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BROMINATION OF BARBARALONE; A NEW ROUTE TO TRIASTERANES

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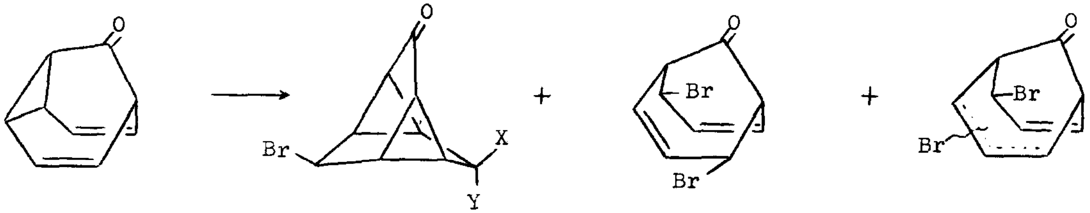
In connection with our interest in bicyclic organopalladium complexes (1), we required halogenated derivatives of bicyclo[3.3.1]-nonadien-9-one. The simplest route to such compounds appeared to be via halogenation of barbaralone, by analogy to the bromination of other bridged homotropilidenes (2). The major product, however, proved to be a substituted triasterane, while the expected bicyclic dibromides accounted for only 15% of the products.

Upon addition of one equivalent of bromine to barbaralone(3) in CH_2Cl_2 at -50°, a mixture of dibromides is formed from which the major product Ia (m.p. 136° dec.) can be crystallized in 70% yield. Three additional isomers Ib, IIa, and IIb can be isolated after repeated thin layer chromatography of the mother liquor on silica gel. Dibromides IIa (m.p. 149°) and IIb (m.p. 128-130°) are assigned the expected bicyclic structures on the basis of spectra, microanalysis, and their smooth debromination to barbaralone by sodium amalgam.

However, dibromides Ia and Ib (m.p. 105°) clearly possess a saturated (and therefore tetracyclic) carbon skeleton, as evidenced by the lack of olefinic NMR signals. The carbonyl absorption at 5.93 μ suggests a cyclopropyl ketone, and therefore Ia and Ib are assigned the triasterane structures:



Ia, X=H Y=Br (70%)
Ib, X=Br, Y=H (~2%)

IIa (8%)

IIb (7%)

TABLE I

A-60-A NMR Spectra in δ($CDCl_3$ + TMS); IR spectra in $CHCl_3$:

Ia: 2.0-2.7(6H, m); 4.94(1H, m); 5.93(1H, br. s); carbonyl at 5.93μ

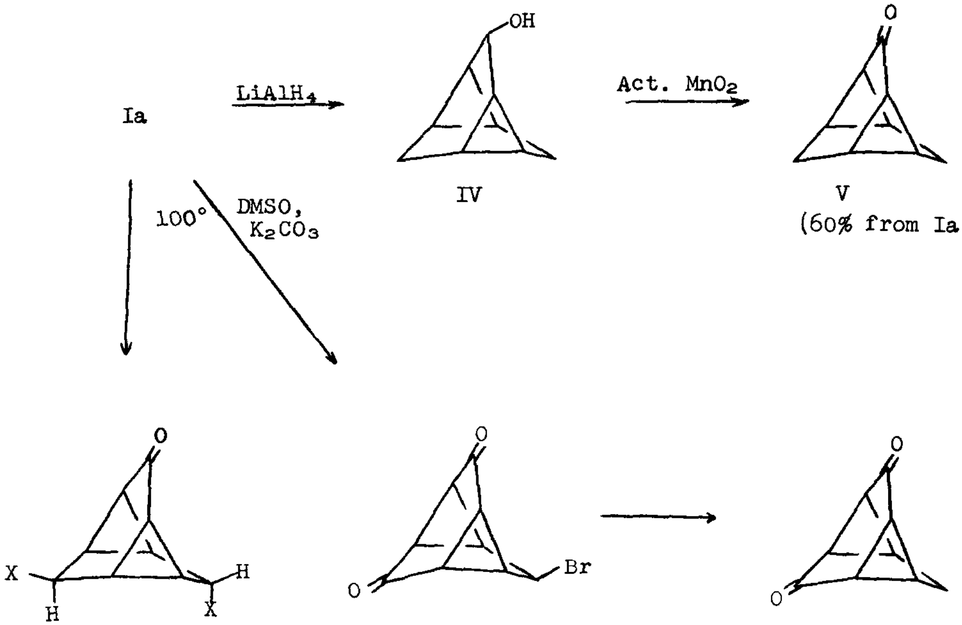
Ib: 2.0-2.7(6H, m); 4.97(2H, br. s); carbonyl at 5.93μ

IIa: 3.38(2H, dxd, J=5Hz and 1.7Hz); 4.87(2H, m); 5.7-6.1(4H, m); carbonyl at 5.71μ

IIb: 3.35(2H, m); 4.8-5.1(2H, m); 5.8-6.3(4H, m); carbonyl at 5.71μ

Several bicyclic (4) and monocyclic (5) 1,4-dienes are known to afford cyclopropanes upon bromination, but the present case is the first example of this reaction with a tricyclic precursor. Also, the facile formation of triasteranes by polar addition of bromine is somewhat surprising in view of the tendency of triasterane carbonium ion precursors to rearrange (6). Accordingly, the major dibromide Ia has been subjected to a more rigorous proof of structure.

Reactive nucleophiles such as tetraethylammonium acetate and sodium azide displace bromide from Ia at room temperature to yield unrearranged products IIIa and IIIb. Consequently, lithium aluminum hydride (LAH) reduction is expected to afford the known triasteranol IV. Treatment of Ia with LAH at -70° followed by ammonium chloride workup results in an unstable alcohol, m.p. 120-130°, which has spectra consistent with structure IV. As expected, active MnO_2 (7) converts the crude alcohol into a ketone V which is identical in all respects with a sample of triasteranone (8,9). Further evidence for the solvolytic stability of the triasterane skeleton is available in the Kornblum-type oxidation of Ia to a bromodione VI in DMSO/K_2CO_3 at 100°. Treatment of VI with LAH followed by active MnO_2 as before yields triasteranedione VII, m.p. 155°. The structures of VI and VII are required by the spectral data of Table II. In addition, the mass spectra of both compounds are characterized by correct molecular ions, and by m/e 91 (tropylium) as the most abundant fragment ion. All efforts to convert Ia or VI into triasterane trione have been unsuccessful.



IV

V
(60% from Ia)

IIIa, X = OAc

IIIb, X = N_3

VI

VII

TABLE II (NMR and IR)

IIIa: 2.08(3H,s); 2.13(3H,s); 1.8-2.4(6H,m); 5.5(1H,m); 5.8(1H, br. s). Carbonyl at 5.8 and 5.94 μ

IIIb: 2.0-2.4(6H,m); 4.28(1H, br. s); 4.53(1H, br. s). Carbonyl at 5.94μ

IV: 0.98(6H, br. s); 2.12(3H, br. s., 1 H Exchanged by D_2O); 2.27(2H, br. s); 4.63(1H, br. s)

VI: 2.3-3.0(6H,m); 5.06(1H, t, J = 3.0 Hz). Carbonyl at 5.88 and 5.93 μ

VII: 2.37 and 2.42 δ, broad overlapping singlets; carbonyl at 5.94 μ.

Sodium amalgam converts Ia or Ib into barbaralone (30-40%), but at least two other ketones are also formed. The structures of these are under investigation and will be described elsewhere.

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9) We are grateful to Prof. Musso for spectra of IV and V, and for a generous sample of the latter.