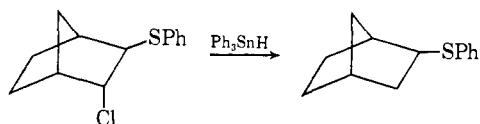


maining phenylthio group to be established by glpc comparison with the known phenyl sulfides.

Benzenesulfonyl chloride was slowly added to a methylene chloride solution of 7,7-dimethylnorbornene containing a small amount of suspended calcium carbonate at -20° .⁶ The crude adduct (IV), a semi-solid, was obtained quantitatively. The pmr spectrum⁹ of IV revealed that it contained about 80% of one major product, V. Recrystallization of IV with petroleum ether (bp $35-37^{\circ}$) yielded 60% of pure V, mp $42.5-43^{\circ}$ (lit.⁶ mp $35-38^{\circ}$). *Anal.* Calcd for $C_{15}H_{19}SCl$: C, 67.52; H, 7.18; S, 12.02; Cl, 13.28. Found: C, 67.70; H, 7.10; S, 12.22; Cl, 13.48. The pertinent pmr data of V are identical with those of II as reported:⁶ a doublet ($J = 4.8$ Hz) at δ 3.73 (1 H) and a doublet of an apparent triplet ($J = 4.8, 4.3, 1.4$ Hz) at δ 4.08 (1 H). The observed splitting patterns and coupling constants indicate a *trans* relationship with an *exo* proton at δ 4.08 and an *endo* proton at δ 3.73. The chemical shifts of the *endo* α -methine proton in V (δ 3.73), its corresponding sulfone (δ 4.37⁶), and 7,7-dimethyl-*exo*-norbornyl chloride (δ 3.90) suggested an *exo*-chloro-*endo*-phenylthio orientation.¹⁰

To achieve the desired hydrodechlorination I was heated for 1 hr at 80° with triphenyltin hydride in the presence of a catalytic amount of azobisisobutyronitrile.⁸ A 62% yield of *exo*-norbornyl phenyl sulfide was realized. Under the same conditions a complete



hydrodechlorination of V was observed. The product showed identical glpc retention time with 7,7-dimethyl-*endo*-norbornyl phenyl sulfide (VI), a minor product from the free-radical addition of thiophenol to 7,7-dimethylnorbornene.¹¹ The *endo*-phenyl sulfide VI was isolated using preparative glpc in 60% yield. *Anal.* Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67; S, 13.80. Found: C, 77.34; H, 8.60; S, 13.69. The pmr spectrum of VI displays a multiplet at δ 3.85 (1 H) characteristic for an *exo* α -methine proton. The small difference in the chemical shift of the two methyl singlets (δ 1.05 and 1.09) also confirms the *endo* orientation of the phenylthio group.¹² No isomerization of VI to its *exo* isomer or *vice versa* has been detected under the hydrodechlorination conditions. Consequently, the major product obtained from the addition of benzenesulfonyl chloride to 7,7-dimethylnorbornene is in fact the *endo*-2-phenylthio-*exo*-3-chloro adduct V,

(9) All the pmr spectra were measured as deuteriochloroform solution on a Varian A-60A spectrometer, with tetramethylsilane as internal references.

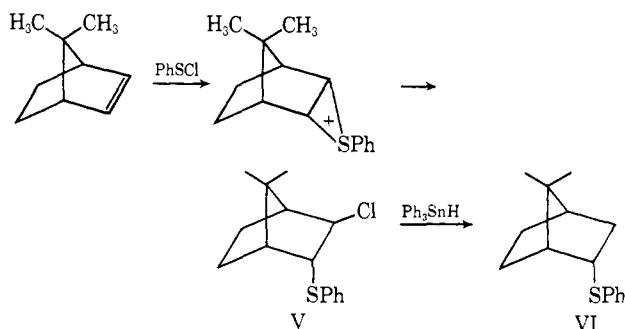
(10) In norbornyl derivatives the effect of the phenylthio group on the *cis*-vicinal proton is shielding, whereas the effect of the benzenesulfonyl group is deshielding. This can be illustrated by the observed chemical shift of the *exo*- α -methine proton in I (δ 3.99), the corresponding sulfone (δ 4.45), and *endo*-norbornyl chloride (δ 4.18).

(11) Glpc analysis was performed with a 150 ft \times 0.01 in. Apiezon L column on a Perkin-Elmer Model 226 gas chromatograph.

(12) For a pair of epimeric 7,7-dimethylnorbornyl derivatives the difference between the two methyl singlets is always larger in the *exo*-substituted epimer than in the *endo* one. For instance, it is 0.18 ppm in 7,7-dimethyl-*exo*-norbornyl tosylate and about zero in the *endo* epimer.¹³ In 7,7-dimethyl-*exo*-norbornyl phenyl sulfide the difference is 0.28 ppm.¹⁴

(13) K.-T. Liu, Ph.D. Thesis, Purdue University, 1968.

(14) J. H. Kawakami, Ph.D. Thesis, Purdue University, 1968.



and not the alternative isomer II as proposed.⁶ The selectivity is at least 80%, since the pmr spectrum indicates the presence of 80% of V in IV, and the hydrodechlorination of IV with triphenyltin hydride reveals 80% of VI (glpc).

The present result therefore removes a major difficulty with the proposal that 7,7-dimethyl substituents exert dominant steric control on addition reactions proceeding through cyclic transition states or intermediates, or the formation of π complexes. Accordingly, this proposal appears capable of providing a tool for exploring and interpreting the mechanisms of additions to norbornenes. For example, oxymercuration of norbornene,¹⁵ 7,7-dimethylnorbornene,¹ and 1,4,7,7-tetramethylnorbornene¹⁶ all give cleanly *exo-cis* adducts. Therefore, a cyclic transition state or intermediate,¹⁶⁻¹⁸ e.g., mercurinium ion, is probably not involved in this addition process.

We continue to test the proposed generalization in an effort to establish its consistency and reliability.

(15) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, No. 19, 14 (1959); *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(16) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).

(17) A. Factor and T. G. Traylor, *ibid.*, **33**, 2607 (1968).

(18) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968), and relevant references cited therein.

(19) Postdoctoral Research Associate on a grant (GP 6492 X) supported by the National Science Foundation.

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Oxygen-Induced Reactions of Organoboranes with Acetylacetylene. A Convenient New Synthesis of α,β -Unsaturated Ketones via Hydroboration

Sir:

Trialkylboranes, readily available *via* hydroboration, undergo facile 1,4 addition to many α,β -olefinic carbonyl compounds.^{1,2} These additions are "spontaneous" for numerous such carbonyl compounds, including methyl vinyl ketone,¹ acrolein,² α -methylacrolein,³ α -bromoacrolein,³ and α -methylene-cyclanones.⁴ However, β -substituted α,β -olefinic carbonyl compounds require radical initiators to achieve a reaction.⁵ Thus trialkylboranes react readily with

(1) A. Suzuki, A. Arase, H. Matsumoto, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(2) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).

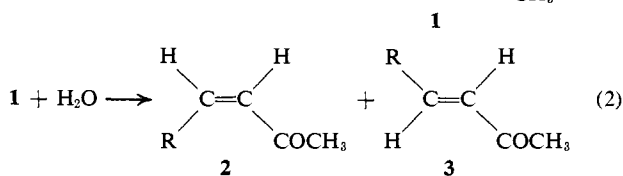
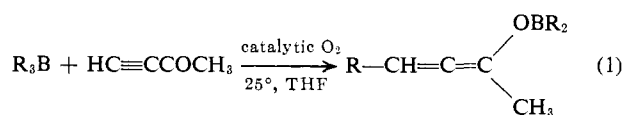
(3) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).

(4) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968).

compounds such as 2-cyclohexenone in the presence of typical radical initiators,⁶ ultraviolet light,⁶ or traces of oxygen.⁷

Following our initial discovery of the "spontaneous" reaction,^{1,2} we examined many other types of derivatives, such as acetylacetylene and acrylonitrile. These molecules failed to undergo the facile addition exhibited by methyl vinyl ketone and acrolein. This limitation of the scope of the 1,4-addition reaction was disappointing. However, the recent discovery that oxygen and other initiators could induce reactions in otherwise inert derivatives, such as crotonaldehyde, ethylideneacetone, and 2-cyclohexenone,^{6,7} led us to reopen our previously unsuccessful explorations.

We now wish to report that acetylacetylene, which fails to undergo the "spontaneous" reaction with trialkylboranes, readily undergoes addition in the presence of catalytic amounts of oxygen (eq 1). Hydrolysis (eq 2) of the initially formed allenic intermediate, **1**, produces the corresponding α,β -unsaturated methyl ketones, **2** and **3**, in good yield.



This reaction emphasizes the versatility of the 1,4-addition reaction of organoboranes. Thus the reaction occurs readily for acetylenic ketones as well as α,β -olefinic aldehydes and ketones, providing a new synthesis of unsaturated ketones. Furthermore, this development indicates the possibility of extending the reaction to many other types of reagents previously considered to be inapplicable.⁸

The mechanism must involve a radical chain analogous to that previously proposed for the 1,4-addition reaction of α,β -unsaturated aldehydes and ketones.^{5,6} Thus, no reaction occurs between triethylborane and acetylacetylene when air and light are carefully excluded from the reaction mixture, even with an extended reaction time of 24 hr. However, a 79% yield of 3-hexen-2-one is obtained under identical conditions by the slow addition of air to the reaction mixture.

The presence of water in the reaction mixture is required to achieve good yields of the desired product. Presumably the allene intermediate (**1**) is highly susceptible to further attack by the free-radical intermediates and this side reaction is minimized by *in situ* hydrolysis of the borinate. Solvolysis of the intermediate may also be achieved through the use of alcohols, such as methanol and ethylene glycol, especially convenient in cases where anhydrous conditions should be maintained.

(5) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970).

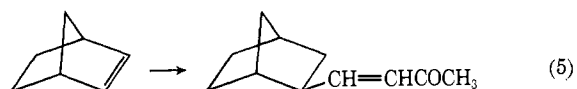
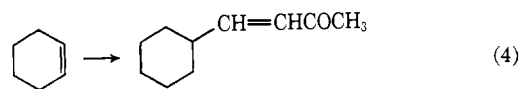
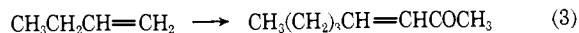
(6) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970).

(7) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970).

(8) Work is now in progress on related systems such as nitriles and the results are very encouraging.

The conclusion that the reaction is proceeding *via* a radical chain reaction is supported by the fact that other typical free-radical initiators may be used to induce the 1,4-addition reaction. As an example, the reaction of triethylborane with acetylacetylene can be induced photolytically⁹ or through the thermal decomposition of azobisisobutyronitrile at 40°. The yields obtained are comparable to those realized when air is used for the initiation.

The reaction appears to be one of wide generality, providing unsaturated methyl ketones from a wide variety of structural types of alkenes (eq 3-5).



In each case the product is a mixture of the *cis* and *trans* isomers, with the *cis* being present in larger amounts than the *trans*. The ratio of the isomers is variable and appears to be dependent on the solvolysis of the allenic intermediate.¹⁰

The experimental results are summarized in Table I.

Table I. Conversion of Olefins into 4-Alkyl-3-buten-2-ones by Reaction of the Corresponding Organoboranes with Acetylacetylene

Organoborane from olefin	Product ^a	Yield, ^b %
Ethylene	3-Hexen-2-one	77
1-Butene	3-Octen-2-one	72
2-Butene	5-Methyl-3-hepten-2-one	47
Isobutylene	6-Methyl-3-hepten-2-one	34
Cyclopentene	4-Cyclopentyl-3-buten-2-one	63
Cyclohexene	4-Cyclohexyl-3-buten-2-one	65
Norbornene	4-(<i>exo</i> -Norbornyl)-3-buten-2-one	67

^a All products exhibited analytical data and spectra in accordance with assigned structures. ^b By glpc analysis.

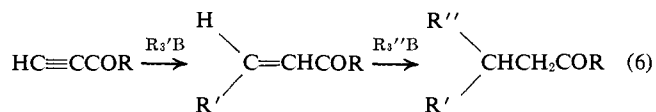
The following procedure is representative. A 25-ml flask, fitted with an inlet carrying a rubber septum cap, a magnetic stirring bar, and a condenser, was flushed with nitrogen. In the flask was placed 11 mmol (5.5 ml of a 2 M solution in THF) of borane. Then 33 mmol (3.3 ml) of cyclohexene was added to form the tricyclohexylborane. The mixture was stirred at 50° for 3 hr to ensure completion of this exceptionally sluggish hydroboration. Then 20 mmol (0.36 ml) of water was added followed by 10 mmol (0.775 ml) of acetylacetylene. Air was then passed into the flask at a rate of 0.5 ml/min through a syringe needle placed through the rubber septum cap to a point just above the reaction mixture. The solution was allowed to stir at room temperature. Samples were removed peri-

(9) A commercially available Sears 250-W sunlamp was used in this study and no attempt was made to filter out the extraneous visible light.

(10) A study is now in progress on the solvolysis of the allene intermediate, **1**, in an attempt to control the *cis*:*trans* isomer ratio.

odically and analyzed by glpc. Analysis after 2 hr (60 ml of air or 0.5 mmol of O₂ was introduced) indicated that 6.5 mmol (a yield of 65%) of 4-cyclohexyl-3-butene-2-one had been formed. The ratio of the *cis:trans* isomer was 1.1:1.0.

The oxygen-induced reaction of organoboranes to acetylacetylene produces α,β -unsaturated ketones. These have previously been shown to undergo 1,4 addition with organoboranes. Consequently, the reaction appears capable of being controlled to introduce two different groups from two different organoboranes, making available a wide variety of ketones (eq 6).



Perhaps even more significant is the fact that this development suggests the possibility of extending this oxygen-catalyzed addition of organoboranes to many other types of structures previously considered not to be applicable.

(11) Postdoctorate research associate on Grant No. GM 10937 from the National Institutes of Health.

(12) National Institutes of Health Postdoctorate Fellow at Purdue University, Lafayette, Ind., 1969-1970.

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Insertion Reactions of ¹S Carbon Atoms in Double Bonds¹

Sir:

Recent studies²⁻⁵ have shown that carbon atoms attack olefins to give allenes, by a formal insertion of the carbon atom into the C=C double bond, and it has also been shown⁶ that the reaction probably involves carbon atoms in the excited ¹S state (excitation energy, 2.7 eV⁷).

Recent studies⁸ have shown that the MINDO/2 method^{9a} can be used successfully to calculate potential surfaces^{9a} for reactions involving hydrocarbons and also to study^{9b} electron-deficient systems of the type involved in the intermediate phases of reactions of carbon atoms. We have accordingly calculated the relevant parts of the potential surfaces for the reaction of ¹S carbon atoms with ethylene and *trans*-2-butene and deduced the corresponding reaction paths. Pre-

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) C. MacKay, P. Polack, H. E. Rosenberg, and R. Wolfgang, *J. Amer. Chem. Soc.*, **84**, 308 (1962).

(3) J. Dubrin, C. Mackay, and R. Wolfgang, *ibid.*, **86**, 959 (1964).

(4) M. Marshall, C. Mackay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964).

(5) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(6) P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967).

(7) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p 142.

(8) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, in press; (c) M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **91**, 7521 (1969).

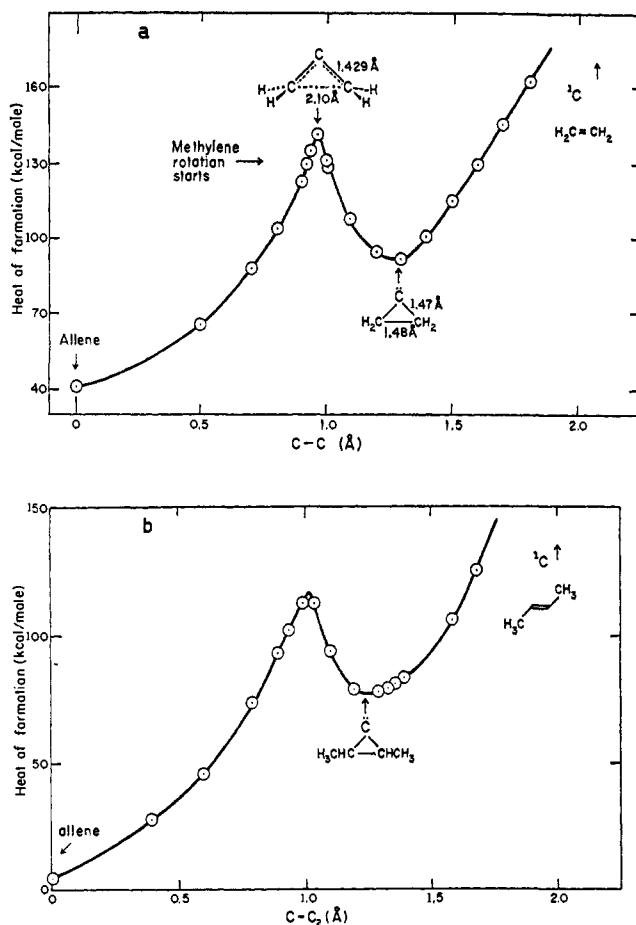
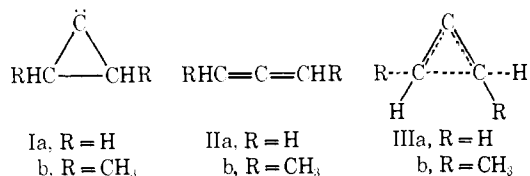


Figure 1. Reaction paths for reactions of carbon atoms with (a) ethylene, (b) *trans*-2-butene.

liminary trials showed that these involved approach of the carbon atoms in the plane bisecting the C=C bonds of the olefins, as one would expect; the perpendicular distance of the atom from the C=C bond axis was therefore taken as the reaction coordinate.

Figure 1a shows a section along the reaction path of the potential surface for the reaction of ethylene, and Figure 1b a corresponding plot for *trans*-2-butene. Each reaction falls into two distinct stages. In the first, a direct exothermic combination of the olefin with the carbon atom leads to a stable intermediate carbene I; in the second, I undergoes an activated rearrangement to the allene II.



The overall reaction involves a relative rotation of the methylene groups of ethylene, or the ethylidene group of *trans*-2-butene, since these are coplanar in the parent olefin but mutually orthogonal in the final allene, II. According to our calculations, this rotation takes place only in the final stages of the reaction, the original unrotated geometry being retained in the transition state, III, for conversion of I to II. The normal twisted form of II is the more stable only for CCC bond angles greater