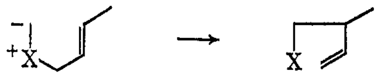
publications.[1] The synthetic potential of the [2,3]-sigmatropic rearrangement in olefin synthesis has been demonstrated.[2] Recently,[3] α-substituted methallyl aryl sulfoxides have been shown to undergo such a rearrangement to allylic sulfenate esters which can be intercepted by nucleophiles, thus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

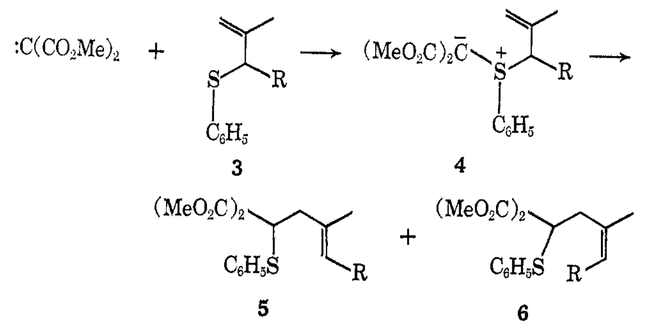
As part of a continuing program aimed at development of the [2,3]-sigmatropic rearrangement for construction of trisubstituted olefinic linkages found in polyisoprenoids, we have examined the stereospecificity which accompanies the [2,3]-sigmatropic rearrangement of α-substituted methallylsulfonium ylides.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



1 **2**

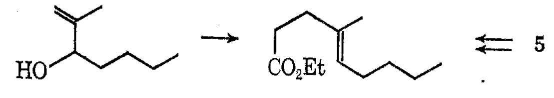
which has recently received much attention in organic synthesis.[5] Allylic sulfonium ylides have previously been generated[6] by the addition of the appropriate carbene precursor; however, no study demonstrating the stereospecificity of this potential trisubstituted olefin forming reaction has been 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.

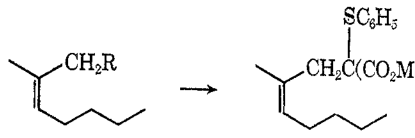


3 **4** **5** **6**

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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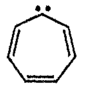
RECEIVED MARCH 26, 1973

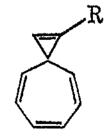
The Addition of Cycloheptatrienylidene to Phenylacetylene. The Possible Intermediacy of a Spiro[2.6]nona-1,4,6,8-tetraene

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 addition of cycloheptatrienylidene (**1**) to carbon–carbon double bonds. Suitable acceptors include dimethylfumarate,[1] 1,3-pentadiene,[2] styrene,[3] and ethylene.[4] As a logical extension of this work as well as possible entry into the theoretically interesting[5] spirononatetraene system **2**, we have now studied the addition of cycloheptatrienylidene to phenylacetylene.

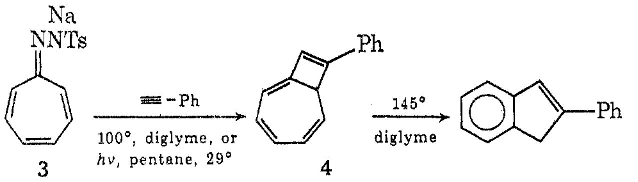


1

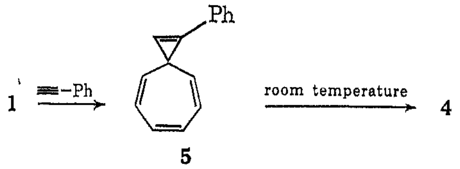


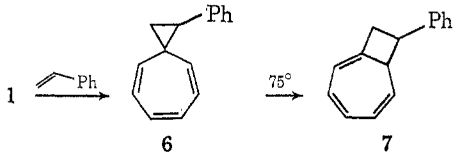
2

Either thermolysis (100°, diglyme) or photolysis (29°, pentane or THF) of the sodium salt of tropone tosylhydrazone (**3**)[1] in the presence of excess phenylacetylene resulted in a $C_{15}H_{12}$ hydrocarbon in 21–25% yield in addition to a trace of heptafulvalene. From its spectral and chemical properties, this material was assigned the structure of 8-phenylbicyclo[5.2.0]nona-1,3,5,8-tetraene (**4**). The nmr spectrum of **4** ($CDCl_3$) shows a multiplet between 7.6 and 7.2 (5 H, aromatic), a doublet at 6.46 (1.4 Hz, 1 H, H_9), a multiplet between 6.35 and 5.65 (5 H, H_2–H_6), and a narrow multiplet at 4.76 ppm (1 H, H_7). The extent of the conjugation is indicated by the uv spectrum which has maxima (in *n*-pentane) at 370 nm (ε 9000) and 269 (31,000).[6] The ir and mass spectra are in agreement with the proposed structure.[9] When **4** was heated at 140° in diglyme, it was smoothly converted to 2-phenylindene,[10] a conversion that is strong supporting evidence for the assigned structure. Additional evidence for this structure was obtained by generating **1** in the presence of β-deuteriophenylacetylene. The nmr spectrum of the product (**4**-d_1) showed no resonance at 6.46 ppm. In addition, the line width of the signal at 4.76 ppm was reduced. When **4**-d_1 was heated at 145°, 2-phenylindene-d_1 was produced. From the nmr spectrum, it was concluded that the deuterium had equilibrated (presumably as a secondary reaction) between the 1 and 3 positions of the indene.



By comparison with the addition of cycloheptatrienylidene to styrene,[2,3] the primary product of the addition of **1** to phenylacetylene is probably the spirononatetraene, **5**.[12] Unstable, even at room temperature, **5** undergoes what is probably a stepwise rearrangement[13] to the tetraene, **4**. The instability of **5** relative to **6** is not surprising, since cyclopropenes undergo thermal ring opening much more readily than cyclopropanes.[14] The thermal conversion of **4** to 2-phenylindene is analogous to the rearrangement of **7** to 2-phenylindan.[2]





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(1) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

(2) E. E. Waali and W. M. Jones, *ibid.*, in press.

(3) (a) K. G. Untch, private communication; (b) L. W. Christensen, E. E. Waali, and W. M. Jones, *J. Amer. Chem. Soc.*, **94**, 2118 (1972).

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(5) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(6) Walborsky and Pendleton[7] reported the uv spectrum of 1-phenyl 1,3,5,7-octatetraene [λ_{max} 365 nm (ε 72,300), 337 (85,000), and 236 (11,000)]. The difference in the maxima and extinction coefficients between **4** and this model compound are expected since **4** has several cis and s-cis bonds and the model compound is all trans.[8]

(7) H. M. Walborsky and J. F. Pendleton, *J. Amer. Chem. Soc.*, **82**, 1405 (1960).

(8) R. M. Silverstein and R. M. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 157.

(9) Ir (neat film) ν 3070 (w), 3010 (m), 2850 (w), 1662 (m), 1482 (m), 1446 (m), 759 (s), 703 (s), 692 (s); mass spectrum *m/e* (rel intensity) 192 (100), 106 (45), 105 (41), 86 (50), 84 (73). The tetraene, **4**, is sensitive to oxygen. It was reduced over Pt/C with the uptake of 4 equiv of hydrogen. The resulting hydrocarbon was shown to have the formula $C_{15}H_{20}$ by mass spectrometry and satisfactory elemental analysis.

(10) Mp 166–167° (lit.[11] mp 167.5); nmr ($CDCl_3$) 7.7 to 7.1 (m, 10 H, aromatic and olefinic) and 3.79 ppm (narrow m, 2 H, benzylic).

(11) F. Mayer, A. Sieglitz, and W. Ludwig, *Chem. Ber.*, **54**, 1397 (1921).

(12) To date, there has appeared no verified two-step addition of cycloheptatrienylidene (or an isomeric cycloheptatetraene) to a multiple bond.

(13) A concerted, thermal [1,7]-sigmatropic shift is unlikely based on orbital symmetry considerations: R. B. Woodward and R. Hoffmann, "The Conversation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim Bergstr., 1970.

(14) In view of (1) the large difference in the activation energy for ring openings of cyclopropenes and cyclopropanes (~30 kcal/mol[15]), (2) the probability that the rearrangement of **5** to **4** is stepwise and (3) the facile rearrangement of **6** to **7**, it is highly unlikely that **5** will be isolable under ordinary conditions. The question remains open whether replacement of the phenyl group by hydrogen (**2**, R = H) will increase the energy of activation for the rearrangement sufficiently to permit isolation of the parent spirononatetraene.

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The Reaction of Alkyl- and Aryldichloroboranes with Ethyl Diazoacetate at Low Temperature[1]

Summary: Ethyl diazoacetate reacts readily at low temperatures with aryl- and alkyldichloroboranes to give after protonolysis the corresponding ethyl arylacetates and alkylacetates in yields ranging from quantitative for the aryl to approximately 60% for the alkyl derivatives.

Sir: Trialkylboranes react with a variety of functionally substituted alkyldiazo compounds.[2] How-

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(1) Joint publication was decided on after we learned of our related research in this area. The Purdue group investigated the alkyl-, the Alberta group the aryldichloroborane series.

(2) (a) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936 (1968); (b) J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); (c) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968); (d) J. Hooz and G. F. Morrison, *Can. J. Chem.*, **48**, 868 (1970); (e) J. Hooz and D. M. Gunn, *J. Amer. Chem. Soc.*, **91**, 6195 (1969).