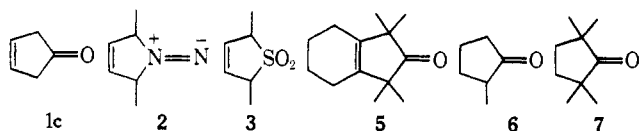


Table II. Fluorescence Lifetimes of Some Cyclopentanones and Cyclopentenones

Ketone	τ_F^a (sec)	Ketone	τ_F^a (sec)
1b	3.0	5	9.9
6	2.7	7	8.7

^a The lifetimes were measured directly using the single photon counting technique.

Neither shows any striking peculiarities when compared to saturated models **6** and **7**. The short lifetime of **1b**



(3×10^{-9} sec)⁷ precludes involvement of significant singlet participation in reaction 2 since even at 0.2 M 1,3-pentadiene only a small fraction of the fluorescence of **1b** is quenched, but under these conditions reaction 2 is strongly quenched.

The striking features of the data in Table I are (a) the very high contribution of *c,c*-**4** from **1a**, (b) an overall high yield of sigmasymmetric products (*c,c*-**4** and *t,t*-**4**), and (c) a nearly 50:50 mix of *t,c*-**4** and *t,t*-**4** from **1b**, the former corresponding to a sigmasymmetric and the latter an axisymmetric product.

These results contrast sharply with those for saturated α,α' -dialkyl cyclic ketones for which a common triplet biradical intermediate appears to be involved starting from either trans or cis starting material.⁸ A common triplet biradical intermediate capable of significant stereochemical loss is clearly incompatible with our data. Partially hindered rotation in specific, biradical conformers also does not appear to be involved. Substantial methyl-methyl, methyl-hydrogen, and methyl-ketyl radical interactions should severely restrict even selective rotations in the ketyl-allylic diradical. Moreover, during the initial stage of formation of the diradical isomer leading to the cis-cis diene, extreme repulsive interactions are encountered before allylic stabilization can be achieved. The relatively high yield of *c,c*-**4** molecule from **1a** suggests to us that we should better consider concerted pathways to explain the data.

Starting from **1a**, the competing sigmasymmetric pathways show relatively little specificity (*t,t*-**4**/*c,c*-**4** \sim 3), a result which suggests a small dependence of the nonbonded $\text{CH}_3 \cdots \text{CH}_3$ interaction in the transition state for formation of *c,c*-**4**. This in turn suggests to us that a *linear*, sterically less demanding symmetric extrusion of CO occurs to keep the $\text{CH}_3 \cdots \text{CH}_3$ interactions from becoming important until the molecule is close to or beyond the transition state. The contrasting much greater degree of stereoselectivity in the competing axisymmetric process from **1b** (*t,t*-**4**/*c,c*-**4** \sim 13) suggests that a nonlinear axisymmetric process is occurring, with a concomitantly high degree of nonbonded interactions occurring in the approach to the transition state.

The higher ratio of sigma/axi products from **1a** (\sim 4/1) relative to the ratio of sigma/axi products from

(7) The observed singlet lifetimes of **1a** and **1b** would necessitate quenching rates from 20 to 40 times those commonly encountered for typical ketone singlets.

(8) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Baltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, **93**, 7213 (1971).

1b (\sim 1/1) is also consistent with a *nonlinear* axisymmetric process, since from **1a** axisymmetric fragmentation must lead to a $\text{CH}_3 \cdots \text{H}$ nonbonded interaction whereas for **1b** only a $\text{H} \cdots \text{H}$ nonbonded interaction occurs in the *nonlinear* axisymmetric fragmentation. Thus for **1b**, the axisymmetric process can compete with the inherently less sterically sensitive *linear* sigmasymmetric process (eq 1 and 2). Finally, we point out the failures of these decarbonylation reactions to conform to the usual nonconcerted, biradical triplet reactions of n,π^* states of ketones may be related to other concurrent electronic-spin coupled processes which have been recently proposed to explain pericyclic reactions.^{9,10} By this we mean that the spin-orbital coupling may be inherent in the "twist motions" of the orbitals involved in the retrocycloaddition reported here and that the reduction of the prohibition of spin flipping is sufficiently reduced so that a *concerted* triplet reaction leading *directly* to singlet products becomes possible.

In conclusion, we report that the unexpected stereochemical results for the triplet, n,π^* retrocycloaddition reactions of **1a** and **1b** can be explained in terms of a *linear* sigmatropic process which is less sterically sensitive than a competing *nonlinear* axisymmetric process.

(9) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973); P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *ibid.*, **95**, 3025, (1973); N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *ibid.*, **95**, 2035 (1973).

(10) The cycloaddition of sulfur monoxide ($^3\Sigma^-$) to *trans,trans*-2,4-hexadiene and *cis,trans*-2,4-hexadiene displays a remarkably high degree of stereoselectivity. See P. Chao and D. M. Lemal, *J. Amer. Chem. Soc.*, **95**, 920 (1973).

Thomas R. Darling, Joseph Pouliquen, Nicholas J. Turro*

Chemistry Department, Columbia University
New York, New York 10027

Received September 6, 1973

Chemical Syntheses with a Quenched Flow Reactor. Hydroxytrihydroborate and Peroxynitrite

Sir:

The technique of mixing two streams of reactant solutions in a reaction tube with downstream injection of a solution containing a quenching reagent has been used for studying the kinetics of fast reactions¹ but does not seem to have been applied to laboratory synthesis. The method is ideal for a synthesis involving the formation of an intermediate species which (1) must be prepared under conditions such that its half-life is in the range between a millisecond and several seconds and (2) can be stabilized by rapid reaction with a quenching reagent. We now report the successful use of this method for preparing solutions of two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite. Each synthesis involves the formation of an unstable intermediate species which is stabilized by deprotonation with hydroxide ion.

The apparatus consists of a Lucite rod bored to a depth of 10 cm with a 3-mm hole. Two 1.5-mm holes for the introduction of the reactants enter from the side of the rod, joining the 3-mm tube tangentially at its

(1) F. J. W. Roughton, "Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience, New York, N. Y., 1953, Chapter 10, Parts 1 and 4.

inner end. A third 1.5-mm hole, for the quenching solution, enters the tube at a point 5 cm from the two reactant holes. The holes are connected to glass tubes on the outside of the rod; these are connected through glass and Teflon needle valves to siphon tubes inserted into three separate bottles. The bottles can be simultaneously pressurized with nitrogen gas at a regulated pressure from a cylinder. Before each run, the needle valves are adjusted so that the flow rates of the three solutions are equal. The reaction tube is mounted vertically, and the quenched product is collected in a beaker placed beneath the open end of the tube.

Wang and Jolly² have shown that, in methanol-water solution at -78° , the borohydride ion reacts very rapidly with strong acid to form H_2OBH_3 . This species hydrolyzes under these conditions with a half-life of about 300 sec, but it can be deprotonated to form the relatively stable BH_3OH^- ion, which has a half-life of several hours at room temperature. An estimated effective activation energy for the H_2OBH_3 hydrolysis of 12 kcal/mol³ corresponds to a half-life of about 20 msec at 0° . Thus, it seemed reasonable to attempt the synthesis of BH_3OH^- using the quenched flow reactor with aqueous solutions initially at 0° and with a reaction time (time between the initial mixing of H^+ and BH_4^- and the quenching with OH^-) of the order of 20 msec or less. Our experimental data are given in Table I. The

relatively stable in alkaline solutions.⁴⁻⁷ The literature procedure for the synthesis of peroxyxynitrite involves the mixing of an acidic peroxide solution with a nitrite solution, immediately followed by treatment with excess base. Yields of 45–50% have been reported.⁵ We have carried out this synthesis with our quenched flow reactor, using equal flow rates of the following solutions at 0° : 0.6 M KNO_2 , a solution 0.6 M in HCl and 0.7 M in H_2O_2 , and 3 M NaOH. The product solution was analyzed spectrophotometrically.⁵ The reaction times (msec) and corresponding percentage yields follow: 44, 44%; 88, 67%; 88, 68%; 230, 77%; 280, 72%; 450, 82%. The relatively low yield obtained for the shortest reaction time (44 msec) was probably a consequence of incomplete reaction of the nitrous acid with the hydrogen peroxide.

Acknowledgment. This work was supported in part by the U. S. Atomic Energy Commission.

(4) H. M. Papee and G. L. Petriconi, *Nature (London)*, **204**, 142 (1964).

(5) M. N. Hughes and H. G. Nicklin, *J. Chem. Soc. A*, 450 (1968).

(6) W. G. Keith and R. E. Powell, *J. Chem. Soc. A*, 90 (1969).

(7) D. J. Benton and P. Moore, *J. Chem. Soc. A*, 3179 (1970).

Janice W. Reed, Hansel H. Ho, William L. Jolly*

Department of Chemistry, University of California
and Inorganic Materials Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received August 16, 1973

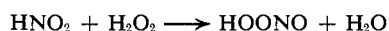
Table I. Data for BH_3OH^- Syntheses

Reaction time, msec	Reagent concn, M			Product temp, ^a $^\circ\text{C}$	Yield of BH_3OH^- , ^b %
	BH_4^-	H^+	OH^-		
26	0.3	0.45	0.6	6	75
21	0.3	0.45	0.6	6	87
16	0.3	0.45	0.6	6	94
10	0.3	0.45	0.6	6	86
10	1.0	2.5	3.0	16	65
10	3.0	4.5	6.0	37	51

^a Temperature of BH_3OH^- solution. Reagent solutions cooled to 0° . ^b Determined from amount of H_2 evolved upon complete hydrolysis.

change in the percentage yield of BH_3OH^- with change in reaction time was qualitatively as expected. Relatively high yields, essentially independent of reaction time, were obtained for reaction times of 10–21 msec; the yield dropped off for a reaction time of 26 msec. The decrease in the percentage yield with increasing concentration of the solutions may be due to the corresponding increase in the reaction temperature caused by the increased heat of reaction.

The reaction of nitrous acid with hydrogen peroxide in acidic solution yields peroxyxynitrous acid.



This acid decomposes to nitric acid with a half-time of 7 sec at 0° , but the conjugate base, peroxyxynitrite ion, is

(2) F. T. Wang and W. L. Jolly, *Inorg. Chem.*, **11**, 1933 (1972).

(3) This is admittedly an optimistically low estimate of the activation energy. At -78° the acid-independent hydrolysis of H_2OBH_3 has a rate comparable to that of the acid-dependent hydrolysis.² The former reaction would be expected to have an activation energy near 20 kcal/mol, thus making the hydrolysis too rapid for a quenched flow reactor operated near room temperature. We have no explanation for the discrepancy.

Hexakis(dimethylamino)- and Hexakis(*tert*-butoxy)dimolybdenum(III)

Sir:

We wish to report the preparation and characterization of Mo_2L_6 where $\text{L} = \text{NMe}_2$ and *O-t*-Bu. These compounds provide¹ (i) the first examples of dialkylamides and alkoxides of tervalent molybdenum, (ii) the first example of oligomerization by metal-metal bond formation in the chemistry of metal-alkoxides and dialkylamides, (iii) synthetically useful starting materials for the synthesis of other metalloorganic compounds of molybdenum(III), and (iv) a unique opportunity for the study of strong homonuclear interactions in the structurally related series $\text{L}_3\text{Mo}\equiv\text{MoL}_3$ where $\text{L} = \text{CH}_2\text{-SiMe}_3$,² NMe_2 , and *O-t*-Bu.

The addition of MoCl_3 to an ice-cooled, magnetically stirred solution of LiNMe_2 (3 mol equiv in 50:50 THF-hexane) gave a dark brown solution. The reaction mixture was stirred for 12 hr at 0° under an atmosphere of dry, oxygen-free nitrogen. Solvent was then removed by vacuum distillation and the residue dried under high vacuum at 60° . Subsequent extraction with pentane yielded a dark, red-brown solution which, on removal of pentane, gave a dark brown solid containing crude $\text{Mo}_2(\text{NMe}_2)_6$. Analytically pure samples of the yellow crystalline solid of $\text{Mo}_2(\text{NMe}_2)_6$ were obtained by vacuum sublimation (100° (10^{-6} cm)) from the crude product.

Addition of *t*-BuOH (>6 mol equiv) to a solution of $\text{Mo}_2(\text{NMe}_2)_6$ in a hydrocarbon solvent led to quantita-

(1) (a) D. C. Bradley, *Advan. Inorg. Chem. Radiochem.*, **15**, 259 (1972); (b) D. C. Bradley and K. Fisher, *MTP (Med. Tech. Publ.) Int. Rev. Sci.*, **5**, 65 (1972).

(2) (a) G. Wilkinson, *et al.*, *J. Chem. Soc., Dalton Trans.*, 533 (1973); (b) G. Wilkinson, *et al.*, *Chem. Commun.*, 1079 (1971).