

Yuzuru Sanemitsu\* (1), Yoshinori Nakayama and Masao Shiroshita

Pesticide Division, Institute for Biological Science, Sumitomo Chemical Co. Ltd., 4-2-1, Takatsukasa,  
Takarazuka, Hyogo 665, Japan

Received March 6, 1981

3,4-Dihydro-1,2,4-triazin-5-(2H)ones were prepared by the reduction of 3-methylthio-1,2,4-triazin-5-(2H)ones with sodium borohydride in dimethylformamide. The synthesis appears to be general.

*J. Heterocyclic Chem.*, **18**, 1053 (1981).

We have recently reported that sodium borohydride reduction of 5-methylthio-1,2,4-triazin-3-(2H)ones in methanol afforded 4,5-dihydro-1,2,4-triazin-3-(2H)ones in good yields (2). Extension of this work led us to the new reductive demethylthiolation of 3-methylthio-1,2,4-triazin-5-(2H)ones (1a-e) by sodium borohydride giving 3,4-dihydro-1,3,4-triazin-5-(2H)ones (2a-e) in high yields (Equation 1).

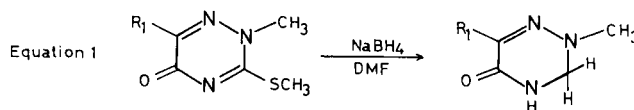
The starting materials (1a-e) were synthesized by the conventional methylation reactions toward 3-methylthio-1,2,4-triazin-5-(2H)ones according to the reported procedure (3, 4). Thus, treatment of compounds (1a-e) with sodium borohydride in dimethylformamide at 70° for 2 hours followed by chromatography on silica gel provided 2-methyl-3,4-dihydro-1,2,4-triazin-5-(2H)ones (2a-e) in yields of 70-82%. Use of methanol as the solvent resulted in a substantial formation of 2-methyl-3-methoxy-1,2,4-tri-

azin-5-(2H)ones along with the expected 3,4-dihydro-1,2,4-triazin-5-(2H)ones.

The structures of compounds (2a-e) were confirmed on the basis of spectroscopic data. The ir spectra gave an absorption at 1660-1685  $\text{cm}^{-1}$ , indicating the existence of a carbonyl group. The pmr spectra of these products in deuteriochloroform exhibit a broad resonance signal at  $\delta$  7.20-8.43 due to the N-H proton which is distinguished by addition of deuterium oxide. Methylene protons, split into a doublet by the adjacent N-H proton, appear at  $\delta$  4.12-4.23. Furthermore, one of the compounds (1a) was identical in physical properties (ir, pmr, mp and elemental analysis) with the authentic sample prepared by the reduction of 2,6-dimethyl-1,2,4-triazin-5-(2H)one with lithium aluminium hydride (5).

In conclusion, this method provides a new efficient route for the synthesis of the 3,4-dihydro-1,2,4-triazin-

Table I  
Synthesis of Some 3,4-Dihydro-1,2,4-triazin-5(2H)ones



Compound No.	R <sub>6</sub>	Yield %	Mp °C	IR $\text{cm}^{-1}$ (nujol)	PMR, $\delta$ (deuteriochloroform)
2a	Methyl	70	115 109-110 Lit. (5)		
2b	Cyclobutyl	82	70	1660	2.95 (s, 3, CH <sub>3</sub> ), 4.21 (d, 2, CH <sub>2</sub> ), 7.30 (br s, 1, NH).
2c	Cyclohexyl	76	119	1670	2.88 (s, 3, CH <sub>3</sub> ), 4.12 (d, 2, CH <sub>2</sub> ), 7.85 (br s, 1, NH).
2d	<i>t</i> -Butyl	82	96	1680	1.25 (s, 9, <i>t</i> -butyl), 2.90 (s, 3, CH <sub>3</sub> ), 4.12 (d, 2, CH <sub>2</sub> ), 7.20 (br s, 1, NH).
2e	Phenyl	79	115	1685	3.03 (s, 3, CH <sub>3</sub> ), 4.23 (d, 2, CH <sub>2</sub> ), 7.30-7.90 (m, 5, phenyl), 8.42 (br s, 1, NH).

Table 2

Compound No.	Formula	Analytical Data for Compounds (2a-e)				Found	
		C	H	N	C	H	N
2a	C <sub>5</sub> H <sub>9</sub> N <sub>3</sub> O	47.23	7.13	33.05	47.29	7.23	32.86
2b	C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O	57.46	7.84	25.13	57.44	8.00	24.97
2c	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O	61.51	8.78	21.52	61.37	8.95	21.15
2d	C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O	56.78	8.94	24.83	56.82	8.94	25.08
2e	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O	63.47	5.86	22.21	63.21	5.89	21.96

-5-(2H)ones.

#### EXPERIMENTAL

Melting points are uncorrected. Pmr spectra were obtained on a Hitachi R-900 spectrometer operating at 90 MHz using TMS as an internal standard. The ir spectra were recorded on a Hitachi 260-10 spectrometer.

#### General Procedure for the Synthesis of Compounds (2a-e).

A solution of sodium borohydride (6 mmoles) dissolved in dimethylformamide (10 ml) was added to a solution of compound **1** (2 mmoles) in the same solvent (5 ml). The mixture was heated at 70° for 2 hours and the solvent was removed *in vacuo*. After cooling, water was added and neutralized with glacial acetic acid. The product was extracted with chloroform, washed with water and then dried over anhydrous sodium sulfate. The crude oily product obtained by removal of chloroform in

*vacuo* was subjected to silica gel column chromatography. Elution with *n*-hexane-acetone (3:1) gave purified compound (2). Physical properties of these compounds are given in Table 1 and 2.

#### Acknowledgement.

The authors thank Dr. K. Yoshioka for helpful discussions and encouragements.

#### REFERENCES AND NOTES

- (1) To whom inquiries should be addressed.
- (2) Y. Nakayama, Y. Sanemitsu, M. Mizutani and K. Yoshioka, *J. Heterocyclic Chem.*, in press.
- (3) J. Gut, M. Prystaš and J. Jonáš, *Collect. Czech. Chem. Commun.*, **26**, 986 (1961).
- (4) J. Daunis, Y. Guindo, R. Jacquier and P. Viallefont, *Bull. Soc. Chim. France*, 1511 (1972).
- (5) J. Daunis and R. Jacquier, *J. Heterocyclic Chem.*, **10**, 559 (1973).