propyl) substrate. The initial reactant and all of the intermediates that will react with solvated electrons protect the electron-free zone until their chemistry is complete. It is after complete reduction that the boundary of the mixing process is advanced with more solvated electrons, and the same chemistry continues at or near the new boundary. The visualization of this in chemical terms is that on the time scale of these reactions the substrate finds it environment as either of two extreme situations, electron-free or electron-rich (see ref 6 and 7).

We propose that this may be another example of unusual chemical observations that may be accounted for by distortions in the product distributions that are the result of nonhomogeneous chemistry rather than the intervention of unusual reaction mechanisms or intermediates.[6-8]

Acknowledgment. We thank Mr. B. Weber for assistance in obtaining 500-MHz NMR spectra and Ms. M. Chan for the GC/MS work. Also we thank Professors J. F. Bunnett and A. Oku for helpful discussions concerning this work.

Registry No. I, 50843-60-2.

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(6) Rys, P. *Acc. Chem. Res.* **1976**, *9*, 345–351 and references therein.

(7) Tremelling, M. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7375–7377. Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *Ibid.* **1980**, *102*, 2852–2854.

(8) Oku, A.; Yoshiura, N.; Okuda, T., private communication. Subsequent work by Oku has shown the same effect in the reduction of bis(*gem*-dihalocyclopropyl) systems of the 1,2-dicyclopropylethane framework. He has also shown that by moderating the rate of electron transfer and/or the lifetimes of the intermediates, partially dehalogenated products can be obtained.

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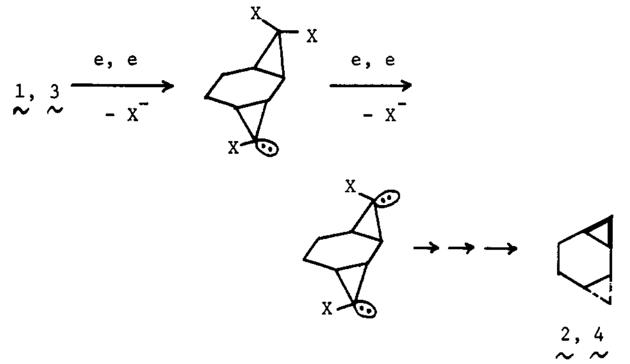
Received October 8, 1982

Nonhomogeneous Phase Effect on the Generation of Carbene Radical Anions in the Birch-Type Reduction of Bis(*gem*-dihalocyclopropyl) Compounds

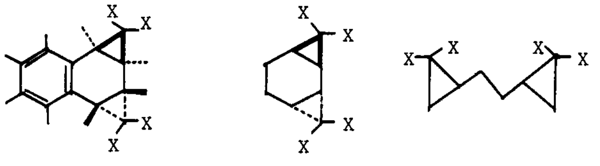
Summary: The reduction of 1,2-bis(*gem*-dichlorocyclopropyl)ethane (**5**) with sodium metal (4 molar equiv with respect to **5**) in a mixed solution of NH$_3$–THF–EtOH, which separated a metallic liquid phase on mixing, gave the parent hydrocarbon product predominantly. On the other hand, analogous reduction of **5** with lithium metal, which produced a homogeneous colored solution, predominantly gave the di- and trichloro intermediate products. The unusual results of the reduction with a nonhomogeneous reductant mixture are explained in terms of a rapid and consecutive electron transfer to the molecule which is taken into or located in the vicinity of the reductant phase. 3,3,8,8-Tetrachlorotricyclo[5.1.0.0^{2,4}]octane behaved analogously.

Sir: We report our observation of the phase effect of a liquid-to-liquid nonhomogeneous reduction system which was produced in the Birch-type reaction of *gem*-dihalides when a cosolvent was employed and which caused rapid and consecutive electron-transfer reactions to organic substrates.

Scheme I



In the preceding paper[1] we reported that the reduction of bis(*gem*-dihalocyclopropyl) compound **1** with alkali metals in NH$_3$/tetrahydrofuran (THF) with or without an added alcohol yielded only product **2** together with unreacted **1** and that the same reaction behavior was observed in the reduction of **3** with sodium metal in NH$_3$/THF/EtOH and also in the reduction of **1** (X = Br) with potassium naphthalenide in THF.[2] We then suggested that the cis-transoid-cis geometry of **1** may allow a 1,4-elimination-type remote ionization effect (Scheme I) under which the reactivity of the intact ring is enhanced by the initially reduced ring.



1, X = Cl or Br
2, X = H
3, X = Cl
4, X = H
5, X = Cl
6, X = H

If this mechanism is correct, it can be applied only to such sterically rigid tricyclic systems as **1** and **3** but not to such a system as 1,2-dicyclopropylethane. In order to verify the validity of this assumption, we studied the reduction of 1,2-bis(*gem*-dichlorocyclopropyl)ethane (**5**)[3] with sodium metal in a mixed solution of NH$_3$–THF–EtOH. Results are shown in Table I, and it turned out that the entirely reduced hydrocarbon **6** was the major product besides unreacted **5**. This finding is analogous to those with regard to **1** and **3** and excludes the involvement of the 1,4-elimination effect. Tremelling and Kaur also proved that this effect is unlikely by examining the reduction of 4,4,8,8-tetrachlorotricyclo[5.1.0.0^{3,5}]octane with potassium metal in NH$_3$/THF.[4]

Then why were the compounds (**1**, **3**, **5**) completely reduced under such reduction conditions? Before any arguments, a peculiar phenomenon which was observed in the reduction solution must be noted. When sodium or potassium metal was added to a mixed solution of NH$_3$ and THF at or below −50 °C (NH$_3$/THF ratio of 60:20 to 20:60, v/v), the solid metal dissolved to give a deep-blue solution. A careful observation, however, showed that a metallic liquid phase (or its dispersed phase) was separated on the

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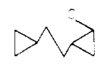
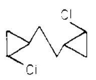
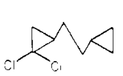
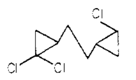
(1) Oku, A.; Tsuji, H.; Yoshida, M.; Yoshiura, N. *J. Am. Chem. Soc.* **1981**, *103*, 1244.

(2) The reduction of 1 with sodium naphthalenide yielded 1,2:3,4-diethylidene-1,2,3,4-tetrahydro-2,3,5,6,7,8-hexamethylnaphthalene (11) and was explained in terms of the rearrangement via a cyclopropylidene intermediate: Oku, A.; Yagi, K. *J. Am. Chem. Soc.* **1974**, *96*, 1966. The reaction of 1 (X = Br) with potassium naphthalenide produced 2 in addition to 11.

(3) A 1:1 mixture of meso and *dl* isomers was used.

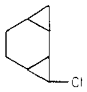
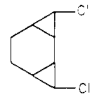
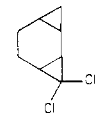
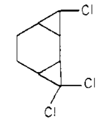
(4) Tremelling, M. J.; Kaur, S., private communication, to be submitted for publication in *J. Org. Chem.*

Table I. Reduction of 5 with Alkali Metal in NH_3/THF Solution at −60 °C

		product distribution, % yield[a]						
NH_3/THF ratio (mL)	metal[d]	5 (unreacted)	6					total yield, %
40/40	Na[b]	31	36	9	7	0	1	84
40/40	Li[c]	29	25	5	13	1	14	87
20/60	Li[c]	3	4	7	54	6	10	84

[a] Determined by VPC with hexadecane as the internal standard. [b] A metallic liquid phase was separated. [c] The entire reaction mixture gave a homogeneous solution. [d] The molar ratio of metal was 4.0 and that of EtOH was 4.5 with respect to 5 (1 g) in all cases.

Table II. Reduction of 3[d] with Alkali Metal in NH_3/THF Solution at −60 °C

					product distribution, % yield[a]				
NH_3/THF ratio (mL)	molar ratio[e] of EtOH	metal[f]	3 (unreacted)	4					total yield, %
40/40	4.5	Na[b]	43	43	5	4	0	1	96
40/40	80	Na[b]	44	36	7	6	0	3	96
40/40	4.5	Li[c]	12	25	4	19	1	14	75
20/60	4.5	Li[c]	3	18	15	32	0	8	76

[a] Determined by VPC using heptadecane as the internal standard. [b,c] See footnotes *b* and *c* in Table I. [d] 1.0 g used in all cases. [e] With respect to 3. [f] The molar ratio was 4.0 with respect to 3 in all cases.

surface of the solution. A more distinct appearance of this metallic liquid was observed in the presence of ethanol or halides: in this mixture the blue color was not diffused in the entire solution but was restricted to only around the surface of the separated phase.

This means that alkali metals (Na, K) cannot form a homogeneous solution in a mixed solvent of liquid ammonia and THF but are separated as a liquid phase which probably consists of the metal and NH_3. A halide molecule which is taken in, or located at the vicinity of, the phase is placed under a high concentration of the reductant[5,6] and probably is subjected to a faster electron transfer than its diffusion.

We thought this assumption could be tested by a homogeneous reductant system where, the entire solution being occupied by solvated electrons (deep colored) in the presence of alcohol, the electron transfer can compete with the protonation of carbanionic intermediates. For this purpose we chose a system of lithium in NH_3/THF/EtOH. A required amount of ammonia was condensed into a THF solution of 3 (or 5) and ethanol at -60 °C to give a clear solution, to which was added a block of Li metal all at once. As the metal dissolved, the entire solution turned dark but did not separate a metallic liquid phase. After the color changed into light gray, the mixture was worked up and analyzed by VPC.

The results in Tables I and II show contrasting product distributions between the nonhomogeneous (Na in NH_3/THF) and the homogeneous (Li in NH_3/THF) reduction phases. In the nonhomogeneous system the completely reduced product was predominantly formed whereas in the homogeneous system half-reduced intermediate products[10] were the major components, particularly when the relative amount of ammonia to THF was decreased.

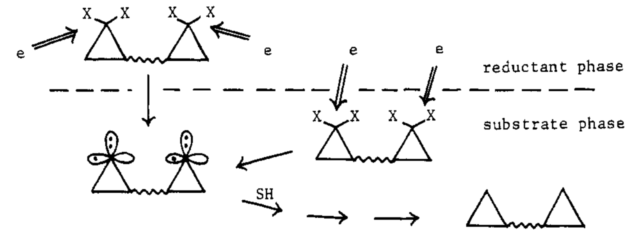


Figure 1.

This difference can be explained as follows. In a homogeneous solution with lithium the rates of electron transfer to *gem*-dihalide and its descendant carbanionic intermediates become comparable to the rates of protonation of the intermediate carbanions because (1) the reducing power of lithium in ammonia is lower than that of sodium or potassium, (2) the stability of carbanionic intermediates increases more with lithium countercation than sodium or potassium, and (3) the concentration of ethanol in the surrounding sphere of carbanionic substrates is relatively higher than in nonhomogeneous systems. When the polarity of the medium is lowered by the decrease of the NH_3/THF solvent ratio, the rate of electron transfer becomes much slower, and the stability of carbanions increases; thus the amount of half-reduced products was increased. In a nonhomogeneous system, or in a pseudononhomogeneous system, as in the case of mixing a THF solution of potassium naphthalenide with a THF (or dimethoxyethane) solution of *gem*-dihalide, the electron transfer to the molecule which is taken in, or locating at the vicinity of, the reductant phase takes place rapidly. Here, most functional groups of the molecule which can potentially be reduced within the time scale of diffusion

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(5) Not the effect of separated phases but a similar effect of reagent mixing was proposed in the $S_{RN}1$ reaction of aryl halides by: (a) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2852. (b) Tremelling, M. J.; Bunnett, J. F. *Ibid.* **1980**, *102*, 7377.

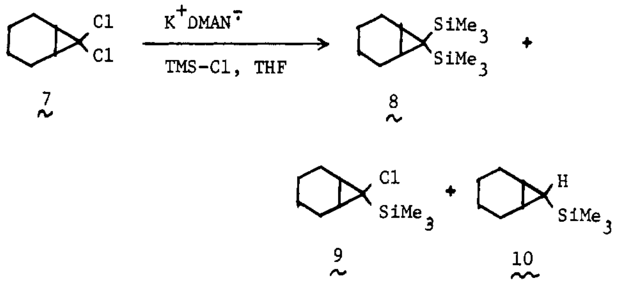
(6) For the electron-transfer reduction from alkali metal surfaces, see: (a) Walborsky, H. M.; Powers, E. J. *Isr. J. Chem.* **1981**, *21*, 210. (b) Walborsky, H. M.; Banks, R. B. *Bull. Soc. Chim. Belg.* **1980**, *89*, 849.

(7) There are references describing the reduction power of alkali metals in solutions. (a) Szwarc, M. *Acc. Chem. Res.* **1972**, *5*, 167. (b) Szwarc, M.; Jagur-Grodzinski, J. "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974; Vol. 2, pp 1–150.

(8) For other examples of generating hypovalent radical anions, i.e., carbene radical anions, see: (a) McDonald, R. N.; Lin, K.-W. *J. Am. Chem. Soc.* **1978**, *100*, 8028 and references cited therein. (b) Sargent, G. D.; Tatum, C. M., Jr.; Kastner, S. M. *Ibid.* **1972**, *94*, 7174.

will undergo consecutive electron transfer before leaving the reduction sphere and being protonated as illustrated in Figure 1.

The phase effect observed here is also compatible with the carbene radical anion mechanism[1] which was proposed to explain the predominant formation of the parent hydrocarbon products in these reactions. Additional evidence for the intermediacy of carbene radical anions in these reaction systems is provided as follows. The reduction of 7,7-dichlorobicyclo[4.1.0]heptane (**7**) with potassium 1-(dimethylamino)naphthalenide (K^+ $DMAN^{-\cdot}$) at −78 °C in the presence of an excess amount of chlorotrimethylsilane (Me_3SiCl) gave 7,7-bis(trimethylsilyl)- (**8**, 17%), 7-chloro-7-(trimethylsilyl)- (**9**, 41%), and 7-(trimethylsilyl)bicyclo[4.1.0]heptane (**10**, 34%).[9] When **9** was independently treated with $K^+DMAN^{-\cdot}$ in the presence of Me_3SiCl, it remained unreacted until the Me_3SiCl was consumed, and it slowly produced **10** instead of **8**. This means that compound **9**, once formed as the result of a stepwise silylation of **7**, must survive its further reduction to **8** in this reductant system which apparently is a pseudononhomogeneous solution reducing *gem*-dihalides. Therefore, **8** must be produced not via **9** but most likely via a cyclopropylidene radical anion. These results are comparable with the in situ quenching by 2-propanol-*d* in the reduction of **1** (X = Cl) with potassium naphthalenide,[1] where the intermediately formed monochlorocyclopropane compounds reacted with naphthalenide more slowly than the starting *gem*-dichloro compound.



Acknowledgment. This work was supported by Grant-in-Aid for Environmental Science from the Japan Ministry of Education (No. 57035024).

Registry No. 1 (X = Br), 36807-30-4; 3, 54082-70-1; 4, 50895-58-4; *meso*-5, 63183-84-6; (±)-5, 63152-30-7; 6, 37520-11-9; 7, 823-69-8; 8, 56431-99-3; 9, 84472-99-1; 10, 67957-93-1; K^+-$DMAN^{-\cdot}$, 82136-09-2; Na, 7440-23-5; Li, 7439-93-2; ethanol, 64-17-5; 1-chloro-2-(2-cyclopropylethyl)cyclopropane, 84473-00-7; 1,2-bis(2-chlorocyclopropyl)ethane, 84473-01-8; 1,1-dichloro-2(2-cyclopropylethyl)cyclopropane, 84473-02-9; 1,1-dichloro-2-[(2-chlorocyclopropyl)ethyl]cyclopropane, 84473-03-0; 3-chlorotricyclo[5.1.0.$0^{2,4}$]octane, 84473-04-1; 3,8-dichlorotricyclo[5.1.0.$0^{2,4}$]octane, 84473-05-2; 3,3-dichlorotricyclo[5.1.0.$0^{2,4}$]octane, 63098-57-7; 3,3,8-trichlorotricyclo[5.1.0.$0^{2,4}$]octane, 84519-58-4; 7,7-dibromobicyclo[4.1.0]heptane, 2415-79-4.

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(9) The yield of **8** increased to 42% when the 7,7-dibromo derivative was treated under the same conditions.

(10) Structures of partially reduced intermediate products appearing in the product column of Tables I and II were determined on the basis of VPC–mass spectral analysis, separation, and further reduction to produce parent hydrocarbon **6** or **4**. Products bearing monochlorocyclopropane ring(s) were obtained as a mixture of stereoisomers with regard to the cis, trans geometry. *gem*-Dichloro products were independently synthesized via a stepwise CCl_2 addition–reduction–CCl_2 addition procedure.

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Received November 15, 1982

Relative Donor-Atom Effects on Rates of Isomerization of 3-Butenenitrile Catalyzed by Anions of the Same Basicity

Summary: For base-catalyzed isomerization of 3-butenenitrile in Me_2SO solution the order of rate constants for anions of the same basicity is $ArS^- > ArO^- > RSO_2NAr^- > 9\text{-G-Fl}^-$ (9-substituted fluorenyl carbanions). The relative rate constants vary somewhat with basicity since the Brønsted β values are 0.77, 1.0, 0.82, and ~0.8, respectively.

Sir: In previous communications we have shown that, in Me_2SO solution, rate constants for both S_N2 and E2 reactions of anions with alkyl halides correlate with the basicity of the anion as long as steric effects and the nature of the donor atom remain constant. Rate constants for anions of the same basicity, but with different kinds of donor atoms, may differ in either kind of reaction by factors greater than 10^4, however, and the relative order for S_N2 and E2 reactions is not the same. For example, toward $PhCH_2Cl$, S_N2 rate constants for anions of the same basicity are in the order $ArS^- \gg 9\text{-G-Fl}^-$ (9-substituted fluorenyl carbanions) $> 2\text{-NpO}^-$ (2-naphthoxide oxanions) $> Cb^-$ (carbazole nitranions),[1a] whereas toward cyclohexyl bromide ($c\text{-}C_6H_{11}Br$) the order of E2 rate constants is $ArS^- \gg 2\text{-NpO}^- > Cb^- > 9\text{-G-Fl}^-$.[2] As a consequence of this difference in order 9-G-Fl^- carbanions react with $c\text{-}C_6H_{11}Br$ almost exclusively by an S_N2 pathway, whereas 2-NpO^- and Cb^- anions react with $c\text{-}C_6H_{11}Br$ almost exclusively by an E2 pathway.[2]

It seemed likely that the difference in reactivity order arose because of different inherent affinities of the various donor atoms in the anions for hydrogen in E2 reactions as compared to carbon in S_N2 reactions. We wondered, however, to what extent the difference was caused by the interaction of the donor atom with hydrogen, per se, i.e., deprotonation, as compared to the interaction of the donor atom with hydrogen in the context of the E2 transition state. As a first step in trying to answer this question we examined the effect of anions of the same basicity on the rate of isomerization of $CH_2{=}CHCH_2CN$ (**1**) to (*E*)- and (*Z*)-$CH_3CH{=}CHCN$ (**2**). Rate constants for the isomerization of **1** to **2** by 9-G-Fl^-, RSO_2NAr^-, ArS^-, and ArO^- ions are summarized in Table I and Brønsted plots are shown in Figure 1.

Examination of Figure 1 shows that the relative rate constants for catalysis of the isomerization of **1** to **2** by anions of the same basicity are as follows: $ArS^- > ArO^-$ (by 0.6 log unit at $pK_a = 10$);[3,4] $ArO^- > RSO_2NAr^-$ (by 0.6 log unit at $pK_a = 13$);[3] $RSO_2NAr^- > 9\text{-G-Fl}^-$ (by 1.4 log units at $pK_a = 14$).[3] The order $S^- > O^- > N^- > C^-$ is the same as was observed for E2 rate constants with $c\text{-}C_6H_{11}Br$,[2] but the total spread of rate constants between S^- and C^- is only about 2.5 log units for the isomerizations compared to over 4 log units for the eliminations. These and earlier results[5,6] suggest that such donor-atom effects

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(1) (a) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 169–170. (b) *Ibid.* **1982**, *47*, 3224–3232.

(2) Bordwell, F. G.; Mrozack, S. R. *J. Org. Chem.* **1982**, *47*, 4813–4815.

(3) Since the slopes of the lines differ slightly, the rate constants vary somewhat with the basicity at which the comparison is made.

(4) Thianions show a higher reactivity than oxanions of the same basicity at $pK_a = 10$ in Me_2SO, but the greater slope for the oxanion line suggests that the lines will cross at $pK_a = 13$ (see the dashed line in Figure 1).

0022-3263/83/1948-0619$01.50/0