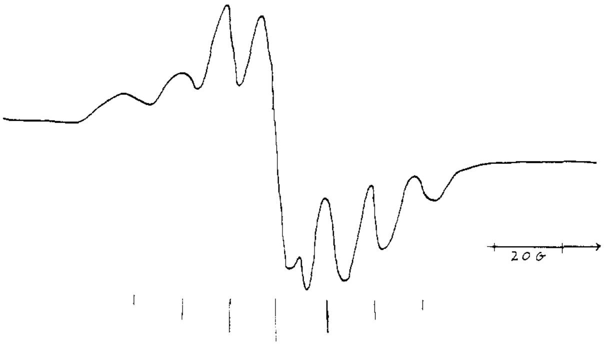
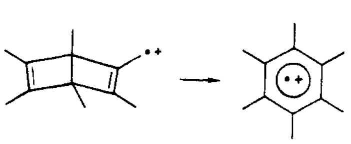


Figure 1. X-band ESR spectrum recorded following γ-irradiation of hexamethyl (Dewar) benzene in $CFCl_2CF_2Cl$ at 77 K, showing features assigned to ($^2A_1$) $HMD^{\bullet+}$ radical cations.

occurred in the spectrum, which became identical with that observed from authentic hexamethylbenzene (HMB) under the same conditions. Therefore, the ring-opening reaction 1 must have


(1)

occurred: this is known to take place extremely rapidly in the liquid phase at higher temperatures.[2] We suggested that, at 77 K, the $CFCl_3$ molecules pack sufficiently rigidly around the HMD molecules to prevent the reaction 1 taking place following ionization.

In order to examine the effect of the matrix material on the properties of the $HMD^{\bullet+}$ cation, we repeated these experiments with $CFCl_2CF_2Cl$ in place of $CFCl_3$. The resulting ESR spectrum (Figure 1) is completely different and appears to comprise of seven lines, which is consistent with a SOMO involving two equivalent methyl groups [$A(H) = 14$ G]. We interpret this as being due to the $^2A_1$ form of the $HMD^{\bullet+}$ cation, in which the unpaired electron is largely confined to the ("stretched") transannular C–C bond. A recent MINDO/3 calculation has predicted that the minimum energy geometry for the parent (Dewar) benzene radical cation does possess an elongated transannular bond,[3] which, taken with the ESR result suggests that the $^2A_1$ state is more stable than the energetically similar $^2B_2$ state; however, we note that ab initio calculations predict the $^2B_2$ state to be the more stable by 8 kcal/mol.[4] The polarization observed in a photo-CIDNP study of HMD with excited (triplet) electron acceptors gave evidence for the formation of both states, proposed to arise via competing pathways.[4]

On annealing the sample, an irreversible change occurred in the ESR spectrum, similar to that observed in the $CFCl_3$ matrix: the resulting spectrum (Figure 2) containing features due to ring-opened ($HMB^{\bullet+}$) radical cations [$A(H) = 6.7$ G]. This strongly supports our assignment of the initial seven line spectrum (Figure 1) as arising from *a different electronic state* of the *same* $HMD^{\bullet+}$ cation.

We tentatively suggest that the difference between the two matrices may be due to a less rigid structure for solid $CFCl_2CF_2Cl$ which can permit the $HMD^{\bullet+}$ framework to relax via stretching of the transannular C–C bond. This appears to be a remarkable demonstration that the structure adopted by a radical cation can be determined by the nature of the matrix material in which it is isolated;[8] hence, we suggest that the more tightly packed $CFCl_3$ matrix hinders the significant elongation of the central C–C bond required for the formation of the $^2A_1$ structure and the alternative $^2B_2$ state is formed.[5]

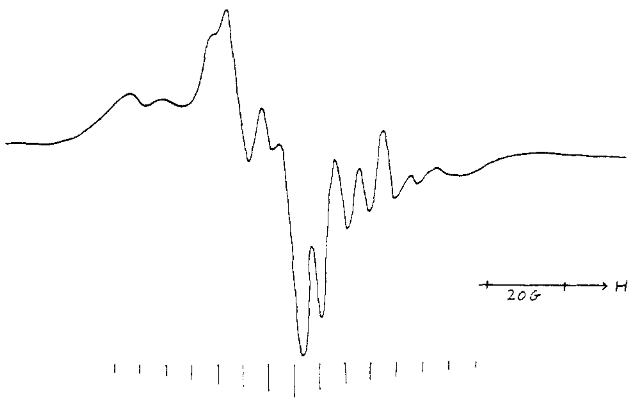


Figure 2. X-band ESR spectrum recorded following annealing of the $CFCl_2CF_2Cl$ matrix containing $HMD^{\bullet+}$ radical cations, assigned to $HMB^{\bullet+}$ radical cations formed by ring opening.

We consider that it is possible that lesser amounts of the $^2B_2$ form may be present along with the $^2A_1$ form in the $CFCl_2CF_2Cl$ matrix; however, the $^2A_1$ form clearly dominates, in contrast with the results in $CFCl_3$.

Acknowledgment. I thank Professor M. C. R. Symons for access to ESR facilities.

---

[2] Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632.

[3] Bews, J. R.; Glidewell, C. *J. Mol. Struct. THEOCHEM* **1982**, *86*, 197.

[4] Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253.

[5] A referee has suggested an alternative explanation, in terms of differences between the abilities of the two matrices to solvate the two cation states, one of which ($^2B_2$) is significantly more delocalized than the other ($^2A_1$). This seems to be a reasonable idea, and although the spectrum assigned to the $^2A_1$ state shows no clear evidence of superhyperfine coupling to solvent nuclei,[6,7] there is a definite broadening of the lines compared with the spectrum of the $^2B_2$ form in $CFCl_3$, which could be due to a weak solvent interaction, but with the additional coupling not fully resolved. We hope that our further experiments will be decisive in this matter.

[6] Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *13*, 393.

[7] Shiotani, M. *Magn. Reson. Rev.* **1987**, *12*, 333.

[8] We note that the radical cation of $CH_3CH_2CH_3$ has been shown to adopt a different electronic state in SF_6 than in freon matrices.[8a,b] (a) Toriyama, K.; Nuromel, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891. (b) Lunnell, S.; Huang, M. B.; Lund, A. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 35.

Substitution Competes with Elimination in a Gas-Phase Anion-Molecule Reaction

Rachel C. Lum and Joseph J. Grabowski*

Department of Chemistry, Harvard University
12 Oxford Street, Cambridge, Massachusetts 02138

Received August 22, 1988

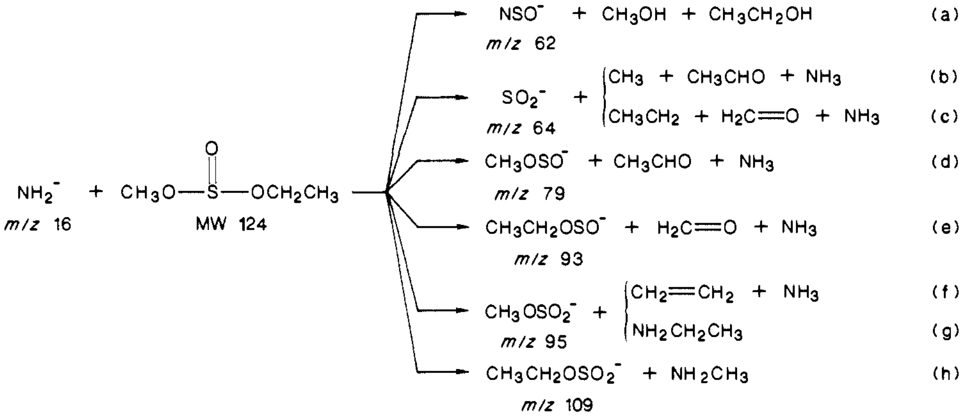
In ethanol solution, ethoxide reacts with propyl bromide to predominantly produce products from substitution; only 8.8% of the reaction proceeds by elimination.[1] However the few studies carried out in the gas phase, which compare substitution to elimination pathways for anion-molecule reactions, indicate that elimination is kinetically preferred over substitution, even when both channels are considerably exothermic.[2] We wish to report that for the strong base amide, interacting with ethylmethyl sulfite in the gas phase, substitution and elimination reactions at saturated carbon are nearly equally favored.

---

[1] Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. D. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4735–4749.

[2] (a) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595–3602. (b) van Doorn, R.; Jennings, K. R. *Org. Mass. Spectrom.* **1981**, *16*, 397–399. (c) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034–5038. (d) King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133–7140. (e) DePuy, C. H.; Beedle, E. C.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1982**, *104*, 6483–6488. (f) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715–1722. (g) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 7602–7608.

Scheme I



The thermally equilibrated (298 ± 1 K) gas-phase reaction of amide and hydroxide ions with dimethyl-, diethyl-, and ethylmethyl sulfite were carried out at 0.3 Torr total pressure (helium) in a flowing afterglow.[3] Ethylmethyl sulfite,[4] following purification by spinning band distillation, was found to be 97.5% pure by GC analysis, the impurities being 1.0% dimethyl sulfite and 1.5% diethyl sulfite.

When amide[5] is allowed to react with ethylmethyl sulfite, rapid reaction occurs, and six product ions are formed; reaction channels for which are shown in Scheme I. The directly observed branching ratio[6] based on three independent measurements[7] is 5.6 ± 0.7% NSO^-, 6.8 ± 0.7% SO_2^-, 9.4 ± 1.7% CH_3OSO^-, 17.8 ± 1.4% $CH_3CH_2OSO^-$, 38.3 ± 0.8% $CH_3OSO_2^-$, and 22.1 ± 1.8% $CH_3CH_2OSO_2^-$.

Several corrections must be applied to the directly observed branching ratio in order to obtain the best estimate of the product yields due solely to amide interacting with ethylmethyl sulfite. The amide signal is contaminated[8] by a small amount of HO^-, which also displays a rapid reaction with ethylmethyl sulfite.[9] As noted above, the ethylmethyl sulfite synthesized here contains measurable amounts of dimethyl sulfite and diethyl sulfite, both of which undergo rapid reaction with either amide or hydroxide.[10] The final consideration is to take into account the natural isotopic distribution of the elements, which we neglect experimentally since we monitor only the strongest isotopic peak.[6,12] Thus the product yield for the gas-phase reaction of amide ion with ethylmethyl sulfite, corrected for these factors, is 6.4% NSO^-, 7.2% SO_2^-, 9.8% CH_3OSO^-, 22.1% $CH_3CH_2OSO^-$, 33.6% $CH_3OSO_2^-$, and 20.9% $CH_3CH_2OSO_2^-$.

Four mechanistic pathways account for the observations found: nucleophilic attack at sulfur yields NSO^- (eq a),[13] elimination across a carbon–oxygen bond produces CH_3OSO^- or $CH_3CH_2OSO^-$ (eq d and e), nucleophilic substitution at carbon yields $CH_3OSO_2^-$ or $CH_3CH_2OSO_2^-$ (eq g and h), and elimination across the carbon–carbon bond gives $CH_3OSO_2^-$ (eq f). We believe the observed SO_2^- (eq b and c) results from fragmentation of a portion of the CH_3OSO^- and $CH_3CH_2OSO^-$ ions formed by pathways d and e.[11]

The ion at *m/z* 95, $CH_3OSO_2^-$, can be formed two ways: either by nucleophilic substitution at the methylene carbon (eq g) or by elimination across the carbon–carbon bond (eq f). If an elimination mechanism is greatly favored over a substitution mechanism for room temperature, gas-phase ion-molecule reactions involving strong bases and substrates with excellent leaving groups,[2] then we would expect to see *only* products from elimination (i.e., eq f, e, d, c, and b; the small amount of sulfur substitution can safely be neglected for these arguments). However, we observe a significant amount of an ion at *m/z* 109, $CH_3CH_2OSO_2^-$, which can *only* arise from nucleophilic substitution (eq h). Thus the conclusion is that the reaction of amide ion with ethylmethyl sulfite undergoes competitive substitution and elimination reactions. Such a conclusion is to be contrasted with gas-phase experimental studies of anions with ethers[2c,e,f] and sulfides[2g] among others which clearly demonstrate that elimination is enormously favored kinetically over substitution. Whether the observation of both substitution and elimination is the result of an extremely reactive system (i.e., having essentially no lifetime as an amide ion/ethylmethyl sulfite complex) or because there is a chance for the system to explore both pathways and find them equally kinetically feasible (i.e., a long-lived ion-dipole complex as has been implicated in many other studies[14]) remains to be seen.

We assume that for every nucleophilic substitution at the methyl group there is at most one nucleophilic substitution at the methylene carbon;[15] therefore, the upper limit of nucleophilic attack at the methylene group is 20.9%. By difference then, at least 12.7% of the overall reaction products (and no more than 33.6%) are formed from the carbon–carbon elimination pathway (eq f). So for the reaction of amide with ethylmethyl sulfite at least 21% and up to 42% of the overall reaction involves nucleophilic substitution, and at least 52% and no more than 73% of the reaction goes by elimination (either across a carbon–oxygen bond or across the carbon–carbon bond). The remaining 6% of the reaction proceeds via nucleophilic attack at sulfur. Thus in situ measurements have been carried out that experimentally

---

(3) (a) Ferguson, E. E.; Feshenfeld, F. C.; Schmeltekopf, A. L. *Advances in Atomic and Molecular Physics*; Bates, D. R., Estermann, I., Eds.; Academic Press: New York, 1969; Vol. 5, pp 1–56. (b) Feshenfeld, F. C. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 151–166. (c) Smith, D.; Adams, N. G. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: Orlando, FL, 1979; Vol. 1, Chapter 1. (d) Graul, S. T.; Squires, R. R. *Mass. Spectrom. Rev.* **1988**, *7*, 263–358. (e) Grabowski, J. J.; Melly, S. J. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 147–164.

(4) Pavlov, V. M.; Bogdanov, N. N.; Sokol'skiii, G. A. *J. Gen. Chem. USSR* (*Engl. Trans.*) **1971**, *41*, 2559–2561. Ethanol was cooled to −15 °C in a dry ice/acetone bath before addition to thionyl chloride.

(5) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229–4235.

(6) As described in the following: Grabowski, J. J.; Zhang, L. *J. Am. Chem. Soc.*, in press.

(7) Errors quoted are standard deviations.

(8) Average amide-to-hydroxide ratio for the ethylmethyl sulfite experiments was 6:1.

(9) The directly observed branching ratio for hydroxide with our synthesized ethylmethyl sulfite is 0.8% HSO_2^-, 3.3% $CH_3CH_2OSO^-$, 64.0% $CH_3OSO_2^-$, and 31.9% $CH_3CH_2OSO_2^-$.

(10) Hydroxide reacts with dimethyl sulfite to give 1.2% SO_2^-, 18.3% CH_3OSO^-, and 80.5% $CH_3OSO_2^-$ and with diethyl sulfite to give 100% $CH_3CH_2OSO_2^-$. By using these data to correct the data for amide ion (contaminated with hydroxide) for the same two substrates, we find that amide and dimethyl sulfite give 5.3% NSO^-, 5.1% SO_2^-, 43.4% CH_3OSO^-, 2.1% CH_3OSONH^-, and 44.1% $CH_3OSO_2^-$, while amide and diethyl sulfite give 7.6% $CH_3CH_2O^-$, 12.1% NSO^-, 11.9% SO_2^-, 15.0% $CH_3CH_2OSO^-$, and 53.4% $CH_3CH_2OSO_2^-$. Reference 11.

(11) Lum, R. C.; Grabowski, J. J. Unpublished data.

(12) (a) *CRC Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985. (b) de Bievre, P.; Barnes, I. L. *Int. J. Mass. Spectrom. Ion Proc.* **1985**, *65*, 211–230.

(13) Bierbaum, V. M.; Grabowski, J. J.; Depuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389–1393.

(14) (a) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153. (b) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565–2571. (c) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192.

(15) Olmstead, W. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219–4228.

demonstrate the successful nature of competition between substitution and elimination channels for gas-phase anion-molecule reactions.

Acknowledgment. We gratefully acknowledge financial support of this work by a National Science Foundation Presidential Young Investigator Award (Grant CHE-8552742).

Registry No. Hydroxide, 14280-30-9; dimethyl sulfite, 616-42-2; diethyl sulfite, 623-81-4; amide, 17655-31-1; ethylmethyl sulfite, 10315-59-0.

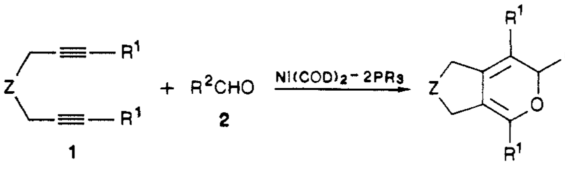
Nickel(0)-Catalyzed Reaction of Diynes with Aldehydes

Tetsuo Tsuda,* Takao Kiyoi, Toshiki Miyane, and
Takeo Saegusa*

Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Yoshida, Kyoto, Japan

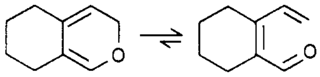
Received June 20, 1988

Transition-metal-catalyzed cycloaddition of diynes with unsaturated compounds is useful for the synthesis of polycyclic compounds and is actively studied recently.[1] The cycloaddition of diynes with a carbonyl group, however, has not been reported except in our recent study of the Ni(0)-catalyzed cycloaddition of diynes with carbon dioxide to bicyclic α-pyrones.[2] Here we investigated the Ni(0)-catalyzed cycloaddition of diynes **1** with aldehydes **2** to bicyclic α-pyrans **3** (eq 1).

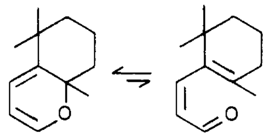


1 **2** **3** (1)

Dihydro- and tetrahydro-α-pyrans are well-known compounds.[3] Those substituted with functional groups, in particular, are important intermediates in the synthesis of natural products.[4] On the contrary, examples of the α-pyran ring system are limited because the α-pyran ring consisting of a dienolic ether structure undergoes electrocyclic ring opening to a dienone. Several monocyclic α-pyrans bearing alkyl and heteroatom substituents are known.[5] It is suggested that the alkyl substituent causes the steric destabilization of the dienone tautomer.[6] The literature on bicyclic α-pyrans is sparse except for 1-benzo-α-pyrans stabilized by the fusion of the benzene ring.[5] The bicyclic α-pyran **4a** exists at room

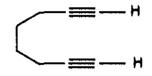
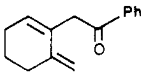
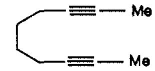
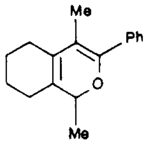
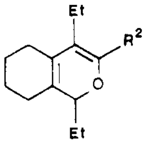
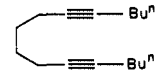
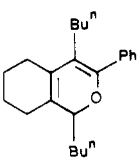
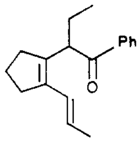
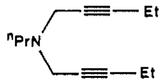
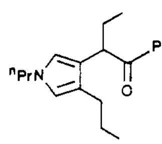


4a **4b** (2)



5a **5b** (3)

Table I. Reaction of Diynes and Aldehydes Catalyzed by the Ni(O)–PR$_3$ Complexes[a]

diyne (1)	aldehyde (2)	PR$_3$	product	isolated yield	%[d]
 **1a**[b]	PhCHO **2d**	PBu$_3^t$ PCy$_3$		**7**	15 1.2
 **1b**[c]	**2d**	PBu$_3^t$ PCy$_3$		**6a**	52 39
 **1c**	MeCHO **2a** ^{n}PrCHO **2b** ^{i}PrCHO **2c** **2d**	PCy$_3$		**6b** (R^2=Me) **6c** (R^2=Pr^n) **6d** (R^2=Pr^i) **6e** (R^2=Ph)	28 90 69 79
		PBu$_3^n$ PPh$_3$			77 78
 **1d**	**2d**	PCy$_3$		**6f**	78
 **1e**	**2d**	PCy$_3$		**8**	71
 **1f**	**2d**	PCy$_3$		**9**	97

[a] Diyne **1**, 1.00 mmol; **2**/**1** = 1.5; Ni(COD)$_2$/**1** = 0.05; PR$_3$/Ni(COD)$_2$ = 2; solvent, THF (10 mL); temperature, 120 °C; time, 5 h. [b] Temperature, 100 °C; time, 20 h. [c] Temperature, 135 °C; time, 5 h. [d] The product has the spectroscopic data and the elemental composition (HRMS) in accord with its structure.