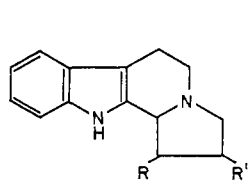
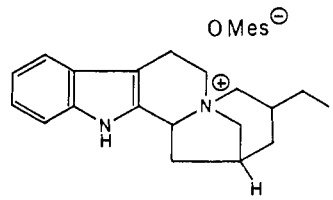
but had lost the characteristic imide absorption in the infrared spectrum. The molecular formula $C_{26}H_{34}N_3O$ was established by high-resolution mass spectrometry which provided the value 390.267 (calcd: 390.267). As already noted previously,[6] this type of molecule fragments rapidly under electron impact to provide a very significant peak at *m/e* 260 due to the ion V (R = $CH_2C_6H_5$).

The amine was treated with excess mercuric acetate (methanol–acetic acid) and the crude product was reduced immediately with sodium borohydride[6] to provide a mixture of six compounds in 42% yield. One of the major components was the desired cyclic amine VI (R = H, R′ = $CH_2CH(Et)CH_2OCH_2C_6H_5$), $C_{26}H_{32}N_2O$ (found: 388.251; calcd: 288.251), no nmr α proton signal on the indole ring and a typical indole chromophore in the ultraviolet spectrum.[10] The mass spectrum of this compound was completely different from that of the amine IV, and with peaks at *m/e* 184, 170, 156, etc., was immediately reminiscent of the analogous compound in the quebrachamine series.[6]

Catalytic debenzylation (palladium on charcoal) converted the benzyloxyamine to the amino alcohol VI (R = H, R′ = $CH_2CH(C_2H_5)CH_2OH$, 85% yield), $C_{19}H_{26}N_2O$ (found: 298.204; calcd: 298.205). Apart from the normal indole ultraviolet spectrum, the nmr spectrum showed a complete absence of the characteristic benzyl ether proton signals mentioned above.



VI



VII

The total synthesis of a *dl*-dihydrocleavamine was completed when the quaternary mesylate, VII, formed directly from the reaction of the amino alcohol with methanesulfonyl chloride in pyridine, was reduced with sodium and liquid ammonia.[6] The reaction product was identical with an authentic sample of 4β-dihydrocleavamine (I; R = H) obtained previously by catalytic reduction of cleavamine. The isomeric 4α-dihydrocleavamine (α-ethyl group at C_4 in I) is also obtained and shown to be identical with an authentic sample prepared from the acid hydrolysis of carbomethoxydihydrocleavamine (infrared, thin-layer chromatography, mass spectrometry in both instances).

Introduction of the ester group to complete the total synthesis of carbomethoxydihydrocleavamine was achieved as follows. Conversion of 4β-dihydrocleavamine to a chloroindolenine was accomplished by means of *t*-butyl hypochlorite.[11] The mass spectrum of the latter compound, $C_{19}H_{25}N_2Cl$, with its molecular ion peak at *m/e* 316 (as well as 318 for ^{37}Cl), its base peak at *m/e* 281 (M − Cl), and peaks normally encountered in the fragmentation of the cleavamine system[12] allowed a normal formulation for this compound.[11] Regeneration of 4β-dihydrocleavamine from lithium aluminum hydride reduction of the chloroindolenine[11] provided further confirmation for its structure.

Reaction of the chloroindolenine with potassium cyanide[11] gave a cyanodihydrocleavamine (I; R = CN), $C_{20}H_{25}N_3$ (found: 307.205; calcd: 307.205), normal indole absorption; ν_{film} 4.5 μ (C≡N); multiplet centered at τ 5.95 in the nmr (HC–CN); typical dihydrocleavamine fragmentation in the mass spectrum.[12] The latter compound on treatment with methanolic hydrochloric acid provided carbomethoxy-4β-dihydrocleavamine (I; R = $COOCH_3$) identical in every respect with an authentic sample of I prepared in our laboratory from the reaction of catharanthine with acetic acid in the presence of zinc dust.[13]

This work now completes the total synthesis of *dl*-coronaridine and *dl*-dihydrocatharanthine in view of our previously reported cyclization.[3] Since the conversion of coronaridine to ibogamine has also been accomplished,[14] our work extends to this series as well.

It is now evident that the transannular cyclization approach is the most general method yet developed for the total synthesis of Aspidosperma, Vinca, and Iboga alkaloids.

Very recently[15] a total synthesis of the Iboga alkaloids has also been achieved by a completely different route.

Acknowledgment. Financial aid from the National Cancer Institute of Canada and the National Research Council of Canada is gratefully acknowledged.

(10) The alternative cyclization product VI (R = $CH_2CH(Et)CH_2OCH_2C_6H_5$; R′ = H) does not lead to a dihydrocleavamine. A further discussion of this reaction will be presented in the detailed paper.

(11) G. Buchi and R. E. Manning, *J. Am. Chem. Soc.*, **88**, 2532 (1966).

(12) M. Gorman, N. Neuss, and N. J. Cone, *ibid.*, **87**, 93 (1965).

(13) Unpublished results from our laboratory. See also ref 12.

(14) M. Gorman, N. Neuss, N. J. Cone, and J. A. Deyrup, *J. Am. Chem. Soc.*, **82**, 1142 (1960).

(15) G. Buchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Ziegler, *ibid.*, **87**, 2073 (1965); **88**, 3099 (1966).

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The Reaction of Trialkylboranes with Dimethyloxosulfonium Methylide

Sir:

The migration of a group from boron to adjacent oxygen and nitrogen is a well-known occurrence which provides the basis for the synthetically important oxidation of organoboranes to alcohols[1-3] as well as their conversion to amines.[4] Organoboranes are known to react with carbon monoxide,[5] isonitriles,[6] diazomethane,[7] and phenyl(bromodichloromethyl)mercury[8] by processes which appear to involve the rearrangement of a group from boron to carbon.

A consideration of these reactions makes it seem

(1) H. G. Kuivila and R. A. Wiles, *J. Am. Chem. Soc.*, **79**, 5659 (1957), and references cited therein.

(2) W. J. Wechter, *Chem. Ind.* (London), 294 (1959).

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(4) H. C. Brown, W. R. Heydkamp, E. Brewer, and W. Murphy, *ibid.*, **86**, 3565 (1964).

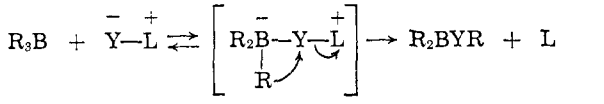
(5) M. E. Hillman, *ibid.*, **84**, 5715 (1962); **85**, 982, 1626 (1963).

(6) (a) G. Hesse and H. Witte, *Angew. Chem.*, **75**, 791 (1963); *Ann.*, **687**, 1 (1965); (b) J. Casanova, Jr., and R. E. Schuster, *Tetrahedron Letters*, 405 (1964); (c) J. Casanova, Jr., H. Kiefer, D. Kuwada, and A. Boulton, *ibid.*, 703 (1965).

(7) C. E. H. Bawn and A. Ledwith, *Progr. Boron Chem.*, 1, 345 (1964), and references cited therein.

(8) D. Seyferth and B. Prokai, *J. Am. Chem. Soc.*, **88**, 1834 (1966).

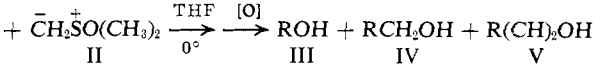
reasonable to expect that any boron-attacking species (*e.g.*, Y^-L^+) which possesses a nucleophilic site and a potentially good leaving moiety should be capable of reacting with an organoborane and inducing the migration of a group from boron to Y.



I

This hypothetical species might or might not bear formal charge on both the nucleophilic terminus, Y, and the leaving terminus, L; however, one can infer that species which do bear appreciable charge on both sites should be especially reactive toward organoboranes since, in such cases, the nucleophilic center would readily react with the electrophilic boron and the migrating group would displace a neutral molecule, L, as the leaving group.

Most ylides would appear to fulfill these requirements satisfactorily; however, methylenetriphenylphosphorane has been reported to react with boron halides,[9] borane,[9,10] and monoalkylboranes[10] (but apparently not with trialkylboranes)[9] to give stable 1:1 adducts. In contrast, we have found that dimethyloxosulfonium methylide[11] (II) reacts with trialkylboranes[12] in the desired manner. Thus, equimolar amounts of trialkylborane (R_3B) and II in tetrahydrofuran react readily at 0° to afford, after alkaline hydrogen peroxide oxidation, homologated alcohol (*i.e.*, IV) in good yield. This procedure is illustrated for the reaction of tri-*n*-heptylborane (20 mmoles) with II (20 mmoles), which gives rise to 1-heptanol (69%), 1-octanol (25%), and 1-nonanol (6%) after oxidation.[15]



II III IV V

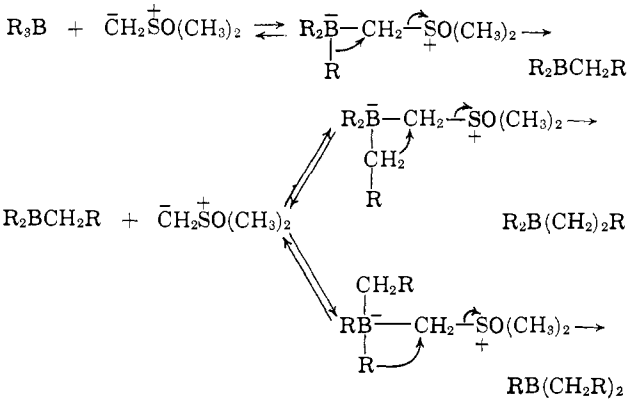
Clearly, the maximum yield of homologated alcohol to be expected from the reaction of equimolar quantities of R_3B and II is 33%. Thus, the reaction, in this instance, is proceeding to afford 79% of the theoretical amount of 1-octanol. The results obtained for a variety of organoboranes are summarized in Table I. It is to be noted that a quantity of doubly homologated alcohol (*i.e.*, V) is formed in each case, possibly due to rapidly reversible betaine formation. Such reversal would permit the exposure of the initially formed homologated organoborane (*i.e.*, R_2BCH_2R) to further reaction with ylide (*cf.* Scheme I). Alternatively, it is also possible that betaine formation is irreversible and the step involving boron-to-carbon migration is faster than the initial attack on boron. We have no direct evidence bearing on this point at this time.

Table I. Product Distribution from the Reaction of Trialkylboranes with II

Hydroborated alkene[a]	II,[b] mmoles[c]	Product distribution,[d] mole % III[e]	IV[e]	V[e]
1-Hexene	20	68	26	6
1-Heptene	20	71	26	3
2,4,4-Trimethyl-1-pentene	20	69	25	6
4-Methyl-1-pentene	40	66	26	8
Norbornene	30	69	26	5

[a] The hydroboration was carried out so as to ensure the formation of trialkylborane. See ref 14. [b] See ref 11. [c] The ylide and organoborane were used in equimolar amounts. [d] The over-all yields of alcohol were 90 ± 10% by vpc. [e] The products were characterized by direct comparison or by comparison of their physical and chemical properties with those reported in the literature.

Scheme I



That the migration of the group from boron to carbon proceeds with retention of configuration can be seen from the results of the reaction of II with the trialkylborane derived from norbornene. The hydroxymethylnorbornane obtained after oxidation was found to be at least 97% *exo* by nmr analysis.[16] This finding is consistent with the stereospecificity observed in the alkaline hydrogen peroxide oxidation of the same borane.[3]

A reasonable alternative[17] to the mechanism suggested above for the organoborane–ylide reaction would involve the insertion of methylene, derived from the decomposition of II, into a boron–carbon bond. Indeed, it has been suggested recently that carbenes may bring about such insertions;[8] however, we tend to favor the former mechanism since the reaction of tri-*n*-hexylborane (20 mmoles) with II (20 mmoles) in the presence of a large excess of cyclohexene (270 mmoles) did not result in the formation of a quantity of norcarane detectable by vpc analysis.

Interestingly, we have found that triarylboranes also react smoothly with dimethyloxosulfonium methylide. Thus, equimolar quantities of triphenylborane and II afford, after oxidation, 89% of the theoretical quantity of benzyl alcohol.

We are currently investigating means to improve the synthetic utility of the reaction between sulfur ylides and organoboron compounds. Moreover, we are seeking to extend the reaction to include other classes of ylides. Details of this work will be reported in a future publication.

Acknowledgment. We wish to thank the National

(9) D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1613 (1961).
(10) M. F. Hawthorne, *ibid.*, **83**, 367 (1961).
(11) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).
(12) Prepared by the hydroboration[13,14] of the requisite olefins.
(13) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.
(14) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).
(15) These percentages include minor amounts of structural isomers since the hydroboration stage does not proceed with the exclusive introduction of boron at the terminal carbon.[13]
(16) *exo*- and *endo*-2-hydroxymethylnorbornane could not be resolved using a variety of gas chromatographic conditions.
(17) Several possible mechanistic variations not explicitly considered herein will be discussed in the full paper.

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Spin Inversion and Bond Rotation in 1,3-Diradicals

Sir:

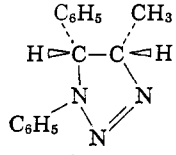
Skell's hypothesis relating electron spin multiplicity and stereospecificity in the addition of carbenes to olefins[1] rests on the assumption that σ-bond rotation is more rapid than spin inversion. The observed nonstereospecific addition of triplet carbene is thus attributed to bond rotations in the intermediate triplet 1,3-diradical prior to the relatively slow spin-inversion process.[2] Singlet carbene addition to olefin occurs with spin conservation and is observed to be stereospecific. Although the validity of Skell's hypothesis is widely recognized, it has been noted that firm evidence supporting the assumption that σ-bond rotation is more rapid than spin inversion in 1,3-diradicals is currently lacking.[3] Furthermore, chemical evidence bearing on this point has been obtained through investigation of carbene and nitrene[4] reactions. Since it is not clear whether additions of singlet carbene to olefin involve 1,3-diradical intermediates,[1,2] valid comparisons of the stereochemical behavior of singlet and triplet 1,3-diradicals have not been possible. We report here our observations of such diradicals, generated by a noncarbene path.

Table I. Direct Photodecomposition[a,b]

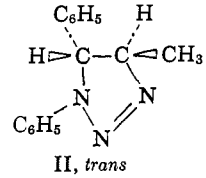
Triazoline[c]	*cis*-Aziridine III, %	*trans*-Aziridine IV, %	Imine V, %
I, cis	65	17	18
II, *trans*	22	66	12

[a] Hanovia Type A, 550 w, Pyrex filter, 25°. [b] ± 4%. [c] Initial concentration: 0.042 *M* in benzene.

Triazolines I and II were prepared by the stereospecific addition of phenyl azide to *cis*- and *trans*-β-methylstyrenes. Structures I and II are fully supported

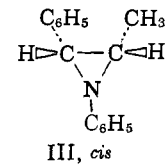


I, *cis*

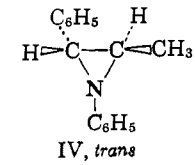


II, *trans*

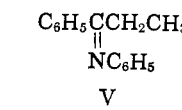
by elemental analysis,[5] nmr spectra,[5] the reported stereospecificity,[6] and the orientational selectivity of azide–olefin addition,[7] as well as by the nature of the decomposition products. Direct irradiation of solutions of I or II produced different mixtures of the same three products: *cis*-aziridine III,[8] *trans*-aziridine IV,[8] and propiophenone anil V (Table I). Interrupted runs revealed no *cis–trans* triazoline interconversion, and the products were photostable under the conditions employed. Within experimental error, the same product distributions were observed (Table I) with oxygen



III, *cis*



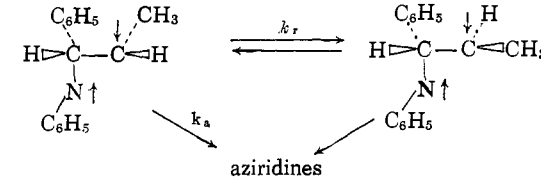
IV, *trans*



V

rigorously excluded from the system or in the presence of 4.9 *M* piperylene. Similarly, quantum yields for nitrogen evolution (313 mμ) from I and II were unaffected by oxygen.

The failure of triplet quenchers to alter the characteristics of the reaction is indicative of reaction from an excited singlet state. The product distribution data (Table I) show predominant retention of initial geometry in the aziridine products. It thus appears that the intermediate singlet 1,3-diradical undergoes ring closure to aziridine more rapidly than bond rotation ($k_a > k_r$).[9] Similar retention of geometry has been



reported for the photo- and thermal decompositions of 1-pyrazolines.[10]

Under photosensitizing conditions (366 mμ, benzophenone), I and II give the products shown in Table II. Appropriate control experiments demonstrated the photostability of the products and the absence of triazoline isomerization prior to decomposition. No other products were detected.

Table II. Benzophenone-Sensitized Photodecomposition[a,b]

Triazoline	*cis*-Aziridine III, %	*trans* Aziridine IV, %	Imine V, %
I, *cis*	60	36	4
II, *trans*	54	42	4

[a] See footnotes *a*, *b*, *c*, Table I. [b] Benzophenone, 0.028 *M*.

Photodecomposition of azo compounds by triplet energy transfer is well documented.[11] Loss of singlet nitrogen[11b] from excited triplet triazoline results in a triplet 1,3-diradical, a species which must undergo spin inversion before closure to aziridine.

(1) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).
(2) For pertinent references see P. P. Gaspar and G. S. Hammond in W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapter 12.
(3) Reference 2, p 260; W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).
(4) W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965); A. G. Anastassiou, *ibid.*, **88**, 2322 (1966).
(5) A full report dealing with the mechanism of triazoline photodecomposition will appear shortly.
(6) R. Huisgen and G. Szeimies, *Chem. Ber.*, **98**, 1153 (1965).
(7) For references see P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libby, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).
(8) J. A. Deyrup and R. B. Greenwald, *ibid.*, **87**, 4538 (1965).
(9) The origin of the imine product and evidence for a one-step expulsion of nitrogen from excited triazoline will be discussed in a forthcoming article.[5]
(10) C. G. Overberger, R. E. Zangaro, and J. P. Anselme, *J. Org. Chem.*, **31**, 2046 (1966); T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **82**, 5251 (1960).
(11) (a) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (b) S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).