Tetrahedron Letters No. 18, pp 1507 - 1508, 1975. Pergamon Press. Printed in Great Britain.

STUDIES IN CLAISEN REARRANGEMENT

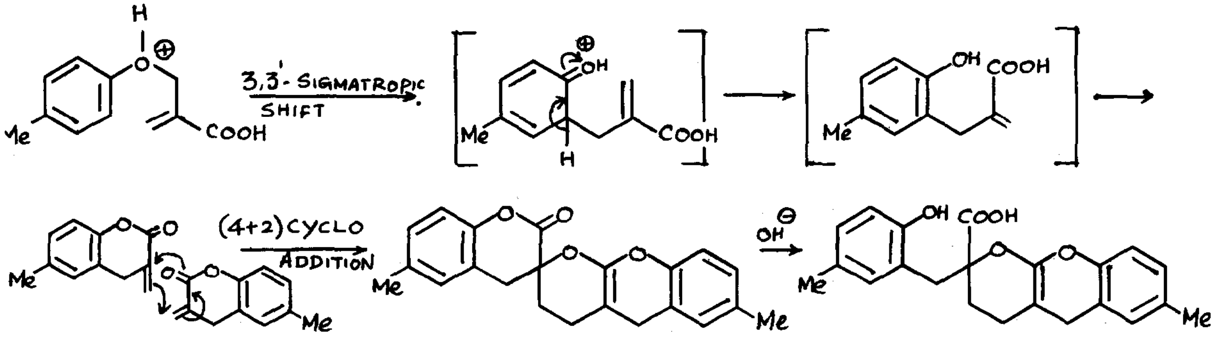
A Novel Transformation of α-Aryloxymethyl acrylic acid[1]

B. Gopalan, K. Rajagopalan, S. Swaminathan*
Department of Organic Chemistry
University of Madras, A.C. College, Madras-600 025
and
K.K. Balasubramanian
Department of Chemistry
Indian Institute of Technology, Madras-600 036

(Received in UK 6 February 1975; accepted for publication 27 March 1975)

In connection with our study on the competitive Claisen vs Fries rearrangement of aryl α-aryloxymethyl acrylates[2], we investigated the acid catalysed condensation of the hitherto unknown α-aryloxymethyl acrylic acids with various phenols. In this communication we report a novel transformation of p-cresoxymethyl acrylic acid I to the spiro dimer II shown in the accompanying chart.

Refluxing a mixture of three equivalents of p-cresol, three equivalents of sodium hydroxide and one equivalent of ββ'-dibromo isobutyric acid[4] in ethanol containing a few drops of dimethylformamide for four hours afforded the α-p-cresoxymethyl acrylic acid, I, m.p. 121-122° (78%). When a mixture of I (1 g), p-cresol (0.55 g) and polyphosphoric acid (10 g) was heated on a steam bath for two hours, a pale red solid (0.95 g, 95%), m.p. 219-220° (methanol), insoluble in water and sodium bicarbonate, was obtained. A similar reaction without employing p-cresol also led to the same product. This solid analysed for $C_{22}H_{20}O_4$ and showed in the mass spectrum peaks at m/e 348 (M^+ 20%), 187 (100%), 188 (99.4%), 174 (M/2, 84.5%), 147 (75.5%) and 145 (44%). Its IR spectrum indicated the presence of a δ-lactone (1740 cm^{-1}) and a double bond (1690 cm^{-1}) while its UV spectrum was similar to that of a dihydro coumarin (λ_{max}^{EtOH} 279 nm, log ε 4.12). This was confirmed by the formation of the monophenolic monocarboxylic acid, III, m.p. 167° (dec.) (molecular ion at 366) when heated with 50% sodium hydroxide solution. This phenolic acid readily underwent a facile lactonisation back to the 219-220° solid when heated at its melting point. The NMR spectrum of the lactone showed no $-OCH_2$ or olefinic proton signals but indicated two aromatic methyl groups at δ 2.3 (s, 3H) and δ 2.4 (s, 3H) and multiplets centered at δ 2.8 (8 H) and δ 7.3 (6 H). These data are consistent with the assigned structure II. The formation of the spiro dimer is rationalised as follows:



II

III

When a solution of the α-p-cresoxymethyl acrylic acid I (1g) in o-dichlorobenzene (10 ml) was refluxed for six hours, the spiro dimer II was straightaway obtained** (60%) on diluting the reaction mixture with ether, in contrast to the extensive tar formation reported in the case of the isomeric γ-phenoxycrotonic acid[5].

Acknowledgement: We thank Professor T.R. Govindachari, Director, CIBA Research Centre, Bombay, for NMR and mass spectral data and R. Balasubramanian, for analytical data. Our thanks are due to Professor A.J. Boulton, University of East Anglia, U.K. for useful discussions. BG gratefully acknowledges the U.G.C. for the award of a JRF and KR acknowledges the C.S.I.R. for a Pool Officer's post.

REFERENCES

1. Preliminary account of this communication was presented at the all-India Convention of Chemists held at Madurai, Tamil Nadu in December, 1974.
2. Unpublished results.
3. All the new compounds described in this communication showed satisfactory elemental analysis and spectral data.
4. A.F. Ferris, J.Org.Chem., 20, 780 (1955).
5. T. Padmanathan and M.U.S. Sultanbawa, J.Chem.Soc., 4210 (1963).

** Several other aryloxymethyl acrylic acids gave the corresponding spiro dimer upon similar treatment.