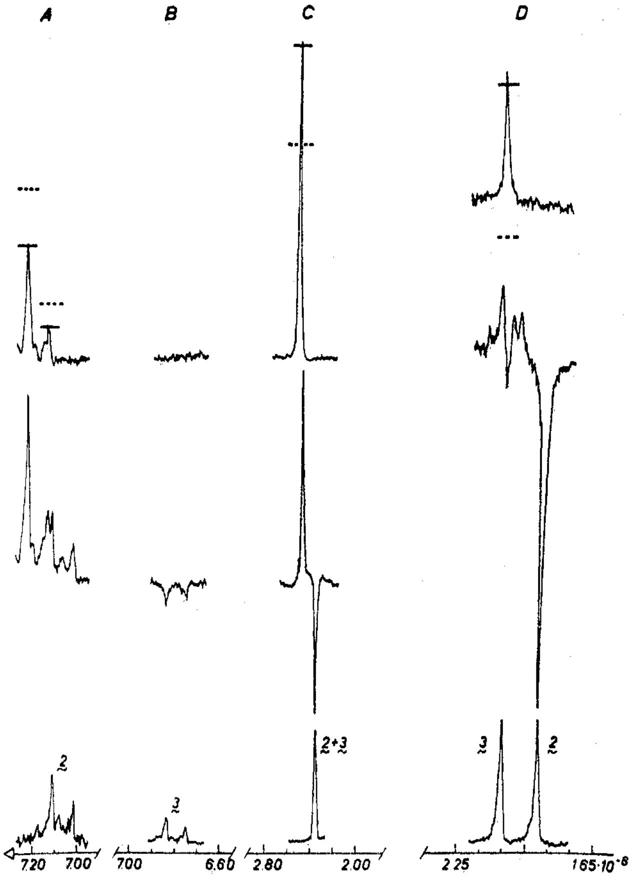
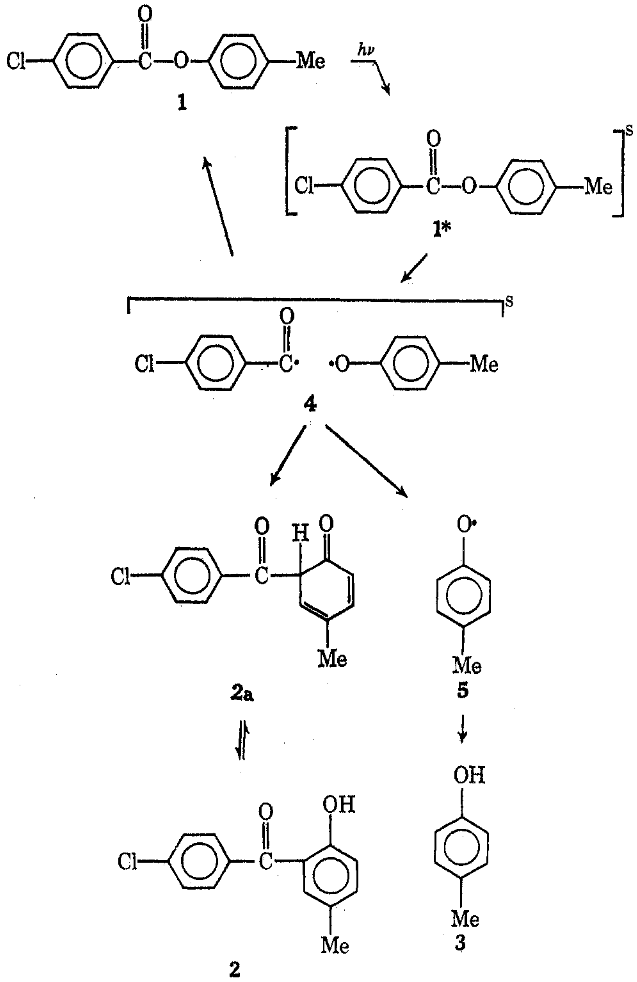


Figure 1.—CIDNP during photolysis of *p*-cresyl *p*-chlorobenzoate (1). Sets A, B, and C are in CH_2Cl_2, set D in C_6H_6. Bars in the top spectra of sets A, C, and D refer to signal intensities of the polarizations in ester 1 during (broken) and after (solid) irradiation. The reference numbers in the bottom spectra of sets A, B, C, and D refer to the proton resonances of authentic *p'*-chlorobenzoyl-*p*-cresol (2) and *p*-cresol (3) products relative to TMS.

the aroyl–aryloxy radical pair **4** prior to intersystem crossing. Cage combination results in ester **1** or phenol **2** *via* its **2a** tautomer, the latter having a lifetime (t) considerably shorter than the relaxation times (T_1) of its polarized protons, *i.e.*, $t \ll T_1$. Some aryloxy radicals **5** escape the cage and on hydrogen abstraction give phenol **3**.

It is unlikely that a concerted pathway[2] is of major importance in the photo-Fries rearrangement of *p*-cresyl *p*-chlorobenzoate (**1**), at least in the solvents used here. For example, measurement[9] of the enhancement factor (V_{exp}) for the *p*-methyl polarization of the rearrangement product **2** gave $V_{exp} = -243 \pm 13$. With the help of Adrian's high field CIDNP treatment,[10] employing a one-proton model and making reasonable assumptions about the time between diffusive pair displacements ($10^{-12} \leqq \tau \leqq 10^{-11}$ sec),[9] the calculated enhancement factor (V_{calcd}) for the formation of **2** entirely from radical pair **4** *via* a singlet reaction is $V_{calcd} = 200 \pm 50$. We anticipate that analogous radical pair mechanisms obtain quite generally for the related photorearrangements of aryl ethers[11] and amides.[12]

SCHEME I



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A Stereoselective Trans-Trisubstituted Olefin Synthesis *via* Rearrangement of Allylic Sulfonium Ylides

Summary: The [2,3]-sigmatropic rearrangement of α-substituted methallylsulfonium ylides results in a stereoselective formation of trans-trisubstituted olefins.

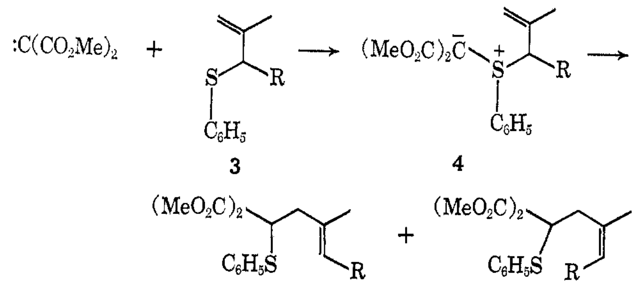
Sir: The need for stereoselective methods for olefin synthesis continues as demonstrated by several recent publications.[1] The synthetic potential of the [2,3]-sigmatropic rearrangement in olefin synthesis has been demonstrated.[2] Recently,[3] α-substituted methallyl aryl sulfoxides have been shown to undergo such a rearrangement to allylic sulfenate esters which can be intercepted by nucleophiles, thus providing a new and useful route to trisubstituted olefins.

As part of a continuing program aimed at development of the [2,3]-sigmatropic rearrangement for construction of trisubstituted olefinic linkages found in polyisoprenoids, we have examined the stereospecificity which accompanies the [2,3]-sigmatropic rearrangement of α-substituted methallylsulfonium ylides. The [2,3]-sigmatropic rearrangement of ylides and related species (*e.g.*, **1** → **2**) represents a well-established reaction[4]

1 **2**

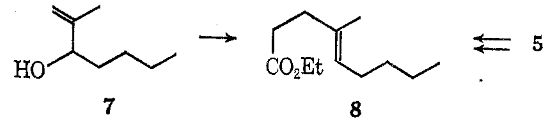
which has recently received much attention in organic synthesis.[5] Allylic sulfonium ylides have previously been generated[6] by the addition of the appropriate carbene precursor; however, no study demonstrating the stereospecificity of this potential trisubstituted olefin forming reaction has been investigated. We wish to describe here a stereoselective trisubstituted olefin synthesis employing allylic sulfonium ylides of type **4**.

Heating a mixture of methyl diazomalonate (1.1 equiv)[7] and the α-substituted methallyl sulfide **3** (R = *n*-Bu) (prepared by treatment of phenyl methallyl sulfide at $-78°$ in anhydrous THF with *n*-BuLi followed by the addition of *n*-BuI and warming to room temperature) in the presence of a catalytic amount of anhydrous cupric sulfate at 100° for ~15 hr (no solvent) results in a 90:10 mixture (indicated by vpc) of the trans and cis olefins **5** and **6** (R = *n*-Bu), respectively, in 70% yield after purification.

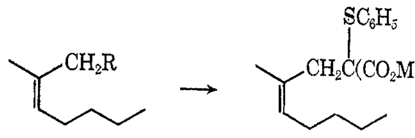


3 **4** **5** **6**

That the major product **5** (R = *n*-Bu) had the stereochemistry indicated was demonstrated by conversion to **8** [decarboxylation, esterification, followed by desulfurization (W-2 Raney Ni)] which was shown to be identical with a sample prepared by Claisen rearrangement[8] of **7** with ethyl orthoacetate. Confirmation of the cis isomer **6** (R = *n*-Bu) was obtained by direct synthesis from **9a**.[9] Conversion of **9a** to the corresponding chloride **9b**[10] followed by alkylation with dimethyl malonate afforded **9c**. Treatment of the sodio derivative of **9c** in anhydrous THF with benzenesulfenyl chloride produced **10** which was identical with the cis isomer **6** (R = *n*-Bu) obtained from the rearrangement described above.



7 **8**



9a, R = OH
b, R = Cl
c, R = CH(CO$_2$Me)$_2$

10

Similarly, reaction of bis(carbomethoxy)carbene with sulfide **3** (R = Et) at 100° resulted in an 89:11 mixture of the trans and cis olefins **5** and **6** (R = Et), respectively, in 71% isolated yield.

The present olefin synthesis complements the existing methods of olefin synthesis.[1,3] In addition, it further demonstrates the potential or [2,3]-sigmatropic rearrangements in olefin synthesis.

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The Addition of Cycloheptatrienylidene to Phenylacetylene. The Possible Intermediacy of a Spiro[2.6]nona-1,4,6,8-tetraene

Summary: The addition of cycloheptatrienylidene to phenylacetylene yields 8-phenylbicyclo[5.2.0]nona-1,3,-5,8-tetraene, possibly *via* a spiro[2.6]nona-1,4,6,8-tetraene.

Sir: Recent studies have shown that spiro[2.6]nona-4,6,8-trienes can be conveniently synthesized by addi-