

STUDIES ON THE OXYMETALATION OF OLEFINS
OXYMERCURATION OF BICYCLO[3.2.1]OCTA-2,7-DIENE

Mitsuru Sakai*

Hanagatami Co., Fukui 915-02, Japan

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In 1939 Lucas, et al.,¹ proposed that the oxymercuration of olefins occurred by a trans addition and that the trans addition proceeded via mercurinium ion intermediates. Recent numerous investigations² of the oxymercuration of unstrained olefins support the proposed formation of an intermediate mercurinium ion, although it was established that strained olefins such as norbornene derivatives undergo exclusive cis-exo oxymercuration³ (eq. 1). Brown and Liu⁴ have compared the stereochemical course of the oxymercuration with that of the addition of benzenesulfonyl chloride to norbornene and 7,7-dimethylnorbornene and concluded that a mercurinium ion is probably not involved in this addition reaction. In contrast, Olah and Clifford⁵ recently reported the direct observation by nmr of mercurinium ion derived from exo-3-hydroxy-exo-2-norbornyl mercuric acetate (eq. 2). Although the experimental conditions are extremely different, the results of these two groups would appear to be in conflict with each other. We wish to report our results on the oxymercuration of bicyclo-[3.2.1]octa-2,7-diene (1)⁶ which contains both the strained norbornene and the unstrained cyclohexene moieties.

The oxymercuration of 1 in acetic acid at 50° for 7 hr followed by usual work-up gave exo-exo-6-acetoxymercuri-7-acetoxycyclo[3.2.1]octene-2 (2), mp 125-127°, in 86 % yield⁷. The nmr spectrum of 2 shows a broad perturbed doublet for C-2 proton at τ 4.20 and a broad doublet for C-3-proton at τ 4.85 but no ab-

* Address correspondence to the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

sorption at τ 3.9 and 4.5 which would indicate the C-6, C-7 double bond. Thus, the mercuriation occurred on the C-6, C-7 double bond and not on the C-2, C-3 double bond. The doublet ($J=6.0$ Hz) for H-7 proton at τ 5.0 indicates that the hydrogens on C-6 and C-7 are cis⁸. The position of the mercury is indicated by the nmr spectra of the acetate λ and λ -D₆ obtained on reducing λ with sodium borohydride in methanol or sodium amalgam in D₂O^{3b,9}, respectively. The nmr spectrum of λ is identical with that of the authentic acetate¹⁰ prepared by the reaction of λ with acetic acid in the presence of p-toluenesulfonic acid. The position of deuterium in λ -D₆ was assigned from its nmr spectrum. Accordingly, no skeletal rearrangement accompanied the addition process.

Similarly, oxidation of λ by palladium acetate in acetic acid proceeds smoothly at 25° to give high yields of monoacetate product, exo-6-acetoxycyclo[3.2.1.0^{2,7}]octene-3 (ξ)¹¹. The only mechanism for the palladium acetate oxidation of λ involves oxypalladation, presumably reversible, of λ to give the adduct λ ¹². This eliminates the elements of HPdOAc to produce ξ ¹³. The nmr and ir spectra of ξ establish that it is a tricyclic acetate. The stereochemistry of ξ was assigned upon comparison of its nmr with that of ξ ^{11a}. Conclusive proof of the exo position of hydroxy group in λ comes from the comparison with its epimer η obtained by CrO₃ oxidation of λ to the ketone ρ , followed by lithium aluminum hydride reduction of the latter to give a 35:65 mixture of λ and η . The alcohol η was also obtained by the reaction of ρ with tetra-n-butylammonium acetate in acetone followed by lithium aluminum hydride reduction.

The addition of acetic acid-D or D₂O (in D₂SO₄) to λ involves specific proton addition to C-6 giving directly the cyclopropylcarbiny cation λ ¹⁰. This cation gives a 1:4 mixture¹⁴ of λ -D₆ and λ -D₈-anti or a 1:8 mixture of λ -OH-D₆ and λ -OH-D₈-anti under acetolysis or hydrolysis, respectively. The above results on the acetolysis or hydrolysis of λ suggest that the oxymercuration of λ may best be described by invoking an intermediate such as λ ¹¹. It has been reported by Traylor^{3b} that "the charge density on the α -carbon controls the extent of rearrangement (e.g., λ -D₈-anti or λ -OH-D₈-anti) and increasing the potential carbon-electrophile bond strength increases the tendency toward an unsymmetrical π -complex or open carbonium ion formation". Thus, rearrangement

decreases as electronegativity of the electrophile decreases. The electronegativity of HgOAc^+ is quite low, so no rearrangement occurs during addition of oxymercuration.

Finally, treatment of bicyclo[3.2.1]octene-2 (1^2) with mercuric acetate in acetic acid resulted in the formation of allylic acetate, exo-2-acetoxycyclo[3.2.1]octene-3 (1^4)¹⁶. Decomposition of the mercurinium ion intermediate is thought to produce a symmetrical cation 1^3 . This cation is known to yield exo acetate 1^4 under acetolysis¹⁶. Further details of this work and its extension to a number of other metal acetates will be reported in near future.

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