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SYNTHESIS OF ETHYL-α- PROPARGYL ACRYLATE - A USEFUL FIVE CARBON SYNTHON

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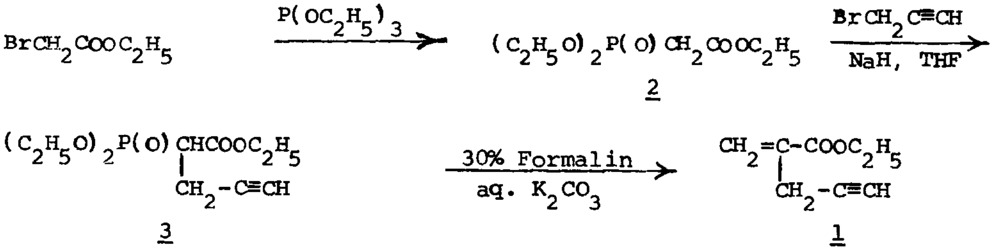
Abstract : The title compound has been synthesised via an alkylation, Wittig-Horner reaction sequence, Michael addition of several active methylene substrates with compound 1 has been carried out.

In connection with our studies on base catalysed rearrangements of oxy-Cope systems[1], we required a five carbon synthon for annulation of cyclo-nones. We report here a three-step synthesis of ethyl-α-propargylacrylate 1 which has the potentials to function as a five carbon Michael acceptor.

Alkylation of triethylphosphonoacetate 2[2] with propargyl bromide, in the presence of NaH in THF at room temperature for 6 h and then at reflux for 3 h gave the alkylated compound 3 as a colourless liquid in 71% yield. Wittig-Horner reaction of compound 3 with 30% formalin in the presence of saturated aqueous potassium carbonate[3], gave the title compound 1 as a colourless liquid in 60% yield.



$$BrCH_2COOC_2H_5 \xrightarrow{P(OC_2H_5)_3} (C_2H_5O)_2P(O)CH_2COOC_2H_5 \xrightarrow[NaH,\ THF]{BrCH_2C\equiv CH}$$

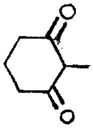
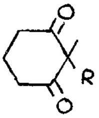
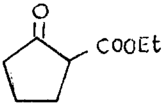
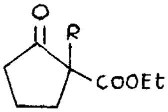
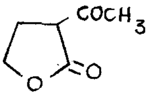
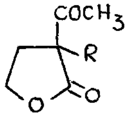
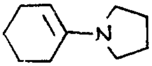
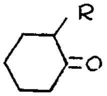
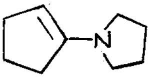
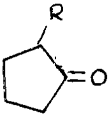
2

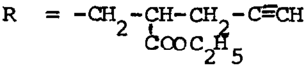
$$(C_2H_5O)_2P(O)\underset{CH_2-C\equiv CH}{CH}COOC_2H_5 \xrightarrow[aq.\ K_2CO_3]{30\%\ Formalin} CH_2=\underset{CH_2-C\equiv CH}{C}-COOC_2H_5$$

3 1

Several active methylene substrates have been found to undergo Michael addition to compound 1 in a clean manner and in fairly good yields only in the presence of a powerful base like sodium methylsulfinyl methide. The results are summerised in Table 1.

TABLE 1

ENTRY	SUBSTRATE	PRODUCT[5]	YIELD(%)[b]
1	$CH_3COCH_2COCH_3$	$CH_3COCH(R)COCH_3$	62
2	$CH_3COCH_2COOC_2H_5$	$CH_3COCH(R)COOC_2H_5$	71
3	$CNCH_2COOCH_3$	$CNCH(R)COOCH_3$	55
4	$C_6H_5CH_2CN$	$C_6H_5CH(R)CN$	64
5	$CH_2(CN)_2$	$R-CH(CN)_2$	65
6			61
7			53
8			55
9			58
10			51



$R = -CH_2-\underset{COOC_2H_5}{CH}-CH_2-C\equiv CH$

b) Isolated yield

Reaction conditions : (a) A mixture of the substrate (0.1 mole), compound 1 (0.11 mole), NaH (0.1 mole) and dry DMSO (75 ml) was stirred at 25°C for 8h and at 80°C for 3-4h under nitrogen and worked up.

We expect the five carbon synthon to be quite valuable in the synthesis of a growing number of natural products[4] containing a fused seven membered ring. We are currently investigating the utility of the synthon towards the synthesis of these compounds.

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(1b) S.Swaminathan, J.Ind.Chem.Soc., LXI, 99(1984).

(2) K.L.Erickzon, J. Org. Chem. 1965, 30, 2208.

(3) J.Villieras, M.Rambaud, Synthesis, 1982, 924.

(4) For example Aciphyllaic acid, Centdarol, Spicatin, Perforenone, Graminiliatrin have fused seven membered rings.

(5) Correct data were obtained for all the new compounds.

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