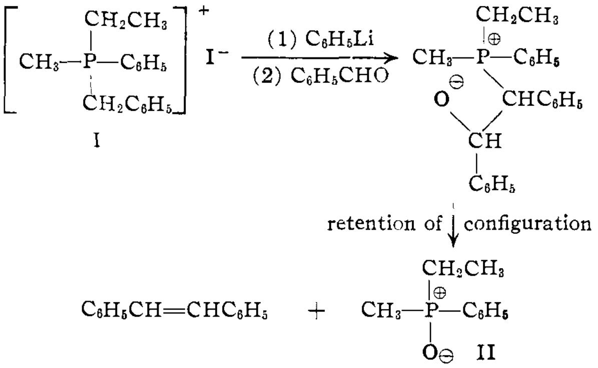
benzaldehyde to the resulting orange mixture, gave a white precipitate of an adduct of II and lithium iodide. Decomposition of the adduct by the action of sodium hydroxide solution, extraction of the phosphine oxide into benzene, and distillation of the extracted material *in vacuo*, gave a 70% yield of II, m.p. 46–50°, $[\alpha]^{25}\text{D}$ 21.5 ± 1.0° (*c*, 2.128 in water).

Anal. Calcd. for $C_9H_{13}PO$: C, 64.30; H, 7.73; P, 18.46. Found: C, 64.54; H, 7.91; P, 18.22.

From the ether filtrate there was isolated *trans*-stilbene in 84% yield and *cis*-stilbene in 5% yield.

When levorotatory I was subjected to the Wittig reaction, there was obtained a 68% yield of II, m.p. 47–51°, $[\alpha]^{25}\text{D}$ −21.0 ± 1.0°, an 82% yield of *trans*-stilbene and a 6% yield of *cis*-stilbene.

Since the available evidence indicates that the Wittig reaction takes place by way of a *quasi*-four-membered ring transition intermediate,[4] it may be assumed that (+)-I and (+)-II belong to the same configurational family. This leads to the conclusion that the decomposition of the phosphonium hydroxides takes place with inversion of configuration since (+)-I gives (−)-II in this reaction.



Consistent with the stereochemical and kinetic data, it may be reasoned that a hydroxide ion can add in a reversible manner to any one of the four faces of the tetrahedral phosphonium cation. Also, the conjugate bases of any of the four trigonal bipyramidal intermediates may be formed by a reversible reaction with a second hydroxide ion. However, owing to the relatively greater stability of the benzyl anion over phenyl, methyl or ethyl anions, only the conjugate base of the pentacovalent phosphorus intermediate in which the negatively charged oxygen atom is colinear with the benzyl group and the phosphorus atom is capable of further reaction to produce II and the benzyl anion. Thus, the stereo-electronic requirements of the decomposition of methylethylphenylbenzylphosphonium hydroxide lead to inversion of configuration of the phosphorus atom.

$$\begin{tikzcd}
\text{(+) Salt} \arrow[r, "\text{OH}^-", "\text{(inversion)}"'] \arrow[d, "\text{Wittig (retention)}"] & \text{(−) Oxide} \\
\text{(+) Oxide} & \text{(−) Salt} \arrow[l, "\text{OH}^-", "\text{(inversion)}"'] \arrow[u, "\text{Wittig (retention)}"']
\end{tikzcd}$$

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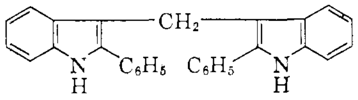
[4] U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

ON THE SYNTHESIS OF 2,2'-DIPHENYL-3,3'-DIINDOLYLMETHANE

Sir:

In a recent paper Leete[1] suggested without evidence that 2,2'-diphenyl-3,3'-diindolymethane (I), m.p. 184–185°, which was synthesized in these



I

laboratories[2] from 2-phenylindole (II) and formaldehyde, was identical with the starting material II (m.p. 187–188°). No definite conclusions about the structure can be drawn from the analytical data as the difference in the percentage composition between I and II is very small. However, these other facts will make the case clear.

(a) The melting point of an admixture of I and II is depressed considerably (150–160°).

(b) The infrared and ultraviolet spectra of I and II show beyond a doubt that the two compounds are not identical.

(c) Treatment of an indole unsubstituted in the 3-position with a 3-dialkylaminomethylindole in glacial acetic acid was found to yield 3,3'-diindolylmethanes.[2] 2,2'-Diphenyl-3,3'-diindolylmethane (I) also can be obtained in this way from 2-phenylindole and the Mannich base 3-(dimethylaminomethyl)-2-phenylindole. The product formed in this reaction is identical with I prepared from II and formaldehyde and different from II (m.p., mixed m.p. and infrared spectra).

It can be concluded, therefore, that the product with m.p. 184–185° from 2-phenylindole and formaldehyde is a new compound and not the starting material.

[1] E. Leete, THIS JOURNAL, **81**, 6023 (1959).

[2] R. Dahlbom and A. Misiorny, *Acta Chem. Scand.*, **9**, 1074 (1955).

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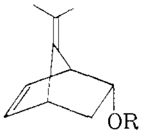
THE SOLVOLYSIS OF *EXO* AND *ENDO*-7-ISOPROPYLIDENEDEHYDRONORBORNYL TOSYLATES

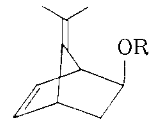
Sir:

Although the stability of homoallylic cations has been well established, the structure and bonding in these intermediates is still a matter of much conjecture.[1] In particular it is not known how many types of non-classical ions might occur, *i.e.*, homoallylic, bi- and tricyclobutonium, *etc.*, nor what role classical ions might play in their reactions. We wish to report results which demonstrate, in a striking manner, the absence of classical cations in some homoallylic solvolyses, and which also place some important restrictions on the type of bonding involved in these cations.

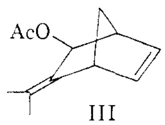
We have reported recently the synthesis of *endo*-7-isopropylidenedehydronorborneol (Ia).[2] Base-catalyzed equilibration of Ia and gas chromatographic separation of the resultant mixture of dienols gave the *exo*-alcohol (IIa). Acetolysis of both *endo*- and *exo*-tosylates (Ib and IIb) proceeded readily at 30° ($k_{\mathrm{Ib}} = 7 \times 10^{-6}$ sec.$^{-1}$, $k_{\mathrm{IIb}} = 6 \times 10^{-5}$ sec.$^{-1}$) showing that both reactions are strongly anchimerically accelerated.[3,4] *Despite the fact that both solvolyses led to positive charge at carbon 2, the reactions are completely stereospecific,* *endo*-tosylate (Ib) leading exclusively to *endo*-acetate (Ic),[5] *exo*-tosylate giving only rearranged acetate (III) as product. Clearly, the cationic center at carbon 2 does not have classical character, since otherwise some mixing of products would have been observed. More importantly, equilibrium between the two homoallylic ions (IV and V) is also ruled out. Similar results were obtained in the solvolysis of the 5,6 dihydro compounds, *exo*- and *endo*-7-isopropylidene-norbornyltosylates,[2] where the same stereospecificity in solvolysis was observed, the *endo* tosylate ($k = 4 \times 10^{-5}$ sec.$^{-1}$) giving only *endo* acetate and the *exo* ($k = 2 \times 10^{-4}$ sec.$^{-1}$) giving only dihydro III.



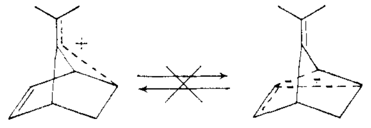
Ia, R = H
b, R = OTos
c, R = OAc



IIa, R = H
b, R = OTos



III



IV V

The absence of common intermediates in the two solvolyses demands an activation energy for the interconversion of the homoallylic ions, and rules out a symmetrical structure in which both sides of the unsaturated center at C_2 are stabilized by interaction with the double bonds. It seems possible that equilibration of the cations may become detectable in solvents in which they have longer lifetimes, and that cations from different sources (*e.g.*, from the amine–nitrous acid reaction) may react differently. Experiments designed to test these points are in progress.

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[1] For recent, comprehensive discussions of the problem see S. Winstein and E. M. Kosower, THIS JOURNAL, **81**, 4399 (1959), and R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[2] C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960).

[3] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

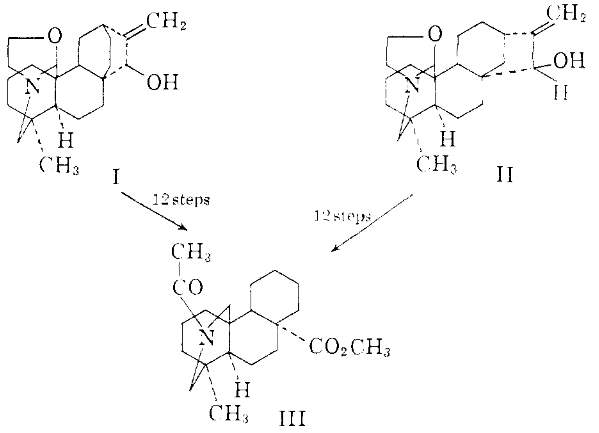
[4] Interaction between the 2 and 7 position of the type displayed in IV has been sought previously without success. See J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957), and E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

[5] As little as 1% of III could have been detected readily by gas phase chromatography.

THE CORRELATION OF THE ATISINE AND VEATCHINE SERIES OF DITERPENE ALKALOIDS[1]

Sir:

The presently accepted structures[2] of atisine (I)[3–6] [*Aconitum heterophyllum*] and veatchine (II)[3,7] [*Garrya veatchii*] differ only in the terminus of the hydroxyl-bearing ring. Because of the failure to interrelate the two series, the possibility has been suggested recently that the allylic alcohol group in atisine may be on the *cis*- (rather than the *trans*-) branch (with respect to nitrogen) of the 2,2,2-bicyclooctane system.[8] As subsequent evidence from this[6] and another laboratory[5] was not compatible with this proposal, the direct correlation of these two important classes of diterpene alkaloids became imperative. This paper reports the successful correlation of atisine and veatchine *via* the degradation product III and provides the first unequivocal evidence for the common stereochemistry of their carbon skeletons.



I II III

Treatment of IV,[9] available from atisine hydrochloride in six steps,[10] with sodium metaperiodate

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[1] This investigation was supported in part by Grants RG 5807 and RG 5807 (C1) from the National Institutes of Health, United States Public Health Service.

[2] The indicated structures assume the *trans–anti* fusion of rings A and B which is common to most diterpenes.

[3] K. Wiesner, *et al.*, *Chemistry and Industry*, 132, (1954); *Experientia* **11**, 255 (1955).

[4] S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **76**, 4496 (1954).

[5] D. Dvornik and O. E. Edwards, *Chemistry and Industry*, 633 (1958).

[6] S. W. Pelletier, *ibid.*, 1116 (1958).

[7] K. Wiesner, *et al.*, THIS JOURNAL, **76**, 6068 (1954).

[8] K. Wiesner and Z. Valenta, *Progress in the Chemistry of Organic Natural Products, XVI*, 52 (1958).

[9] S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **78**, 4144 (1956).

[10] The intermediate azomethine acetate was prepared by the method of Dvornik and Edwards, *Canad. J. Chem.*, **35**, 860 (1957).