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### References and Notes

- (1) J. L. Margrave and P. W. Wilson, *Acc. Chem. Res.*, **4**, 145 (1971).
- (2) W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).
- (3) W. Kirmse, Ed., "Carbene Chemistry", Vol. 1, 2nd ed, Academic Press, New York, N.Y., 1971, Chapters 7, 8.
- (4) J. C. Thompson, J. L. Margrave, and P. L. Timms, *Chem. Commun.*, 566 (1966).
- (5) A. Orlando, C. S. Liu, and J. C. Thompson, *J. Fluorine Chem.*, **2**, 103 (1973).
- (6) C. S. Liu, J. L. Margrave, and J. C. Thompson, *Can. J. Chem.*, **50**, 465 (1972).
- (7) C. S. Liu and C. W. Cheng, *J. Am. Chem. Soc.*, **97**, 6746 (1975).
- (8) D. L. Perry and J. L. Margrave, *J. Chem. Educ.*, **53**, 696 (1976).
- (9) P. L. Timms, R. A. Kent, T. C. Ehler, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).
- (10) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, **88**, 940 (1966).
- (11) J. S. Binkley and J. A. Pople, *Chem. Phys. Lett.*, **45**, 197 (1977).
- (12) T. L. Cottrell, "The Strengths of Chemical Bonds", 2nd ed, Butterworths, London, 1958.
- (13) P. L. Timms et al., *J. Am. Chem. Soc.*, **87**, 3819 (1965).

Chao-shiuan Liu,\* Tsai-lih Hwang

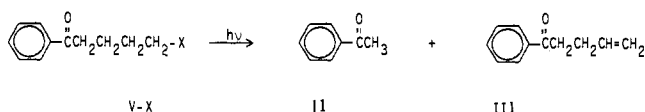
Department of Chemistry  
National Tsing Hua University  
Hsinchu, Taiwan, ROC

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### Rates of Radical $\beta$ Cleavage in Photogenerated Diradicals<sup>1</sup>

Sir:

The Norrish type II photoreaction<sup>2</sup> provides a unique probe for studying substituent effects on radical reactions, since intramolecular hydrogen atom abstraction is so regioselective. Because of the intense interest in  $\beta$ -haloalkyl radicals,<sup>3</sup> we have studied the photochemistry of three  $\delta$ -haloalderophenones. They each undergo loss of HX competitive with type II photoelimination. The halogens are eliminated from the 1,4-diradical intermediate involved in type II photoelimination.<sup>2</sup> Moreover,  $\delta$ -benzoyl sulfides, sulfoxides, and sulfones behave similarly. Our combined results provide the first extensive set of relative  $\beta$ -cleavage rates of radicals.



We had noted previously that V-Cl undergoes a minor reaction in competition with type II elimination.<sup>4</sup> We have now identified 4-benzoyl-1-butene (III) as a minor product from V-Cl, the major product for V-Br, and the only volatile product for V-I.<sup>5</sup> Table I lists quantum yields for product formation and for ketone disappearance in benzene containing 0.1 M pyridine. The pyridine captures the HBr and HI which otherwise react with products<sup>6</sup> and maximizes type II yields.<sup>7</sup> Under these conditions, the material balance for the chloro and bromo ketones is close to 100%.

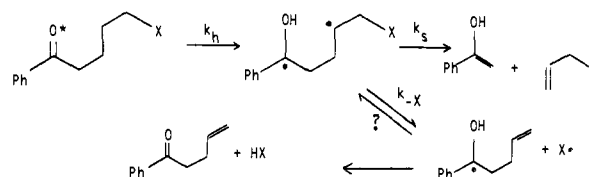
Neither 1 M ethyl iodide nor 1 M butyl bromide measurably quenches the photoelimination of butyrophenone. Likewise, irradiation of  $\beta$ -chloropropiophenone and  $\gamma$ -chloro- and  $\gamma$ -bromobutyrophenone does not form benzoylalkenes. These experiments indicate that the carbon-halogen bonds are not broken by direct interaction with the excited ketone. The only remaining mechanism for product formation involves competitive reactions of the diradicals formed by triplet state  $\gamma$ -hydrogen abstraction. The hydroxy radical formed by  $\beta$  elimination of a halogen atom<sup>8</sup> from the diradical should either

**Table I.** Product Quantum Yields for  $\delta$ -Substituted Valerophenones  $\text{PhCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{X}^a$

X	$\Phi_{II}^b$	$\Phi_{III}^c$	Rel $k_{-X}^c$
Cl <sup>d</sup>	0.58	0.10	1
Br <sup>d</sup>	0.048	0.55	65
I <sup>d</sup>	<0.002	0.43	>1260
SCN	0.003 <sup>f</sup>	0.25 <sup>f</sup>	490
SBU <sup>e</sup>	0.21 <sup>f</sup>	0.006 <sup>f</sup>	0.16
SOBu <sup>e</sup>	0.03 <sup>f</sup>	0.39 <sup>f</sup>	76
SO <sub>2</sub> Bu <sup>e</sup>	0.39 <sup>f</sup>	0.03 <sup>f</sup>	0.46
SPh	0.02 <sup>f</sup>	0.28 <sup>f</sup>	110
SOPh	0.003 <sup>f</sup>	0.32 <sup>f</sup>	630
SO <sub>2</sub> Ph	0.19 <sup>f</sup>	0.22 <sup>f</sup>	6.8
SCOCH <sub>3</sub>	0.78 <sup>f</sup>	0.02 <sup>f</sup>	0.15
Cl <sup>d,g</sup>	0.54	0.08	
Cl <sup>d,h</sup>	0.36	0.06	
Cl <sup>d,i</sup>	0.045	0.008	
Cl <sup>d,j</sup>	0.63	0.07	

<sup>a</sup> Degassed benzene solutions containing 0.1 M ketone irradiated at 313 or 366 nm, 25 °C. <sup>b</sup> An extra 12% cyclobutanol is also formed for V-Cl and presumably for the other ketones. <sup>c</sup> Some data from ref 4. <sup>d</sup> In the presence of 0.1 M pyridine. <sup>e</sup> Bu = *n*-C<sub>4</sub>H<sub>9</sub>. <sup>f</sup> In the presence of 1 M dioxane. <sup>g</sup> In CH<sub>3</sub>CN. <sup>h</sup> In CH<sub>3</sub>OH. <sup>i</sup> *p*-MeO. <sup>j</sup> *p*-CF<sub>3</sub>.

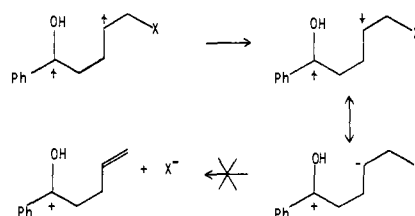
### Scheme I



disproportionate or couple with the halogen atom in high yield, perhaps involving a rapid oxidation of the organic radical by X.<sup>9</sup> Both Br<sub>2</sub> and I<sub>2</sub> are formed from V-Br and V-I; so there is some diffusion apart of the radical pairs.

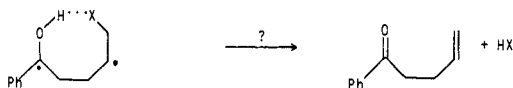
Since thiyl radicals also add reversibly to olefins,<sup>8,10</sup> we extended our studies to some  $\delta$ -benzoyl sulfides, sulfones, and sulfoxides and found that they all undergo both forms of elimination, as noted in Table I. The corresponding  $\gamma$ -benzoyl homologues give only type II products. Unlike alkyl halides, sulfur compounds do quench excited ketones efficiently,<sup>11</sup> but do not undergo sensitized elimination themselves in the process. We conclude that all products come from the usual 1,4 diradical. With V-SR observation of disulfide as a minor product indicates the formation of thiyl radicals. With V-SOR, the expected coupling product of sulfinyl radicals, RS-SO<sub>2</sub>R,<sup>12</sup> is observed.

Since it is now well established that photogenerated diradicals undergo typical monoradical rearrangements<sup>13</sup> and bimolecular trapping,<sup>14</sup> we expected them to also undergo  $\beta$ -elimination of labile halogen and sulfur-centered radicals. Therefore Scheme I represents the expected and most likely explanation for this novel and highly specific form of photoelimination. II/III product ratios vary only slightly with solvent polarity and with para substituents; so a strong zwitterionic contribution to the elimination is unlikely.



A cyclic concerted elimination has already been suggested for  $\beta$ -alkoxy ketones<sup>15</sup> and remains a possibility here. Because an eight-membered ring is necessary, we doubt that this con-

certed mechanism can compete with radical cleavage except possibly for the worst leaving groups.



Relative rates of  $\beta$  cleavage can be obtained directly from the product ratios, given the plausible assumption that  $k_s$  is largely independent of X.<sup>16</sup> Recent measurements<sup>17</sup> indicate that  $k_s = 1 \times 10^7 \text{ s}^{-1}$ ; so a  $k_{-X}$  value of  $2.7 \times 10^5 \text{ s}^{-1}$  is indicated for X = *n*-BuS. Actual rate constants for  $\beta$  elimination in solution have not been reported previously. The 7.5-kcal activation energy estimated for  $\beta$ -bromoethyl radical<sup>18</sup> is certainly consistent with our estimated  $k_{-Br} = 1 \times 10^8 \text{ s}^{-1}$ , given an *A* factor of  $10^{13} \text{ s}^{-1}$ .

Comparison of the relative  $k_{-X}$  values is revealing. As expected,  $I > Br > Cl$  and  $PhS \gg n\text{-BuS}$ <sup>19</sup> as leaving groups. The order  $RSO \gg RS$ ,  $RSO_2$  confirms Kice's suggestion<sup>20</sup> that sulfinyl radicals have the greatest relative kinetic stability of the three. That  $SCN \gg SCOCH_3$  may reflect the known weak conjugative stabilization in  $\alpha$ -keto radicals<sup>21</sup> and further indicates that  $\delta$ -X leaves as a radical rather than an anion.

The most surprising result is that Cl is eliminated more rapidly than thyl radicals. Kineticists usually assume a much smaller value of  $k_{-X}$  for  $\beta$ -chloroethyl<sup>22</sup> than we estimate. Therefore it is possible that the cyclic concerted mechanism contributes for X = Cl. However, the amount of Cl loss in the radical addition of mercaptans to allyl chloride<sup>23</sup> is consistent with our separate observations that loss of  $\delta$ -Cl and trapping by mercaptans<sup>14a</sup> compete comparably with type II cleavage. It is not inconceivable that studies on monoradicals have indicated too low a value for  $k_{-Cl}$  because of rapid reverse addition. Our  $k_{-X}$  values are *minimum* values uncorrected for reverse addition. However, since the diradicals can generate caged radical pairs, in-cage radical-radical reactions are probably faster even than addition of Cl atoms to double bonds and thus minimize the effects of reversibility on relative  $k_{-X}$  values.

## References and Notes

- (1) We thank the National Science Foundation for partial support of this work.
- (2) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
- (3) (a) For a review, see P. S. Skell and K. J. Shea in "Free Radicals", J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., Vol. II, p 809; (b) D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6485 (1972); (c) K. S. Chen, P. J. Krusic, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2014 (1974); (d) R. V. Lloyd and D. E. Wood, *J. Am. Chem. Soc.*, **97**, 5986 (1975); (e) D. Griller and K. U. Ingold, *ibid.*, **96**, 6715 (1974).
- (4) P. J. Wagner and A. E. Kempainen, *J. Am. Chem. Soc.*, **94**, 7495 (1972).
- (5) III was collected by preparative GC and identified by comparison of its NMR and mass spectra with those of independently synthesized material. None of the ketones V-X produces III in the dark or during analysis.
- (6) NMR spectra indicated no *N*-alkylpyridinium halide formation in our solution. Pyridine does not affect triplet state decay: P. J. Wagner, T. Jelinek, and A. E. Kempainen, *J. Am. Chem. Soc.*, **94**, 7512 (1972).
- (7) P. J. Wagner, I. E. Kochevar, and A. E. Kempainen, *J. Am. Chem. Soc.*, **94**, 7489 (1972).
- (8) (a) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p. 302; (b) E. S. Huyser, "Free-Radical Chain Reactions", Wiley-Interscience, New York, N.Y., 1970, p 212.
- (9) P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. C. Hamilton, *J. Am. Chem. Soc.*, **98**, 8135 (1976).
- (10) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).
- (11) J. B. Gutenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **95**, 200 (1973).
- (12) (a) R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962); (b) D. Barnard and E. J. Percy, *Chem. Ind. (London)*, 1332 (1960).
- (13) (a) A. Padwa, *J. Am. Chem. Soc.*, **87**, 4205 (1965); (b) N. Shimizu, M. Ishikawa, K. Ishikura, and S. Nishida, *ibid.*, **96**, 6456 (1974); (c) P. J. Wagner and K.-C. Liu, *ibid.*, **96**, 5952 (1974).
- (14) (a) P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 287 (1972); (b) J. Grotewold, C. M. Previtali, D. Soria, and J. C. Scaiano, *J. Chem. Soc., Chem. Commun.*, 207 (1973); (c) M. Hamity and J. C. Scaiano, *J. Photochem.*, **4**, 229 (1975); (d) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Am. Chem. Soc.*, **96**, 3351 (1974); (e) J. C. Scaiano, *ibid.*, **99**, 1494 (1977); (f) R. D. Small and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828 (1977).
- (15) P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **93**, 4958 (1971).
- (16) If the rate-determining step for triplet generated diradical reaction is T  $\rightarrow$  S intersystem crossing,<sup>14c</sup> heavy-atom effects of  $\delta$  substituents might in-

crease  $k_s$ .

- (17) R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).
- (18) (a) R. Barker and A. Maccoll, *J. Chem. Soc.*, 2839 (1963); (b) P. I. Abell and R. S. Anderson, *Tetrahedron Lett.*, 3727 (1964).
- (19) D. N. Hall, A. A. Oswald, and K. Griesbaum, *J. Org. Chem.*, **30**, 3829 (1965).
- (20) J. L. Kice in ref 3a, pp 715-718.
- (21) (a) G. A. Russell and J. Lokensgard, *J. Am. Chem. Soc.*, **89**, 5059 (1967); (b) K. D. King, D. M. Golden, and S. W. Benson, *ibid.*, **92**, 5541 (1970).
- (22) (a) R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Meyers, and S. Smoes, *Chem. Ber.*, **93**, 3014 (1960); (b) P. B. Ayscough, A. J. Cocker, F. S. Dainton, S. Hirst, and M. Weston, *Proc. Chem. Soc. London*, 244 (1961).
- (23) D. N. Hall, *J. Org. Chem.*, **32**, 2082 (1967).

Peter J. Wagner,\* James H. Sedon  
Michael J. Lindstrom

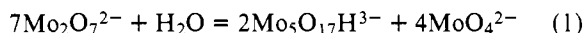
Department of Chemistry, Michigan State University  
East Lansing, Michigan 48824

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## Synthesis and Characterization of the Pentamolybdate Ion, $Mo_5O_{17}H^{3-}$

Sir:

We recently reported the synthesis and characterization of the dimolybdate ion,  $Mo_2O_7^{2-}$ , as a tetrabutylammonium salt.<sup>1</sup> This compound contains the most basic polymolybdate ion isolated to date and is reactive toward a wide variety of reagents. We report here its reaction with water to form a labile pentamolybdate ion:



The instability of this novel, protonated isopolymolybdate in nonaqueous solution provides new insights into the kinetics and mechanism of polymolybdate transformations.

Although addition of water to a  $CH_3CN$  solution of  $[(n-C_4H_9)_4N]_2Mo_2O_7$  (**1**) produces no significant change in its solution IR spectrum,<sup>1</sup> the pentamolybdate ion can be synthesized according to eq 1 by forcing the equilibrium to the right using two different approaches. In the first approach, the low solubility of the pentamolybdate ion in  $CH_3CN/(C_2H_5)_2O$  is exploited. Slow addition ( $\sim 15 \text{ mL/min}$ ) of 80 mL of  $(C_2H_5)_2O$  to a clear solution of 1.0 g of **1** and 1.0 mL of  $H_2O$  in 10 mL of  $CH_3CN$  with rapid stirring yields 190 mg of an amorphous precipitate having the empirical formula<sup>2</sup>  $[(n-C_4H_9)_4N]_3Mo_5O_{17}H$  (**2**). In the second approach, the high solubility of  $[(n-C_4H_9)_4N]_2MoO_4$  in  $H_2O$  relative to **1** and **2** is exploited. When a suspension of 1.0 g of **1** in 10 mL of pH 5-6 aqueous HCl is stirred for  $\sim 1 \text{ min}$  and filtered, compound **2** (460 mg) is obtained as an amorphous powder.

Structural characterization of **2** is rendered difficult by its instability in solution (see below) which has thus far ruled out recrystallization, conductivity measurements, and the measurement of  $^{17}O$  NMR parameters. Nonetheless, elemental analysis<sup>2</sup> and IR spectroscopy strongly suggest the anion structure for **2** shown in Figure 1, where  $MoO_4^{2-}$  and  $OH^-$  groups are connected to opposite sides of an  $Mo_4O_{12}$  ring by weak ( $>2.2 \text{ \AA}$ ) Mo-O bonds yielding the structural formula<sup>3</sup>  $(MoO_4^{2-})(OH^-)(Mo_4O_{12})$ . This structure is closely related to the  $(CH_3)_2AsMo_4O_{15}H^{2-}$  structure<sup>4</sup> by replacement of the bidentate  $MoO_4^{2-}$  subunit with a bidentate  $(CH_3)_2AsO_2^-$  group.<sup>5</sup> Structural isomorphism between the anions in **2** and  $[(n-C_4H_9)_4N](CH_3)_2AsMo_4O_{15}H$  (**3**) should imply similar IR spectra for the two compounds in the 500-4000- $cm^{-1}$  region with the exception of absorptions characteristic of the  $MoO_4^{2-}$  and  $(CH_3)_2AsO_2^-$  subunits. Such a similarity is in fact observed. Both **2** and **3** exhibit sharp OH absorptions at 3610  $cm^{-1}$  and their spectra in the 500-1000- $cm^{-1}$  region (see Figure 2a and 2b) bear a striking resemblance outside of the 725-850- $cm^{-1}$  region. In the 725-850- $cm^{-1}$  region, **3** displays