C, 42.63; H, 3.34; N, 22.21; S, 10.55.

4-(2-Chloro-5-nitro)benzalamino-5-mercpto-3-methyl-*s*-triazole (**1b**) was obtained as yellow crystals in 74% yield, mp 252°; ir and uv spectrum were similar to those of **1a**.

Anal. Calcd for $C_{10}H_8ClN_5O_2S$: C, 40.35; H, 2.71; N, 23.51. Found: C, 40.27; H, 2.80; N, 23.43.

3-Alkyl-8-nitrobenzo(7,8)-*s*-triazolo[3,4-*b*](1,3,4)thiadiazepines.—Equimolar amounts of 3-alkyl-4-(2-chloro-5-nitro)benzalamino-5-mercapto-*s*-triazoles and sodium ethoxide in ethanol were heated under reflux for 4 hr. The product was separated by filtration, washed with water, and recrystallized from methanol.

3-Ethyl-8-nitrobenzo(7,8)-*s*-triazolo[3,4-*b*](1,3,4)thiadiazepine (**2a**) was obtained as yellow crystals in 67% yield: mp 240°; ir 1605 and 1520 cm^{-1}; uv max 237 nm (log ϵ 3.24) and 278 (infl) (3.08); nmr (DMSO-d_6) δ 1.33 (t, 3 H, CH_2CH_3), 2.82 (q, 2 H, CH_2CH_3), 7.91 (d, 1 H, C-10 H), 8.41 (q, 1 H, C-9 H), 8.62 (d, 1 H, C-7 H), and 8.86 (s, 1 H, CH=N).

Anal. Calcd for $C_{11}H_9N_5O_2S$: C, 48.00; H, 3.30; N, 25.45. Found: C, 48.24; H, 3.52; N, 25.16).

3-Methyl-8-nitrobenzo(7,8)-*s*-triazolo[3,4-*b*](1,3,4)thiadiazepine (**2b**) was obtained in 70% yield: mp 275°; ir 1605 and 1520 cm^{-1}; uv max 233 nm (log ϵ 4.34) and 277 (infl) (4.03).

Anal. Calcd for $C_{10}H_7N_5O_2S$: C, 45.98; H, 2.70; N, 26.81. Found: C, 46.16; H, 2.92; N, 27.07.

3-Ethyl-5-imino-7-nitro-5*H*-*s*-triazolo[3,4-*b*]-1,3-benzothiazine (**3a**). **Method A. From 1a.**—To a solution of sodium (0.253 g, 12 mg-atoms) in ethanol (70 ml) was added compound **1a** (3.12 g, 0.01 mol). A crystalline solid began to separate when the reaction mixture was heated under reflux with stirring for 1 hr. The refluxing was continued for 4 hr, the reaction mixture cooled, and the product was filtered, washed with water and ethanol, and recrystallized from methanol to give **3a** as pale yellow crystals: yield 1.8 g (66%); mp 176°; ir 3350, 3260, and 1650 cm^{-1}; uv max 218 nm (log ϵ 4.48) and 320 (3.93); nmr (DMSO-d_6) δ 1.35 (t, 3 H, CH_2CH_3), 2.80 (q, 2 H, CH_2CH_3), 7.72 (d, 1 H, C-9 H), 8.43 (q, 1 H, C-8 H), and 9.50 (d, 1 H, C-6 H).

Anal. Calcd for $C_{11}H_9N_5O_2S$: C, 48.00; H, 3.30; N, 25.45. Found: C, 48.29; H, 3.43; N, 25.31.

Method B. From 2a.—Compound **2a** (8.25 g, 0.03 mol) was added to a solution of sodium (0.23 g, 10 mg-atoms) in ethanol (150 ml) and the reaction was carried out and worked up as above to obtain a yield of 5.6 g (68%).

Method C. From 4a and 5.—From **4a** (1.29 g, 0.01 mol) and **5** (1.83 g, 0.01 mol) using sodium ethoxide from sodium (0.25 g, 12 mg-atoms) in ethanol (60 ml) **3a** was obtained in 43.5% yield.

5-Imino-3-methyl-7-nitro-5*H*-*s*-triazolo[3,4-*b*]-1,3-benzothiazine (**3b**).—Compound **2b** (2.61 g, 0.01 mol) was added to ethanol (100 ml) to which sodium (0.23 g, 10 mg-atoms) had been added previously. The mixture was stirred and heated under reflux for 6 hr. The precipitate formed on cooling was filtered and recrystallized from ethanol to afford 0.8 g (31%) of **3b**: mp 191°; ir 3350, 3260, and 1645 cm^{-1}; uv max 218 nm (log ϵ 4.48) and 323 (3.93).

Anal. Calcd for $C_{10}H_7N_5O_2S$: C, 45.98; H, 2.70; N, 26.81. Found: C, 46.33; H, 2.91; N, 27.05.

The filtrate was concentrated under reduced pressure and cooled to give 80 mg of **4b** which on recrystallization from 2-propanol melted at 94°: ir 2240, 1600, 1580, 1030, and 750 cm^{-1}; uv max 296 nm (log ϵ 4.37) and 233 (infl) (4.21); nmr ($CDCl_3$) δ 1.51 (t, 3 H, CH_3), 4.33 (q, 2 H, OCH_2), 7.14 (d, 1 H, aromatic proton), and 8.45 (m, 2 H, aromatic protons).

Anal. Calcd for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.11; H, 4.39; N, 14.44.

3-Ethyl-5-(chloroacetyl)imino-7-nitro-5*H*-*s*-triazolo[3,4-*b*]-1,3-benzothiazine (**3c**).—To a stirred suspension of **3a** (2.75 g, 0.01 mol) in dry toluene (50 ml) containing pyridine (1 ml), a solution of chloroacetyl chloride (1.24 g, 0.01 mol) in toluene (10 ml) was added dropwise. The mixture was heated under reflux for 4 hr and cooled. The precipitated product was filtered and washed with water and ethanol. Recrystallization from methylene chloride–hexane gave 1.7 g (49.35%) of **3c** as colorless crystals: mp 218°; 1700 and 1650 cm^{-1}; uv max 323 nm (log ϵ 4.04) and 235 (infl) (3.96).

Anal. Calcd for $C_{13}H_{10}ClN_5O_3S$: C, 44.39; H, 2.87; N, 19.91. Found: C, 44.69; H, 3.16; N, 20.01.

3-Ethyl-7-nitro-5-oxo-5*H*-*s*-triazolo[3,4-*b*]-1,3-benzothiazine (**3d**).—Compound **3a** (1.37 g, 0.005 mol) was warmed with concentrated HCl (5 ml) and ethanol (10 ml). A homogeneous solution was formed and after 5 min the crystaline precipitate which was formed was filtered, washed with dilute sodium bicarbonate, and recrystallized from ethanol to give 0.3 g (22%) of **3d**: mp 193°; ir 1710 and 1610 cm^{-1}; uv max 236 nm (log ϵ 4.36) and 323 (3.81).

Anal. Calcd for $C_{11}H_8N_4O_3S$: C, 47.83; H, 2.92; N, 20.29. Found: C, 47.70; H, 3.17; N, 20.06.

7-Amino-3-ethyl-*s*-triazolo[3,4-*b*](1,3,4)benzothiadiazepine (**2c**).—A mixture of compound **2a** (4.0 g), Raney Nickel W-2 (2.5 g), and methanol (200 ml) was shaken with hydrogen at ambient temperature and atmospheric pressure until the absorption ceased which corresponded to absorption of nearly 3 mol of hydrogen. The suspension was filtered and the filtrate was evaporated to give a crystalline solid which melted at 160°. Recrystallization from ethanol gave 2.9 g (81%) of **2c** as yellow crystals: mp 181°; ir 3320 and 3200 cm^{-1}; uv max 246 nm (log ϵ 4.53).

Anal. Calcd for $C_{11}H_{11}N_5S$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.49; H, 4.86; N, 28.55.

Treatment of **2c** (2.45 g) with sodium ethoxide under conditions described for **2a** gave back unchanged material.

6-Imino-8-nitro-6*H*-benzimidazolo[2,3-*b*]-1,3-benzothiazine (**6a**).—The above compound was obtained in 65% yield from 2-mercaptobenzimidazole and 2-chloro-5-nitrobenzonitrile **4a** using sodium ethoxide under conditions described for **3a** and recrystallized from methanol: mp 287°; ir 3280, 1600, and 1580 cm^{-1}; uv max 225 nm (log ϵ 4.31), 245 (4.16), and 345 (3.63).

Anal. Calcd for $C_{14}H_8N_4O_2S$: C, 56.76; H, 2.72; N, 18.91. Found: C, 56.43; H, 2.89; N, 18.87.

8-Nitro-6-oxo-6*H*-benzimidazolo[2,3-*b*]-1,3-benzothiazine (**6b**).—Compound **6a** (1.48 g) was added to ethanol (15 ml) containing

concentrated HCl (8 ml) and heated under reflux with stirring for 4 hr. Filtration of the product followed by treatment with dilute sodium bicarbonate solution and ethanol gave yellow crystals of **6b**: yield 1.3 g (88%); mp >305°; ir 1702 and 1612 cm^{-1}; uv max 222 nm (log ϵ 4.26), 260 (4.35), and 335 (4.05).

Anal. Calcd for $C_{14}H_7N_3O_3S$: C, 56.57; H, 2.37; N, 14.14. Found: C, 56.86; H, 2.67; N, 13.90.

Registry No.—**1a**, 24848-32-6; **1b**, 29669-34-9; **2a**, 24848-33-7; **2b**, 29669-36-1; **2c**, 29913-47-1; **3a**, 29669-37-2; **3b**, 29669-38-3; **3c**, 29669-39-4; **3d**, 29669-40-7; **4b**, 29669-41-8; **6a**, 29669-42-9; **6b**, 29669-43-0.

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Synthesis of Pyrido[1,2-*a*]pyrimido[4,5-*b*]pyridine and Related Tricyclic Systems

T. GEORGE,* D. V. MEHTA, AND D. A. DABHOLKAR

Contribution No. 217 from the CIBA Research Centre, Goregaon, Bombay-63, India

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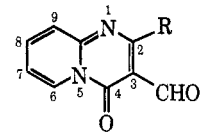
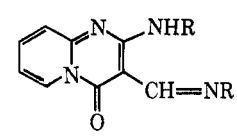
It has been reported earlier[1] that the pyrido[1,2-*a*]-pyrimidine nucleus can be functionalized by the Vilsmeier–Haack reaction to obtain 2-chloro-3-formyl-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**1a**). We are describing below a facile synthesis of some tricyclic systems starting from **1a**.

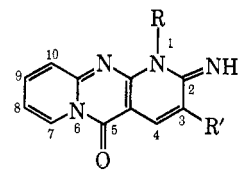
Reaction of **1a** with methylamine and benzylamine took place exothermically to give the aldimines **2a** and **2b**. The nmr spectrum of **2a** showed the presence of the $CH{=}NCH_3$ moiety, the methyl as a doublet at δ 3.42, and the methine proton as a quartet at δ 8.78 ($J_{CH,NCH_3} = -1.6$ Hz);[2] **2b** showed the presence of the $CH{=}NCH_2C_6H_5$ moiety, the methylene group as a doublet at δ 4.72, and the methine proton as a triplet at δ 9.03 ($J_{CH,NCH_2} = -1.3$ Hz). Acid hydrolysis of **2a** gave the aldehyde **1b**. Treatment of **2a** with malononitrile gave in excellent yield 3-cyano-2-imino-1-methyl-4-oxo-4*H*-pyrido[1,2-*a*]pyrimido[4,5-*b*]pyridine (**3a**) which showed in the ir spectrum the imino group at 3300 cm^{-1} and the conjugated cyano group at 2210 cm^{-1}. In general, the formation of the above tricyclic system was very facile using compounds containing active methylene groups adjacent to a cyano group. Thus, ethyl cyanoacetate, cyanoacetamide, and benzoyl acetonitrile[3] reacted with **2a** to give compounds **3b–d** and benzoyl acetonitrile with **2b** to give **3e**. The course of the reaction can be envisaged to proceed through the addition of the anions of the above reagents followed by elimination of methylamine or benzylamine to give compounds **3a–e**. Aminoacetonitrile and cyanamide



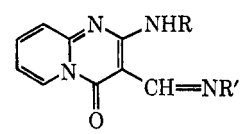
1a, R = Cl
b, R = $NHCH_3$



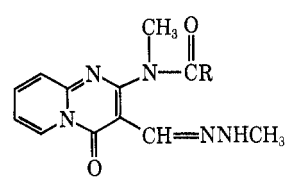
2a, R = CH_3
b, R = $CH_2C_6H_5$



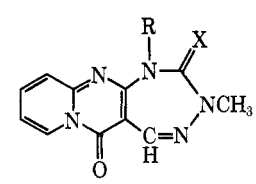
3a, R = CH_3; R′ = CN
b, R = CH_3; R′ = $COOC_2H_5$
c, R = CH_3; R′ = $CONH_2$
d, R = CH_3; R′ = COC_6H_5
e, R = $CH_2C_6H_5$; R′ = COC_6H_5



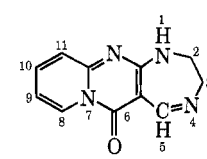
4a, R = CH_3; R′ = $NHCH_3$
b, R = $CH_2C_6H_5$; R′ = $NHCH_3$
c, R = CH_3; R′ = $-N(CH_3)-CO-Cl$
d, R = CH_3; R′ = $-N(CH_3)-CO-N$⟨morpholine⟩
e, R = $CH_2C_6H_5$; R′ = $-N(CH_3)-CS-Cl$
f, R = $CH_2C_6H_5$; R′ = $-N(CH_3)-CS-N$⟨morpholine⟩
g, R = CH_3; R′ = $-N(CH_3)-CO-COOC_2H_5$



4c′, R = Cl
d′, R = N⟨morpholine⟩



5a, X = O; R = CH_3
b, X = S; R = $CH_2C_6H_5$



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failed to react with **2a** and **2b**. Active methylene compounds such as acetylacetone, phenacyl chloride, or chloroacetone did not give tricyclic systems from **2a**, the only product which could be isolated and characterized being **1b**, the aldehyde corresponding to **2a**.

Methylhydrazine reacted with **2a** and **2b** to give the corresponding *N*-methylhydrazones **4a** and **4b**. On reaction with phosgene in toluene, **4a** gave a product

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