

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

ARYLGLYOXYLIC ESTERS VIA ARYLLITHIUM COMPOUNDS

R. G. Micetich^a; R. Raap^a

^a R & L Molecular Research Ltd., Edmonton, Alberta, Canada

To cite this Article Micetich, R. G. and Raap, R.(1971) 'ARYLGLYOXYLIC ESTERS VIA ARYLLITHIUM COMPOUNDS', *Organic Preparations and Procedures International*, 3: 4, 167 – 169

To link to this Article: DOI: 10.1080/00304947109356062

URL: <http://dx.doi.org/10.1080/00304947109356062>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

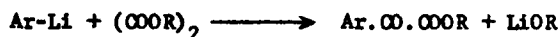
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ARYLGLYOXYLIC ESTERS VIA ARYL LITHIUM COMPOUNDS

R. G. Micetich* and R. Raap*
R & L Molecular Research Ltd.,
8045 Argyll Road, Edmonton 82, Alberta, Canada.

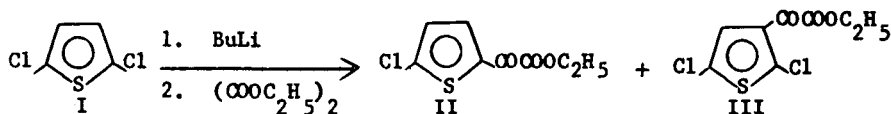
Arylglyoxylic esters may be prepared from the aroyl chlorides¹ or via a Friedel-Crafts reaction on the hydrocarbon². Recently Nyberg³ reported that while thienyl Grignard reagents reacted with dimethyl oxalate to form methyl thienylglyoxalate and methyl dithienylglycolate, 2- and 3-lithiothiophene reacted with dimethyl oxalate to form the corresponding 2,2'- and 3,3'-thenoin. In these latter reactions none of the glyoxylic esters could be detected.

We have found that the reverse addition of an aryl or hetero-aryl lithium compound to an excess of an oxalate ester is a convenient method of preparing certain glyoxylic esters. 2-Lithiothiophene by this



method gave 84% of the ketoester. In the case of 3-lithiothiophene a mixture of the 2- and 3-glyoxylic esters resulted, probably because the temperature of the 3-lithiothiophene was not rigorously kept below -70° during the transfer into the oxalate solution⁴. An attempt to make ethyl 5-chloro-2-thienylglyoxylate from 2,5-dichlorothiophene by this method resulted in a 90% yield of a 1:1 mixture of ethyl 5-chloro-2-thienylglyoxylate II and ethyl 2,5-dichloro-3-thienylglyoxylate, III. This composition was determined by a comparison of the n.m.r. spectrum of the product with the spectra of authentic samples².

R. G. MICETICH AND R. RAAP



EXPERIMENTAL⁵

n-Butyllithium in hexane (125 ml. of a 1.6 molar soln., 0.20 mole) was added slowly to a stirred, cold (-60°) solution of the hydrocarbon (thiophene, thiazole or isothiazole) or the halo compound (2,3,5-tri-bromothiophene or 1-bromonaphthalene) (0.20 mole) in anhydrous THF (300 ml.) under a nitrogen atmosphere. After an additional 30 minutes at this temperature, the resulting aryllithium solution was slowly siphoned (ca. 20 minutes) into a stirred mixture of diethyl oxalate (0.60 mole) and dry ether (200 ml) while the temperature was maintained at ca. -60°. After the transfer was completed the reaction mixture was warmed to ca. -40° and then poured into 200 ml. of ice-cold 2 N hydrochloric acid. The product was extracted with ether (3 x 100 ml.). The combined organic layers were dried (MgSO₄), the solvent removed and the residue distilled under reduced pressure. The arylglyoxylic esters made by this route are listed in the Table.

Acknowledgments The authors thank Dr. R. U. Lemieux, Director of Research for his advice and interest in this work and Messers V. Baker, R. Fortier, R. Thomas and P. Wolfert for their technical assistance.

TABLE ArCOCOOC₂H₅

<u>Ar</u>	<u>bp.°/mm.</u>	<u>Yield%</u>	<u>Ref.</u>	<u>Elemental Analysis</u> ^e
2-Thienyl ^a	90-93/0.9	84	2	-----
2-(3,5-Dibromothieryl) ^b	135-137/0.5 mp. 65-66	75	-	C,H,Br,S
2-Thiazolyl ^c	88-90/0.4	72	-	C,H,N,S
2-Isouthiazolyl ^d	105-106/0.3 mp. 19-20	71	-	C,H,N,S
1-Naphthyl	154-155/0.5	80	6	-----

ARYLGLYOXYLIC ESTERS VIA ARYLLITHIUM COMPOUNDS

- a. Methyl ester. In this experiment THF was used in place of ether since dimethyl oxalate is not appreciably soluble in ether.
- b. N.m.r. in CDCl_3 : 2.80 τ (s, 1H); 5.55 τ (q, 2H); 8.58 τ (t, 3H).
- c. N.m.r. in CDCl_3 : AB type 1 proton doublets centered at ca. 1.78 τ and 2.06 τ ($J=3$ Hz); 5.47 τ (q, 2H); 8.57 τ (t, 3H).
- d. N.m.r. in CCl_4 : AB type 1 proton doublets centered at ca. 1.49 τ and 2.06 τ ($J=1.8$ Hz); 5.60 τ (q, 2H); 8.57 τ (t, 3H).
- e. The elemental analysis were within $\pm 0.4\%$ of the calculated values.

REFERENCES

1. M. Julia and M. Baillarge, *Bull. Soc. Chim. France*, 850 (1959)
 2. R. G. Micetich, *Org. Prep. Proced.*, 2, 249 (1970)
 3. K. Nyberg, *Acta Chem. Scand.*, 23, 1087 (1969)
 4. S. Gronowitz, "Advances in Heterocyclic Chemistry", A. R. Katritzky, Ed. Vol 1, p. 75, Academic Press, New York, 1963
 5. The infrared spectrum of the glyoxylic esters showed two sharp strong bands in₁ the carbonyl stretching region at 1730 to 1740 and 1670 to 1680 cm^{-1} .
 6. J. Hoch and J. M. Choisy, *Compt. rend.*, 248, 3314 (1959)
- * Present Address. Raylo Chemicals Limited, 8045 Argyll Road, Edmonton 82, Alberta, Canada.

(Received April 26, 1971)