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Received April 19, 1978

Evidence for a New Mode of Neighboring-Group Participation by the Azo Group

Sir:

During the last 8 years studies involving azo compound reactions have shown that the $-N{=}N-$ group is one of the mechanistically most versatile functional groups in chemistry.[1-9] Cases of reaction by radical,[2,3] zwitterion,[4] carbene,[5] and cationic[6] mechanisms have been reported. Examples of concerted reaction pathways without formation of reactive intermediates[7,8] and reverse Diels–Alder processes[9] also have appeared.

One of our current research interests is concerned with the reaction of azo compounds by mechanisms which involve cationic intermediates. Recently we found that solvolysis of azo *p*-bromobenzenesulfonate **1** occurs with neighboring-group participation and elimination of nitrogen via diazonium-ion intermediate **2**.[6a,b] We now wish to report that solvolysis of 3-OBs involves a new and entirely different kind of neighboring-group participation.
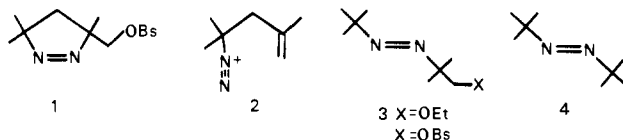
The synthetic sequence used to prepare 3-OBs is outlined in eq 1.[10] The **5 → 7** conversion is analogous to a reported diaziridinone synthesis.[11]
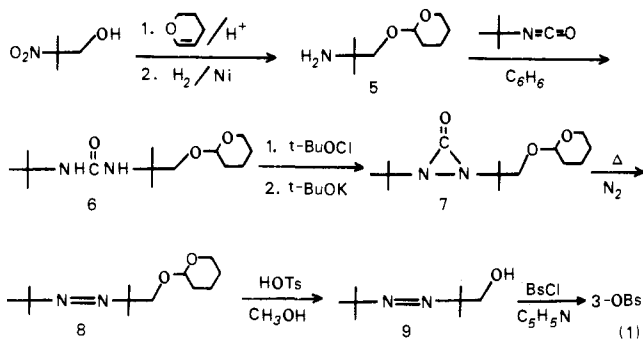
Azo *p*-bromobenzenesulfonate 3-OBs was solvolyzed under anhydrous conditions in ethanol buffered with 2,6-lutidine. Rate measurements were made by the usual sealed ampule method. Titration of the developing *p*-bromobenzensulfonic acid was performed using methyl red as the indicator.[13] Rates also were measured by ¹H NMR spectroscopy. All rate constants were nicely first order and the two methods gave essentially the same rate constant values. Some representative kinetic data are summarized in Table I. Reactivity comparisons of 3-OBs with 3-OEt, 2,2′-azobisisobutane (**4**),[14] neophyl *p*-bromobenzenesulfonate (**10a**), and neopentyl *p*-bromobenzenesulfonate (**10b**)[15] also are included.

Products derived from ethanolysis of 3-OBs were found to vary with the amount of oxygen (air) present. Under oxygen-free reaction conditions[16] hydrazinium salt acetal **11** was the sole product detected.[17,18] On the other hand, excess air (O_2)

Table I. Ethanolysis Rate Data[a] and Reactivity Comparisons for 3-OBs

| compd	temp, °C	$10^4 k$, s⁻¹	rel rate
3-OBs	50.0	0.147 ± 0.01[b]	2×10^7, 1×10^4
	74.9	1.64 ± 0.13[b]	
	75	2.2[c]	
3-OEt	184.4	2.66 ± 0.05[d]	
	159.8	0.181 ± 0.01[d]	
	50.0	7.6×10^{-9}[e]	1
4	184.7	2.81 ± 0.01[d]	
	185.0	2.51 ± 0.1[f]	
	50.0	9.3×10^{-9}[g]	1
10a	50.0	8.4×10^{-3}[h]	1×10^6, 5×10^2
10b	50.0	1.5×10^{-5}[h]	2×10^3, 1

[a] Dry EtOH with 0.010 M 2,6-lutidine and 0.005–0.008 M 3-OBs. [b] Titrametric rate. An aliquot of reaction solution was quenched with purified dioxane. The sample was then back-titrated with 0.011 M $HClO_4$ in dioxane using methyl red indicator.[13] [c] Measured in EtOH-d_6 (containing 0.1 M 3-OBs and 0.2 M lutidine) by NMR integration of changes of reactant and product ¹H against the ¹H of 1,1,2,2-tetrachloroethane internal standard. [d] Liquid phase in EtOH in sealed Pyrex tubes which had been placed under N_2 by repeated freeze–pump–thaw cycles. The rate was obtained by monitoring the disappearance of the UV absorption at 370 nm. [e] Extrapolated from the higher temperature data. [f] Gas phase data.[14] [g] Extrapolated from gas phase data.[14] [h] Estimated from reported EtOH data using $\Delta H^{\ddagger}$ for AcOH.[15] The treatment also uses the well known approximation factor of 3 for $k_{ROBs} > k_{ROTs}$.

afforded only azo acetal **12**.[17] When solvolysis involved limited amounts of air, mixtures of **11** and **12** were obtained. A control experiment demonstrated the complete conversion of **11** to **12** in ethanol/air. These relationships are shown in eq 2.[17]
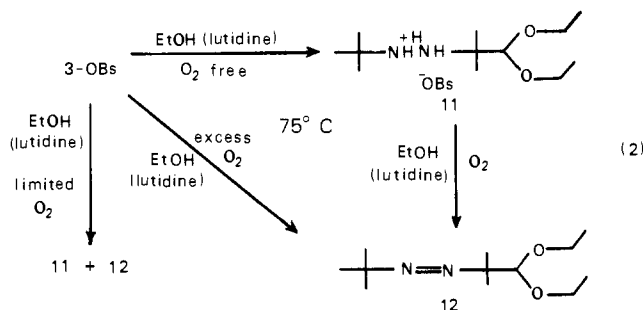

The reactivity comparisons in Table I are instructive. A near identity of reaction rates for **4** and reference compound 3-OEt in ethanol makes it clear that the latter reacts by the usual free-radical process.[2] The exceptionally high reactivity ratio of 10^7 for 3-OBs compared with 3-OEt indicates reaction of 3-OBs by some other kind of mechanism. This kinetic evidence is substantiated by the nature of the products observed (eq 2) and by the lack of nitrogen formation.[17]

These considerations and the titrametric method used to follow the reaction strongly suggest that ethanolysis of 3-OBs involves some sort of cationic mechanism. Two plausible
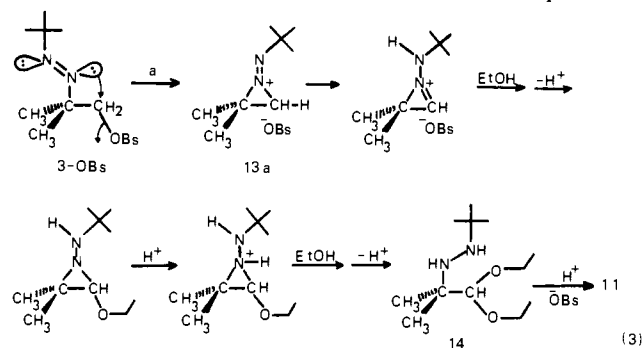
possibilities are illustrated by eq 3 and 4. An equilibrium between **11** and **14**[19] with accompanying oxidation of **14** (eq 5) readily accounts for formation of azo acetal **12**. A comparison

$$11 \rightleftharpoons 14 \xrightarrow{O_2} 12 \qquad (5)$$
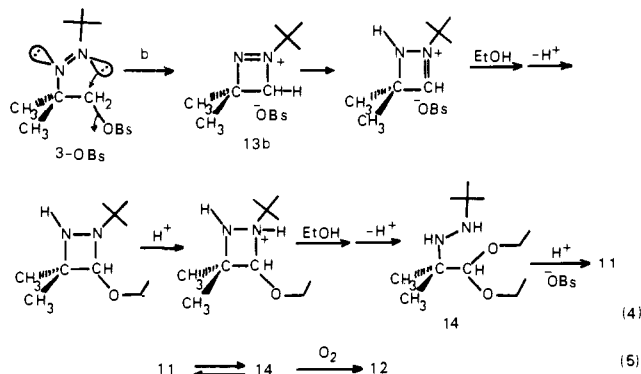
of the mechanistic features of processes 3 and 4 show that the only intrinsic difference between them occurs in the initial achimerically assisted ionization step a or b.

Evidence for **13a** or **13b** as an intermediate in the ethanolysis of **3-OBs** was sought from information about the chemical properties of trialkyldiazenium ions. The literature failed to show any reaction results for the conditions of eq 2.[20] Consequently, we examined the ethanolysis (lutidine) of **15**[21] as a model system. Pertinent products were acetaldehyde diethyl
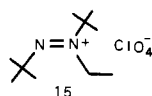
acetal (**16**, 35%), isobutylene (**17**, 50%), and ethyl *tert*-butyl ether (**18**, 40%).[22] A substantial yield of **16** demonstrates that diazenium ions containing a $-CH_2-N^+$ moiety react with ethanol to give acetal. The combined formation of **17** and **18** is diagnostic of the high propensity of diazenium ions with *t*-$C_4H_9-N^+$ to react with the loss of *tert*-butyl cation. This finding suggests that ethanolysis of **3-OBs** occurs by eq 3 via **13a**.[23]

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant No. CHE76-01129.

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(16) The EtOH solution of **3-OBs** in a Pyrex tube was purged with nitrogen, freed of air (O_2) by repeated freeze–pump–thaw cycles, and sealed.
(17) Hydrazinium salt **11** was identified by its ^1H NMR spectrum which was in complete accord with the assigned structure. A recovered, purified sample of **11** had satisfactory elementary analyses. Azo acetal **12** had the expected ^1H NMR and UV spectra. The yield of product was estimated by NMR integration of ^1H signals against 1,1,2,2-tetrachloroethane internal standard. Within the limits of this method **11**, **12**, or **11** + **12** were formed quantitatively. GC analysis did not show formation of other primary products (isobutylene and/or ethyl *tert*-butyl ether might have been expected from the solvolysis results with **16**a).[18] No nitrogen elimination was detected by the previously described method.[6a]
(18) Control experiments indicated that prolonged heating of **11** in EtOH caused decomposition. In this case isobutylene was observed as a secondary product. For this reason the product measurement cited in note 17 for **11** is for <30% ethanolysis.
(19) It is also probable that equilibria are important in either process 3 or 4.
(20) Experimental work for solvolysis of trialkyldiazenium ions is very limited: J. P. Snyder, M. L. Heyman, and M. Gundestrup, *J. Chem. Soc., Perkins Trans. 1*, 1551 (1977).
(21) Alkylation of 1,2-di-*tert*-butylhydrazine with triethyloxonium fluoroborate followed by treatment with KOH gave 1-ethyl-1,2-di-*tert*-butylhydrazine. Oxidation with AgClO₄ yielded **15** (mp 117–118 °C) with the proper NMR spectrum and elemental analysis.
(22) Determined by a combination of GC and NMR analyses.
(23) Further study with **3-OBs** and related systems is in progress.

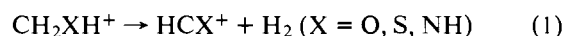**Evan L. Allred,*** **Joseph E. Oberlander, Paul F. Ranken**

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Received March 31, 1978

Kinetic Energy Release in the Fragmentation of CSH₃⁺ Ions

Sir:

It is well established[1,2] that the reaction

$$CH_2XH^+ \rightarrow HCX^+ + H_2 \ (X = O, S, NH) \qquad (1)$$

occurs with significant release of kinetic energy. This has been interpreted[2] in terms of a symmetry-forbidden 1,2-H_2 elimination reaction which imposes an activation energy barrier greater than the endothermicity of the reaction. Recent theoretical calculations[3,4] have confirmed the presence of such a barrier. By contrast 1,1-H_2 elimination is not symmetry forbidden and it has been observed that such fragmentation reactions show little kinetic energy release.[5] This suggests that the reaction

$$CH_3X^+ \rightarrow HCX^+ + H_2 \ (X = O, S, NH) \qquad (2)$$
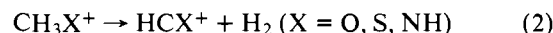
for CH_3X^+ ions, isomeric with CH_2XH^+, should occur with little kinetic energy release. For X = O it has been noted[6] that reaction 2 ($CH_3O^+ \rightarrow HCO^+ + H_2$) is thermoneutral or exothermic[7] and no metastable ion is observed. Indeed, because of the facile loss of H_2 the m/e 31 ion (COH_3^+) is of very low abundance, compared with HCO^+, in compounds where simple bond rupture to give the methoxy cation might be expected.[6]

By contrast, the CSH_3^+ ion (nominally CH_3S^+) is abundant in the mass spectra of compounds of the general formula CH_3SR.[7] In addition, the available thermochemical data[8,9] suggest similar heats of formation for CH_3S^+ and CH_2SH^+. These observations lead to the possibility that for the sulfur