Reductive Cleavage of 9,9-Diarylfluorenes by Potassium in 1,2-Dimethoxyethane[1]

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Abstract: Reduction of 9,9-diarylfluorenes by potassium in 1,2-dimethoxyethane results in cleavage of one of the aryl rings to form 9-arylfluorenyl anions. Product analyses and kinetic studies indicate that cleavage occurs via dianions, produced by disproportionation of the initially formed radical anions.

Reduction of aromatic hydrocarbons (Ar) often results in C–C bond cleavage. The question of whether the radical anion ($Ar^{-}\cdot$) or the dianion (Ar^{2-}) is the species undergoing cleavage is often difficult to answer, because disproportionation of radical anions produces dianions, even if a deficiency of reducing agent is employed. If Ar^{2-} is much more susceptible to cleavage than $Ar^{-}\cdot$, reaction can occur through the former, even if it is present only in minute amounts.

To our knowledge, dianion intermediacy has been unequivocally demonstrated in only one report of reactions of this type. For the reductive cleavage of 1,2-di(α-naphthyl)ethane to α-methylnaphthyl carbanions, Lagendijk and Szwarc observed a kinetic rate law which is second order in $[Ar^{-}\cdot]$ and inversely proportional to [Ar], as required for dianion intermediacy by Scheme I.[2]

Gilman and Gorsich[3] and Janzen, Harrison, and Pickett[4] have reported cleavage of 9,9-diphenylfluorene by alkali metals in ethereal solvents, as shown in Scheme II. Since this reaction occurs at a convenient rate at room temperature, thus avoiding many of the problems encountered by Tabner and co-workers in their extensive studies of C–H cleavages of fluorenes,[5] we have investigated this system further.

Results

Product Studies. A series of compounds, **1**, was reduced with potassium in 1,2-dimethoxyethane (DME) at room temperature (conditions in which $1^{-}\cdot$ is observed[4]). Relative cleavage aptitudes were established by GC analyses of the product mixtures obtained after quenching with methanol and are listed in Table I. Runs 4 and 6 ensured incomplete reduction of **1** prior to cleavage. Run 4, in which potassium biphenylide was used as the reducing agent, shows somewhat less selectivity than the others; run 6, involving only three momentary mirror contacts, has the same product ratio as run 5.

Kinetic Studies. The disproportionation mechanism of Scheme I requires a rate law of the form

$$-d[Ar^{-}\cdot]/dt = k_2K[Ar^{-}\cdot]^2/[Ar] \qquad (1)$$

Assuming constant [Ar] throughout the reaction, and validity of the Beer–Lambert law for $Ar^{-}\cdot$, where $A = \epsilon b[Ar^{-}\cdot]$, this becomes

$$R \equiv -dA/dt = kA^2 = k'A^2/[Ar] \qquad (2)$$

where $k' = k_2K/\epsilon b$.

Scheme I

$$2Ar^{-}\cdot = Ar + Ar^{2-} \qquad K = k_1/k_{-1}$$
$$Ar^{2-} \rightarrow \text{products} \qquad k_2$$

Scheme II

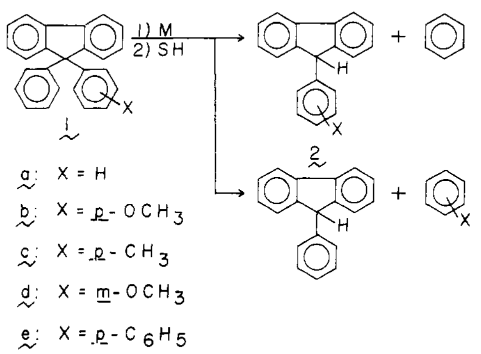

Table I. Products of the Reductive Cleavage of **1** by K in DME

compd no.	run no.	ratio[a]	conversion, %	K contact time, min
1b	1	0.118	34	35
1c	2	0.360	17	*b*
	3	0.360	46	20
	4	0.487[c]	29	
1d	5	2.76	100	110
	6	2.76[d]	24	0.25
1e	7	*e*	100	20

[a] Mole ratio of 9-phenylfluorene (**2a**) to 9-arylfluorene (**2b–e**). [b] Solution used for five kinetic runs (solution D in Table II). Contact time not measured. [c] Reduction by successive small portions of potassium biphenylide in DME, allowing complete conversion to products between additions. [d] Only three momentary contacts with K mirror, allowing complete conversion to products between contacts. [e] No **2e** observed.

The required second-order rate law was observed for **1b**, **1c**, and **1d**. Table II shows that set of values of the apparent second-order rate constant, *k*, obtained by the usual treatment utilizing the integrated rate expression. Similar values were obtained by two other methods of data treatment (see Experimental Section). The inverse dependence on [Ar] is clear. Values of *k′* are also listed, obtained by multiplying *k* by [Ar]. The greatest discrepancies for each compound can be seen in those runs with low [**1**], reflecting the uncertainty in measuring [**1**]. Also, [**1**] was assumed to be unchanged from one run to another when using the same solution. In one case (compound **1c**) in which products were analyzed after five kinetic runs, 17% of the starting material had been consumed.

Discussion

We are led to conclude that reduction of 9,9-diarylfluorenes by potassium in DME results in cleavage according to Scheme I, with the dianion, formed by disproportionation of the initially formed radical anion, producing a 9-arylfluorenyl anion and a σ aryl anion as primary products.

That the aryl substituent leaves as an anion is shown by the large polar effect on cleavage aptitude. Excluding **1e**, a Hammett plot yields $\rho = 3.4$. This compares favorably with other studies

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(1) Taken from the M.S. Thesis of T.L.M., UNCC, 1980. A preliminary report was presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, March 1980.

(2) Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359–5363.

(3) Gilman, H.; Gorsich, R. D. *J. Org. Chem.* **1958**, *23*, 550–551.

(4) Janzen, E. G.; Harrison, W. B.; Pickett, J. B. *J. Organomet. Chem.* **1969**, *16*, P48–P50.

(5) Tabner, B. J.; Walker, T. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1304–1306 and earlier papers in the series.

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Table II. Kinetics of Reductive Cleavage of **1** by K in DME at 25.0 °C

					$k' \times 10^6$, M s^{-1}		
compd no.	run no.[a]	$[1] \times 10^4$, M	A_0	$k \times 10^4$, s^{-1} [b]	int[b]	TL[c]	IR[d]
1b	A1	3.7	0.100	25	0.94		1.8
	B1	30	0.560	5.2	1.6	1.9	1.7
	B2		0.733	3.0	0.89	0.87	0.82
	B3		0.767	3.2	0.97	1.0	0.97
	B4		0.505	3.9	1.2	0.89	1.1
	B5		0.328	3.7	1.1		1.0
	C1	9.2	0.580	7.3	0.67	0.65	0.63
	C2	42[e]	0.881	2.0	0.82		0.85
				average	1.0 ± 0.3	1.1 ± 0.5	1.1 ± 0.4
1c	D1	15	0.722	6.9	1.0	0.92	0.71
	D2		0.635	8.2	1.2	1.3	0.91
	D3	48[e]	0.776	1.6	0.77	0.79	0.70
	D4	76[e]	0.764	1.6	1.2	1.2	1.0
	D5		0.887	1.6	1.2	1.2	1.1
				average	1.1 ± 0.2	1.1 ± 0.2	0.9 ± 0.2
1d	E1	4.7	0.211	110	5.2		3.3
	F1	28	0.533	18	5.0		3.5
	F2		0.486	20	5.5	5.9	3.7
	G1	82	0.487	6.6	5.4		5.2
				average	5.3 ± 0.2		3.9 ± 0.9

[a] Letters designate the solutions used. [b] Integrated rate expression. [c] Time lag method of ref 18. [d] Initial rate method. [e] Portions of solid **1** were added between runs to increase $[1]_0$.

of formation of σ aryl anions ($\rho = 2.2$,[6] 4[7]). The high cleavage aptitude of the *p*-biphenylyl anion is also consistent with findings by Streitwieser[8] and Shatenshtein[7] that the acidity of the 4 position of biphenyl is about three times greater than that of benzene, even though σ for a *p*-phenyl group is close to 0. Finally, the order of cleavage is inconsistent with that expected for free radical leaving groups.[9]

Table II shows that **1d** reacts about five times faster than either **1b** or **1c**, which have comparable rates.[10] Since **1b** and **1c** predominantly cleave an unsubstituted phenyl group, this indicates that the stability of the incipient 9-arylfluorenyl anion is not the rate-controlling factor. This conclusion is also supported by the product studies. Cleavage of **1e** yields 9-phenylfluorenyl and *p*-biphenylyl anions, not the more stable 9-*p*-biphenylylfluorenyl anion. Also, trends in cleavage do not correspond to fluorenyl anion stabilities, as shown by the pK_a values of aryl-substituted fluorenes,[11] but rather to σ aryl anion stabilities.[12]

Finally, preliminary results with **1a** and sodium in DME indicate first-order kinetics. A change of kinetic order with metal has been reported by Tabner and co-workers in several examples of 9-hydrofluorene cleavages, but was not attributed to the presence or absence of disproportionation.[5] In fact, the trends toward second-order kinetics in Tabner's compounds run counter to those favoring disproportionation. In one case in which a second-order rate law was observed, the rate was shown not to depend on [Ar].[13] In our case, the shift in kinetic order is consistent with the report that disproportionation is favored with potassium relative to sodium in DME.[14]

Experimental Section

All fluorenes were prepared by reaction of the Grignard reagent of 2-bromobiphenyl with the appropriate carbonyl compound, followed by ring closure with HCl in acetic acid.[15] Recrystallization from aqueous methanol afforded products whose properties agreed with literature values where available.[11,16] Purities were checked by GC (Dexsil 300, 320 °C, He 35 mL/min). For 9-phenyl-9-*p*-biphenylylfluorene (**1e**): mp 169–170 °C, *m/e* 394.1729 (100%, calcd for $C_{31}H_{22}$ 394.1723), 317 (38), 271 (29), 267 (14), 241 (13), 239 (13), 193 (32).[17]

Dimethoxyethane was purified by standard techniques and stored over Na/K alloy. Reactions were conducted using vacuum line techniques in an all-glass apparatus, with break-seals for reagent transfer. Potassium metal was triply distilled into a side arm tube which was separated by a coarse frit or by glass beads from the main reaction compartment. Products were analyzed by GC.

Kinetic studies utilized an attached optical cell; the absorption maximum at 624–626 nm was monitored. Since OD_∞ values were unreliable over the time span required, a computer program calculated the OD_∞ which gave the smallest standard deviation from the desired linear second-order relation. This was 1.3% or better for all runs except A1 (3.9%). No satisfactory fit could be obtained for a first-order rate law. The data were also treated by the time lag method of Espenson,[18] which allows determination of both OD_∞ and the apparent second-order rate constant, *k*. In those cases in which data covered more than 75% of the reaction, OD_∞ calculated by the two methods agreed to within ±0.009. Rate constants calculated with the time lag method showed standard deviations from 0 to 7% for runs covering more than 75% of the reaction (average 3.5%). Runs B1 (7.8%) and B4 (13.3%) were of shorter duration. Initial rates were obtained by differentiation of the best polynomial fit to the absorption-time data. With these initial rates, values of *k'* were obtained by use of eq 2.

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(7) Shatenshtein, A., as cited by Streitwieser, A., Jr. "Progress in Physical Organic Chemistry"; Interscience: New York, 1965; Vol. 3, p 70.

(8) Streitwieser, A., Jr.; Lawler, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 2854–2855; corrected in ref 6.

(9) (a) Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5504–5507. (b) Solomon, S.; Wang, C. H.; Cohen, S. G. *Ibid.* **1957**, *79*, 4104–4107.

(10) This assumes equal molar absorptivities for all compounds. Since the 9-aryl substituents are formally isolated from the fluorenyl ring system, this is probably valid, at least to the extent required here.

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(12) Alternatively, the dianion might possess some excess electron density in the ring which cleaves, a situation favored by electron-withdrawing groups and especially **1e**.

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(16) (a) Nakamura, M.; Nakamura, N.; Oki, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1097–1101. (b) Hart, H.; Sedor, E. *J. Am. Chem. Soc.* **1967**, *89*, 2342–2347.

(17) Mass spectra were obtained from the NSF Regional Instrumentation Facility, The Johns Hopkins University, Baltimore, Maryland.

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