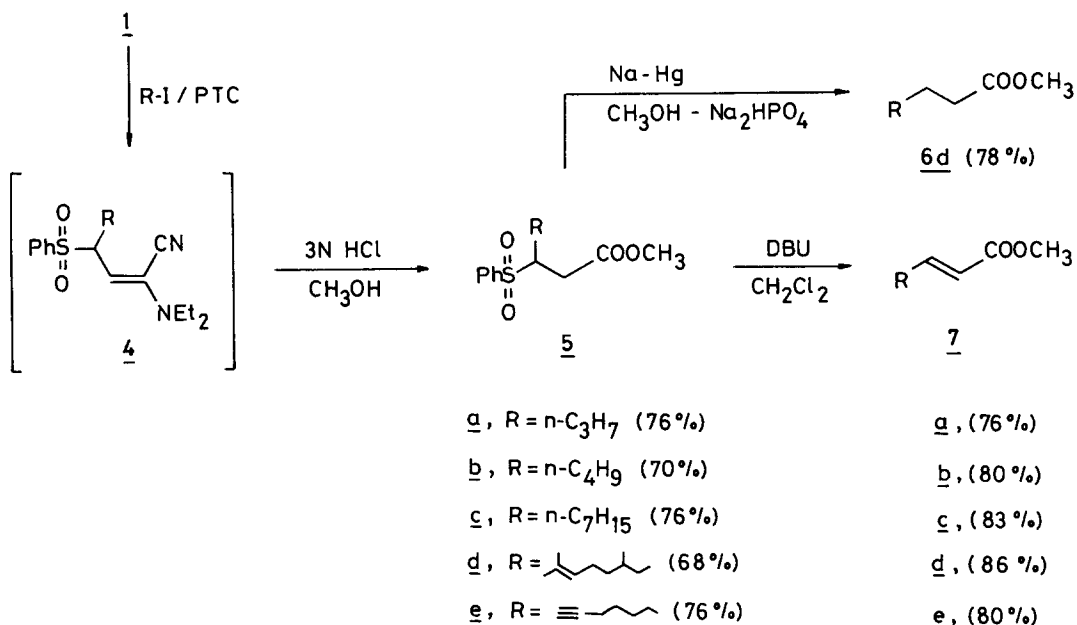


As a result of the enhanced acidity of the allylic proton in 1, γ -alkylation can be performed in the presence of a wide variety of bases (BuLi or LDA in THF, NaH in THF or DME, tAmOK in tAmOH/THF).

The most practical procedure involves catalytic solid-liquid phase-transfer conditions using solid potassium hydroxyde as the base in THF⁴ (Scheme 2). Typically, a solution of 1 (7.4 mmoles) and alkyl halide (7.4 mmoles) in THF (6ml) containing a few drops of tricaprilmethylammonium chloride (Aliquat 336[®]) was added to a suspension of finely ground KOH (1g) in THF (4 ml) under vigorous stirring. The reaction time is about 2 hours. The white solid (potassium salt) is removed by filtration through alumina to give the practically pure α -cyanoenamine 4 as the single (E) isomer. Methanolysis (1.1 equiv. of 3N HCl, CH₃OH, 20°C, 3-15h) gave the sulfone-ester 5 which was purified by chromatography on silica gel (ethyl acetate-petroleum ether, 1:4).

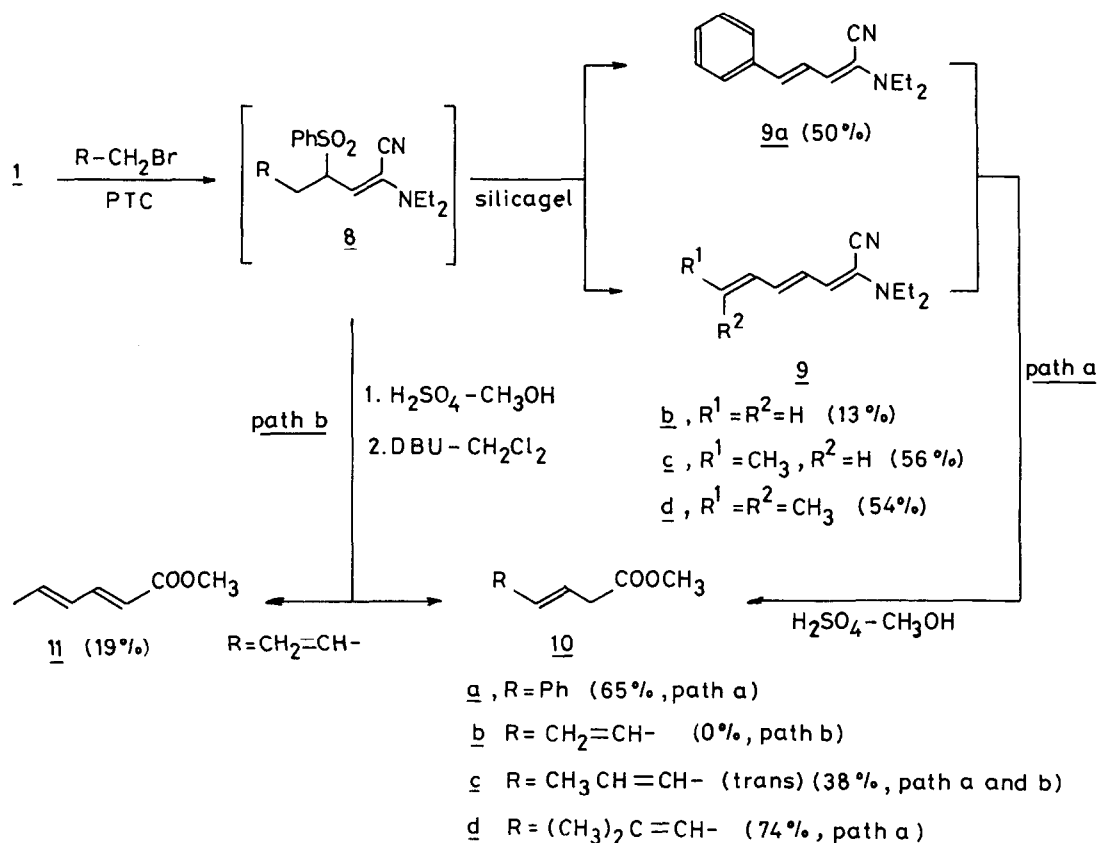


Scheme 2

The sequence proceeds with good yields when the alkylating agent is a primary alkyl iodide. The resulting ester can be readily desulfonylated with sodium-amalgam to give 6⁵. Furthermore, base-catalyzed elimination of sulfonic acid smoothly converts 5 into the corresponding α,β ethylenic esters 7. Sequence 1 \rightarrow 6 and 1 \rightarrow 7 demonstrate the capacity of α -cyanoenamines 1 to act as a synthetic equivalent of both homoenolate or β -carboxyl vinyl anions 6,7.

It must be mentioned here that the dianion derived from 3-phenylsulfonylpropanoic acid could in principle, serve for the same purpose. However its formation requires fairly drastic conditions and its alkylation proceeds in modest yields⁸. Moreover, our attempts to deuterate or directly alkylate the anion derived from 2 only led to tars.

Secondary alkyl iodides and primary alkyl bromides react only sluggishly with 1 under the standard phase transfer conditions. The use of more basic systems (NaH or tBuOK in DMF or DMSO) leads to decomposition of 1. However, with more reactive bromides, the alkylation proceeds quantitatively under the standard conditions (Scheme 3) but the methanolysis gives low yields of sulfone ester as a result of a competing elimination of benzene sulfinic acid. The lability of the benzenesulfonyl group in α -cyanoenamines 8 bearing benzylic or allylic substituents at C-4 is further demonstrated by their facile conversion into the new "capto-dative"⁹ trienes 9 on heating at 50°C in a slurry of silicagel in benzene. Compounds 9 were obtained as mixtures of configurational isomers in which the all (E) isomers predominate (e.g. 70% for 9d). Methanolysis of 9 selectively yields the β,γ trans-unsaturated ester 10.



Scheme 3

As shown for 10c, these esters can be even more conveniently prepared in a one pot sequence : alkylation of 1, acidic methanolysis and base-catalyzed elimination of benzenesulfonic acid. However, under these conditions, compound 10b ($R=CH_2=CH-$) is isomerized into the fully conjugated methyl sorbate 11.

In conclusion, we have shown that the readily available synthon 1 can be very conveniently used for the preparation of saturated or unsaturated (α,β or α,γ) esters as well as of new "capto-dative" polyenes.

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