Monatshefte für Chemie 126, 103–105 (1995)

Monatshefte für Chemie
Chemical Monthly

Heterocycles from Heterocycles: 1,3-Dialkyl-4,5-imidazolidinediones from 1,3,5-Trialkyl-hexahydro-1,3,5-triazines and Oxalyl Chloride

G. Verardo, A. G. Giumanini*, F. Gorassini, and **P. Strazzolini**

Department of Chemical Sciences and Technologies, University of Udine, I-33100 Udine, Italy

Summary. 1,3-Dialkyl-4,5-imidazolidinediones (**5**) were prepared by the reaction of oxalyl chloride (**3**) with the corresponding 1,3,5-trialkyl-hexahydro-1,3,5-triazines (**4**), followed by addition of ethanol, in good to fair yields and fully characterized by MS, IR, ^1H and ^{13}C NMR.

Keywords. 4,5-Imidazolidinediones; Hexahydro-1,3,5-triazines; Oxalyl chloride.

Heterocyclen aus Heterocyclen: 1,3-Dialkyl-4,5-imidazolidindione aus 1,3,5-Trialkyl-hexahydro-1,3,5-triazinen und Oxalylchlorid

Zusammenfassung. Durch die Reaktion von Oxalylchlorid (**3**) mit den entsprechenden 1,3,5-Trialkyl-hexahydro-1,3,5-triazinen (**4**) und anschließender Ethanolzugabe wurden 1,3-Dialkyl-4,5-imidazolidindione (**5**) in zufriedenstellenden bis guten Ausbeuten hergestellt. Die Produkte wurden mit spektroskopischen Methoden charakterisiert.

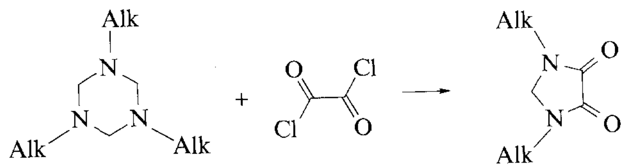
Introduction

Aromatic 1,3,5-hexahydro-1,3,5-triazines (**1**) were found to produce 1,3-diaryl-4,5-imidazolidinediones (**2**) in fair to good yields when treated with oxalyl chloride (**3**) in dichloromethane, followed by quenching of the reaction mixture with ethanol [1]. On the other hand, their alkyl counterparts **4** appeared to be quite unreactive.

We wish to report now that change of solvent and order of addition of reagents allowes to obtain the four derivatives **5** from the corresponding **4** in yields ranging from 51% to 66% without any real optimization attempt (Table 1).

Results and Discussion

The solvent effect is shown by the low yield of cyclic product from **4a** and oxalyl chloride in ethyl ether compared with a 66% yield in hexane. The initial substrate consumption was always fast, but variable amounts of the open diamides were obtained in all experiments. The more pronounced reactivity of the aromatic imines could be ascribed to their fast thermal equilibrium of monomer and dimer forms which are both very active species. The aliphatic compounds **4** are much more stable



3

4a: Alk = Me
4b: Alk = Et
4c: Alk = *c*-Hex
4d: Alk = Ph–CH$_2$

5a: Alk = Me
5b: Alk = Et
5c: Alk = *c*-Hex
5d: Alk = Ph–CH$_2$

Table 1. 1,3-Dialkyl-4,5-imidazolidinediones (**5**)

Triazine (R)	Product	mol (**1**)/mol (**3**)	Solvent	Yield (%)	mp (°C)	Recrystallized from
4a (CH_3)	**5a**	1/2.5	Hexane	66	182	Et_2O/MeOH
4b (C_2H_5)	**5b**	1/1.2	Et_2O	57	178	*t*-Bu–O–Me/MeOH
4c (C_6H_{11})	**5c**	1/1.2	Et_2O	51	211	*t*-Bu–O–Me/CH_2Cl_2
4d (C_7H_7)	**5d**	1/3	Et_2O	53	230	Hex/CH_2Cl_2

thermically, and it is highly likely that their cleavage is caused by attack of **3**. The role of the solvent might be that of dissolving some reaction intermediates and favouring the ring closure with ethanol, but the specific action is still unclear.

Only one compound having the general structure **5** was recorded to date in the chemical literature, namely the dimethyl derivate **5a**, which was obtained in extremely low yield by preparative electrolysis (anodic *bis*-acetoxylation) of tetramethyloxamide [2] but could not be prepared by the reaction of N',N''-dimethylpolymethylene diamines (n = 2, 3) with dialkyl oxalates [3].

Experimental

Materials

Oxalyl chloride and primary aromatic amines are commercially available (Aldrich, Milano, Italy); they were purified and used to prepare 1,3,5-trialkyl-hexahydro-1,3,5-triazines according to the amine paraformaldehyde method [4]. Dry solvents were obtained following standard procedures [5].

Equipment

Infrared spectra were recorded with a Jasco DS-702G spectrophotometer (KBr pellets). Electron impact (70 eV) mass spectra were obtained with a Finnigan 1020 spectrometer. ^1H and ^{13}C NMR data were acquired with a Bruker AC-F 200 spectrometer.

Table 2. Properties of 1,3-dialkyl-4,5-imidazolidinediones (**5**) isolated

Compound	IR, ν (cm^{-1})	^{1}H NMR, δ (ppm), *J* (Hz)	^{13}C NMR, δ (ppm)	MS, *m/z* (%)
5a	3450s, 2920 vs, 1730vs, 1490s, 1460s, 1430s, 1240s, 990s, 805s	3.08 (s, 6H), 4.60 (s, 2H)	28.93, 62.57, 158.28	128 (M$^+$, 63), 100 (23), 56 (8), 49 (12), 43 (82), 42 (100)
5b	2980s, 1730vs, 1460vs, 1430vs, 1370s, 1330s, 1230vs, 810s	1.20–1.35 (tr, 3H, *J* = 7.3), 3.55–3.68 (q, 2H, *J* = 7.3), 4.66 (s, 2H)	12.86, 37.20, 58.45, 158.05	156 (M$^+$, 42), 128 (3), 72 (3), 57 (64), 56 (22), 42 (100)
5c	2920vs, 2850s, 1720vs, 1700vs, 1430vs, 1340s, 1270s, 1225vs	1.05–1.98 (m, 20H), 4.05–4.50 (m, 2H), 4.58 (s, 2H)	25.15, 25.23, 30.59, 51.48, 53.39, 157.96	264 (M$^+$, 12), 183 (67), 182 (10), 101 (100), 100 (36), 82 (23), 68 (12), 67 (15), 56 (34), 55 (45)
5d	2320s, 1730vs, 1650s, 1470s, 1450s, 1425s, 1230s, 695s	4.34 (s, 2H), 4.66 (s, 4H) 7.19–7.41 (m, 10H)	46.39, 58.48, 128.26, 128.53, 129.14, 134.34,	280 (M$^+$, 14), 189 (10), 132 (11), 92 (15), 91 (100), 71 (7), 65 (15), 57 (12)

Preparation of 1,3-dialkyl-4,5-imidazolidinediones (**5**)

A solution of 1,3,5-trimethyl-hexahydro-1,3,5-triazine (**4a**, 10.0 mmol) in anhydrous hexane (5.0 ml) was slowly added to a mixture of oxalyl chloride (25 mmol) and anhydrous hexane (5 ml) kept at 0 °C under efficient stirring in an atmosphere of argon. About 10 minutes after the end of the addition, anhydrous ethanol was slowly added at 0 °C. The precipitation of **5a** was completed at room temperature by addition of ether. The precipitate, separated by filtration, was recrystallized from a suitable solvent.

The spectroscopic and MS properties of the new products are collected in Table 2.

Acknowledgments

This work was supported in part by grants to *AGG* (CNR 91.03291.CT03 and 92.01213.CT06; MPI 1989–91 40% and 60%) and to *GV* (MPI 1987–89 40% and 1989–92 60%). *FG* is the recipient of a postdoctoral scholarship from the Department of Agriculture of the Autonomous Region of Friuli-Venezia Giulia.

References

[1] Giumanini A. G., Verardo G., Gorassini F., Strazzolini P., Tolazzi M. (1993) Tetrahedron **46**: 10609

[2] Eberson L., Hlavaty J., Jonsson L., Nyberg K., Servin R., Sternerup H., Wistrand L. G. (1979) Acta Chem. Scand., Ser. B, **33**: 113

[3] Isaksson R., Liljefors T., Sandstrom J. (1981) J. Chem. Res. (S): 43

[4] Giumanini A. G., Verardo G., Randaccio L., Bresciani-Pahor N., Traldi P. (1987) J. Prakt. Chem. **327**: 748

[5] Perrin D. D., Armarego W. L. F., Perrin D. R. (1980) Purification of Laboratory Chemicals, 2nd ed. Wheaton & Co. Ltd., Great Britain

Received June 1, 1994. Accepted (revised) June 20, 1994