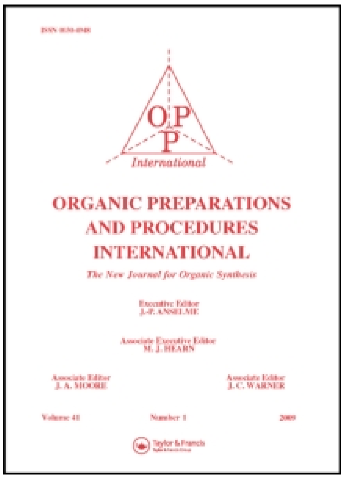

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# ARYLGLYOXYLIC ESTERS, FRIEDEL-CRAFTS REACTION

R. G. Micetich[a]
[a] R & L Molecular Research Ltd., Edmonton 82, Alberta

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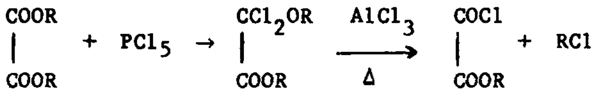
# ARYLGLYOXYLIC ESTERS. FRIEDEL-CRAFTS REACTION

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



$$\begin{array}{c} COOR \\ | \\ COOR \end{array} + PCl_5 \rightarrow \begin{array}{c} CCl_2OR \\ | \\ COOR \end{array} \xrightarrow[\Delta]{AlCl_3} \begin{array}{c} COCl \\ | \\ COOR \end{array} + RCl$$

$$ArH + ClCO.COOR \xrightarrow[CH_3NO_2]{AlCl_3} Ar.CO.COOR + HCl$$

During the course of our work we had occassion to require fairly large quantities of various aryl and heteroarylglyoxylic esters. We have found the Friedel-Crafts reaction using alkyl oxalyl chloride[1] to be a very convenient method. Large amounts of alkyl oxalyl chloride are conveniently made from the commercial dialkyl oxalates[2] using a modification of the procedure described by Anschütz in 1889[3].

## EXPERIMENTAL

Methyl or Ethyl oxalyl chloride. Dimethyl or diethyl oxalate (2.0 moles)[2] and phosphorous pentachloride (2.1 mole) were stirred and heated under reflux in an oil bath at 130-135° for 16 hours after which the reaction mixture was distilled. In the case of dimethyl oxalate the phosphorous oxychloride formed could be removed completely by distillation under slightly reduced pressure. The residue of methyl 2,2-dichloro-2-methoxyacetate on heating at 120° with a catalytic amount of anhydrous aluminium chloride, underwent a very rapid decomposition, evolving methyl chloride. Distillation then gave methyl oxalyl chloride, b.p. 117-120° (95%). Reported b.p. 125°[3].

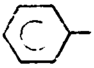
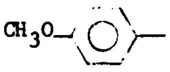
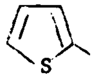
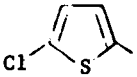
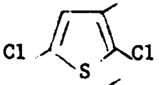
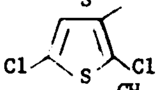
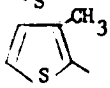
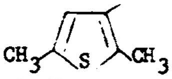
In the case of diethyl oxalate, ethyl oxalylchloride was formed directly during the initial reaction and co-distilled with the phosphorous oxychloride. This mixture could however be used as such in the Friedel-Crafts reaction.

Friedel-Crafts Reaction. Preparation of glyoxylic esters. A solution of anhydrous aluminium trichloride (100 g, 0.75 mole) in nitromethane (200 ml) was added slowly to a stirred mixture of the alkyl oxalylchloride (0.75 mole) and the aryl or heteroaryl compound (0.50 mole) cooled in an ice-bath, at such a rate as to maintain the reaction temperature below 10°. After the addition was completed the reaction mixture was stirred at 10° for one hour more and then at ambient temperature for another hour, after which it was poured carefully into a mixture of ice and water (1.5 l), layered with ether (150 ml). The aqueous layer was extracted with ether (3 x 100 ml) and the combined ether layers washed with dilute aqueous sodium carbonate, dried ($MgSO_4$), filtered and solvent removed. The residue was distilled under reduced pressure. The arylglyoxylic esters made by this route are described in the table.

In every case the infrared spectrum of the glyoxylic esters showed two sharp strong bands in the carbonyl stretching region at 1730 to 1740 and 1670 to 1680 $cm^{-1}$. The n.m.r. spectrum in every instance was in agreement with the assigned structure, and in cases where more than one isomer could be formed (2 and 7 in Table), the n.m.r. spectrum of the purified compound showed the presence of only one isomer.

TABLE[a]

Ar.CO.COOR

| No. | Ar | R | b.p.°C/mm | Yield % |
|---|---|---|---|---|
| 1 |  | $CH_3$ | 100-102/2.3 | 58 |
| 2 |  | $CH_3$ | 114-117/0.7<br>m.p. 46-48°C | 60[b]<br>33[c] |
| 3 |  | $CH_3$ | 90-92/0.9 | 53[d] |
| 4 |  | $C_2H_5$ | 100-112/1.0<br>m.p. 43-45°C | 78[e] |
| 5 |  | $CH_3$ | m.p.58-60°C | 78 |
| 6 |  | $C_2H_5$ | 110/0.8 | 82 |
| 7 |  | $C_2H_5$ | 94-95/0.5 | 66[f] |
| 8 |  | $CH_3$ | 95-97/0.5 | 70 |

a. All new compounds had C and H analysis within ± 0.4% of the calculated values.

b. A 60% yield of the distilled product was obtained as a pale yellow oil which could be crystallized as white needles from hexane. Although the liquid and solid had identical n.m.r. spectra, the solid was obtained in 33% yield owing to its solubility in hexane.

c. N.m.r. in $CCl_4$: $A_2B_2$ type doublets centered at ca. $\tau$ 2.12 and 3.12, J = 9cps (4H); 6.11s (3H) and 6.20s (3H).

d. N.m.r. in $CCl_4$: Thiophene proton multiplets centered at ca. $\tau$ 2.00, 2.27 and 2.89; 6.11s (3H).

e. N.m.r. in $CDCl_3$: AB type doublets centered at ca. $\tau$ 2.03 and 2.96, J = 4.5cps (2H); 5.58q (2H); 8.60t (3H).

f. N.m.r. in $CCl_4$: AB type doublets centered at ca. $\tau$ 2.42 and 3.07, J = 5cps (2H); 7.47s (3H) and 8.60 (3H).

## ACKNOWLEDGEMENTS

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1. L. Bouveault, Bull. Soc. Chim. Fr., 17, 363 (1897).
2. The dialkyl oxalates used were obtained from Raylo Chemicals Limited, 8045 Argyll Road, Edmonton 82, Alberta, Canada.
3. R. Anschütz, Ann., 254, 1 (1889).

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