Pergamon

Tetrahedron Letters, Vol. 36, No. 32, pp. 5801-5804, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)01132-3

Reactions of Stilbene Dibromides with 2-Nitropropan-2-yl Anion in DMSO. A Competing Ionic and SET Mechanism

Bong Rae Cho*, Eun Kyung Lee, and Hyun Soo Kim

Department of Chemistry, Korea University
1-Anamdong, Seoul 136-701, Korea

Abstract: Reactions of *dl*- and *meso*-stilbene dibromides with 2-nitropropan-2-yl anion in DMSO proceed by the E2 mechanism, whereas that of *erythro*-*p*-nitrostilbene dibromide proceeds by a competing ionic and SET mechanism.

A fundamental postulate in electron transfer theory is that electrons may only be transferred one at a time.[1] But, in organic chemistry, electrons have been considered to move in pairs at least in polar reactions. Recently, the notion that polar organic reactions may also proceed by the SET processes has become more widely accepted due to the discovery of many such examples.[2-6] In contrast, little is known about the elimination reactions that proceed by the SET mechanism.[7-9]

Very recently we have investigated the debromination reactions of 1-aryl-1,2-dibromo-2-nitropropanes under various conditions in an attempt to find the examples of elimination reactions that proceed by the SET mechanism. When the compounds were reacted with $[(CH_3)_2C(NO_2)]^-Li^+$ in DMSO or R_2NH in MeCN, the ionic pathway predominated.[10,11] The SET mechanism was observed only when the compounds were electrochemically debrominated.[12]

Another possible substrate that may react by the SET mechanism is *p*-nitrostilbene dibromide. It has been demonstrated that *p*-nitrobenzyl halides react with 2-nitropropan-2-yl anion in DMF by the competing S_N2 and $S_{RN}1$ mechanisms to produce O- and C-alkylation products, respectively.[13] As the competing S_N2 reaction is made more difficult by utilizing a poorer leaving group, the yield of the latter increased. However, benzyl halides substituted in the *para* position by a less electron-withdrawing substituent gave only oxygen alkylation. Since stilbene dibromide can be regarded as the dimer of benzyl bromide, it is expected to react with 2-nitropropan-2-yl anion by an ionic mechanism. On the other hand, *p*-nitrostilbene dibromide should be able to accept an electron from the base, as does *p*-nitrobenzyl bromide, to produce an anion radical, which may subsequently lose bromide to form a benzylic radical and undergo β-cleavage to afford the debromination product. To probe this possibility, we have investigated the reactions of stilbene dibromides **1**-**3** with 2-nitropropan-2-yl anion in DMSO under various conditions (eq 1).

$$XC_6H_4\underset{Br}{C}H\underset{Br}{C}HPh + (CH_3)_2\bar{C}NO_2 \longrightarrow ArCH{=}CHPh \quad (1)$$

1; X = H (*dl*), **2**; X = H (*meso*), **3**; X = *p*-NO_2 (*erythro*)

Stilbene dibromides **1-3** and lithium salt of 2-nitropropan-2-yl anion were prepared by the literature methods.[13,14] The reactions were conducted by stirring a solution of 0.02-0.06 M of **1-3** and an excess amount of the base in 10 mL of DMSO under argon. The products were isolated and identified by conventional methods. The rates of the reactions were followed by monitoring the increase in the absorption at the λ_{max} for the stilbenes in the range 312-362 nm under argon at 25.0 °C.[11]

Reaction of *dl*-stilbene dibromide **1** with 2-nitropropan-2-yl anion in DMSO produced only *trans*-α-bromostilbene in quantitative yield. In contrast, *meso*-stilbene dibromide **2** produced *trans*-stilbene as the major product. Neither the yields nor the rates were significantly influenced by the addition of the radical inhibitors (Table 1), indicating that the reactions must proceed by the ionic mechanism. Assuming similar reactivity of the base toward the proton and the bromine, the results can be attributed to the favorable steric interactions in the anti transition states.[15] Similarly, the 13-fold slower rate of dehydrobromination from **2** than from **1** can also be explained with the greater steric hindrance in the former transition state. However, the production of *trans*-stilbene as the major product from **2** is in contrast with the exclusive formation of *cis*-α-bromostilbene from the reaction of the same compound with acetate, cyanide, and chloride in DMF,[14] and can be attributed to the greater softness of the 2-nitropropan-2-yl anion.

When *erythro*-*p*-nitrostilbene dibromide **3** was reacted under the same conditions only *trans*-*p*-nitrostilbene was produced in quantitative yield. Considering that the compound **3** has the identical stereochemistry to that of **2** and the *p*-nitro group should increase the acidity of the benzylic H, the rate of

Table 1. Yields and Second-order Rate Constants for the Reactions of Stilbene Dibromides with 2-Nitropropan-2-yl anion in DMSO at 25.0 °C.[a]

			Yield (%)[b,c]			
Compds	[*p*-DNB][d,e]	[DBNO][e,f]	ArCH=CHPh[g]	ArCBr=CHPh[h]	$k_2^{-Br_2}$[c,i,j]	k_2^{-HBr}[c,j,k]
1				100		0.198
	1.1			100		0.189
		1.0		100		0.193
2			85.1	14.9	0.0827	0.0145
	1.0		82.0	18.0	0.0717	0.0157
		1.7	81.7	18.3	0.0672	0.0150
3			100		41.8	
	0.07		100		6.34	
	0.21		100		5.67	
	1.05		100		4.40	
		1.0	100		15.9	

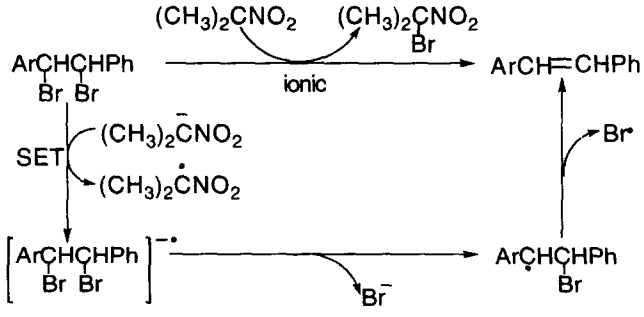
[a][Stilbene dibromide] = (1.6 -1.8) x 10^{-5} M, [$(CH_3)_2\bar{C}NO_2Li^+$] = (1.0 - 3.0) x 10^{-3} M. [b]Yields were determined by comparing the UV absorbance of the infinity samples of the kinetic runs with those of authentic samples. [c]Estimated uncertainty, ± 5 %. [d]*p*-DNB = *p*-dinitrobenzene. [e]Number of equiv of the scavengers based on the base concentration. [f]DBNO = di-*tert*-butylnitroxide. [g]*trans*-stilbene. [h](Z)- and (E)-isomer for **1** and **2**, respectively. [i]$k_2^{-Br_2} = k_{obs}$ x fractional yield of *trans*- stilbene/[$(CH_3)_2\bar{C}NO_2Li^+$]. [j]$M^{-1}s^{-1}$. [k]$k_2^{-HBr} = k_{obs}$ x fractional yield of α-bromostilbene/[$(CH_3)_2\bar{C}NO_2Li^+$].

dehydrobromination from **3** should be much faster than that from **2** to increase the yield of *cis*-α-bromostilbene.[14] On the other hand, it may also decrease the strength of the C-Br bond and lower the energy of the LUMO of the dibromide to increase the rates of debromination reactions that proceed by both the ionic and SET pathways. Therefore, the exclusive formation of *trans*-*p*-nitrostilbene from **3** reveals that the latter two effects are more important.

The positive evidence for the onset of the SET process is provided by the 500-fold faster rate of debromination from **3** than from **2**. For the $S_{RN}1$ reactions of benzyl system with 2-nitropropan-2-yl anion, the rate of *p*-nitro derivative was more than 100-fold faster than that for the corresponding unsubstituted compound. However, the rates of the S_N2 reactions differed only slightly.[13] Thus, the 500-fold rate acceleration caused by the *p*-nitro group in the debromination of **3** could be taken as evidence for the SET mechanism. Furthermore, the rates are retarded by the radical scavengers. *p*-Dinitrobenzene is expected to accept an electron from the anion radical of **3** to decrease the rate. Similarly, di-*tert*-butylnitroxide should also be able to intercept the benzylic radical to retard the rate of product formation. Therefore, the modest rate retardation caused by the scavengers provides additional support for the SET mechanism. In addition, the rate of debromination from **3** is 50-fold faster than that from **2** even though the SET pathway is suppressed by the addition of an excess amount of the scavengers, indicating that the ionic pathway should also operate. The faster rate of ionic debromination for **3** can be attributed to the weaker strength of the C-1-Br bond (*vide supra*).

These results can most reasonably accommodated by the competing ionic and SET mechanism shown in Scheme 1. The *erythro*-*p*-nitrostilbene dibromide **3** would either undergo ionic debromination induced by the attack of the base at the C-1-Br bond[10,11] or accept an electron from the base to form an anion radical. Since the *p*-nitrobenzyl moiety is expected to be reduced preferentially and the unpaired electron should remain on the same side of the scissile bond throughout the fragmentation processes,[16] the anion radical is expected to lose bromide to form the *p*-nitrobenzyl radical, which rapidly decomposes to the product. The much greater retardation effect of the *p*-dinitrobenzene indicates that electron transfer step should be rate-determining.

In conclusion, the reactions of of *dl*- and *meso*-stilbene dibromides with 2-nitropropan-2-yl anion in DMSO proceed by the E2 mechanism, whereas that of *erythro*-*p*-nitrostilbene dibromide proceeds by the competing ionic and SET mechanism shown in Scheme 1.



(Scheme 1)

Acknowledgement. This research was supported in part by OCRC-KOSEF, Korea Research Foundation, and Basic Science Research Institute Program, Ministry of Education, 1994 (Project No. BSRI-94-3406).

REFERENCES AND NOTES

(1) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, 18, 79.
(2) Bunnett, J. F. *Acc. Chem. Res.* **1992**, 25, 2.
(3) Bordwell, F. G.; Lynch, T. Y. *J. Am. Chem. Soc.* **1989**, 111, 1052.
(4) Bacaloglu, R.; Bunton, C. A.; Cerichelli, G.; Orgeta, F. *J. Am. Chem. Soc.* **1988**, 110, 3945.
(5) Ashby, E. C. *Acc. Chem. Res.* **1988**, 21, 414.
(6) Kochi, J. K. *Acc. Chem. Res.* **1992**, 25, 39.
(7) There are some evidences that the conversion of *vic*-dibromides to olefins by stabilized carbanions in liquid ammonia may proceed by the SET mechanism.[8] Although the denitration reaction of *vic*-dinitro compounds with sulfide may also proceed by the same mechanism, no mechanistic study has been conducted.[9]
(8) Korzan, D. G.; Chen, F.; Ainsworth, C. *J. Chem. Soc. Chem. Comm.* **1971**, 1053.
(9) Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, 93, 4316.
(10) Cho, B. R.; Suh, Y. S.; Lee, S. J.; Cho, E. J. *J. Org. Chem.* **1994**, 59, 3681.
(11) Cho, B. R.; Lee, S. J.; Kim, Y. K. *J. Org. Chem.* **1995**, 60, 2072.
(12) Cho, B. R.; Cho, E. J.; Lee, S. J.; Chae, W. S. *J. Org. Chem.* **1995**, 60, 2077.
(13) Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1965**, *87*, 4520.
(14) Avraamides, J.; Parker, A. J. *Aust. J. Chem.* **1983**, 36, 1705.
(15) March, J. *Advanced Organic Chemistry*; Wiley, New York, **1985**, p. 875.
(16) Channon, M.; Rajzmann, M.; Channon, F. *Tetrahedron*, **1990**, 46, 6193.

(*Received in Japan* 14 *March* 1995; *revised* 2 *June* 1995; *accepted* 16 *June* 1995)