NEW ACETYLENIC MICHAEL RECEPTOR EQUIVALENTS.

PART I : SYNTHESIS OF Q-SULFENYL - AND Q-SULFINYL ACRYLIC DERIVATIVES.

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 $\frac{Abstract}{P} \quad The synthesis of \alpha-thioarylated B-unsubstituted acrilic derivatives is reported$

Electron deficient olefins like substituted vinyl ketones¹, nitroolefins², charge protected conjugated carbonyl compounds³, α,β -unsatured thioamides⁴, vinyl phosphorus compounds⁵, vinyl sulfoxydes⁶ and ketene thioacetals² have revealed to be versatile building blocks in organic synthesis as receptors in the Michael addition reaction of organometallic or carbanionic nucleophiles. Some of these receptors have efficiently been used in the trapping of regiounstable kinetically generated "copper enolates" ¹b,c,8,9

As an outgrowth of our interests in the electrophilic trapping of such enclates, we expected that structural subunits of type \underline{A} might be accessible in a single operation by a tandem 1,4-addition-functionalisation reaction



In principle, propiolic esters or ethynylketones could be considered as equivalents for the required electrophiles <u>B</u> In fact, the very few examples reported of acetylenes as Michael receptors towards enolates show that only disubstituted ones have so far led to satisfactory yields¹⁰

Herein we wish to report on the synthesis of reagents of type I and II Their effectiveness as trapping agents equivalent to electrophiles B was expected



considered that

- sulfenyl and sulfinyl substituents stabilise carbanions in a-position
- sulfinylated compounds are prone to easy conversion into olefins

The most convenient means of obtaining these α -substituted acrylic derivatives involved a thermal dehydrohalogenation as the key step. Thiophenoxylation of the starting



 ι OSH, Et_3N, Et_2O, $\Delta/24h$, $_{f}$ SO_2Cl_2, O° , k distillation on 220°/Toluene , l. m-CPBA, CH_2Cl_2, O° overnight

 α -bromoesters <u>1</u> and subsequent treatment with sulfuryl chloride in the cold¹¹, led to the chlorothiophenoxyesters <u>2</u> in yields better than 80% Whereas dehydrohalogenation of ester <u>2b</u> occured smoothly during bulb-to-bulb distillation, the esters <u>2a</u> and <u>2c</u> underwent only partly the elimination under distilling conditions Pyrolysis of the latters as IM solutions in toluene, at 200° through a glass column (30 cm length, 2 5 cm i d, packed with 24 g of glass wool, <u>15 mm Hg</u>) and at a flow-rate of 10 ml/hour, brought the reaction to completion, but with a less satisfactory yield in the case of the t-butyl ester <u>3c</u>

These acrylates *polymerise* completely within 5 days at room temperature Fortunately, the corresponding sulfoxydes¹² were obtained (yield > 90%) as perfectly stable liquids (4b and 4c) or crystalline product (4a, m p = 41° C)

The same sequence has been applied to the synthesis of the α -phenylsulfenylmethylvinylketone 3d Pyrolysis at 200° (vide supra, in the presence of one equivalent of



pyridine) afforded the vinyl ketone 3d in 70% yield This ketone, in contrast with the

parent esters, upon standing at room temperature for a few hours, *dimerises* into a white cristalline product TLC analysis showed a main product (Ez/AcOEt 5 1, Rf 0,69) beside two minor unidentified components (Rf 0,60 and 0,52). Two recristallisations in pentane afforded a pure compound in 90% yield which appeared, upon spectral analysis, to be the sole regionsomer 5d. The latter undergoes very cleanly the retrodimensation at 230°, and therefore constitutes a usefull storage compound of the vinyl ketone 3d. Use of these reagents in enolate trapping reactions will be outlined in a forthcoming communication¹³.

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Note added in proof for related vinyl sulfones, see C N SHIAO and H SHECHTER, Tetr Lett 23, 3455 (1982)

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