

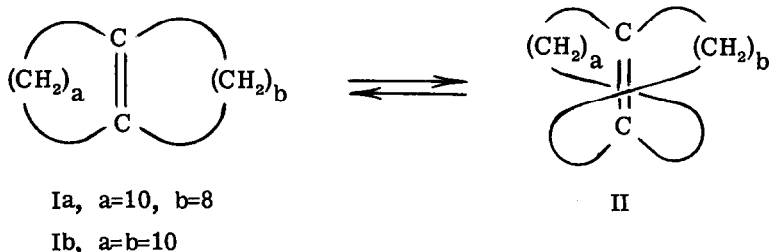
ACID CATALYZED ISOMERIZATION OF LARGE RING BICYCLIC ALKENES:
 A REEVALUATION OF SOME BETWEENANENE SYNTHETIC STRATEGY

James A. Marshall, * T. Howard Black, and Robert L. Shone

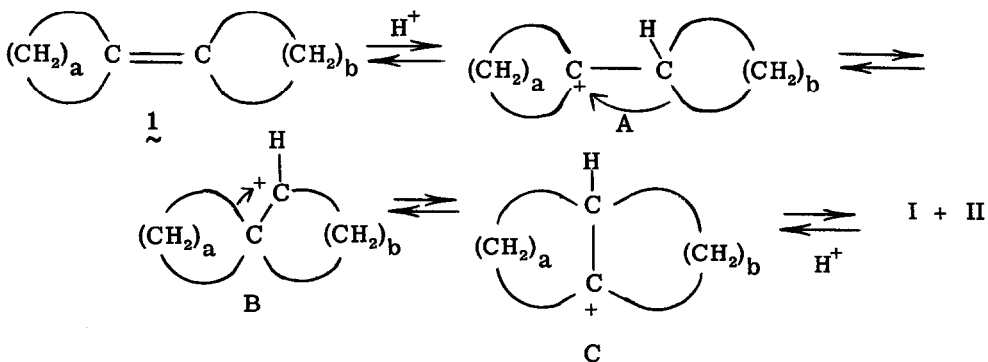
Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Acid treatment of *cis*-bicyclo[10.10.0]docos-1(12)-ene (Ib) affords bicyclo[10.10.0]docos-1-ene (I) as the sole product. Contrary to a previous report, [10.10]betweenanene (II) is not produced under acidic conditions. Attempts to convert cycloalkylidenecycloalkanes and spiro systems to fused ring alkenes by acid treatment were also unsuccessful.

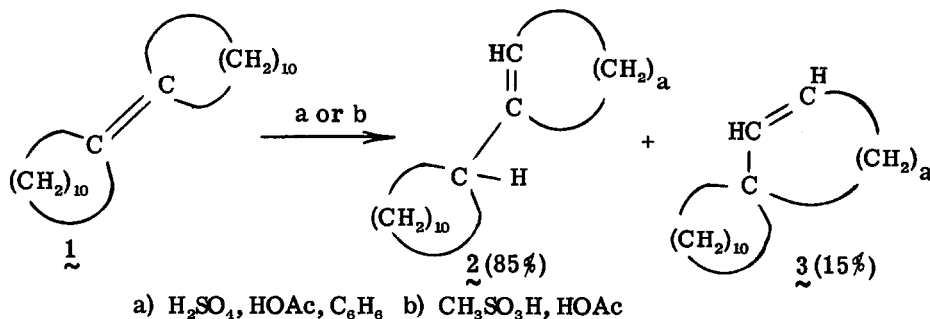
We recently described a remarkable acid-catalyzed isomerization of bicyclic alkenes Ia and Ib to the betweenanenes IIa and IIb.¹ This finding suggested that certain larger ring betweenanenes might possess unusual stability relative to double bond isomers and might thus be derivable from readily available bicyclic compounds via equilibrating processes. In this report we describe several attempts at implementation of this strategy which led us to question the validity of the reported isomerization.



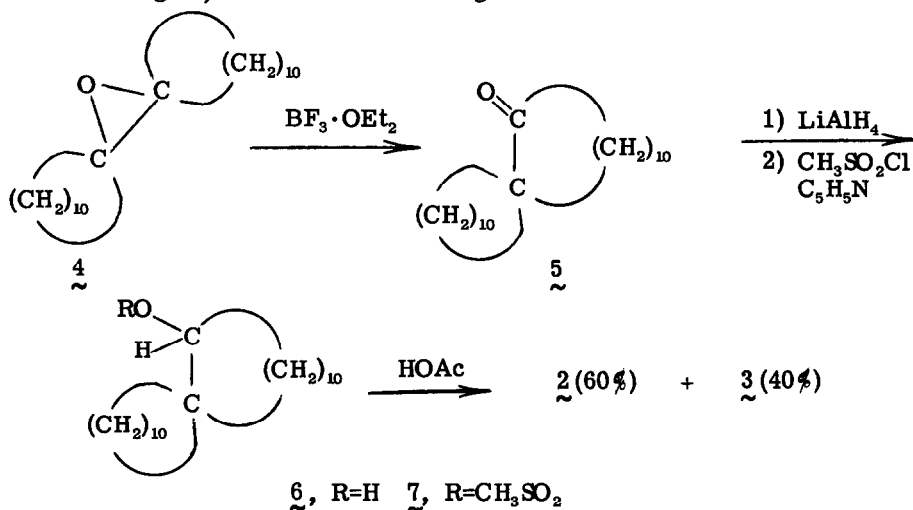
Initially we hoped to convert cycloalkylidenecycloalkanes (I) to betweenanenes II by the rearrangement sequence A→B→C.



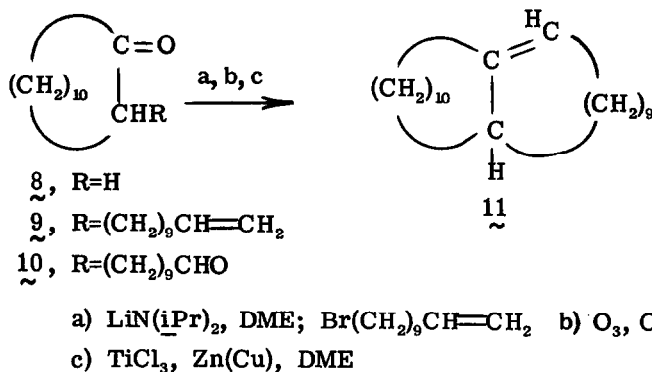
Cycloundecylidencycloundecane (1, mp 80°), was readily prepared (97% yield) via titanium promoted coupling of cycloundecanone. Treatment with sulfuric acid in acetic acid-benzene¹ or, better, methanesulfonic acid in acetic acid afforded an 85:15 mixture of isomerized olefins 2 and 3.³ The fused ring alkenes Ib and IIb were totally absent from the reaction mixture.



Since the first ring expansion step (A→B) in the above rearrangement scheme seemed to be unfavorable, we examined a variation whereby the epoxide derivative 4 of olefin 1 was subjected to BF_3 -promoted rearrangement⁵ giving the spiro ketone 5 in high yield. The methanesulfonate derivative 7 of the derived alcohol 6 yielded a 60:40 mixture of olefins 2 and 3 upon heating in acetic acid. Once again, none of the fused ring olefins Ib or IIb could be detected.



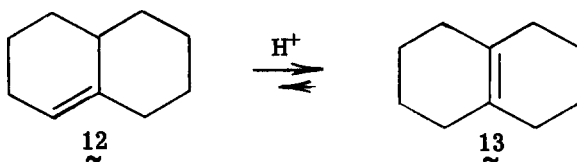
These findings suggested that the ring expansion B→C might also be unfavorable. We therefore examined an alternative approach employing olefin 11 prepared from cyclododecanone (8) through alkylation with 10-undecenyl bromide, ozonolysis and titanium-induced cyclization. Surprisingly acid treatment, as above, effected no change on olefin 11, even after prolonged reaction time. Again, not a trace of olefin Ib or IIb could be detected by gas chromatography.



The apparent acid stability of olefin $\tilde{11}$ cast serious doubt on the validity of our assumption regarding the unusual stability of betweenanene IIb and prompted a reexamination of the experimental basis for that conclusion. To that end olefin Ib was treated with sulfuric acid in benzene-acetic acid or, better, methanesulfonic acid in acetic acid whereupon smooth isomerization was observed leading not to [10.10]betweenanene, as originally reported, but to the trisubstituted alkene $\tilde{11}$. The gas chromatogram of the reaction mixture showed not a trace of [10.10]-betweenanene (IIb).⁶ Furthermore, exposure of authentic [10.10]betweenanene (IIb) to acid failed to produce Ib, $\tilde{11}$, or any related isomer. Instead, we observed slow decomposition to numerous products having distinctly shorter g.c. retention times.

In light of the experiments described above we must conclude that the reported acid isomerization of I to II¹ is in error. Photoisomerization, however, proceeds readily (II/I > 10).⁷

The apparent preference for tri vs tetrasubstituted double bonds in these systems (e.g. $\tilde{2}$ over $\tilde{1}$ and $\tilde{11}$ over Ib) stands in sharp contrast to acyclic and smaller ring olefins where tetrasubstitution is generally highly favored. For example, octalin $\tilde{12}$ ⁸ isomerizes readily to the tetrasubstituted isomer $\tilde{13}$ ⁹ in methanesulfonic acid-acetic acid ($\tilde{13}/\tilde{12} \sim 7$). The anomaly appears to be associated with the ring size¹⁰ and may well arise from steric effects.



Acknowledgements - We thank the National Science Foundation for support of this work through a research grant (CHE-7801755). R. L. Shone is indebted to G. D. Searle Co. for their support through a continuing education grant.

References and Notes

1. J. A. Marshall, R. E. Bierenbaum, and K.-H. Chung, Tetrahedron Lett., 2081 (1979).
2. J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krupski, J. Org. Chem., **43**, 3255 (1978).
3. The structures of these olefins were surmised from their spectral properties and through ozonolysis to a keto acid and an aldehyde acid, respectively. The keto acid afforded cycloundecanol and cycloundecanedicarboxylic acid upon Baeyer-Villiger oxidation followed by saponification.
4. Epoxidation was effected with m-chloroperoxybenzoic acid in bicarbonate-buffered benzene.
5. Cf. G. D. Ryerson, R. L. Wasson, H. O. House, Org. Syn., Coll. Vol. IV, 957 (1963).
6. It is worth noting that the g. c. retention times of 11 and Ib are nearly identical. Furthermore, 11 reacts only slowly with m-chloroperoxybenzoic acid whereas Ib reacts rapidly. In addition the vinylic hydrogen of 11 is easily overlooked in the nmr spectrum owing to coupling and cis/trans isomers appearing at differing chemical shifts. These factors may well have led to erroneous identification of 11 as Ib.
7. Cf. M. Nakazaki, K. Yamamoto, and J. Yanagi, J. Am. Chem. Soc., **101**, 147 (1979).
8. J. F. Sauvage, R. H. Baker, and A. S. Hussey, J. Am. Chem. Soc., **83**, 3874 (1961).
9. 1,2-Dimethylcyclododecene yields 75% of the 1,12-dimethyl isomer (cis/trans mixture) upon equilibration with iodine in dioxane.¹⁰
10. J. A. Marshall, L. Karas, and R. Royce, J. Org. Chem., **44**, 2994 (1979).

(Received in USA 7 September 1979)