*J. Org. Chem.* **1994**, *59*, 3681−3682

# Reactions of 1-Aryl-1,2-dibromo-2-nitropropanes with 2-Nitro-2-propyl Anion in DMSO

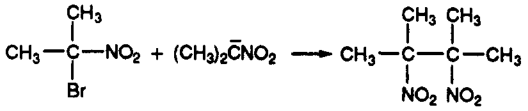
Bong Rae Cho,* Young Sung Suh, Seung Jae Lee, and Eun Jeong Cho

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

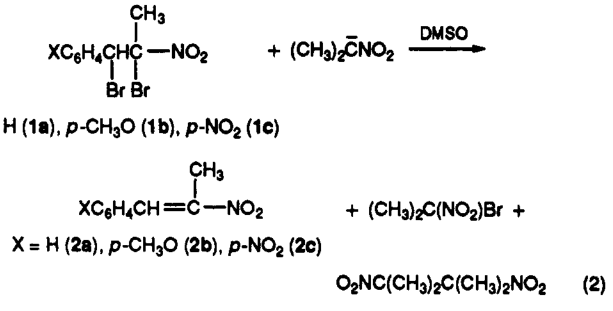
*Received December 29, 1993*

Many reactions traditionally classified as polar have recently been found to proceed via single-electron transfer (SET) mechanisms. Examples include dehalogenation reactions,[1] $S_N2$ reactions,[2] $S_NAr$ reactions,[3] carbonyl addition reactions,[4] and electrophilic aromatic substitution reactions.[5] Similarly, the transition state for the nucleophilic addition to electron-deficient olefins has also been demonstrated to possess some radical anionic character.[6] In contrast, except for the reductive elimination of $\beta$-substituted alkyl halides[7] and $\beta$-nitro compounds[8] by reducing agents, little is known about the base-promoted elimination reactions that proceed via a SET mechanism.

Perhaps the simplest reaction that proceeds via the SET pathway is that between 2-bromo-2-nitropropane and 2-nitro-2-propyl anion (eq 1).[9,10] The latter is assumed to donate an electron to the former to form an anion radical, which rapidly decomposes to 2-nitro-2-propyl radical and bromide. The free radical is then assumed to react with the anion to produce the dimer anion radical which propagates the chain reaction.[10] If this compound had a scissile bond adjacent to the free radical, it might undergo a $\beta$-elimination reaction as shown in Scheme 1. To probe this possibility, we have synthesized 1-aryl-1,2-dibromo-2-nitropropanes **1a−c** and studied their reactions with 2-nitro-2-propyl anion in DMSO under various conditions (eq 2).



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-NO_2 + (CH_3)_2\bar{C}NO_2 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}-\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}-CH_3 \qquad (1)$$



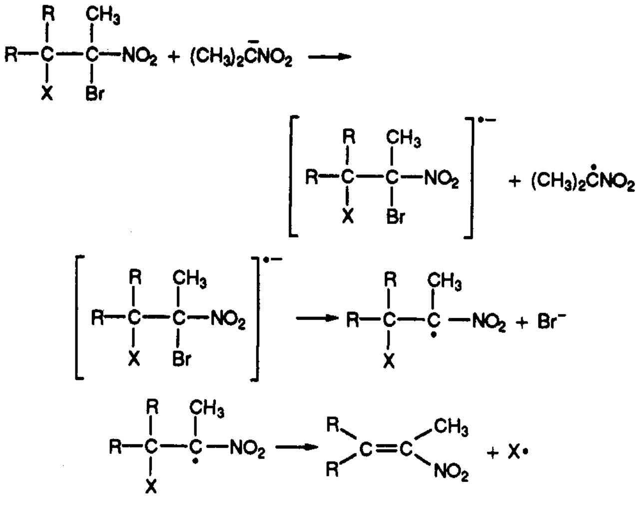
$$XC_6H_4\underset{\displaystyle Br}{CH}\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-NO_2 + (CH_3)_2\bar{C}NO_2 \xrightarrow{DMSO}$$

X = H (**1a**), *p*-CH$_3$O (**1b**), *p*-NO$_2$ (**1c**)

$$XC_6H_4CH=\overset{\displaystyle CH_3}{C}-NO_2 + (CH_3)_2C(NO_2)Br + O_2NC(CH_3)_2C(CH_3)_2NO_2 \qquad (2)$$

X = H (**2a**), *p*-CH$_3$O (**2b**), *p*-NO$_2$ (**2c**)

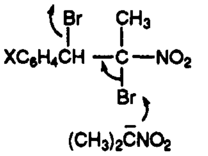
**Scheme 1**



## Results and Discussion

Reactions of **1a−c** with 2-propanenitronate in DMSO were almost instantaneous, producing **2a−c**, 2-bromo-2-nitropropane, and 2,3-dimethyl-2,3-dinitrobutane. Attempts to measure the rates of the reactions with a stopped-flow spectrophotometer failed because the reaction was finished within 5 ms. Therefore, the products were analyzed by GC under various conditions. The results are summarized in Table 1.

When **1a** was reacted with 2-propanenitronate in 1:1 ratio, 2-bromo-2-nitropropane, 2,3-dimethyl-2,3-dinitrobutane, and **2a** were produced in 79, 7, and 82% yields, respectively. Use of 2 equiv of the anion increased the yield of both substitution and debromination products. For all reactions, the sum of the yields of 2-bromo-2-nitropropane and 2,3-dimethyl-2,3-dinitrobutane was nearly the same as those of **2a−c**. Since 2,3-dimethyl-2,3-dinitrobutane is produced by eq 1,[9] the results indicate that the debromination is much faster than the substitution reaction and that 2-bromo-2-nitropropane and **2a** must have been produced at the same rates. The result can readily be explained by the polar mechanism as shown below. On the other hand, if the reaction proceeded by the SET mechanism, the yield of 2-bromo-2-nitropropane should have been much lower because the only plausible pathway of its formation would be the reaction of 2-nitro-2-propyl radical with bromine radical or bromide ion, which is not expected to be very efficient.



The conclusion is supported by the negligible effects of the scavengers on the debromination reaction. Addition of 1 equiv of *p*-dinitrobenzene or di-*tert*-butyl nitroxide decreased the yield of 2,3-dimethyl-2,3-dinitrobutane and increased the yields of 2-bromo-2-nitropropane and **2a**. The debromination reaction is not inhibited but enhanced by these additives. Since the substitution reaction is retarded by the scavengers,[10] the yield of 2,3-dimethyl-2,3-dinitrobutane should decrease and thus more of the 2-bromo-2-nitropropane and the base should be left unreacted. In addition, the yield of **2a** should also increase

---

[1] Bunnett, J. F. *Acc. Chem. Res.* **1992**, *25*, 2.

[2] Bordwell, F. G.; Lynch, T. Y. *J. Am. Chem. Soc.* **1989**, *111*, 1052.

[3] Bacaloglu, R.; Bunton, C. A.; Cerichelli, G.; Orgeta, F. *J. Am. Chem. Soc.* **1988**, *110*, 3495.

[4] Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

[5] Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39.

[6] Hoz, S. *Acc. Chem. Res.* **1993**, *26*, 69.

[7] Kochi, J. K.; Singleton, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1582 and references cited therein.

[8] Ono, N. Nitro Compounds; Feuer, H., Nielson, Eds.; VCH Publishers: New York, 1990; pp 113−116.

[9] Seigle, L. W.; Hass, H. B. *J. Org. Chem.* **1940**, *5*, 100.

[10] (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663. (b) Russell, G. A.; Jawdosiuk, M.; Makoza, M. *J. Am. Chem. Soc.* **1979**, *101*, 2355.

0022-3263/94/1959-3681$04.50/0

**Table 1. Products of Reactions[a,b] between $XC_6H_4CHC(Br)C(Br)(NO_2)CH_3$ and 2-Nitro-2-propyl Anion in DMSO at Ambient Temperature**

| | | | yield (%)[c,d] | | |
|---|---|---|---|---|---|
| X | PDNB[e] | DBNO[f] | $(CH_3)_2C(Br)NO_2$ | $[(CH_3)_2CNO_2]_2$ | $XC_6H_4CH{=}C(NO_2)CH_3$ |
| H | | | 79.0 | 7.0 | 82.0 |
| H[g] | | | 72.0 | 31.0 | 93.0 |
| H | 1.0[h] | | 91.0 | 3.1 | 95.0 |
| H | | 1.0[h] | 92.0 | 0.0 | 90.0 |
| *p*-MeO | | | 76.0 | 11.0 | 84.0 |
| *p*-$NO_2$ | | | 84.0 | 6.0 | 92.0 |

[a] Equivalent amounts of **1a**−**c** and the anion were reacted for 10 min except as otherwise noted. [b] [Substrate] = $4.1 - 10.0 \times 10^{-2}$ M. [c] Average of at least two runs. [d] Estimated reproducibility ±3%. [e] *p*-Dinitrobenzene. [f] Di-*tert*-butyl nitroxide. [g] Two equivalents of base were used. [h] Number of equivalents of the additive.

because more base is available for the debromination reaction. The complete absence of the substitution product in the presence of di-*tert*-butyl nitroxide reflects its greater retardation effect.[11] Finally, the reactions were not significantly influenced by the electron-withdrawing ability of the $\beta$-aryl substituent.

Why would this reaction proceed by an ionic mechanism? One plausible explanation might be the high exothermicity of this reaction. Since the strengths C-2−Br bond of **1a** and $C_\alpha$−Br bond of 2-bromo-2-nitropropane should be nearly identical, and those of C-3−Br bond of **1a** and the $\pi$ bond of **2a** should be very similar,[12a] there should be little difference in the bond energy between the reactant and the product. On the other hand, the p$K_a$ values of 2-nitropropane and HBr are approximately 7.7[12b] and −4.7,[13] respectively, from which the $\Delta G°$ value of −17 kcal/mol is calculated for this reaction. Although the value may vary depending upon the solvent, the large difference in the p$K_a$ values would undoubtedly provide enough driving force for this reaction.[14] In contrast, the redox potentials of 2-nitro-2-propyl anion and **1a** in DMSO are 0.30 and 0.025 V vs Ag/AgCl, respectively, indicating that the SET process should be endothermic by 6.3 kcal/mol. Therefore, it seems reasonable to expect that the ionic pathway is more favored.

## Experimental Section

**Materials.** Lithium salt of 2-nitropropane was prepared by a literature method.[16] 1-Aryl-2-nitropropenes **2a**−**c** were synthesized by the reactions of appropriate aryl aldehydes with nitroethane in the presence of ammonium acetate in acetic acid.[17] 1-Aryl-1,2-dibromo-2-nitropropanes **1a**−**c** were prepared by brominating **2a**−**c** in dichloroethane.[18] The NMR and IR spectra and combustion analysis data for these new compounds were consistent with the proposed structures. The melting point (°C), NMR ($CDCl_3$, ppm), IR (KBr, $NO_2$, $cm^{-1}$), and combustion analysis data for **1a**−**c** are as follows. $C_6H_5CH(Br)C(Br)(NO_2)CH_3$ (**1a**): mp 76−78; IR 1332, 1556; NMR $\delta$ 7.58 (m, 2H), 7.42 (m, 3H), 5.99 (s, 1H), 2.44 (s, 3H). Anal. Calcd for $C_9H_9Br_2NO_2$: C, 33.47; H, 2.81; N, 4.33. Found: C, 33.31; H, 2.80; N, 4.39. *p*-$CH_3OC_6H_4CH(Br)C(Br)(NO_2)CH_3$ (**1b**): mp 56−58; IR 1256, 1564; NMR $\delta$ 7.51 (d, 2H), 6.92 (d, 2H), 5.96 (s, 1H), 3.86 (s, 3H), 2.42 (s, 3H). Anal. Calcd for $C_{10}H_{11}Br_2NO_3$: C, 34.02; H, 3.14; N, 3.97. Found: C, 33.99; H, 3.03; N, 3.86. *p*-$NO_2C_6H_4CH(Br)C(Br)(NO_2)CH_3$ (**1c**): mp 56−58; IR 1350, 1528, 1560; NMR $\delta$ 8.36 (d, 2H), 7.83 (d, 2H), 6.08 (s, 1H), 2.48 (s, 3H). Anal. Calcd for $C_9H_8Br_2N_2O_4$: C, 29.40; H, 2.19; N, 7.61. Found: C, 29.66; H, 2.14; N, 8.01.

**Product Studies.** The reactions were conducted by adding an equivalent amount of **1a**−**c** to a solution of lithium 2-propanenitronate in 1.0 mL of DMSO under argon. The solution was stirred for 10 min and diluted by addition of 10 mL of acetone. The products were analyzed by gas chromatography on a 10-m HP5-530 column with mesitylene as an internal standard.

**Cyclic Voltammetry.** Cyclic voltammetric experiments were performed by the literature procedure[19] except that platinum wire was used both as the working electrode and as the auxiliary electrode, a Ag/AgCl electrode was used as the reference electrode, and $LiClO_4$ was used as the supporting electrolyte. Voltammograms were recorded at sweep rates of 100 mV/s. The cyclovoltammograms of both compounds were irreversible. For lithium 2- propanenitronate, two broad oxidation peaks were observed at 300 and 650 mV. On the other hand, **1a** showed one broad reduction peak at 25 mV. The peak potentials were reproducible within 3 mV for successive runs.

**Acknowledgment.** This research was supported by OCRC-KOSEF, Basic Science Institute Program, Korea Ministry of Education (1994).

---

(11) Kornblum, N. *Angew. Chem. Int. Ed.* **1975**, *14*, 734.

(12) (a) Dean, J. A. Handbook of Organic Chemistry; McGraw-Hill: New York, 1987; pp 3-18−3-27. (b) *Ibid.* pp 8-44.

(13) Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 67.

(14) A reviewer has made an interesting suggestion that, if the identity reaction between 2-bromo-2-nitropropane and 2-nitro-2-propyl anion that is shuttling the bromide between 2-nitropropyl groups is very fast, we have stopped the passing of the bromide by an E1cb elimination reaction. Indeed there is one literature precedent for the bromine atom transfer between 2-bromo-2-nitropropane and diethyl ethylmalonate.[15] However, a variety of cyano-stubstituted anions such as the anions of ethylmalononitrile, ethyl α-cyanopropionate, and 2-cyano-4,4-dimethyl-3-pentanone with the same substrate reacted without extensive bromine atom transfer.[15] Therefore, it is not clear whether the identity reaction between 2-bromo-2-nitropropane and 2-nitro-2-propyl anion would be very fast or not. Furthermore, even if it were very fast, it is difficult to make a mechanistic decision with the available data whether the present debromination reaction would proceed via E1cb or E2 mechanism with E1cb-like transition state.

(15) Russell, G. A.; Norris, R. K.; Panek, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5839.

(16) Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1965**, *87*, 4520.

(17) Catherine, B. G.; Gerald, R. L. *J. Org. Chem.* **1953**, *18*, 1.

(18) Priebs, B. *Ann.* **1884**, *225*, 342.

(19) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.