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ENE REACTION OF α-THIOCARBOCATION: SIMPLE SYNTHESIS OF E,E-2,4-ALKADIENOIC ESTERS FROM 1-ALKENES

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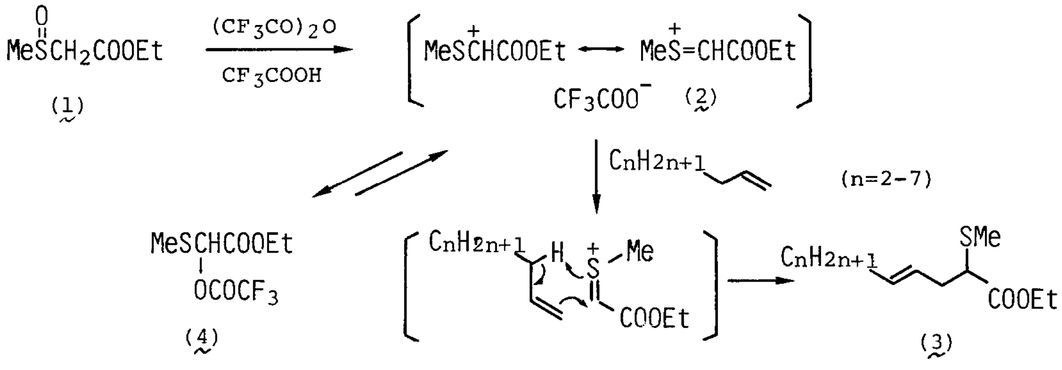
Summary: Pummerer reaction intermediate **2** of α-methylsulfinylacetate(**1**) has been found to react with 1-alkenes to afford ene adducts **3**. E,E-2,4-decadienoic ester (**5**) was synthesized from the adduct **3** (n=5).

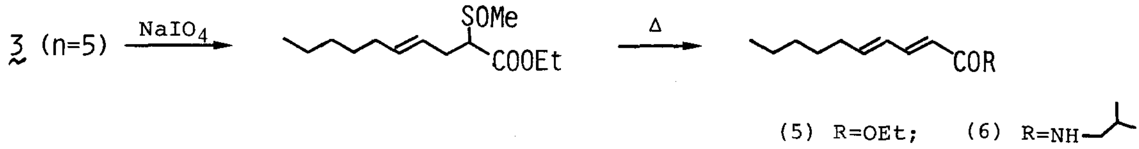
While the electrophilic aromatic substitution of α-thiocarbocations have been widely investigated,[1] the reaction of α-thiocarbocation to olefinic compounds has received scant attention; two examples so far reported involves the Friedel-Crafts type substitution reaction of ethylthiomethyl fluoroborate to trisubstituted olefin[2] and the addition reaction of dithienium cation to 1,1-disubstituted olefin.[3] The present communication describes a novel ene reaction of the α-thiocarbocation **2**, Pummerer reaction intermediate of α-methylsulfinylacetate(**1**),[4] with 1-alkenes, which yields the adducts **3**. This ene reaction provides a new convenient way to E,E-2,4-alkadienoic esters *via* oxidative desulfurization of the adducts **3**.



In a typical procedure, trifluoroacetic anhydride (2 mmol) and 1-pentene (2 mmol) were successively added to a stirred solution of the sulfoxide **1** (2 mmol) in trifluoroacetic acid (2 ml) at 0°. After stirring at the same temperature for 1 hr, trifluoroacetic acid was removed *in vacuo* and the residue was chromatographed on silica gel to give ethyl 2-methylthio-E-4-heptenoate (**3**, n=2) in 75% yield. The corresponding Z isomer was not detected by nmr spectrum of the crude product. The structure of **3** (n=2) was confirmed by the following spectral evidence. The nmr spectrum exhibits the signals at δ 0.96 (t, 3H, J=7Hz, CH_3 on C-7), 1.28 (t, 3H, J=7Hz, $OCH_2C\underline{H}_3$), 1.7-2.7 (m, 4H, $CH_2\times2$ on C-3 and C-6), 2.15 (s, 3H, SCH_3), 3.20 (t, 1H, J=7Hz, CH on C-2), 4.20 (q, 2H, J=7Hz, $OC\underline{H}_2CH_3$), and 5.49 (dd, 2H, J=9 and 5Hz, -CH=CH-). The ir spectrum reveals a strong absorption band at 965 cm^{-1} due to E configuration of the double bond. Other adducts 3 (n=3-7) were similarly obtained in 72-79% yields.

When the above reaction was carried out in methylene chloride, the product was a Pummerer rearrangement product 4, which gave also the ene adducts 3 on treatment with 1-alkenes in trifluoroacetic acid.

The addcuts 3 can readily be converted into E,E-2,4-alkadienoic esters by oxidation with $NaIO_4$ in aq MeOH and successive pyrolysis of the resulted sulfoxides in refluxing benzene. Thus E,E-2,4-decadienoic ester(5) was prepared from the adduct 3 (n=5) in 89% yield. The present sequence of reactions for the ester 5 means the synthesis of Pellitorine (6), an insecticidal compound isolated from *Anacyclus pyrethrum*, since 6 was already reported to be prepared from the ester 5.[5]



The investigation of this ene reaction with other types of olefin is now in progress.

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4) Ethyl phenylsulfinylacetate similarly reacted with 1-alkenes to give the ene adducts of type 3, through the reactivity was lower than the sulfoxide 1.

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