

AN OXYGEN¹⁸-ISOTOPE STUDY OF THE
CONDENSATION OF METHYL
PHENOXYACETATE AND ANISALDEHYDE

THE potassium *tert*-butoxide catalysed condensation of aryloxyacetates and aryl aldehydes result in the formation of α -aryloxyacrylic acids and esters^{1,2}.

the aldehyde and phenoxyacetic acid were also studied (Table I).

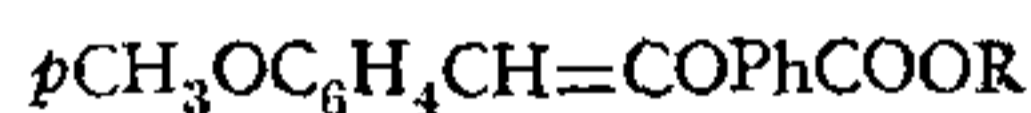
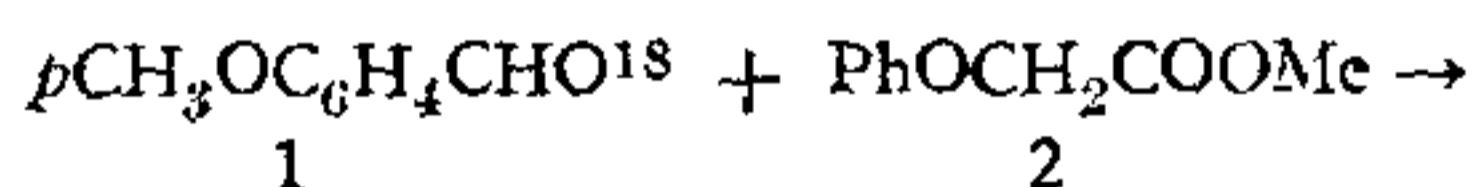
The data clearly indicated that in the Claisen/Stobbe reaction, the O¹⁸ of the aldehyde is incorporated in the acrylic acid (3a), but is not found in the acrylic ester (3b).

TABLE I
O¹⁸ Enrichment in the products

Sl. No.	Aldehyde	Product	$\frac{(M+2) \times 100^a}{M}$	$\frac{(M+2) \times 10^a}{M+1}$
1.	Normal anisaldehyde	3a	3.49, 3.33, 3.21 (3.34)	1.71, 1.71, 1.66 (1.69)
		3b	3.59, 3.54, 3.30 (3.48)	1.71, 1.68, 1.62 (1.67)
2.	O ¹⁸ -anisaldehyde	3a	3.97, 4.19, 4.04 (4.07)	2.04, 2.10, 2.06 (2.07)
		3b	3.41, 3.41, 3.26 (3.36)	1.64, 1.68, 1.63 (1.65)
Perkin reaction:				
3.	Normal anisaldehyde	3a	3.37, 3.24 (3.30)	1.70, 1.61 (1.66)
4.	O ¹⁸ -anisaldehyde	3a	3.52, 3.38, 3.61 (3.50)	1.71, 1.75, 1.86 (1.77)

* The mean value is given in brackets.

Anisaldehyde-O¹⁸ prepared by a method similar to that described by Stasiuk, Sheppard and Bourns³ for benzaldehyde-O¹⁸, was condensed with methyl phenoxyacetate (2) in butanolic *tert*-butoxide at room temperature. Acidification of the reaction mixture yielded the acrylic acid (3a) m.p. 200° and the acrylic ester (3b) m.p. 92-3° in 32% and 66% yields.



3a: R=H

3b: R=Me

The decarboxylation of these acrylates does not proceed smoothly⁴ as do diphenylvinyl acetic acid⁵ and thiophene 2-carboxylic acid⁶ used for isotopic studies in the Stobbe and Hinsberg condensations. Closer examination of the mass spectra (Finnigan 1015 Quadrupole Mass Spectrometer) showed that the (M+2)⁺ ion peak at 272 was more intense in the acid 3a from O¹⁸-anisaldehyde than obtained from normal anisaldehyde, suggesting a different approach to the analysis of the problem.

The intensity of the (M+2)⁺ peak (at a recorder attenuation of 100) was compared with the M⁺ ion peak in these acids, and they showed a consistency which could be employed for studying the incorporation of O¹⁸ into the reaction products. The same acrylic acids obtained by the Perkin condensation of

The (M+2)⁺/(M+1) ion peak ratios also led to similar observations and conclusions.

The experimental results are in agreement with the hypothesis of simultaneous oxidylic and aldol routes, though an alternative hydrolytic pathway is not excluded completely⁷.

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