particularly with the finding by Kuivila, *et al.*,[11a] and by Sisido, *et al.*,[3] that optically active halides lose their activity when reduced with organotin hydride. This apparent discrepancy can be explained, however, by the *gem*-dihalo structure of the substrates; the halogen atom which remains intact in the reaction, *i.e.*, the fluorine, might form a complex with tin compounds, to restrict the radical from inverting its configuration before it reacts with tri-*n*-butyltin hydride. The extremely high reactivity of organotin hydride with radicals and their potential use to trap configurationally labile radicals have already been pointed out by Kaplan,[20] who found that 2,2,2-triphenylethyl radical, which normally possesses a great tendency to rearrange to 1,2,2-triphenylethyl radical, can react with triphenyltin hydride before rearrangement occurs.

Further studies on these and the related reactions are now in progress.

Acknowledgment. We are indebted to the Hitachi Seisakusho Co., Ltd., for measurements of the fluorine nmr spectra.

[20] L. Kaplan, *J. Am. Chem. Soc.*, **88**, 4531 (1966).

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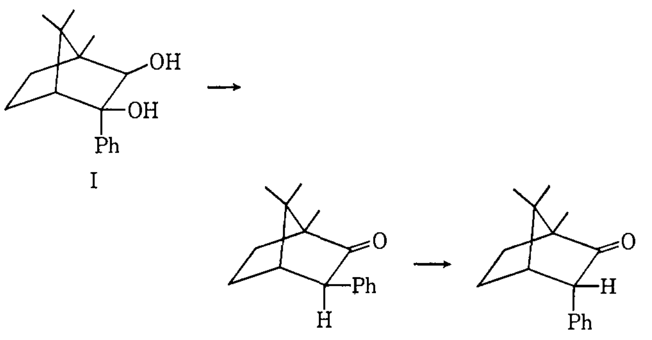
The Pinacol Rearrangement of 3-*endo*-Phenyl-2,3-*exo,cis*-bornanediol. An *endo–endo* Hydride Migration

Sir:

Recent studies[1-3] of the pinacol rearrangement of 3-*endo*-phenyl-2,3-*exo,cis*-norbornanediol prompted us to investigate the corresponding bornanediols as a possible synthetic route to alkyl- and aryl-substituted bornanones of known stereochemistry.

We have treated 3-*endo*-phenyl-2,3-*exo,cis*-bornanediol (I) with 1 : 100 $HClO_4$–HOAc for 4 hr at room temperature and have obtained results which are highly significant in terms of their theoretical implications. The product, obtained in approximately 80% yield, is 3-*exo*-phenylcamphor (II) (*Anal.* Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.04; H, 8.86), whose structure has been unambiguously established by its nmr spectrum and its rearrangement to 3-*endo*-phenylcamphor (III). *Anal.* Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.25; H, 8.74. The *exo*-phenyl ketone exhibits a one-proton singlet at 3.22 ppm as well as three methyl singlets at 0.59, 0.92, and 0.95 ppm. The signal at 0.59 ppm has been assigned to the *syn*-7-methyl which, as models clearly show, is shielded by the *exo*-phenyl group.



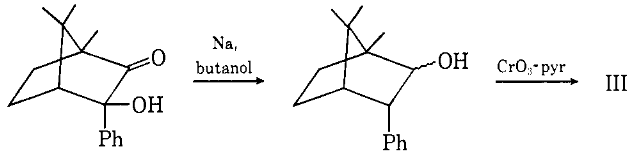
I

II

III

When the reaction is continued beyond the 4-hr period, the ketone formed initially undergoes slow epimerization to the *endo*-phenyl ketone III, whose nmr spectrum exhibits a one-proton doublet ($J_{3,4}$ = 4.5 cps) at 3.79 ppm, the methyl at 0.59 ppm having merged with the other methyl signals at approximately 1.0 ppm. Complete epimerization can be effected by stirring II with dilute NaOH for a few hours. It is significant that ketone III is thermodynamically more stable than ketone II while 2-*exo*-phenylnorbornanone, on the other hand, is clearly more stable than the 2-*endo*-phenyl epimer.[1,4] This observation undoubtedly is a result of the spatial requirement of the *syn*-7-methyl which makes the *exo* side of the bornanone more encumbered than the *endo*.

Ketone III has been independently synthesized from 3-*endo*-phenyl-3-*exo*-hydroxycamphor[5] (IV) by reaction with sodium in butanol[6] and oxidation of the epimeric alcohols with CrO_3–pyridine complex.



IV

3-*endo*-Phenyl-2,3-*exo,cis*-bornanediol (*Anal.* Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.94; H, 8.96) was prepared from hydroxy ketone IV by reduction with lithium aluminum hydride. The *cis* structure of the diol was established by its infrared trace and its acid-catalyzed reaction with acetone to form an acetonide. *Anal.* Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.89; H, 9.23. The infrared spectrum of the diol showed bands at 3527 and 3632 cm^{-1} ($\Delta\nu$ = 105 cm) indicative of strongly intramolecularly bonded hydroxyl.

Our results indicate that rearrangement takes place *via* an *endo–endo 2,3-hydride shift.* We have confirmed this hypothesis by subjecting the deuterated diol V to the same conditions that effected rearrangement of diol I. The product ketone, VI, contained more than 90% of the deuterium at the 3-*endo* position. Its nmr spectrum in deuteriochloroform was identical with the protonated form except for the signal at 3.22 ppm. When the deuterated ketone was heated for several hours at 70°, a doublet at 3.79 ppm appeared representing conversion to ketone III through enolization and exchange. We believe that these observations represent the first case of an *endo–endo* migration in the bicyclo[2.2.1]heptyl series.[1,4,7]

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[1] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964).

[2] B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

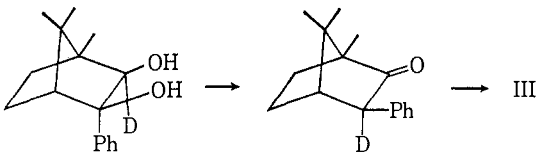
[3] D. C. Kleinfelter and T. E. Dye, *ibid.*, **88**, 3174 (1966).

[4] D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **83**, 2329 (1961).

[5] J. Gripenberg, *Suomen Kemistilehti*, **18B**, 53 (1945); *Chem. Abstr.*, **41**, 739*e* (1947).

[6] H Rupe and A. Wirz, *Verhandl. Naturforsch. Ges.* (Basel), **38**, 164 (1927); *Chem. Abstr.*, **23**, 1405 (1929).

[7] J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, p 159.


V VI III

Finally, these results provide strong evidence for the structure of the intermediate carbonium ion. In the norbornyl system evidence has been presented in support of open, classical ions at the expense of nonclassical, σ-bridged intermediates.[3,8] Our results are inconsistent with a nonclassical carbonium ion intermediate and can only be accommodated either (1) by open, classical intermediates in which product formation is determined by steric and possibly torsional effects,[9] or (2) by a concerted hydrogen migration whose driving force is greater than that for bridging.[10]

Acknowledgment. The support of this research by Research Grant CA-4298 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, is gratefully acknowledged.

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[8] (a) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 3898, 3900 (1967); (b) P. von R. Schleyer, *ibid.*, **89**, 3901 (1967).

[9] P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

[10] We wish to express appreciation to a referee for several helpful suggestions.

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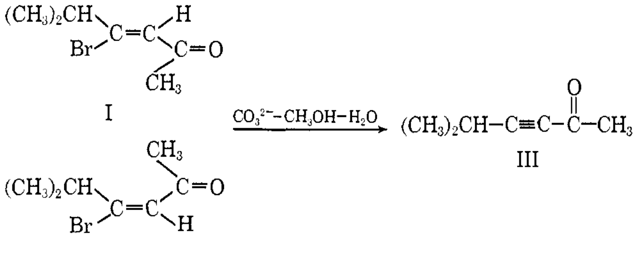
Conjugated Acetylenic Ketones. 2-Cyclooctynone[1]

Sir:

We have found that conjugated acetylenic ketones can be prepared in excellent yield by the reaction of β-bromo α,β-unsaturated ketones with mild base. The reaction is very much more facile than might have been anticipated and provides a fine method for the preparation of these interesting compounds from readily accessible starting materials.[2]

Both *trans*- (I) and *cis*-5-methyl-4-bromo-3-hexen-2-one (II)[3] react readily with 0.13 *M* potassium carbonate in aqueous methanol (1:2) or sodium phenoxide in aqueous acetone (1:4) at room temperature to give 5-methyl-3-hexyn-2-one (III). Reaction of 10 mmoles of the *trans* isomer with an equal amount of the base is complete within 2 hr and affords the acetylenic ketone in 87% isolated yield even on this small scale. The reaction is very fast; the first half-life is passed within 5 min. Reaction of the *cis* isomer is about an order of magnitude slower, but the desired product is still obtained in good yield. Similarly, *trans*-4-bromo-3-penten-2-one and *cis*-4-bromo-3-buten-2-one have been converted into the corresponding acetylenic ketones.


I II III

Little is known about the mechanism of elimination reactions from π-bonded systems activated by strong electron-withdrawing groups. It is clear that neither the β,γ-olefinic isomer of the starting bromo enone nor the allene isomer of the product acetylene is an intermediate in the reactions reported here; β-bromo β,γ-enones form conjugated allenyl ketones, and these, in turn, add methanol to give β-methoxy β,γ-enones. For the isomeric pairs of β-bromo α,β-enones we have examined, *trans* elimination is faster than *cis* elimination. This is in accord with previous work on elimination reactions from other olefinic systems.[4] We have shown that elimination of hydrogen bromide from compound II is much faster than exchange of the α-vinyl hydrogen with deuterium from the solvent. Thus, the elimination reaction is either concerted or the intermediate α-vinyl anion collapses with expulsion of bromide ion faster than reprotonation can occur. It is a moot point as to whether the conjugated π system of the α,β-unsaturated ketone is maintained throughout the reaction or is interrupted to allow the transition state to assume a geometry similar to that of an allenolate anion.

The ease of these elimination reactions across vinylic systems is really quite remarkable. A good case in point is the ready generation of 2-cyclooctynone (IV), a very strained system, by the reaction of 3-bromo-2-cyclooctenone (V) with base. This cyclic, acetylenic ketone is very reactive; it cannot be isolated, but its formation can be demonstrated easily. Reaction of V with potassium carbonate in deuterated aqueous methanol leads to an excellent yield of 3-methoxy-2-cyclooctenone (VI) in which better than 90% of the vinyl hydrogen is heavy. No exchange of the vinyl hydrogen in reisolated, unreacted starting material can be detected, nor, under the conditions of the reaction, is the vinyl hydrogen of light 3-methoxy-2-cyclooctenone exchangeable. Hence, the majority of the reaction product can be accounted for by the addition of deuteriomethanol to 2-cyclooctynone. More direct evidence for the formation of 2-cyclooctynone has been secured from Diels–Alder trapping experiments. Reaction of 3-bromo-2-cyclooctenone with base in nonhydroxylic solvents in the presence of 1,3-diphenylisobenzofuran or cyclopentadiene gives, respectively, 80 and 50% isolated yield of the Diels–Alder adducts VII and VIII of these dienes to 2-cyclooctynone.[5]

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[1] The National Science Foundation and the National Institutes of Health contributed generously to the support of this work.

[2] Many of the methods for the preparation of β-chlorovinyl ketones discussed in the review article of A. E. Pohland and W. R. Benson, *Chem. Rev.*, **66**, 161 (1966), are applicable to the synthesis of the corresponding bromo compounds. In some cases the chloro compounds might suffice.

[3] The *cis–trans* designation applies to the geometry of the carbon substituents about the ethylenic bond except for *cis*-4-bromo-3-buten-2-one in which the carbon chain is not long enough. In this one case, the prefix relates the bromo and acetyl groups.

[4] S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, 74, 629 (1952); S. J. Cristol and A. Begoon, *ibid.*, 74, 5025 (1952); W. E. Truce in "Organic Sulfur Compounds," Vol. 1, N. Kharash, Ed., Pergamon Press, London, 1961, p 112; J. C. Craig and M. Moyle, *J. Chem. Soc.*, 3712 (1963).

[5] Neither diene reacts with 3-bromo-2-cyclooctenone.