Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 2881-2883

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis and Characterization of Chrysanthemic Acid Esters

QINGWEI DING[1,*], YONGHONG LI[2] and MINGANG ZHANG[1]

[1]College of Material Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, P.R. China
[2]Key Laboratory of Pesticide Chemistry and Application, Ministry of Agriculture, Institute of Plant Protection Chinese Academy of Agricultural Sciences, Beijing 100193, P.R. China

*Corresponding author: E-mail: dingqingweiding@163.com, liyh2012@163.com

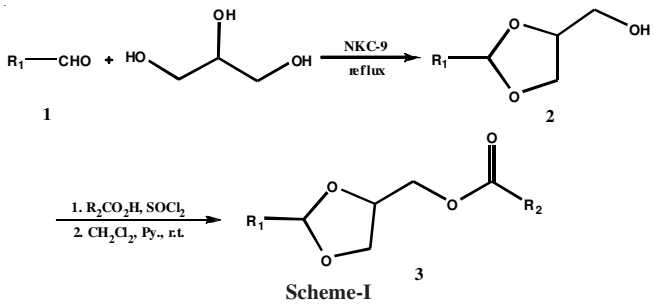
(*Received*: 14 June 2011; *Accepted*: 1 February 2012) AJC-11026

A short and convenient synthesis for a series of novel chrysanthemic acid esters from aldehyde and chrysanthemic acid is reported.

Key Words: Chrysanthemic acid ester, Synthesis, Aldehyde.

INTRODUCTION

Chrysanthemic acid esters are essential building blocks of the pyrethroids, a class of nature insecticides. These insecticides can be isolated from white chrysanthemum flowers (*Chrysanthemum cineriaefolium*) and they combine a low mammalian toxicity with high insecticidal activity[1]. Synthetic pyrethroids are widely used as insecticides in agriculture, forestry, domestic, horticulture, public health and veterinary applications throughout the world because of their general high potent bioefficacy, enhanced stability, and relatively low toxicity to birds and mammals[2,3]. These compounds have been improved physical and chemical properties and biological activity compared to their natural analogues. Pyrethroids are the most potent lipophilic insecticides[4]. They have been detected as surface water contaminants and impacts on the environment leading to effects on ecosystem health have been reported[5]. Many of the toxicological studies on pyrethroids focused on nontarget invertebrates and aquatic animals[6-8], which are extremely sensitive to the neurotoxic effects of these insecticides. This paper reports the preparation of chrysanthemic acid esters compounds involving a novel improved method for the acetalization of aldehydes with glycerol (**Scheme-I**).



Scheme-I

Generally, acetalization reactions are carried out by treatment of carbonyl compounds with alcohols in presence of an acid catalyst and proceed with azeotropic removal of water, using Dean-Stark apparatus. Previously, the catalysts used in the acetalization reaction were generally protic acids, Lewis acids and a number of transitional metal complexes including Rh, Pd, and Pt.[9-12] Although good results have been obtained, the separation of the product from the catalyst system after the reaction was still difficult and the noble metal catalysts used were quite expensive and usually unstable[13].

EXPERIMENTAL

^{1}H NMR spectra were acquired using Bruker DPX300 NMR Spectrometer in $CDCl_3$ solution with TMS as the internal standard. The elemental analyses were performed at the Institute of Chemistry, Chinese Academy of Sciences. Analytical thin-layer chromatography was carried out using MN Kieselgel G/UV254 (Art. 816320) glass-backed plates. Resin NKC-9 was purchased in Nankai University. Commercial available organic compounds were used with further purification and solvents for the reactions were dried on 4-Å molecular sieves before use.

General procedure for the preparaton of products 2: A mixture of the carbonyl compounds (**1**) (10 mmol), 1,2,3-propanetriol (11 mmol) and resin 10 % (w/w) in toluene (25 mL) was refluxed for 5-10 h, using a Dean-Stark trap separator. After the reaction was complete (TLC), the resin was separated by filtration. The toluene was removed under reduced pressure. The product was obtained by distilling the residue under oil-pump reduced pressure (Table-1).

General procedure for the preparaton of products 3a-3m: A solution of the chrysanthemic acid and excess of $SOCl_2$

TABLE-1
YIELDS, PHYSICAL PROPERTIES OF ACETALS (**2**)

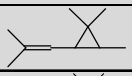
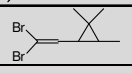
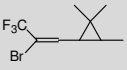
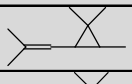
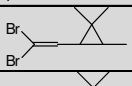
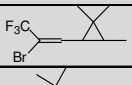
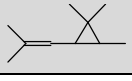
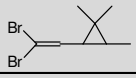
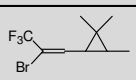
	R_1	Yield (%)*	b.p. (ºC)	^{1}H NMR ($CDCl_3$/TMS) (δ), *J* (Hz)	Elemental analyses (found)	
					C	H
2a[a]		87	134-137 /0.30 KPa	2.20-2.29 (m, 1H), 3.68-3.71 (m, 1H), 3.76-3.87 (m, 1.5H), 3.99-4.09 (m, 1H), 4.18-4.23 (m, 0.5H), 4.33-4.39 (m, 1H), 6.11 (s, 0.5), 6.24 (s, 0.5H), 6.98-7.02 (m, 1H), 7.15-7.19 (m, 1H), 7.33-7.36 (m, 1H)	51.39 (51.60)	5.39 (5.41)
2b[b]		85	150-152 /0.98 KPa	2.23-2.36 (m, 1H), 3.54-4.36 (m, 5H), 5.39-5.94 (4s, 1H), 7.34-7.41 (m, 3H), 7.44- 7.51 (m, 2H)	66.38 (66.65)	6.68 (6.71)
2c[b]		87	172-174 /1.30 KPa	2.03 (s, 1H), 3.85-4.38 (m, 5H), 5.82-6.25 (3s, 1H), 7.28-7.57 (m, 3H), 7.57-7.72 (m, 1H)	56.18 (55.96)	5.19 (5.17)

*Isolated yield based on aldehyde; a) colourless liquid; b) pale yellow liquid

was stirred at 50-60 ºC, after 4 h, the excess of $SOCl_2$ was removed under reduced pressure to give the crude chrysanthemoyl chloride. Then to a solution of the acetal (1 mmol) in 10 mL CH_2Cl_2 and pyridine (1.1 mmol) stirred at room temperature, was added dropwise a solution of the chrysanthemoyl chloride (1.1 mmol) in 5 mL CH_2Cl_2; the reaction progress was monitored by TLC. Upon completion, the reaction mixture was acidified with 1.5 N aqueous HCl and then partitioned with water (30 mL). The organic phase was washed with brine (3 × 30 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated on a rotary vacuum evaporator to afford the crude product. The crude product obtained after work-up was purified by flash column chromatography on silica gel (300-400 mesh).

As described above, the final compounds **3a-3m** were prepared from different aldehyde and 1,2,3-propanetriol in various yield (Table-2). Data of magnetic resonance spectroscopy and elemental analyses are collected in Table-3.

TABLE-2
YIELDS, PHYSICAL PROPERTIES OF COMPOUNDS **3**

Comp.	R_1	R_2	Yield (%)*	Flash column chromatography petroleum ether: ethyl acetate
3a[a]			82	9 : 1
3b[a]			76	9 : 1
3c[a]			85	9 : 1
3d[b]			78	9 : 1
3e[c]			73	9 : 1
3f[a]			84	4 : 1
3g[c]			81	9 : 1
3h[a]			77	4 : 1
3i[a]			82	4: 1
3j[a]			80	9 : 1
3k[a]			79	4 : 1
3l[c]			77	9 : 1
3m[a]			79	4 : 1

*Isolated yield based on acetal; a) Pale yellow viscous liquid; b) White crystalline solid; c) Yellow viscous liquid

RESULTS AND DISCUSSION

The key step of the present route is that the acetalization was performed using cation-exchange resin NKC-9 as catalyst, which has been little used in this context. Cation-exchange resin NKC-9 is a copolymer of divinylbenzene (DVB) and styrene; the sulfonic acid group is the active site (Brønsted acidity), which is the same as Amberlyst-15.[14,15] Resin NKC-9, however, is a commercial domestic product. Unlike Amberlyst-15 (US), it can be obtained easily and cheaply. Unlike dry HCl, corrosive acid HF, saturated H_2SO_4 and *p*-TsOH, it can be recycled, does not corrode the apparatus and the products separates easily and the reaction does not involve any other additive. The preparation of the starting material acetals (**2**) by acetalization has been reviewed in the literature[16].

The biological activity of compounds **3** indicates that they display better sterilization bioactivities and some insecticidal activity[17]. This simple, inexpensive, efficient, recyclable and highly ecofriendly acid catalyst has been shown to be useful in acetalization reactions.

ACKNOWLEDGEMENTS

The authors thank the Natural Science Foundation for Young Scientists of Shanxi Province, China (No. 2009021007-3) and the Municipal Science and Technology Development Program of Shanxi Province, China (No. 20081028, 20091022) for financial support.

REFERENCES

1. Y. Katsuda, *Pestic Sci.*, **55**, 775 (1999).
2. J.P. Leahey, The Pyrethroid Insecticides; Taylor and Francis: London, UK, Chapter 5, pp. 263 (1985).

TABLE-3
ANALYTICAL AND SPECTRAL DATA OF COMPOUNDS **3a-3m**

Compound	^{1}H NMR ($CDCl_3$/TMS) (δ), J (Hz)	Elemental analyses (Found)	
		C	H
3a	1.141-1.145 (d, *J* = 1.188 Hz, 3H), 1.246-1.293 (m, 3H), 1.444-1.461 (d, *J* = 5.34 Hz, 1H), 1.700-1.715 (d, *J* = 4.422 Hz, 6H), 2.054-2.098 (t, 1H), 3.784-3.843 (m, 1H), 4.211-4.291 (m, 3H), 4.476-4.535 (m, 1H), 4.876-4.907 (m, 1H), 6.251 (s, 1H), 6.977-7.006 (m, 1H), 7.162-7.174 (d, *J* = 3.522 Hz, 1H), 7.325-7.345 (m, 1H)	64.26 (64.21)	7.19 (7.24)
3b	1.048-1.353 (m, 6H), 1.869-2.030 (m, 2H), 3.968-4.023 (m, 1H), 4.090-4.327 (m, 3H), 4.02-4.459 (m, 1H), 6.128 (s, 1H), 6.725-6.784 (m, 1H), 6.979-7.008 (m, 1H), 7.167-7.202 (m, 1H), 7.330-7.368 (m, 1H)	41.22 (40.86)	3.89 (3.73)
3c	1.290-1.321 (m, 6H), 2.009-2.060 (t, 1H), 2.168-2.234 (m, 1H), 3.772-3.834 (m, 1H), 4.214-4.303 (m, 3H), 4.485-4.548 (m, 1H), 6.259 (s, 1H), 6.882-6.192 (m, 1H), 6.986-7.015 (m, 1H), 7.163-7.181 (m, 1H), 7.336-7.357 (m, 1H)	49.70 (49.27)	4.42 (4.24)
3d	1.187-1.191 (d, *J* = 1.407 Hz, 6H), 1.246-1.253 (d, *J* = 2.208 Hz, 7H), 3.775-3.825 (m, 1H), 4.167-4.186 (t, 2H), 4.231-4.282 (m, 1H), 4.479-4.541 (m, 1H), 6.246 (s, 1H), 6.970-6.999 (m, 1H), 7.157-7.175 (m, 1H), 7.317-7.338 (m, 1H)	61.91 (61.86)	7.14 (7.19)
3e	0.687-0.710 (d, *J* = 6.687 Hz, 3H), 1.014-1.055 (m, 3H), 2.267-2.351 (m, 1H), 3.104-3.204 (m, 1H), 3.832-3.977 (m, 1H), 3.991-4.042 (m, 1H), 4.120-4.282 (m, 2H), 4.343-4.381 (m, 1H), 6.077 (s, 1H), 6.957-6.988 (m, 1H), 7.147-7.161 (t, 1H), 7.270-7.275 (d, *J* = 1.683 Hz, 1H), 7.298-7.340 (m, 4H)	59.91 (59.82)	5.56 (5.47)
3f	1.127-1.144 (t, 3H), 1.260-1.278 (t, 3H), 1.435-1.472 (m, 1H), 1.699-1.712 (d, *J* = 3.9Hz, 6H), 2.061-2.079 (d, *J* = 5.34 Hz, 1H), 3.806-3.973 (m, 1H), 4.107-4.286 (m, 3H), 4.452-4.491 (m, 1H), 4.877-4.908 (m, 1H), 5.819 (s, 0.5H), 5.953 (s, 0.5H), 7.3577.392 (m, 3H), 7.462-7.546 (m, 2H)	72.70 (72.65)	7.93 (7.99)
3g	1.222-1.289 (m, 6H), 1.647-1.675 (d, *J* = 8.4 Hz, 2H), 3.680-3.750 (m, 2H), 4.363-4.414 (m, 2H), 4.984-5.050 (m, 1H), 5.473 (s, 1H), 6.290-6.316 (d, *J* = 7.92Hz, 1H), 7.353-7.397 (m, 3H), 7.466-7.498 (m, 2H)	46.98 (46.57)	4.38 (4.20)
3h	1.255-1.314 (m, 6H), 1.944-2.004 (m, 1H), 4.126-4.407 (m, 3H), 4.984-5.050 (m, 1H), 5.471 (s, 1H), 6.863-6.919 (t, 2H), 7.358-7.396 (m, 2H), 7.461-7.493 (m, 2H)	56.37 (56.29)	4.98 (4.90)
3i	1.172-1.196 (m, 6H), 1.215-1.263 (m, 7H), 3.786-3.999 (m, 1H), 4.101-4.300 (m, 3H), 4.458-4.514 (m, 1H), 5.832-5.959 (2s, 1H), 7.356-7.402 (m, 3H), 7.459-7.519 (m, 2H)	71.03 (70.98)	7.95 (8.01)
3j	1.129-1.163 (m, 3H), 1.245-1.315 (m, 3H), 1.432-1.475 (m, 1H), 1.685-1.745 (m, 6H), 2.054-2.097 (m, 1H), 3.871-4.164 (m, 1H), 4.113-4.307 (m, 3H), 4.462-4.535 (m, 1H), 4.876-4.907 (m, 1H), 6.187(s, 0.5H), 6.290 (s, 0.5H), 7.278-7.365 (m, 3H), 7.588-7.696 (m, 1H)	65.84 (65.79)	6.91 (6.96)
3k	1.210-1.300 (m, 6H), 1.898-1.936 (d, *J* = 11.58 Hz, 2H), 4.153-4.300 (m, 5H), 6.184-6.311 (m, 1H), 6.737-6.780 (m, 1H), 7.276-7.372 (m, 4H)	43.71 (46.57)	3.87 (4.20)
3l	1.219-1.343 (m, 6H), 1.998-2.069 (m, 1H), 2.148-2.225 (m, 1H), 3.792-3.841 (t, 0.5H), 3.957-4.002 (m, 0.5H), 4.108-4.162 (m, 0.5H), 4.211-4.298 (m, 2.5H), 4.470-4.528 (m, 1H), 6.179 (s, 0.5H), 6.286 (s, 0.5H), 5.898-5.941 (m, 1H), 7.253-7.311 (m, 2H), 7.335-7.379 (m, 1H), 7.579-7.659 (m, 1H)	51.95 (56.29)	4.36 (4.90)
3m	1.102-1.253 (m, 12H), 1.268-1.320 (m, 1H), 3.820-4.007 (m, 1H), 4.107-4.300 (m, 3H), 4.451-4.527 (m, 1H), 6.188 (s, 0.5H), 6.289 (s, 0.5H), 7.270-7.302 (m, 2H), 7.329-7.366 (m, 1H), 7.590-7.699 (m, 1H)	63.81 (70.98)	6.84 (8.01)

3. E. Miadokova, V. Vickova, M. Trebaticka, L. Garajova, J. Grolmus, S. Podstavkova and D. Vieck, *Mutal. Res.*, **280**, 161 (1992).
4. J. Angerer and A. Ritter, *J. Chromatogr. A.*, **695**, 217 (1997).
5. A. Moore and C.P. Waring, *Aquat. Toxicol.*, **52**, 1 (2001).
6. J.R. Coates, D.M. Symonik, S.P. Branbury, S.D. Dyer, L.K. Timson and G.J. Atchison, *Environ. Toxicol. Chem.*, **8**, 671 (1989).
7. K. Haya, *Environ. Toxicol. Chem.*, **8**, 381 (1989).
8. S.C. Schimmel, R.L. Garnas, J.M. Patrick Jr. and J.C. Moore, *J. Agric. Food Chem.*, **31**, 104 (1983).
9. J. Ott, G.M.R. Tombo, B. Schmid, G. Wang, T.R. Ward and L.M. Venanzi, *Tetrahedron Lett.*, **30**, 6151 (1989).
10. Z. Zhu and J.H. Espenson, *Organometallics*, **16**, 3658 (1997).
11. B.H. Lipschutz, D. Pollart, J. Monforte and H. Kotsuki, *Tetrahedron Lett.*, **26**, 705 (1985).
12. R.V. Hoffman, *Tetrahedron Lett.*, **15**, 2415 (1974).
13. M. Cataldo, E. Nieddu, R. Gavagnin, F. Pinna and G. Strukul, *J. Mol. Catal.*, **142**, 305 (1999).
14. G.P. Kalena, A. Jain and A. Banerji, *Molecules*, **2**, 100 (1997).
15. P.K. Paakkönen and A.O.I. Krause, *Appl. Catal. A.*, **245**, 289 (2003).
16. Y.H. Li, X.J. Zhang, T.R. Ren and J.J. Zhou, *Synth. Commun.*, **36**, 1679 (2006).
17. The Biological Activity was Evaluated by the Research Institute of Elemento-Organic Chemistry of Nankai University.