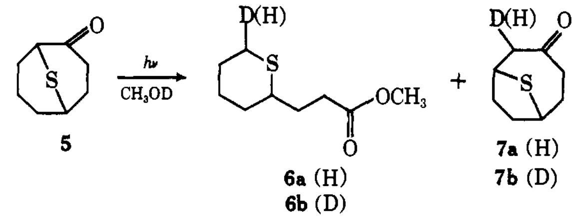
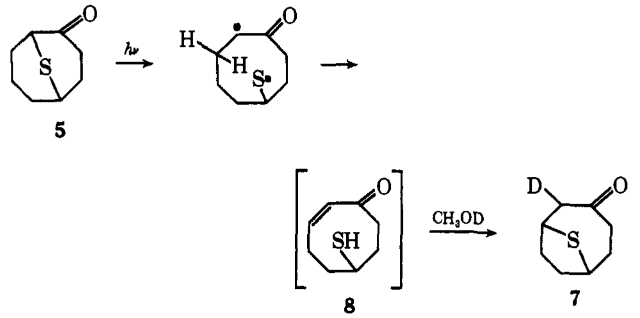
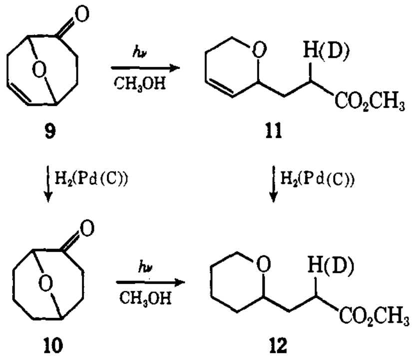


ester **6** (30%) and ketone **7** (32%) as major products.[11] The structure of **6** was established by its independent synthesis (catalytic reduction) from **4**. The mass spectrum of **6** clearly indicates that the deuterium atom is located on the thiapyran portion of the molecule. This product has prominent peaks at *m/e* 115 (corresponding to loss of methyl acetate) and 102 (base). The structure of **7a** (mp 148–149°) was elucidated on the basis of the physical and chemical data cited. The infrared spectrum of **7a** was characterized by bands at 3.41, 5.85, 7.41, and 8.96 μ. The ultraviolet spectrum (95% ethanol) has maxima at 320 and 231 $m\mu$ (ϵ 90 and 570). The nmr spectrum ($CDCl_3$) shows a two-proton multiplet at τ 6.30 and a ten-proton multiplet between τ 7.15 and 8.35. The mass spectrum of **7b** included peaks with *m/e* 157 (parent), 129, and 101. The deuterium atom adjacent to the carbonyl group could be readily washed out with potassium carbonate in methanol. Chemical confirmation of structure **7** was obtained by reaction with Raney nickel. The product obtained was identical with an authentic sample of cyclooctanol.

Compound **6** may be rationalized by a path analogous to the one outlined above (Scheme III). The formation of **7** from **5** may be visualized as occurring by scission of the C–S bond followed by internal hydrogen abstraction and subsequent intramolecular cyclization of the transient intermediate (**8**). This latter step may be either a ground state or photoinduced process. This rationalization readily accommodates the incorporation of deuterium at the α position and is mechanistically similar to previous results encountered in the photochemistry of 2-oxo-6-hydroxy-9-thiabicyclo[3.3.1]nonane.[4]



At this point we recognized that the influence of the heteroatom on the photochemistry of 9-heterobicyclo[3.3.1]non-2-ones needed to be assessed. We therefore turned our attention to the related oxa system in order to make a comparison with the photochemistry of the above β-keto sulfides. Our initial experiments were involved with the photochemistry of 9-oxabicyclo[3.3.1]non-6-en-2-one (**9**) and 9-oxabicyclo-[3.3.1]non-2-one (**10**).[12] A critical difference between the two systems under consideration is that the oxa system is devoid of an excited-state interaction of the two chromophores (uv (95% ethanol) of **9**, 290 $m\mu$ (ϵ 35); **5**, 251 and 304 $m\mu$ (ϵ 300 and 250)). Irradiation of **9** in methanol afforded ester **11** in high yield. Similarly, irradiation of **10** gave ester **12** as the sole photoproduct. The structure of **12** was established by its



independent synthesis by treatment of tetrahydropyran-2-methyl bromide with sodium ethyl malonate followed by hydrolysis and esterification.

Most importantly, when the irradiation of **9** (or **10**) was carried out in deuteriomethanol the product formed incorporated the deuterium atom adjacent to the carbonyl group as evidenced by mass spectroscopy (*i.e.*, fragment peaks for **11** appear at *m/e* 96 (P − CH_2-DCO_2CH_3) and 83 (base)). This may be rationalized by initial formation of a ketene *via* Norrish type I cleavage and internal disproportionation. The behavior of the oxa system is substantially different from the thia system and suggests that carbonyl–sulfur interactions in the excited state play an important role in the photochemistry of cyclic β-keto sulfides.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. CA-12195-04).

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[12] The syntheses of **9** and **10** and their physical properties will be described in our full paper. All new compounds were analyzed by ir, nmr, and mass spectroscopy and gave satisfactory carbon and hydrogen analyses.

(13) Alfred P. Sloan Fellow, 1968–1970.

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A Convenient Procedure for the Conversion of 1-Alkynes into Alkylcyclopropanes and *trans*-1-Halo-2-alkylcyclopropanes *via* the Hydroalumination Reaction[1]

Sir:

We wish to report a novel technique for the conversion of 1-alkynes into cyclopropyl derivatives which, in view of its experimental simplicity, should have broad synthetic utility. Thus, 1-alkenylalanes, which are readily prepared *via* the cis addition of dialkylaluminum hydrides to 1-alkynes,[2] react with methylene bromide in the presence of a zinc–copper couple[3] to

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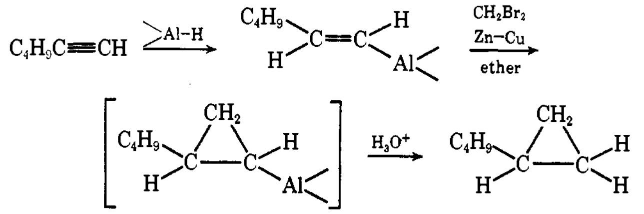
(1) This research was supported by the National Science Foundation through Grant No. GP-9398.

(2) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

(3) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

produce cyclopropylalanes.[4–10] These intermediates may be hydrolyzed to give alkylcyclopropanes or halogenated to afford *trans*-1-halo-2-alkylcyclopropanes.

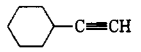
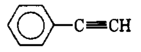
A representative example of the procedure for the preparation of alkylcyclopropanes from 1-alkynes is as follows. To 75 mmol of 1-hexyne in 15 ml of *n*-hexane was added 75 mmol of diisobutylaluminum hydride, while maintaining the temperature during the addition at 25–30°. The solution was stirred at ambient temperature for 30 min, then heated at 50° for 4 hr. After cooling the mixture to room temperature, the solvent was removed under reduced pressure and 23 ml of dry ether was added at 0°. To the resulting solution was added a mixture of 14.8 g of zinc–copper couple (prepared from 0.225 g-atom of 60–200 mesh zinc granules)[3] and 0.112 mol of methylene bromide. The mixture was maintained at reflux under a nitrogen atmosphere for 24 hr and the resulting diisobutylcyclopropylalane was then hydrolyzed with dilute sulfuric acid. Glpc analysis of the ether extract revealed the formation of 73% *n*-butylcyclopropane along with some isobutyl bromide (<5%).[11,12]



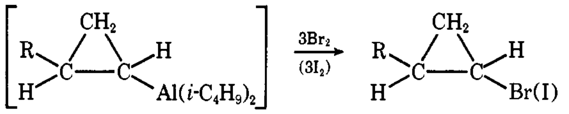
This reaction appears to have wide applicability.[13] Thus, increasing the size of the alkyl group attached to the triple bond from *n*-butyl to *tert*-butyl has little effect on the yield of the cyclopropane formed, as is shown in Table I. It should be noted, however, that a relatively low yield of phenylcyclopropane is obtained from phenylacetylene. This results because of partial metallation of the phenylacetylene during hydroalumination.[14]

It is known that cleavage of the carbon–aluminum bond in vinylalanes with halogens proceeds with retention of configuration.[15] This observation, coupled with the fact that the zinc–copper couple–methylene bromide reagent adds cis to double bonds,[3] suggested that cleavage of cyclopropylalanes with bromine or iodine should afford cyclopropyl halides of defined stereochemistry, and this has been borne out by experiment. Thus, addition of bromine to butylcyclopropylalane in a 3:1 ratio produced, as evidenced by glpc analysis, a 64% yield of *trans*-1-bromo-2-butylcyclopropane. Similarly, treatment of the cyclopropylalane with iodine afforded *trans*-1-iodo-2-butylcyclopropane in 50% yield. These results, along with those for the reactions of several other cyclopropylalanes, are shown in Table I. It is apparent that the bromination and iodination reactions are general and may be applied to variously substituted cyclopropylalanes.

Table I. Yields of Alkylcyclopropanes and *trans*-1-Halo-2-alkylcyclopropanes Derived from Various 1-Alkynes[a]

Vinylalane derived from	Cyclopropane, %	Cyclopropyl bromide, %	Cyclopropyl iodide, %
$C_4H_9{\equiv}CH$	62 (73)	58 (64)	47 (50)
	58 (71)	51 (54)	53 (61)
	51 (61)	51 (54)	
	35 (40)		

[a] Values in parentheses are glpc yields. The others are isolated yields.



The following procedure for the synthesis of *trans*-1-iodo-2-butylcyclopropane is representative. A solution of diisobutyl-*n*-butylcyclopropylalane in ether was prepared as described earlier starting with 50 mmol of 1-hexyne. To the mixture was then added at −65° a solution of iodine (0.15 mol) in tetrahydrofuran (90 ml) over a 2-hr period.[16] The reaction mixture was kept at −65° for an additional hour, and then allowed to warm up to room temperature before being poured slowly into a mixture of 10% H_2SO_4 (100 ml) and ether (100 ml) which had been precooled in an ice bath. The organic phase was separated, and the aqueous layer was extracted with ether. The combined ether extracts were washed successively with saturated sodium chloride, 10% sodium thiosulfate, saturated sodium bicarbonate, and finally again with saturated sodium chloride. Distillation through a short Vigreux column gave 5.30 g (47%) of *trans*-1-iodo-2-butylcyclopropane: bp 88–89° (26 mm); $n^{24}D$ 1.4975. The ir and nmr spectra were identical with those of the authentic iodide.[17]

Finally, it is important to note that diisobutyl(*trans*-1-alken-1-yl)alanes are much more reactive toward the methylene bromide–zinc–copper couple reagent than are 1-alkenes. Thus, the reaction of an equimolar mixture of diisobutyl(*trans*-1-hexen-1-yl)alane and 1-octene with the methylene transfer reagent gave, after hydrolysis, only traces of *n*-hexylcyclopropane. How-

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(4) It has been shown that vinyl derivatives of silicon, germanium, and tin react similarly with methylene iodide and a zinc–copper couple to give the corresponding cyclopropyl metal derivatives: D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(5) Tricyclopropylalane has been prepared by exchange between triethylalane[6] and dicyclopropylmercury.[7] However, monocyclopropylalanes have not previously been reported.

(6) P. Binger and R. Köster, *Angew. Chem., Int. Ed. Engl.*, **1**, 508 (1962).

(7) D. A. Sanders and J. P. Oliver, *J. Amer. Chem. Soc.*, **90**, 5910 (1968).

(8) It should be noted that the reaction of vinylalanes with diazomethane results in insertion into the vinylaluminum bond.[9] Halomethylalanes, which may be formed by exchange in the reactions of the present investigation, have been shown to be efficient methylene transfer reagents.[10]

(9) H. Hoberg, *Angew. Chem., Int. Ed. Engl.*, **5**, 513 (1966).

(10) H. Hoberg, *Justus Liebigs Ann. Chem.*, **656**, 1 (1962).

(11) The butylcyclopropane may also be prepared by treating the vinylalane with methylene iodide and zinc–copper couple. However, using this procedure a large amount of isobutyl iodide is formed.

(12) It is possible that part of the butylcyclopropane is derived from a cyclopropylzinc intermediate arising from transmetallation.

(13) Methylenation of the vinylalane derived from 3-hexyne resulted in the formation of a complex mixture of products.

(14) J. R. Surtees, *Aust. J. Chem.*, **18**, 14 (1965).

(15) G. Zweifel and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 2753 (1967).

(16) For the bromination reaction of the cyclopropylalane derived from 0.10 mol of 1-hexyne, a solution of bromine (0.30 mol) in methylene chloride (100 ml) was added to the reaction mixture over a 2-hr period.

(17) N. C. Yang and T. Marolewski, *J. Amer. Chem. Soc.*, **90**, 5644 (1968). We thank Dr. Yang for supplying the ir and nmr spectra of both the cis and trans isomers of 1-iodo-2-butylcyclopropane.

ever, an 86% yield of *n*-butylcyclopropane was obtained. Since the triple bond of 1-alkynes may be selectively hydroaluminated in the presence of double bonds,[18,19] it is thus conceivable that enynes containing a terminal acetylene group may be converted into alkenylcyclopropanes *via* the hydroalumination–methylenation reactions. We are currently exploring the feasibility of such transformations.

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(18) V. V. Markova, V. A. Kormer, and A. A. Petrov, *Zh. Obshch. Khim.*, 37, 226 (1967); *J. Gen. Chem. USSR*, 37, 208 (1967); and preceding papers.

(19) G. Zweifel, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, 90, 7139 (1968); G. M. Clark, unpublished results.

(20) National Defense Education Act Fellow (Title IV) at the University of California, Davis, 1968–1970.

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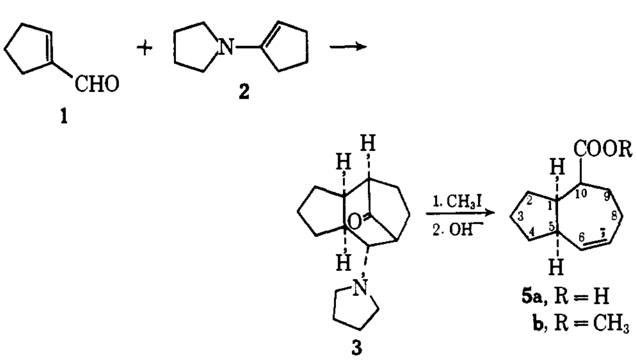
Received November 7, 1970

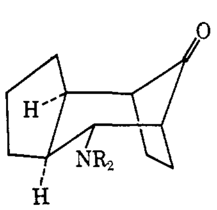
Sesquiterpenes. VI. A Short Stereospecific Synthesis of Functionalized Perhydroazulenes[1]

Sir:

Simple stereospecific syntheses of perhydroazulenes are rare[1,2] and limited in applicability for creating models in conformational studies[3] or for constructing the many sesquiterpenes bearing this skeleton.[4] We offer here a new synthesis of this system which is short and stereospecific and produces in good overall yield a functionalized perhydroazulene capable of elaboration in many different ways. The central design principle in this synthesis is that, while medium rings cannot usually be constructed viably by cyclization, they can be made with facility through cleavages of bicyclic molecules composed of common-size rings. These bicyclics are in turn easily made by standard cyclization reactions. Stork's elegant reaction for creating bridged bicyclic ketones[5] is an excellent example, so far little exploited in synthesis, since he also showed the capability of the products for further cleavage to medium rings, with functions usefully sited on opposite sides of the ring.

We have utilized this principle in the construction of **3** from 1-cyclopentenylcarboxaldehyde[6] (**1**) and the pyrrolidine enamine of cyclopentanone (**2**). The reaction forms five asymmetric centers but its stereospecificity may be predicted from the presumption that the sequence of mechanistic steps includes no irreversible reactions. Hence the thermodynamically most stable product **3** should result; the 5–6 ring fusion has the more stable cis orientation and of the two cis forms, it should be the exo isomer which places axial substituents on opposite (rather than the same) sides of the chair cyclohexanone **4**.





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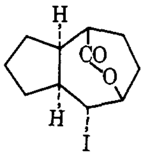

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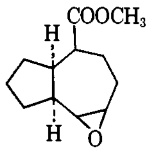

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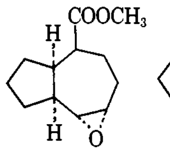

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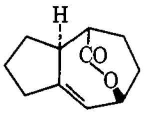

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When the components **1** and **2** were allowed to stand 20 hr in dioxane at room temperature to form a crude amino ketone **3** and this (without isolation) was methylated with methyl iodide and boiled 3 hr with 15% aqueous alkali, up to 25% of crystalline bicyclic acid **5a** could be isolated [mp 68–70°; nmr τ −1.0 (s, 1), 4.25 (m, 2)].[7]

Proof of the stereochemistry of **5** was deduced from the easy formation of an iodolactone, **6**, mp 120°, on treatment of the acid **5a** in bicarbonate solution with iodine (as KI_3) at room temperature. The formation of a seven-ring lactone bridge is sterically impossible with a trans-fused 5–7 ring system. Of the two possible cis-fused isomers of **5** the one shown was selected since treatment of the iodolactone **6** with alkali followed by diazomethane esterification yielded epoxide **7** [bp 120° (bath temperature) (0.4 mm); nmr τ 6.45 (s, 3), 7.05 (t, 2, $J = 3$ Hz)], which in turn was the *minor* of two epoxides (1:3) formed on epoxidation of **5b** with perbenzoic acid. The epoxide formed from iodolactone **6** must possess a cis relation of epoxide and carboxyl so that the other, major epoxide, **8** [bp 130° (bath temperature) (0.5 mm); nmr τ 6.40 (s, 3), 7.07 (t, 1, $J = 5$ Hz), 7.38 (dd, 1, $J = 5$, 9.5 Hz)], from peracid must be the trans isomer. The preponderance of **8** in the peracid oxidation in turn implies peracid attack from the less hindered convex face of the bicyclic olefin and so a product **8** with epoxide cis to the ring juncture protons.[8]

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(1) Part V: J. B. Hendrickson, C. Ganter, D. Dorman, and H. Link, *Tetrahedron Lett.*, 2235 (1968).

(2) J. A. Marshall and W. F. Huffman, *J. Amer. Chem. Soc.*, 92, 6358 (1970), and references cited therein.

(3) Part IV: J. B. Hendrickson, *Tetrahedron*, 19, 1387 (1963).

(4) F. Sorm and L. Doleja, Ed., "Guaianolides and Germacroanolides," Holden-Day, San Francisco, Calif., 1960; "Selected Constants: Sesquiterpenoids," Pergamon Press, Elmsford, N. Y., 1966.

(5) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, 78, 5129 (1956).

(6) J. B. Brown, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950).

(7) Spectra and analyses of all compounds reported were consistent with the assignments illustrated.

(8) This steric preference for the convex face is especially clear in Woodward's discussion of his reserpine synthesis.[9] The 3:1 predominance of **8** reported is only a minimum expression of steric preference since any direction of peracid cis to (and by) the ester group would produce the minor isomer **7**.

(9) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, 2, 1 (1958).