Rearrangement during Acid-catalyzed Solvolyses of Benzobicyclo[3,2,1]octenyl and Benzobicyclo[2,2,2]octenyl Derivatives

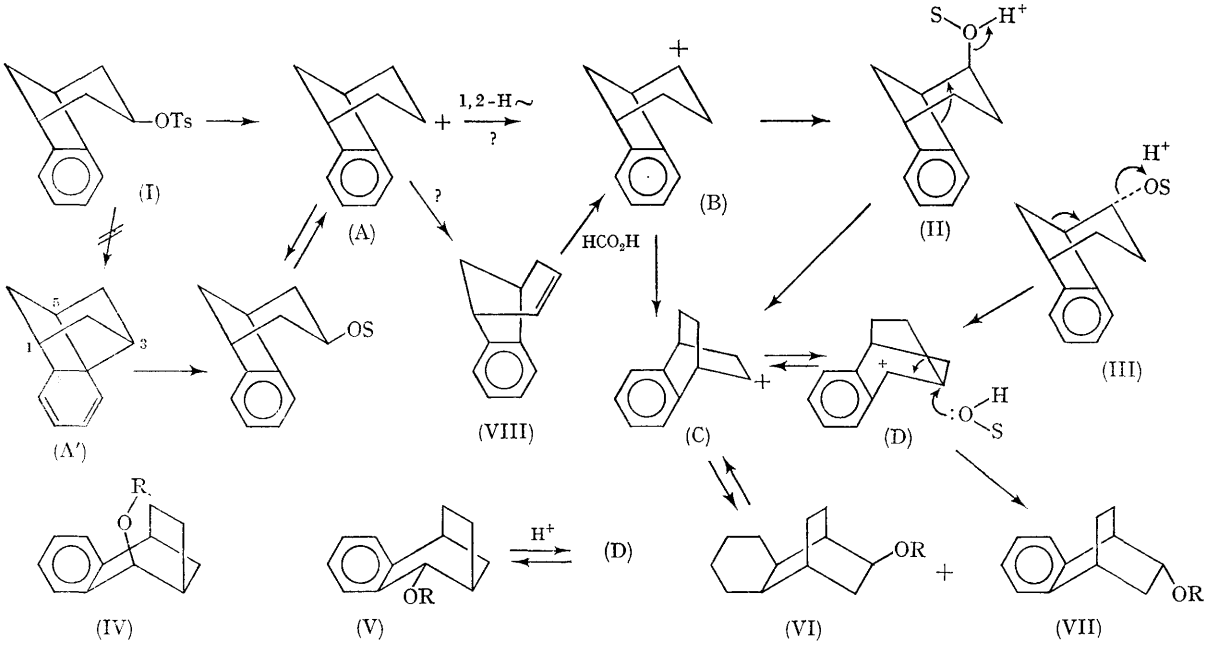
By PETER T. LANSBURY* and NORMAN T. BOGGS, TERT.

(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

TANIDA and his co-workers[1] have recently reported solvolysis rates and products of apparent kinetic control for the buffered acetolysis of *exo*- and *endo*-5,6-benzobicyclo[2,2,2]octen-2-yl bromosulphonates. Of particular note, the *endo*-isomer afforded the epimeric 3,4-benzobicyclo[3,2,1]octen-2-yl acetates. During the *unbuffered* formolysis and acetolysis of *exo*-6,7-benzobicyclo[3,2,1]octen-3-yl toluene sulphonate (I), we have encountered similar compounds;† however, our conditions lead to *thermodynamic* product control, with results in striking contrast to Tanida's.[1] Such variation in product composition by changing conditions was also noted by Cristol and his colleagues[2] in the related dibenzobicyclo[2,2,2]octadienyl system.

Our preliminary results, which do not allow detailed mechanistic conclusions to be drawn for each Wagner–Meerwein rearrangement,‡ are summarized in the Chart. We have obtained no evidence from these products§ (see following Communication also) or acetolysis kinetics¶ that (I) ionizes with Ar_1-4 participation,[3] which was an original goal of this research.

Formates (VI) and (VII) are the major products



(OR=O·CHO, O·COMe)

CHART

Equilibria among benzobicycloctenyl esters.

† Buffered acetolysis of (I) gives mainly the olefin (VIII) from elimination and unrearranged, inverted *endo*-acetate. Minor amounts of acetates (II) and (VI) (15% of total products) are also formed.

‡ As indicated in the chart, we do not yet know whether (VIII) is an intermediate in the conversion of ion A to B, or if this involves an intramolecular 1,2-hydride shift.

§ If 1,3-phenyl rearrangements were to occur in the ion derivable from (I), then isotopic labels or substituents can scramble between positions 1, 3, and 5.

¶ (I) undergoes acetolysis at 50° *ca.* five times *slower* than *exo*-bicyclo[3,2,1]oct-3-yl toluene-*p*-sulphonate, a reasonable model not containing aryl groups, which was studied by C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 1965, 3405.

of unbuffered solvolysis of (I), the latter being the most stable and the former the kinetic product. Addition of formic acid to olefin (VIII) likewise proceeds rapidly and gives mainly formates (VI) and (VII) although, with no sulphonic acid catalyst, some formate (II) appears at short reaction times. Ion (A) can also be generated by formolytic cyclization of 1-allylindene and gives product spreads similar to those from (VIII), as seen in the following Communication.

Formates (II)—(V) were not detectable among the solvolysis products from (I). These structures could be implicated, as shown in the total reaction scheme, by studying toluene-*p*-sulphonic acid-catalyzed acetolyses of the independently prepared acetates. Thus, acetate (II) rapidly rearranges (with phenyl migration) to give acetate (VI), which slowly epimerizes to acetate (VII), whereas acetate (III) rearranges more slowly (with apparent C(8)-methylene migration) to acetate (VII) directly or first to give (IV) and (V) *via* ion (D). The latter compounds, however, are not observable under the equilibrating reaction conditions but rather rearrange rapidly (as shown in a separate experiment) to acetate (VII). In contrast, under kinetic control, the bromosulphonate (VII) is reported[1] to give acetates (IV) and (V) and the bromosulphonate (VI) gives mainly acetate (II).

The alcohols and acetates corresponding to structures (II—VII) were prepared from the parent ketones.[1] Acetates and formates from solvolysis reactions were reduced by lithium aluminium hydride in ether and the derived alcohols analyzed by v.p.c. (using a 6 ft. "Tide" on Chromosorb-P column operated at *ca.* 175°) with the aid of authentic samples. The toluene-*p*-sulphonate (I) was prepared by sodium–ethanol reduction of 3,5-(*o*-phenylene)cyclohexanone[4] to give the equatorial alcohol,* which was subsequently converted to form (I). Satisfactory elemental analyses and consistent spectroscopic data (i.r., u.v., and n.m.r.) were obtained for all compounds discussed.

We thank the Alfred P. Sloan Foundation for financial support.

(*Received, August 10th*, 1967; *Com.* 848.)

* Reduction of this ketone by lithium aluminium hydride gave both epimeric alcohols, whose stereochemistry was confirmed *inter alia* by the chemical shifts of the acetate methyl signals (in the *axial*-acetate the higher field methyl resonance results from positioning the group above the aryl ring), and the coupling patterns of the carbinyl protons. These data will be discussed fully later.

[1] H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1967, **89**, 3212.
[2] S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, 1965, **87**, 2879.
[3] B. Capon, *Quart. Rev.*, 1964, **18**, 45.
[4] P. T. Lansbury and E. J. Nienhouse, *J. Amer. Chem. Soc.*, 1966, **88**, 4290.