

## 1,2,4-Triazines X: Dimerizations of 1,2,4-Triazines

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5,5'-Bi-1,2,4-triazinyl compounds are obtained by the treatment of 5-unsubstituted 1,2,4-triazines with either sodium methoxide or with aqueous potassium cyanide.

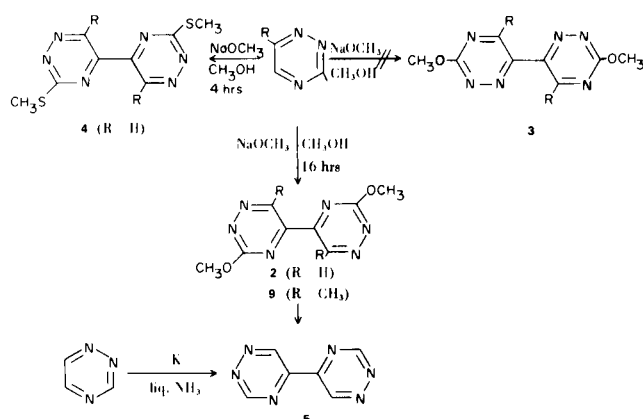
5,5'-Bi-1,2,4-triazinyl is also obtained by the reaction of 1,2,4-triazine with potassium cyanide.

It is proposed that the sodium methoxide catalyzed dimerizations occur *via* a carbanionic intermediate; the aqueous potassium cyanide catalyzed reactions *via* a cyanide addition product and the potassium in liquid ammonia reaction *via* a free radical dimerization process.

The treatment of 3-methylthio-1,2,4-triazine (**1**) with sodium methoxide, which had been generated by dissolving fresh sodium metal in absolute ethanol, affords, along with the expected 3-methoxy-1,2,4-triazine, a higher melting material of molecular formula  $C_8H_8N_6O_2$  (**1**). This compound becomes the exclusive product when sodium metal is added to a solution of 3-methylthio-1,2,4-triazine in absolute methanol.

The pmr spectrum of this substance shows two singlets, in a 1:3 area ratio, at  $\tau$  1.01 and 6.66, respectively. This pattern in conjunction with the molecular weight (220) and elemental analysis of this compound allows one to suggest that the compound is either 3,3'-dimethoxy-5,5'-bi-1,2,4-triazinyl (**2**) or 3,3'-dimethoxy-6,6'-bi-1,2,4-triazinyl (**3**) (see Scheme 1).

SCHEME 1



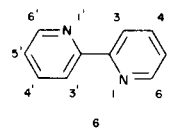
In order to differentiate between these two possibilities, we dimerized 6-methyl-3-methylthio-1,2,4-triazine and obtained the product (**9**) in 50% yield. Thus, it appears that we are dealing with a 5,5'-dimer (**2**).

Final confirmation of this structural assignment came from an examination of the dimer obtained by conversion of the methoxy compound (**2**) to its dihydrazino derivative, followed by oxidative removal of the hydrazino function.

Since the pmr spectrum of the resulting bi-1,2,4-triazinyl (**5**) shows the presence of an AB system (*cf.* Table I), indicative of *para*-coupling rather than two singlets, we are indeed dealing with a 5,5'-dimer (**2**). The same compound is also readily and directly obtained by the slow addition of sodium metal to a solution of 1,2,4-triazine in liquid ammonia (Scheme 1).

It is of some interest to note that, if the dimerization reaction is interrupted, one obtains, instead of the methoxy dimer, the methylthio dimer **4**. Thus, the dimerization process occurs more rapidly than the displacement of the methylthio grouping.

In order to assign the AB system of the 5,5'-bi-1,2,4-triazinyl (**5**) properly, recourse was taken to the pmr spectrum of 2,2'-bipyridyl (**6**) (**2**), where we note that the



$\beta$ -proton ( $\tau$  2.73) becomes considerably more deshielded ( $\tau$  1.60) in going from pyridine to the dimer (H-3). This deshielding ( $\tau$  1.13) would also be expected to occur in H-6 of the triazine dimer when compared to 1,2,4-triazine (H-6:  $\tau$  = 0.76). Thus, if the most deshielded pmr signal of the dimer ( $\tau$  = -0.37) is assigned to H-6, one finds that this proton is more deshielded by  $\tau$  1.13 than it is in 1,2,4-triazine. Thus, the assignments, as shown in Table I are verified (**3**).

Dimerizations of pyridinoid heterocyclic compounds are well-known phenomena. For example, when dry pyri-



Table II  
Potassium Cyanide Catalyzed Dimerizations  
of Some 1,2,4-Triazines

Starting Material (Compound No.)	Product (Compound No.)	% Yield	%C	Elemental Analyses					
				Calcd. (a)	Found		Found		
				%H	%N	%C	%H	%N	
1 a	4	94.0	38.10	3.18	33.33	38.23	3.65	33.15	
1 b	2	93.0	43.63	3.66	38.13	43.34	3.57	37.91	
1 c	7 (b)	80.5	42.85	4.28	30.00	42.97	4.41	30.18	
1 d	8 (c)	91.4	37.89	3.15	58.94	38.05	3.22	59.17	
1 e	5	89.2	44.99	2.51	52.49	44.77	2.31	51.87	

(a) Calcd. for the appropriate dimer. (b) M.p. 116.5-118°. (c) M.p. 350° dec.

### 3,3'-Dimethoxy-5,5'-bi-1,2,4-triazinyl (2).

3-Methylthio-1,2,4-triazine (5.08 g., 0.04 mole) was dissolved in ice-cold absolute methanol. To this solution was added 1.2 g. of sodium metal in two portions during a 30 minute interval. The mixture was allowed to stand at room temperature for 16 hours, saturated with dry-ice and filtered. The solid was washed with 200 ml. of methanol and the washings were combined with the filtrate. The combined solution was evaporated to dryness and residue was extracted with chloroform. The chloroform extract, after evaporation to dryness afforded a yellow solid which was recrystallized from methanol to afford 2.8 g. (63.6%) of 3,3'-dimethoxy-bi-1,2,4-triazinyl (2), m.p. 175-176.5°, identical in every respect (m.p., mass spec., pmr spectrum) with the minor product described in the previous paragraph.

### 3,3'-Dimethylthio-5,5'-bi-1,2,4-triazinyl (4).

The above procedure was repeated with the exception that the reaction was interrupted after four hours. Repeated fractional recrystallization on the reaction products afforded 0.8 g. (20%) of a compound (m.p. 168.5-170°; mass spec. mol. wt. 252) identified as 3,3'-dimethylthio-5,5'-bi-1,2,4-triazinyl (4) by its elemental analysis and pmr spectrum.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>6</sub>S<sub>2</sub>: C, 38.10; H, 3.18; N, 33.33. Found: C, 38.23; H, 3.65; N, 33.15.

### 5,5'-Bi-1,2,4-triazinyl (5).

a) From 3,3'-dimethoxy-5,5'-bi-1,2,4-triazinyl (2).

A solution of 6 g. (0.027 mole) of compound 2 was dissolved in 100 ml. of ethanol and 4 g. of 95% aqueous hydrazine was added. The resulting solution was refluxed for 24 hours and the precipitated product was collected, from the cooled reaction mixture, by filtration. The material (5.9 g.) was dissolved in 100 ml. of absolute ethanol and 18 g. of yellow mercuric oxide was added. The suspension was then heated under reflux for 5.5 hours, the cooled reaction mixture was filtered and the ethanol was removed by filtration. The solid residue thus obtained was sublimed at 150° (0.5 mm) to afford 1.4 g. of a yellow solid.

This compound was purified by recrystallization from ethanol to afford, 5,5'-bi-1,2,4-triazinyl (5) (m.p. 210-212°).

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>N<sub>6</sub>: C, 44.99; H, 2.51; N, 52.49. Found: C, 44.77; H, 2.31; N, 51.87. Mass spec. mol. wt. 160 (Calcd. 160); pmr spectrum, see Table I.

### 6,6'-Dimethyl-3,3'-dimethoxy-5,5'-bi-1,2,4-triazinyl (9).

6-Methyl-3-methylthio-1,2,4-triazine (5.3 g., 0.04 mole) was treated in the same manner as described for the preparation of 3,3'-dimethoxy-5,5'-bi-1,2,4-triazinyl (2) (experiment 2 of this experimental section), to afford 2.3 g. (47%) of 6,6'-dimethyl-3,3'-dimethoxy-5,5'-bi-1,2,4-triazinyl (9), m.p. 159-161.5°, mass spec. mol. wt. 248 (theor. 248).

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub>: C, 48.38; H, 4.84; N, 33.87. Found: C, 48.54; H, 4.77; N, 33.91.

Potassium Cyanide Catalyzed Dimerizations of 5-unsubstituted 1,2,4-triazines. (General Procedure).

A solution of 200 mg. of the appropriate triazine derivative in 15 ml. of water was stirred and heated on a steam bath until complete dissolution of the solid. To this warm solution (approx. 40°) was added excess potassium cyanide as a solid (500 mg.). An immediate precipitate (intensely colored) was formed. This solution was then stirred with 250 ml. of ethyl ether for 15 minutes and the organic layer was separated and dried over anhydrous sodium sulfate. The ether was then evaporated *in vacuo* to yield the corresponding triazine dimer. (See Table II for analytical data).

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- (8) The nmr spectra were obtained with a Varian HA-100 instrument as dilute solutions in the solvents indicated in Table I. The mass spectrometric molecular weights of all compounds were obtained with a Hitachi-Perkin Elmer RMU-6E instrument. The elemental analyses were done by Mrs. V. Gindlesberger of this department.