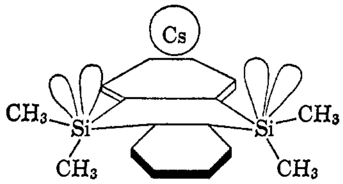
At room temperature the potassium ion jump is rapid enough so that an average coupling constant for H_a and H_b is observed but, as the temperature is lowered, the ion jump becomes slower, H_a and H_b become distinguishably different, and line broadening sets in. At temperatures below −115° (in DEE) further broadening takes place because the pairs of previously equivalent hydrogens now also become slightly different. This could be the result of the potassium ion locating itself nearer one benzene than the other.

Further evidence for this interpretation is found when cesium is used as gegenion. In DME, THF, and DEE a 12-line spectrum is obtained. The splitting pattern is consistent with approximately equal coupling to four equivalent hydrogens and one cesium ion ($I = {}^7/_2$) of 2.17, 2.16, and 2.44 gauss at room temperature and 2.15, 2.55, and 2.44 gauss at −60° for DME, THF, and DEE, respectively. In THF and DEE the 12 lines have approximately the intensities predicted. These results clearly point to a contact ion pair which may in fact have a chelate structure.[9]



It is clear that much can be learned about the structure and bonding in organosilane radical anions from temperature studies of the esr spectra of the ion pairs. To the extent bonding to potassium takes place in the ion pairs silicon can be considered pentacoordinated.[10] Trigonal-bipyramidal structures have been suggested in some cases.[11] However, all our data when taken together are more consistent with the use of unhydridized silicon 3d orbitals for delocalization of spin from neighboring aromatic π systems. Further studies of organosilane radical ion pairs are in progress.[12]

Acknowledgment. We are grateful to Dr. W. H. Atwell of the Dow Corning Corporation for providing us with the organosilanes used in this study.

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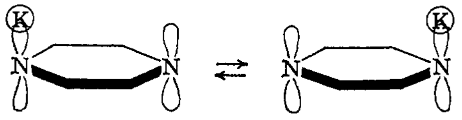
[9] Spectra of sodium and potassium ion pairs of pyrazine radical anion also exhibit line-width alternation at −68° in THF and −58° in DME, respectively. A similar mechanism for line broadening has been suggested (approximately 45% of the spin resides on each nitrogen atom): N. M. Atherton and A. E. Goggins, *Mol. Phys.*, **8**, 99 (1964); J. D. Santos-Veiga and A. F. Neiva-Correia, *ibid.*, **9**, 395 (1965); see also C. A. McDowell and K. F. G. Paulus, *Can. J. Chem.*, **43**, 224 (1965).



[10] C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3170 (1964); C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961).

[11] J. Y. Corey and R. West, *ibid.*, **85**, 4034 (1963); R. Rudman, S. Novick, and W. C. Hamilton, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967, No. R188; see also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

[12] Preliminary results have been obtained on the carbon analog of I, 9,9,10,10-tetramethyldihydroanthracene radical anion. However, these spectra are different and not well understood at this time.

[13] NASA Traineeship, 1965–1967.

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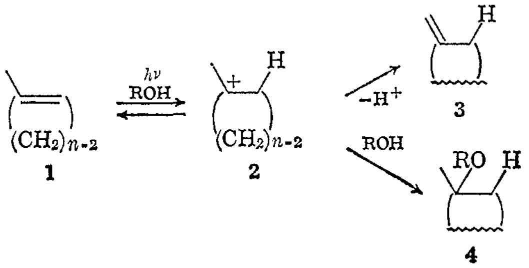
Received March 18, 1967

Photochemistry of Cycloalkenes. II. Cyclopentenes and Norbornenes

Sir:

Recent studies have shown that irradiation of alcoholic solutions of 1-alkylcyclohexenes and -heptenes (*cf.* **1**) in the presence of aromatic hydrocarbon photosensitizers such as benzene, toluene, or xylene results in protonation of the double bond followed by three competing processes: (a) formation of the corresponding exocyclic isomer **3**, (b) addition of solvent to afford a tertiary cycloalkyl ether (**4**), and (c) regeneration of the starting olefin **1**.[1,2] As a consequence of this behavior, irradiation in methanol-O-*d* leads to extensive incorporation of deuterium in both the products and the recovered starting olefin.[1] Analogous behavior is exhibited by cyclohexenes and -heptenes bearing no substituents about the double bond, except that in these cases photosensitized cyclodimerization competes with ether formation.[1,3] By contrast, larger ring cycloalkenes and their acyclic analogs, which are well known to undergo facile *cis–trans* photoisomerization,[4] show no evidence of either isomerization or ether formation under these conditions.[1] The difference in behavior of these various systems is almost surely related to the relative ease with which the carbon skeleton can accommodate an orthogonally oriented π,π* triplet species and, perhaps, a *trans*-substituted double bond.[1] We wish now to report yet another type of behavior, of a radical rather than ionic nature, displayed under these conditions by norbornenes and cyclopentenes—olefins which are substantially less flexible than those previously found to exhibit ionic behavior.



Irradiation of 1-methylcyclopentene in methanol–xylene affords principally 1-methylcyclopentane (46%), accompanied by a smaller amount of methylenecyclopentane (24%) but no methyl 1-methylcyclopentyl ether,[5] the expected product of ionic addition.[1,2,6] Although some exocyclic isomer is formed in this case, labeling studies have shown that *the isomerization does not involve protonation of the starting olefin:* irradiation of 1-methylcyclopentene in xylene–methanol-O-*d*, under conditions in which 1-methylcyclohexene and its photoproducts incorporated deuterium extensively (33–92%), afforded 1-methylcyclopentane and methylenecyclopentane *without any measurable incorporation of*

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[1] Part I: P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

[2] J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

[3] P. J. Kropp, unpublished observations.

[4] See, for example, the discussion by R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

[5] Direct comparison was made with an authentic specimen prepared independently by acid-catalyzed addition of methanol.

[6] All products were identified by direct spectral comparison with commercial samples or authentic specimens prepared as previously described in the literature.

Table I. Photosensitized Irradiation of 2-Norbornene (**5**)[a]

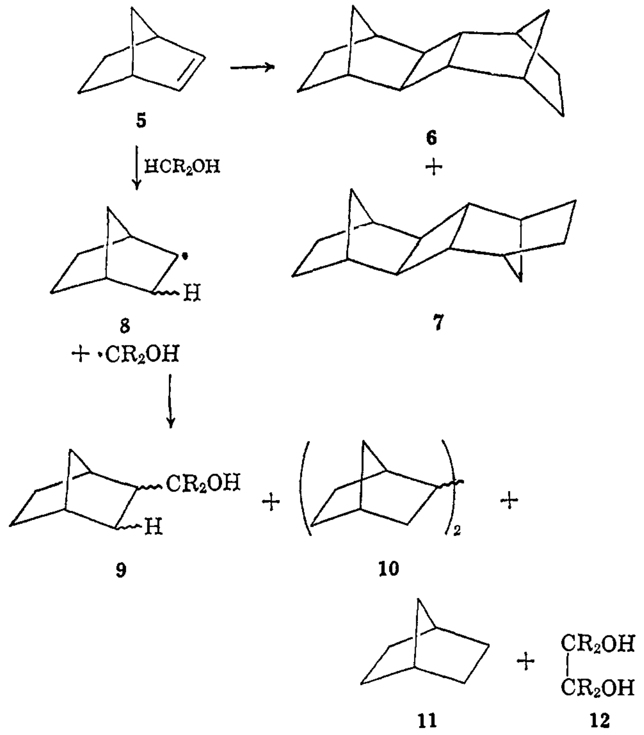
Solvent	Sensitizer	Time, hr	Yield, %[b]						
			5	**6**	**7**	**9**	**10**	**11**	**12**
CH_3OH	Xylene	4	1	26	3	24	11	8	28
CH_3OH		8	88	...	...	...	...	...	...
$(CH_3)_2CHOH$	Xylene	4	*c*	16	2	33	14	*c*	21
$(CH_3)_3COH$	Xylene	4	*c*	51	7	...	8	*c*	...
Benzene	Benzene	8	37	22	3	...	...	...	...

[a] Irradiations were conducted using a Hanovia 450-w lamp, a Vycor immersion well, and 150 ml of solution containing 3.00 g of **5** and 3.0 ml of sensitizer. [b] Determined by gas chromatographic analysis of an aliquot removed from the irradiation mixture. The results reported are those of a typical run. [c] Not determined because of overlap by the solvent peak.

deuterium in either of the photoproducts or in the recovered starting olefin.

Reduction also occurs on irradiation of 2-norbornene (**5**) in methanol– or 2-propanol–xylene mixtures, but is accompanied by formation of the additional products **9**, **10**, and **12** as well as the *endo,trans,exo* and *exo,trans,exo* dimers **6** and **7**[7] (see Table I).[6] Only the latter two products result from irradiation in either benzene or a *t*-butyl alcohol–xylene mixture, conditions under which no readily abstractable hydrogens are available. No methyl 2-norbornyl ether could be detected from irradiations conducted in methanol.[5] Formation of the products **9–12** apparently involves an initial abstraction of hydrogen from the alcohol by 2-norbornene.[8] Products analogous to **9–12** but arising from benzylic hydrogen abstraction are formed on irradiation in toluene or xylene in the absence of an alcohol.[9]

Chart I



2-Methyl-2-norbornene exhibits similar behavior except that the presence of the methyl group impedes the formation of dimeric products analogous to **6**, **7**, and **10**. The principal products from a typical run in methanol–xylene were 2-methylnorbornane (24%) and a mixture of methanol adducts analogous to **9** (44%), accompanied by only a small amount of the exocyclic isomer 2-methylenenorbornane (6%).

The photochemistry of cycloalkenes is now seen to follow a clear pattern which suggests the following tentative interpretation. In the case of exocyclic, larger ring cyclic, and acyclic olefins the availability of a relatively unstrained orthogonal π,π^* triplet and decay to either a *cis* or *trans* isomer serves as an efficient means of removing energy from the system and precluding intermolecular processes such as proton or radical abstraction. In cyclohexenes and -heptenes either the orthogonal π,π^* triplet or, if formed, the corresponding extraordinarily strained *trans*-cycloalkene achieves relief of strain by principally undergoing rapid protonation in hydroxylic media. With cyclopentenes and norbornenes the formation of an orthogonally oriented excited species is inconceivable, much less decay to a *trans* olefin. Return can occur only to *cis* olefin. Hence the triplet state is sufficiently long-lived and/or energetic to participate in intermolecular processes; the result in this case, however, is hydrogen abstraction,[10] a behavior not unprecedented for excited π systems.[11] These points will be discussed in more detail separately, along with the results of current studies designed to further test this working hypothesis.[11a]

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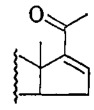
(7) Obtained previously by acetone- or acetophenone-sensitized dimerization of **5**: (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); (b) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(8) Numerous detailed schemes for the formation of products **9–12** from **5** can be envisioned. Chart I is intended to illustrate no particular pathway, or set of pathways, except for the important point that hydrogen abstraction by the olefin occurs, presumably from the alcoholic solvent. Control experiments suggest that hydrogen abstraction from the alcohol by the aromatic hydrocarbon sensitizer does not occur to any significant extent under these conditions.

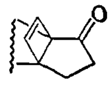
(9) It has been proposed that 2,2′-binorbornane (**10**), which was obtained previously by irradiation of **5** in acetone solution, arises as a secondary product *via* "Substratdehydrierung intermediärer Photoprodukte."[7a] However, this proposal is not consistent with the present data, which clearly show that generation of **10** is directly related to the availability of abstractable hydrogen atoms on solvent molecules and does not occur under otherwise identical conditions in the absence of available hydrogens.

(10) A small amount (1–3%) of reduction competes with the ionic reactions of cyclohexenes and -heptenes, but no reduction of larger ring or acyclic olefins has been observed.

(11) It has previously been reported that the ketones i and ii undergo saturation of the carbon–carbon double bond upon irradiation in ethanol or methylene chloride, respectively. Such examples may well be closely related mechanistically to the present results; see I. A. Williams and P. Bladon, *Tetrahedron Letters*, 257 (1964); R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Am. Chem. Soc.*, **88**, 1330 (1966).



i



ii

(11a) Note Added in Proof. Recent results from these laboratories have shown that under specialized conditions, such as the presence of phenyl substitution or the possibility of intramolecular protonation, norbornenes can be induced to exhibit at least partial ionic behavior.

Acknowledgment. The excellent technical assistance of Mr. H. J. Krauss is gratefully acknowledged.

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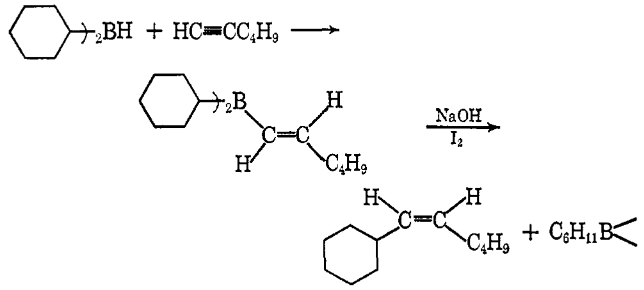
Received April 12, 1967

A Convenient Stereoselective Synthesis of Substituted Alkenes *via* Hydroboration–Iodination of Alkynes[1]

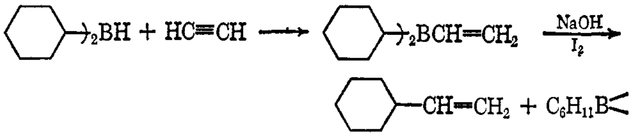
Sir:

The addition of bromine to vinylboronic esters results in the formation of 1,2-dibromoalkaneboronic esters. These may be converted to vinyl bromides by treatment with water or sodium hydroxide.[2] Matteson and Liedtke[3] have suggested that bromine adds *trans* to the vinylboronic esters. Also, they have established that the deboronobromination involves a stereospecific *trans* elimination. In concurrence with these results, Brown and Bowman[4] have reported that bromination of the vinylborane derived from hydroboration of 1-hexyne with bis(3-methyl-2-butyl)borane yields *cis*-1-bromo-1-hexene on work-up.

We now wish to report that iodination of vinylboranes does not afford the corresponding vinyl iodides, but results in a transfer of one alkyl group from boron to the adjacent carbon to give high yields of substituted olefins. Thus, addition of iodine to the vinylborane derived from the hydroboration of 1-hexyne with dicyclohexylborane gives an 81% yield of *cis*-1-cyclohexyl-1-hexene with 92% isomeric purity. If sodium hydroxide is added prior to the iodination step, a 75% yield of pure *cis* olefin (99%) is obtained.



The hydroboration of acetylene with dicyclohexylborane in tetrahydrofuran proceeds readily to the vinylborane stage,[5] and iodination of this organoborane in the presence of sodium hydroxide produces 83% of vinylcyclohexane.



Finally, vinylboranes derived from the hydroboration of disubstituted alkynes with dialkylboranes may be converted by this procedure to trisubstituted olefins. The experimental results are summarized in Table I.

It is apparent that the utility of this reaction depends on the availability of the starting dialkylboranes.[6] Fortunately, most cyclic and many acyclic olefins are readily converted to substituted boranes.[7] Consequently, the iodination of vinylboranes offers a novel route for the introduction of olefinic side chains onto both cyclic and acyclic systems.

The following procedure for the synthesis of *cis*-1-cyclohexyl-1-hexene is representative. A solution of 4.1 g (50 mmoles) of cyclohexene in tetrahydrofuran (20 ml) was placed in a 100-ml flask equipped with a thermometer, a pressure-equalizing funnel, and a magnetic stirrer. The flask was immersed in an ice–water bath and hydroboration was achieved by the dropwise addition of 13.9 ml of a solution of borane (25 mmoles) in tetrahydrofuran. The precipitate formed (R_2BH) was stirred at 0–5° for 1 hr, and then the reaction mixture was diluted with 2.05 g of 1-hexyne (25 mmoles) in 10 ml of tetrahydrofuran while the temperature was maintained at 15–20°. After the precipitate had dissolved, the resulting solution was stirred for an additional 30 min at room temperature. To this mixture was then added at $-10°$ 15 ml of 6 *N* sodium hydroxide, followed by the dropwise addition of a solution of iodine (6.35 g, 25 mmoles) in tetrahydrofuran (10 ml) over a period of 15 min. After the reaction mixture had warmed up to room temperature, any excess iodine was decomposed by adding a small amount of aqueous sodium thiosulfate. The olefin product was extracted into pentane and dried. Distillation gave 3.1 g of *cis*-1-cyclohexyl-1-hexene (75%), bp 44–45° (1 mm), $n^{20}D$ 1.4586.

Table I. Conversion of Vinylboranes into Olefins by Iodine in the Presence of Sodium Hydroxide

Vinylborane derived from	Olefin produced (isomeric purity, %[a])	Yield, %[b]
$(C_6H_{11})_2BH$ + acetylene	Vinylcyclohexane	83[c]
+ 1-hexyne	*cis*-1-Cyclohexyl-1-hexene (99)	75
+ cyclohexylacetylene	*cis*-1,2-Dicyclohexylethylene (92)	77
+ 3-hexyne	3-Cyclohexyl-3-hexene[d]	85
$((CH_3)_2CHCHCH_3)_2BH$ + 1-hexyne	*cis*-2,3-Dimethyl-4-nonene (98)	63

[a] The analytical and spectral data for each of these products are consistent with their structures. [b] The yields are based on the theoretical production of 1 mole of olefin from 1 mole of dialkylborane. [c] By glpc analysis. [d] The configuration of this olefin has not been established.

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(1) This research was supported by National Science Foundation Grant No. GP-6633.

(2) B. M. Mikhailov and P. M. Aronovich, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1961); *Chem. Abstr.*, 55, 24541 (1961); D. S. Matteson and K. Peacock, *J. Org. Chem.*, 28, 369 (1963); W. G. Woods and I. S. Bengelsdorf, *ibid.*, 31, 2769 (1966).

(3) D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, 87, 1526 (1965).

(4) H. C. Brown, private communication.

(5) H. Arzoumanian, unpublished results.

(6) We are currently exploring the possibility of using monoalkylboranes for the iodination reaction.

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.