A Convenient One-Pot Preparation of 1,3-Disubstituted 6-Methylthio-2,4-dioxo-1,2,3,4-tetrahydro-1,3,5-triazines [6-Methylthio-1,3,5-triazine-2,4(1*H*, 3*H*)-diones]

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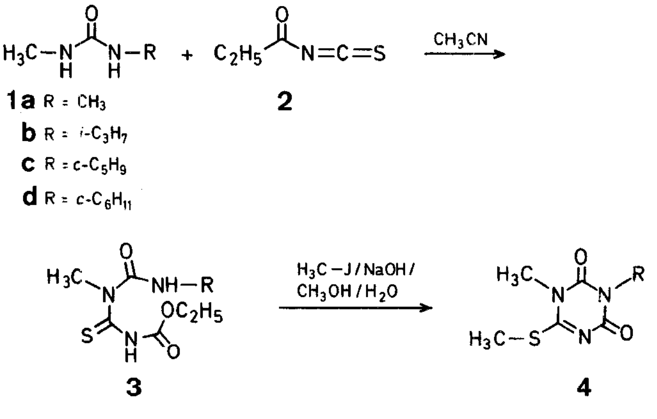
The present communication deals with a convenient one-pot preparation for the synthesis of 1,3-disubstituted 6-methylthio-1,3,5-triazine-2,4(1*H*,3*H*)-diones (**4**). These compounds are of interest from a phytotoxic standpoint[1] and one example is a precursor of a potent herbicide (Hexazinone)[2]. The hitherto reported syntheses of compounds **4** are not satisfactory with respect to the total yield, versatility, and the use of less accessible starting materials[3,4]. Recently, we have reported a convenient one-step synthesis of compounds **4** by reaction of *N*-substituted *N'*-ethoxycarbonyl-*S*-methylisothioureas with isocyanates[5]. This result prompted us to study the behaviour of *N*-alkyl-*N'*-methylureas (**1**) toward ethoxycarbonyl thiocyanate (**2**). We found a facile one-pot preparation of compounds **4**.



Reaction of easily accessible *N*-alkyl-*N'*-methylureas (**1**) with **2** in acetonitrile at room temperature for 24 h afforded *N*-aminocarbonyl-*N'*-ethoxycarbonylthioureas (**3**). Compounds **3** were easily converted to the 1,3,5-triazinediones **4** by treatment with aqueous sodium hydroxide followed by *S*-methylation without prior purification. The structures of all products **4** were confirmed by microanalysis, I. R., and ^{1}H-N.M.R. spectra.

Due to the simple procedure, and easy availability of the starting ureas **1**, this method provides an attractive synthetic method to 6-methylthio-1,3,5-triazine-2,4(1*H*,3*H*)-diones (**4**).

6-Methylthio-2,4-dioxo-1,2,3,4-tetrahydro-1,3,5-triazines (4); General Procedure:

To a solution of the *N*-alkyl-*N'*-methylurea (**1**; 10.0 mmol) in acetonitrile (50 ml), ethoxycarbonyl isothiocyanate (**2**; 1.5 g, 10.0 mmol) is added. The mixture is stirred at room temperature for 24 h. To the reaction mixture is added methyl iodide (2.0 g, 14.0 mmol) and 10% aqueous methanolic solution (20 ml) of sodium hydroxide (0.4 g, 10.0 mmol). The solution is stirred for 30 min and evaporated in vacuo. After adding water (50 ml) to the residual mixture, the product is extracted with chloroform (2 × 50 ml). The combined chloroform extract is dried with magnesium sulfate and concentrated under reduced pressure. The crude residue is purified by column chromatography on silica gel with hexane/acetone (4/1) as eluent yielding pure products **4** (Table).

Table. 6-Methylthio-1,3,5-triazine(1*H*,3*H*)-diones(**4**) prepared

Product	Yield[a] [%]	m.p. [°C][b]	
		found	reported
4a	36	140°	137–139°[4]
4b	72	74°	73–75°[4]
4c	76	85°	80–83°[2]
4d	78	141°	135–137°[4]

[a] Yield of pure isolated products; all compounds gave satisfactory microanalysis.

[b] Uncorrected.

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[1] Fuchs, J. J., Lin, K., *German Patent (DBP)* 2326312 (1973), E. I. du Pont de Neumours; *C. A.* **1974**, *80*, 59971.

[2] 1 - Methyl - 3 - cyclohexyl -6 - dimethylamino -1,3,5 - triazine - 3,5(1*H*,3*H*) - dione (Hexazinone) was easily prepared by the reaction of 6-methylthio-1,3,5-triazine-3,5(1*H*,3*H*)-dione (**4d**) with dimethylamine: Lin, K., *U.S. Patent* 3902887 (1975), E. I. du Pont de Neumours; *C. A.* **1976**, *84* 44169.

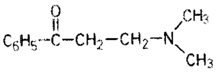
[3] Ogawa, M., Matsui, T., Tobitsuka, J., Kitamura, H., *Agric. Biol. Chem. (Japan)* **1980**, *44*, 2161.

[4] Schlee, H. G., Sasse, K., Eue, L., *German Patent (DBP)* 2254200 (1974), Bayer A.G.; *C. A.* **1974**, *81*, 37583.
Zumach, G., Kühle, E., *Synthesis* **1970**, 542.

[5] Sanemitsu, Y., Nakayama, Y., *Synthesis* **1984**, 770.

Errata and Addenda 1985

K. Matsumoto, A. Sera, T. Uchida, *Synthesis* **1985** (1), 1–26:
The structure of the second product in Table 16 (p. 18) should be:



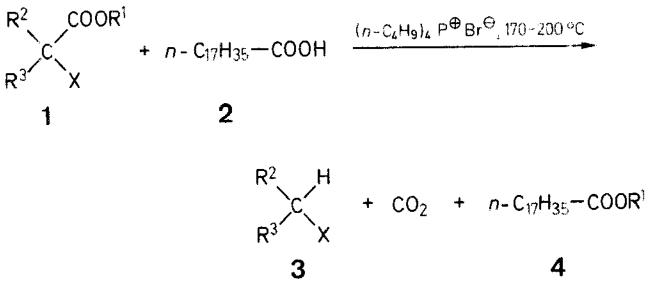
$C_6H_5-C(=O)-CH_2-CH_2-N(CH_3)_2$

Y. Vo Quang, D. Carniato, L. Vo Quang, F. Le Goffic, *Synthesis* **1985** (1), 62–64:
The substituents R^1 for the compounds **2–4b** and **c** (p. 63) should be $C_6H_5-CH_2-O-CO-$ and $C_2H_5-O-CO-$, respectively.

K. N. Mehrotra, I. S. Singh, J. Roy, *Synthesis* **1985** (1), 81–83:
In the Table (p. 82), the I. R. assignment (C=O) should read (C=C) for all products.

J. M. Aizpurua, C. Palomo, *Synthesis* **1985** (2), 206–207:
The following paragraph should be added:
The procedure described is a specific adaption of Roesky's method [H. W. Roesky, H. H. Gieve, *Z. Naturforsch. [b]* **25**, 773 (1970)]. The authors regret the omission of this acknowledgement in the above communication.

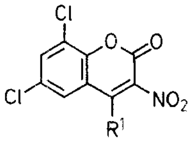
E. V. Dehmlow, E. Kunesch, *Synthesis* **1985** (3), 320–321:
The first formula scheme (p. 320) should be:



$X = COOC_2H_5, COOCH_3, CO-CH_3, -CN$

R. J. K. Taylor, *Synthesis* **1985** (4), 364–392:
The heading for the experimental procedure on p. 379 should be:
2-Benzyl-3-*n*-butylcyclopentanone (23)[90]**:**

A. Caşcaval, *Synthesis* **1985** (4), 428–429:
The structure of product **5** (p. 428) should be:



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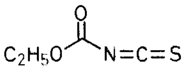
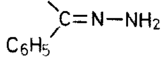
Y. Sanemitsu, *Synthesis* **1985** (4), 429–430:
The structure of compound **2** (p. 429) should be:



2

L. Lapatsanis, G. Milias, S. Paraskewas, *Synthesis* **1985** (5), 513–515:
The structure of compound **2** should be:

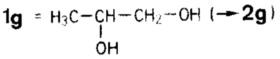


2

T. Eicher, R. Rohde, *Synthesis* **1985** (6/7), 619–625:
The heading for the last experimental procedure on p. 621 should be:
***endo/exo*-6a-Dimethylamino-6-oxo-4,5-diphenyl-2a,6,6a,7-tetrahydro-7*H*-cyclobuta[b]pyrrolizin (*endo/exo*-3d):**
The heading for the 3rd experimental procedure on p. 624 (left-hand column) should be:

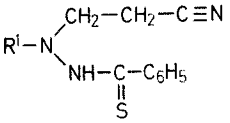
11a-Dimethylamino-1,2-diphenyl-3-oxo-5,6,11,11a-tetrahydro-3*H*-pyrrolo[2,1-b] [3]benzazepin (17):

Xue-Ping Gu, I. Ikeda, M. Okahara, *Synthesis* 1985 (6/7), 649–651:
The structure of product **1g** (p. 650) should be:



1g $= H_3C-CH(OH)-CH_2-OH$ (→**2g**)

I. Yamamoto, K. Fukui, S. Yamamoto, K. Ohta, K. Matsuzaki, *Synthesis* **1985** (6/7), 686–688:
The structure of compounds **3e, f** should be:

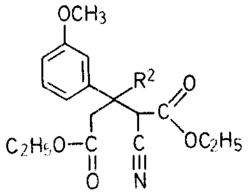


3e,f

I. Monkovic, H. Wong, C. Bachand, *Synthesis* **1985** (8), 770–773:
Reference 9 (p. 772) should be:
[9] Scherer, C. A., Dorschel, C. A., Cook, J. M., Le Quesne, P. W. *J. Org. Chem.* **1972**, *37*, 1083.

A. Cornelis, P. Laszlo, *Synthesis* **1985** (10), 909–918:
Footnotes a and b of Table 10 (p. 916) should be:
[a] 5-Methyl-2-nitro product.
[b] 3-Hydroxy-4-nitro product.

Abstract 7192, *Synthesis* **1985** (11), 1079:
The structure of product **3** should be:



3

D. Moderhack, *Synthesis* **1985** (12), 1083–1096:
The abbreviated name of compound **23** (p. 1087) should read 3-amino-4-imino-2-azetine.

S. M. Fahmy, R. M. Mohareb, *Synthesis* **1985** (12), 1135–1137:
The heading for the last experimental procedure on p. 1136 should be:
3-Amino-*N*^{5}-(2-aminophenyl)-2-cyano-2-pentenediamide (15):

F. Fülöp, G. Bernáth, *Synthesis* **1985** (12), 1148–1149:
The heading for the first experimental procedure on p. 1148 should be:
2-Substituted-1,2,3,4,5,6,7,8-octahydroquinazolines (3); General Procedure: