ACETOLYSIS OF 2-(ENDO-5-NORBORNEN-2-YL)ETHYL

p-BROMOBENZENESULFONATE

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RECENTLY it has been demonstrated that for certain solvolytic reactions it
is possible to arrange for anchimeric assistance by the π-electrons of a
remotely located carbon-carbon double bond. Pertinent examples are the
solvolyses of the Δ^3-cyclopentenylethyl system I (1,2), Δ^3-cyclohex-
enylethyl p-bromobenzenesulfonate II (3), and the 5-hexenyl system III. (4).
In these cases anchimerically assisted ionization leads to non-classical
cations.
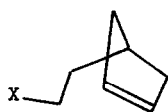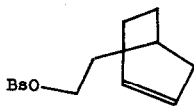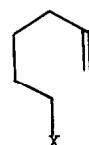
I   II   III

This current interest prompts us to report the results of our
preliminary investigation of the acetolysis of 2-(endo-5-norbornen-2-yl)
ethyl p-bromobenzenesulfonate (IVb). This system seems especially in-
triguing because of the possibility that rearrangement might accompany
anchimeric assistance to give more than one new tricyclic structure. In
this event, scrutiny of the mechanistic details should be particularly in-
formative in regard to carbonium ion theory.

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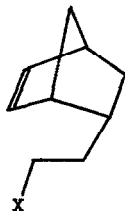
IVa X = OH
  b X = OBs
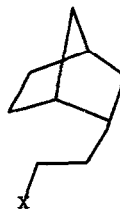
Va X = OH
 b X = OBs

The necessary endo-alcohol IVa,[2] b.p. 93–94° (6 mm.), $n_D^{25\cdot 3}$
1.4930, was obtained from endo-5-norbornen-2-yl-methyl chloride, b.p.
70–71° (12.5 mm.), via a Grignard reaction with formaldehyde. The chlor-
ide was available from the treatment of endo-5-norbornen-2-yl-methanol,
b.p. 76–76.5° (4.5 mm.), n_D^{25} 1.4887, with thionyl chloride. The latter
alcohol was obtained from the lithium aluminum hydride reduction of endo-
5-norbornene-2-carboxylic acid (5). A sample of the saturated alcohol Va,
b.p. 94.5–95.5° (5.5 mm.) was prepared by hydrogenation (5% palladium on
carbon) of IVa. The bromobenzenesulfonates IVb (liquid at room temperature,
purified by exhaustive water extraction of an ether solution and low tem-
perature recrystallization from pentane-ether) and Vb (m.p. 57–58°) were
prepared by the usual pyridine method.

Pertinent kinetic data for acetolysis are summarized in Table I.
The p-bromobenzenesulfonate IVb solvolyzed ca. fifteen times faster than
Vb in acetic acid. For Vb in pure acetic acid steady first-order kinetics
were observed. In the presence of sodium acetate the rate, when treated
as first-order, drifted downward for ca. 25% reaction, and then remained
essentially steady during the rest of the acetolysis. The initial drift
most probably is due to a small bimolecular contribution involving acetate
ion. This indicates that at a rate level of 1 x 10⁻⁸ sec.⁻¹ the nucleo-

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[2] Satisfactory analytical data were obtained for the alcohols and their
derivatives.

philic substitution by acetate ion for a structure like Vb is just discern-
ible. Therefore, for IVb a bimolecular contribution by acetate ion is
negligible during acetolysis.

For the acetolysis of IVb, ionization clearly is anchimerically
accelerated. In this regard $k_{unsat.}/k_{sat.}$ is certainly a minimum estimate

TABLE I

Acetolysis Rates of 0.01 M p-Bromobenzenesulfonates
IVb and Vb at 75.0°

Compound	Added Salt	$10^6 k$, sec.$^{-1}$	$k_{unsat.}/k_{sat.}$
IVb	None	$17.5-0.5$ [a]	14
	0.015 M NaOAc	$20.2-9.9$ [b]	16
Vb	None	1.25 ± 0.03 [c]	--
	0.015 M NaOAc	1.26 [d]	--

[a] Downward drifting rate. Instantaneous k's evaluated from the slopes on
a plot of ln(a/a-x) vs. time; ca. 0-65% reaction range.

[b] Instantaneous k's evaluated over a 0-80% range.

[c] Integrated k value.

[d] Initial instantaneous k.2 and drifting downward. Steady first-order k
from ca. 30-70% reaction.

of k_Δ/k_s (the ratio of anchimerically to solvent assisted rates).[3] A
better estimate is 35-40.[4] This means that more than 97% of the reaction
proceeds by way of the π-route.

It is interesting that for IVb in pure acetic acid there was a
continuous drift in rate of more than 35 during the course of the reaction,
while with added excess sodium acetate this was reduced to 2.2. It is

[3] A comparison of the relative acetolysis rates of n-butyl p-bromobenzene-
sulfonate (k = 1.49 x 10^{-6} sec.$^{-1}$ at 75.0°, reference (6) and Vb indicates
nothing unusual in the kinetic behavior of Vb; $k_{n-Bu}/k_{sat.}$ (Vb) = 1.18.

[4] This value corrects for the inductive effect of the double bond as es-
timated from the data of reference (7).

tempting to attribute this difference in magnitude of drift to the preven-
tion of a portion of ion pair return by sodium acetate (8). At least a
part of the diminishing rate in pure acetic acid, however, must be ascribed
to concomitant double bond removal by acid catalyzed addition of acetic
acid. For norbornene the first-order rate constant for addition of acetic
acid was 9.07×10^{-5} sec.$^{-1}$ at a concentration of 0.005 M p-toluenesulfonic
acid (the acid catalyst concentration at one-half of the acetolysis of
IVb). In the presence of excess sodium acetate, and hence sodium p-bromo-
benzenesulfonate, no such diversio. of the double bond occurred. In the
case of norbornene in the presence of 0.005 M sodium acetate and 0.005 M
sodium p-toluenesulfonate there was no double bond disappearance during a
period corresponding to more than ten acetolysis half-lives of IVb.

The kinetic behavior of IVb with added sodium acetate is indica-
tive of extensive rearrangement and ion pair return to a new p-bromoben-
zenesulfonate with solvolyzes considerably more slowly. In this connec-
tion, it was observed for the acetolysis with sodium acetate that after
ten half-lives only ca. 95% of the stoichiometric p-bromobenzenesulfonic
acid was liberated. During an additional twenty half-lives the value
became stoichiometric.

Product from the total acetolysis of IVb with excess sodium ace-
tate at 75.0° was recovered and reduced with lithium aluminum hydride. Analy-
sis of the reduced material by gas phase chromatography showed a mixture
which contained only ca. 5% unrearranged alcohol IVa. Moreover, the rear-
ranged product consisted of four other components in the approximate ratio
of 1:2:8:2, in the order of elution.[5] All of the components had similar
retention times. The unrearranged alcohol IVa and the latter two compon-
ents, so far, have defied complete separation on a number of gas phase

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[5] The sample of alcohol IVa used to prepare IVb was >96% pure according to
gas phase chromatography.

chromatographic columns. Examination of the infrared spectrum of the re-
duced product mixture revealed a strong hydroxyl absorption at 3.0 μ. No
absorption band was detected at 3.3 μ, a value diagnostic of ethylenic
C-H stretching vibration (9). Only a trace of a band was visible at 14.0 μ,
a region presumed to be characteristic of a cis-ethylenic double bond (9,10).
The unsaturated alcohol IVa (and its precursors) showed a medium intensity
band at 3.3 μ and a strong absorption near 14 μ. At present, the exact
identity of the rearranged product alcohols has not been established.

The kinetic results and the multiplicity of products indicate
that more than one discrete carbonium ion intermediate is involved in the
solvolysis of IVb. Two attractive a priori possibilities are the non-
classical carbonium ions VI and VII. Tricyclic ring systems which are
likely to result from these intermediates are VIII, IX and X. We are now
pursuing the identification of the products and the elucidation of the in-
timate mechanistic details of solvolysis.

VI   VII   VIII

IX   X
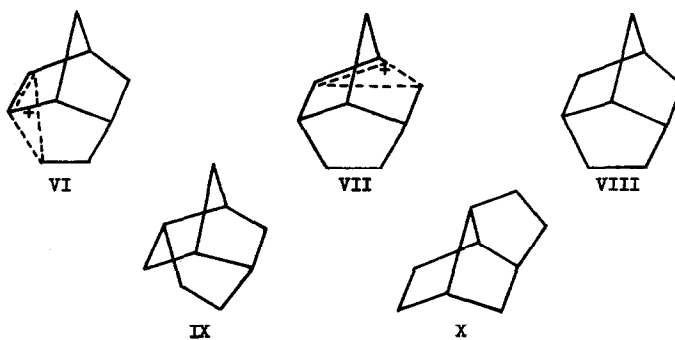
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