Tetrahedron Letters No.24, pp. 2739-2744, 1966. Pergamon Press Ltd.
Printed in Great Britain.

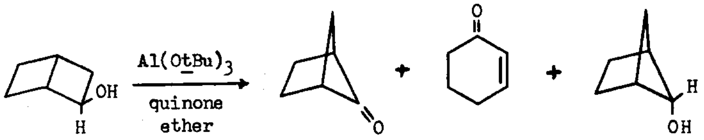
STRAINED RING SYSTEMS. III.[1] SOME OXIDATIONS OF exo-BICYCLO[2.2.0]HEXAN-2-OL

Richard N. McDonald and Charles E. Reineke[2]

Department of Chemistry, Kansas State University
Manhattan, Kansas 66502

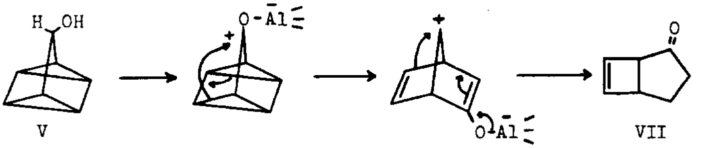
(Received 31 March 1966)

Attempts in our laboratories to oxidize exo-bicyclo[2.2.0]hexan-2-ol[1] (I) to the corresponding ketone have resulted in the observation of the oxidative rearrangement of I under Oppenauer oxidation conditions[3] to bicyclo[2.1.1]hexan-5-one (II) as the major product (12% isolated yield).[4] Two minor products have been identified as cyclohexen-3-one (III, ~1% yield) and endo-bicyclo[2.1.1]hexan-5-ol (IV, ~ 1% yield).[5]



I II III IV

Similar rearrangements under Oppenauer oxidation conditions have been observed for quadracyclanol (V)[6] and cyclopropyl carbinol (VI).[7] The oxidative rearrangement of V to bicyclo[3.2.0]hepta-3,6-dien-2-one (VII) was proposed[6] to proceed by way of the 7-quadracyclyl carbonium ion, formed by loss of hydride from the 7-quadracyclyl aluminum alkoxide. Rearrangement of this carbonium ion to the 7-norbornadienyl carbonium ion followed by

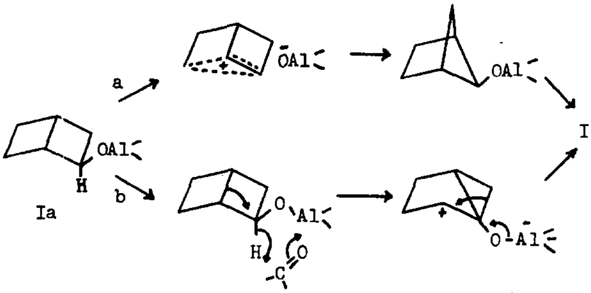


V VII (1)

further rearrangement and dissociation of the aluminum complex would give VII (equation 1). It was further observed[6] that aluminum tert-butoxide alone in refluxing benzene had no effect on quadracyclanone (VIII), while under the oxidation conditions, VIII did rearrange to VII. This observation indicates an important function of hydroquinone and quinone in the rearrangement mechanism.

The rearrangement of VI was suggested[7] to be aluminum alkoxide induced causing formation of the cyclopropyl carbinyl cation followed by rearrangement to the observed cyclobutyl system.

Two mechanisms, therefore, appear reasonable for the oxidative rearrangement of I to II. A mechanism analogous to the rearrangement of VI would involve dissociation of the aluminum alkoxide Ia to the bicyclo[2.2.0]hexyl carbonium ion-aluminate anion ion pair (path a, equation (2)) which with rearrangement, ion pair return, as observed in the acetolysis of the tosylate of I[1], and oxidation would lead to II as observed. In order to test the possibility of path a, I was treated with aluminum tert-butoxide



(2)

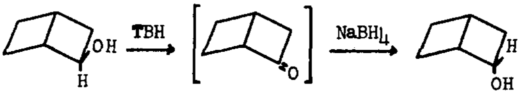
under the oxidation conditions with the exclusion of quinone. exo-Bicyclo[2.1.1]hexan-5-ol (IX), the expected product if the rearrangement proceeded by path a, was not observed as a product. Instead, the starting alcohol I was recovered in 50% yield and endo-bicyclo[2.1.1]hexan-5-ol (IV) was produced in 5% yield (v.p.c. integration). This result seems to rule out rearrangement by path *a* as the principal source of II. It does, however, explain the observation of the small amount of IV in the oxidation products.

A rearrangement mechanism similar to that proposed for V appears most favorable for I. Migration of the 1,4-bridge *σ* bond of the bicyclo-[2.2.0]hexyl alkoxide Ia with loss of hydride would lead to a 2-bicyclo-[3.1.0]hexyl carbonium ion (path b, equation 2). In order to explain the absence of norbornyl type rearrangement,[8] we believe that *this shift must be a simultaneous shift in the hydride transfer step to the hydrogen acceptor*. The driving force for this rearrangement may be the formation of a cyclopropylcarbinyl cation.[9] Further rearrangement of the bicyclo[3.1.0]-hexyl carbonium ion, with the driving force of dissociation of the aluminum alkoxide complex, would give rise to the observed ketone II.

In view of the apparent rearrangement mechanism for I under the Oppenauer conditions, it is expected that *endo*-bicyclo[2.2.0]hex-2-yl tosylate will exhibit an enhanced rate of solvolysis.

The ease with which rearrangements occur in the substituted bicyclo-[2.2.0]hexanes is further illustrated by the oxidation of I with *tert*-butyl hypochlorite (TBH). The results appear to be best explained by the intermediacy of bicyclo[2.2.0]hexan-2-one (X).

When I was allowed to react with TBH under conditions similar to those previously described,[10] an unstable product which exhibited infrared absorption at 5.61 μ was obtained.[11] The structure of X was assigned on the basis of immediate reduction[12] of the oxidation reaction mixture with sodium borohydride in ethanol to give *endo*-bicyclo[2.2.0]hexan-2-ol (XI, ~ 10% yield). The structural assignment for XI is based on the following spectral data. The mass spectrum showed a parent peak at *m/e* 98 and a cracking pattern differing only slightly from that of the exo isomer I. The infrared spectrum showed no unsaturation and was unlike the infrared spectra of all other possible bicyclic isomers. The n.m.r. spectrum[13] of XI exhibited a multiplet at τ 5.3-5.9 (C-2 methine),[14] a singlet at τ 6.4 (hydroxyl) and continuous absorption from τ 6.7-8.3 (bridgehead methine and methylene protons).

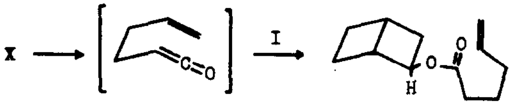


I X XI

Reduction of the TBH oxidation reaction mixture[12] with lithium aluminum hydride gave varying results apparently because of partial decomposition of X before or during reduction. The cleanest such reduction with lithium aluminum hydride gave recovery of the starting alcohol (I, 51% yield) and 5-hexen-1-ol[15] (XII, 20% yield).

When the oxidation of I with TBH was performed at room temperature with no attempt to isolate or trap X, 5-hexenoic acid (XIII, 30% yield) and exo-bicyclo[2.2.0]hex-2-yl 5-hexenoate (XIV, 23% yield) were isolated. Acid XIII was identified by its infrared spectrum and by reduction with lithium aluminum hydride to XII. The structure of ester XIV was assigned on the basis of spectral data and by reduction with lithium aluminum hydride to the corresponding alcohols, I and XII. The infrared spectrum of XIV exhibited absorption at 5.75 (C=O), 6.08 (C=C), and 10.95 µ ($C=CH_2$). The n.m.r. spectrum[13] exhibited absorptions at τ 3.8-4.7, 4.8-5.3, and 8.6-7.1.

The formation of XIV is reasonably explained by the spontaneous ring-



XV XIV

opening of X to 4-butenylketene (XV) which would easily be trapped by I to give XIV. Acid XIII could arise by hydrolysis of XIV or XV. Similar ring-opening reactions of some substituted cyclobutenones to ketenes have been reported.[1e]

The authors wish to express their gratitude to the National Science Foundation (GP-1916 and GP-4888) for the financial support of this research.

REFERENCES

1) For paper II in this series see R. N. McDonald and C. E. Reineke, *J. Am. Chem. Soc.*, **87**, 3020 (1965).

2) This represents a portion of a dissertation presented by C. E. Reineke to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

3) The conditions were those previously employed for the oxidation of *endo*-bicyclo[2.1.1]hexan-5-ol to II (K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961)) with the reaction time increased to 34 hr.

4) Vapor phase analysis before v.p.c. collection of II indicated a 20% yield.

5) The major product II was identified by comparison of its infrared and n.m.r. spectra with those of an authentic sample. The structures of the minor products were assigned by comparison of their infrared spectra with those of the known compounds.

6) P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **87**, 1623 (1965).

7) C. C. Lee and I. S. Bhardwaj, *Can. J. Chem.*, **41**, 1031 (1963).

8) The loss of hydride prior to the rearrangement in path b would lead to a 2-bicyclo[2.2.0]hexyl carbonium ion, which would correspond to the aluminum *tert*-butoxide complex of bicyclo[2.2.0]hexan-2-one. Bicyclo-[3.1.0]hexan-2-one, the expected product of a norbornyl type rearrangement of such an ion, was not observed as a product of the oxidation.

9) K. B. Wiberg and A. J. Ashe, *Tetrahedron Letters*, 4265 (1965) and references therein.

10) a) C. A. Grob and H. J. Schmid, *Helv. Chim. Acta*, **36**, 1763 (1953); b) F. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 1270 (1964); c) The temperature of the highly exothermic reaction was maintained at 2-4°.

11) Attempts to isolate this product by vapor phase chromatography resulted in the disappearance of the 5.61 μ infrared band. On standing at room temperature in carbon tetrachloride solution the 5.61 μ band slowly diminished with the appearance of additional bands at 5.49 μ and at least two bands between 5.7 and 5.8 μ. Over longer periods the 5.49 μ band diminished and a band at 5.75 μ became the major absorption band.

12) All reductions were performed directly on the oxidation reaction mixture from which the precipitated pyridinium hydrochloride had been removed by either filtration or aqueous base washes.

13) All n.m.r. spectra were recorded in carbon tetrachloride solution with tetramethylsilane as internal standard.

14) The C-2 methine proton resonance of I appeared as a triplet.

15) Alcohol XII was identified by its infrared, n.m.r. and mass spectra and by comparison with a sample prepared by mono-hydroboration of biallyl according to G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

16) a) E. F. Jenny and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 2005 (1956); b) E. F. Jenny and J. Druey, *ibid.*, **82**, 3111 (1960).