Kinetics of the Oxidation of Fluorenes to Fluorenones by Hypobromite in Aqueous Dioxane[1]

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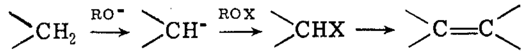
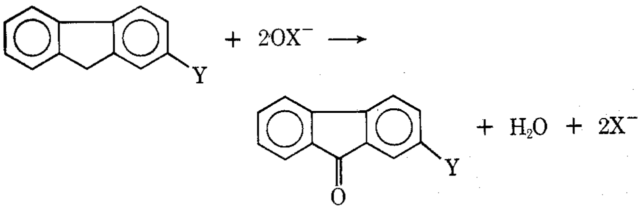
Oxidation of 2-substituted fluorenes to the fluorenones with alkaline hypobromite in aqueous dioxane has been kinetically studied by means of uv spectrophotometry and glc analysis. The rate is expressed as $v = k_1$[fluorene][NaOH] at [NaOH] < 0.4 *M*, and $v = k_2$[fluorene][OBr$^-$]/[Br$^-$] at [NaOH] > 0.6 *M*. The effect of 2 substituents on the reaction of fluorenes with a mixture of Br_2–NaOH at 25° and at [NaOH] = 0.01–0.1 *M* gives a ρ value of +4.40. The reaction of 2-bromofluorene with alkaline hypobromite at higher concentrations of NaOH (2.1 *M*) and NaBr (1.0 *M*) afforded 2,9-dibromofluorene. A mechanism is postulated, which involves a proton abstraction from the 9 position of the fluorene followed by a rapid hypobromite attack to give the 9-bromofluorene and then the fluorenone. The rate-determining step changes from proton abstraction to oxidation of 9-bromofluorene with increasing the concentration of NaOH. For the elucidation of later steps, the rate of hypobromite oxidation of 2,9-dibromofluorene to 2-bromofluorenone was measured; the observed rate expression, $v = k_3$[2,9-dibromofluorene][OBr$^-$]/[Br$^-$], suggests a mechanism involving elimination of Br$^-$ from 9-bromofluorene followed by an attack of OBr$^-$ to give the fluorenone.

The compounds bearing an active methylene group are oxidized by hypohalite to give dimeric olefinic derivatives in alkaline solutions[2-4] with some exceptions such as haloform reaction. For example, benzyl cyanides react with hypohalite to give α,α'-dicyanostilbenes.[2] A number of workers[2-4] have studied these reactions and suggested mechanisms involving an initial formation of carbanion, which is halogenated and then condensed to dimeric products.



9-Halofluorene reacts also with alkali to give bifluorenylidene (**9**),[5] but 2-acetylfluorene is oxidized by potassium hypochlorite to fluorenone-2-carboxylic acid, but not the expected dimer.[6] We observed that fluorenes often yielded the corresponding fluorenone by the hypohalite oxidation under certain conditions.



The mechanism of these oxidations of fluorenes has not yet been studied and there is no appropriate explanation for the different oxidation behaviors between fluorenes giving fluorenones and others giving dimer.

The authors wished to clarify these phenomena and the mechanism concerning oxidation of fluorenes. The present paper reports a study on kinetics and mechanism for the hypobromite oxidation of fluorenes and 9-bromofluorene, a probable intermediate, in alkaline aqueous dioxane by following the formation of fluorenone by uv spectrophotometry or glc analysis.

Results

Products. Fluorenes were treated with alkaline hypobromite in aqueous dioxane (27% water) at 25°. Fluorenones were produced in good yields from fluorenes with electron-attracting groups and no other products were detected. Their yields were estimated by means of glc and shown in Table I. On the other hand, 2,9-dibromofluorene was obtained by the treatment of 2-bromofluorene with sodium hypobromite in the presence of excess sodium hydroxide (2.1 *M*) and sodium bromide (1.0 *M*) in aqueous dioxane (27% water) at 25°.

Table I
Products and Yields[a] of the Reaction[b] of Fluorenes with Hypobromite in Alkaline Aqueous Dioxane (27% Water) at 25° for 5 hr

Substituent of fluorene, 10^{-3} *M*	Registry No.	Products yields: Fluorenone, %	Products yields: Bifluorenylidene, %
2-NO_2 (1.85)	607-57-8	100	
2-CN (2.30)	2523-48-0	100	
2-Br (1.95)	1133-80-8	96	
2-Ac (2.21)	781-73-7	99[c]	
2-MeO (2.03)	2523-46-8	15	
None (2.42)	86-73-7	5	
2,9-diBr (1.53)[d]	6633-25-6		100
2,9-diBr (0.306)		100	
2,9-diBr (1.53)		98	Trace
2,9-diBr (30.6)		87	13

[a] Yields were calculated by measurement of glc analysis of product and starting fluorene, since there is no by-product. [b] $[NaOBr]_0$ = 0.125 *M*, $[NaOH]_0$ = 0.125 *M*. [c] Fluorene-2-carboxylic acid. [d] Reaction with NaOH alone (0.125 *M*).

The reaction of 2,9-dibromofluorene with alkaline hypobromite under the same conditions as fluorenes gave 2-bromofluorenone and 2,2′-dibromobifluorenylidene but no other products detectable by glc analysis. The yield of bifluorenylidene increased with increasing the concentration of 2,9-dibromofluorene (Table I).

Kinetics. The rate of the reaction of 2-bromofluorene (2.00×10^{-5} *M*) with sodium hypobromite (0.0199–0.199 *M*) in alkaline (NaOH, 0.007–0.687 *M*) aqueous dioxane (75% water) was measured by means of uv spectrophotometry of product at 25°.

The pseudo-first-order rate constants in the rate equation of $v = k_{obsd}([\text{2-bromofluorene}]_0 - [\text{2-bromofluorenone}])$ are listed in Table II, where $[\ ]_0$ means initial concentration. The k_{obsd} value is proportional to the concentration of alkali up to 0.4–0.5 *M* sodium hydroxide, but is independent of the concentration of BrO$^-$ and Br$^-$.

$$v = k_1[\text{2-bromofluorene}][OH^-] \qquad (1)$$

Table II
Pseudo-First-Order Rate Constants for the Reaction of 2-Bromofluorene with NaOBr in Alkaline Aqueous Dioxane (75% Water) at 25°

Initial concn					
$[NaOBr]_0$, 10^{-2} M	$[NaOH]_0$,[a] 10^{-2} M	$[NaBr]_0$,[b] 10^{-2} M	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_1$,[c] M^{-1} sec^{-1}	$10^4 k_2$,[d] sec^{-1}
1.99	17.7	3.99	5.39	30.5	
1.99	17.7	4.49	5.30	29.9	
1.99	17.7	4.99	5.35	30.2	
1.99	17.7	6.99	3.53		12.3
1.99	17.7	11.99	2.12		12.8
1.99	0.7	1.99	0.267	37.4	
1.99	9.2	1.99	2.60	28.3	
1.99	17.7	1.99	5.33	30.1	
1.99	26.2	1.99	7.22	27.6	
1.99	34.7	1.99	10.00	28.8	
1.99	43.2	1.99	10.7	(24.8)[e]	(10.7)[e]
1.99	51.7	1.99	12.2	(23.7)[e]	(12.2)[e]
1.99	60.2	1.99	12.2		12.2
1.99	68.7	1.99	12.3		12.3
4.99	17.7	4.99	5.33	30.1	
7.50	17.7	7.50	5.32	30.1	
9.98	17.7	9.98	5.33	30.1	
15.0	17.7	15.0	5.26	29.7	
19.9	17.7	19.9	5.32	30.1	
1.91	100	97.2	0.249		12.7
3.82	100	99.1	0.467		12.1
5.73	100	101	0.704		12.4
7.64	100	103	0.995		13.4

[a] Added concentration. [b] Total concentration. [c] $k_1 = k_{obsd}/[NaOH]_0$. [d] $k_2 = k_{obsd}[NaBr]_0/[NaOBr]_0$. [e] These values are in the break point of the plot of k_{obsd} *vs.* $[NaOH]_0$; hence the k_1 and k_2 values deviate.

However, when the concentration of alkali is over 0.6 M, the rate is independent of $[OH^-]$ and expressed as

$$v = k_2[\text{2-bromofluorene}][OBr^-]/[Br^-] \quad (2)$$

The rate of the oxidation of 2,9-dibromofluorene, a probable intermediate, was measured in aqueous dioxane (75% water) at 25°. The formation of bifluorenylidene was negligible at this low concentration of 2,9-dibromofluorene (2.12×10^{-5} M). The data are listed in Table III. The pseudo-first-order rate constant, k_{obsd}', in the equation of $v = k_{obsd}'([\text{2,9-dibromofluorene}]_0 - [\text{2-bromofluorenone}])$ is proportional to the concentration of OBr^- and inversely proportional to the concentration of Br^-. Thus the rate is expressed as

$$v = k_3[\text{2,9-dibromofluorene}][OBr^-]/[Br^-] \quad (3)$$

The rate constant k_3 is approximate to the k_2 value in eq 2.

Substituent Effect. Relative rates for the reaction of 2-nitro-, 2-cyano-, 2-acetyl-, 2-bromo-, 2-methoxy-, and unsubstituted fluorenes with sodium hypobromite were measured in alkaline aqueous dioxane (27% water, $[OH^-] = 0.0125–0.125$ M) at 25° by means of glc. The data are listed in Table IV, which gives a ρ value of 4.40 ($r = 0.986$) with Hammett's σ(meta).

Discussion

Initial Stage. Carbanion Formation. In our previous paper[2] on the kinetics for the oxidative coupling of benzyl cyanides with alkaline hypohalites, we suggested a mechanism which involves a rate-determining α-proton abstraction from benzyl cyanide followed by a rapid hypohalite attack to give α-halobenzyl cyanide. The analogous kinetic data, *i.e.*, the rate law (eq 1) and substituent effect at $[NaOH] < 0.4$ M, are also obtained in the oxidation of fluorenes to fluorenones and these data suggest a rate-determining abstraction of the 9 proton of fluorenes **1** to give carbanion **2** at an initial stage. In other words, rate eq 1 implies that one molecule of fluorene and a base should participate in the rate-determining step. The large ρ value of 4.40 is similar to those ρ values of 3–4 for a number of reactions which involve a rate-determining deprotonation to give carbanion.[2,7]

Table III
Pseudo-First-Order Rate Constants for the Oxidation of 2,9-Dibromofluorene with NaOBr in Alkaline Aqueous Dioxane (75% Water) at 25°

Initial concn				
$[NaOBr]_0$, 10^{-2} M	$[NaOH]_0$,[a] 10^{-2} M	$[NaBr]_0$,[b] 10^{-2} M	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_3$,[c] M^{-1} sec^{-1}
1.91	100	97.2	0.251	12.8
3.82	100	99.1	0.495	12.8
5.73	100	101	0.758	13.5
7.64	100	103	1.01	13.6
1.52	100	9.55	2.03	12.8
1.52	100	19.1	0.906	11.4
1.52	100	23.9	0.834	13.1
1.52	100	28.7	0.699	13.2
1.52	100	38.2	0.582	14.6
1.91	100	1.91	12.5	12.5
1.91	50.0	1.91	13.3	13.3
1.91	20.0	1.91	13.5	13.5
1.91	10.0	1.91	12.3	12.3
5.73	100	5.73	11.7	11.7

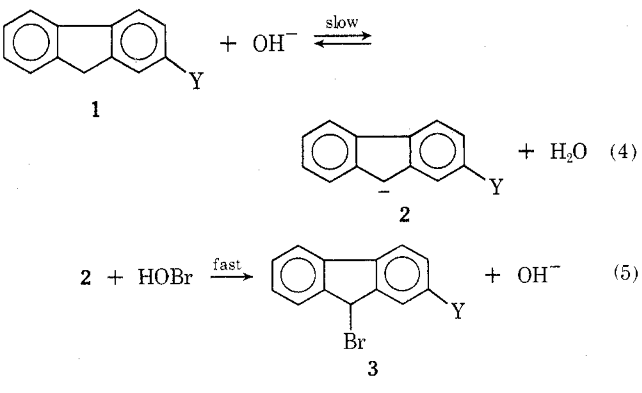
[a] Added concentration. [b] Total concentration. [c] $k_3 = k_{obsd} \cdot [NaBr]_0/[NaOBr]_0$.

Table IV
Relative Rates for the Reaction of 2-Substituted Fluorenes with NaOBr in Alkaline Aqueous Dioxane (27% Water) at 25°

Substituent of fluorene	k_{rel}	Substituent of fluorene	k_{rel}
2-NO_2[a]	802	2-Ac[a,b]	83.3
2-CN[a]	141	2-OMe[b]	3.10
2-Br[a,b]	60.3	None[b]	1.00

[a] $[NaOH] = 0.0125$ M. [b] $[NaOH] = 0.125$ M.

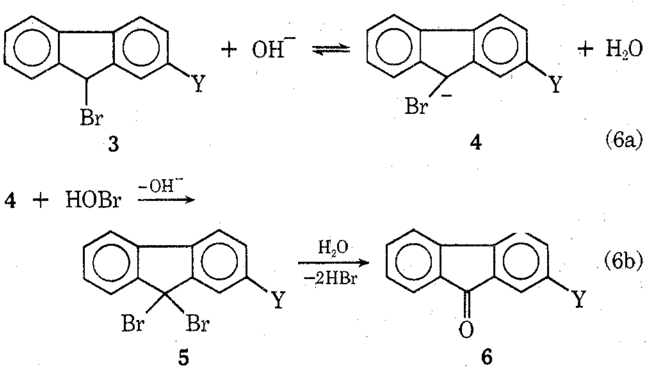
Scheme I



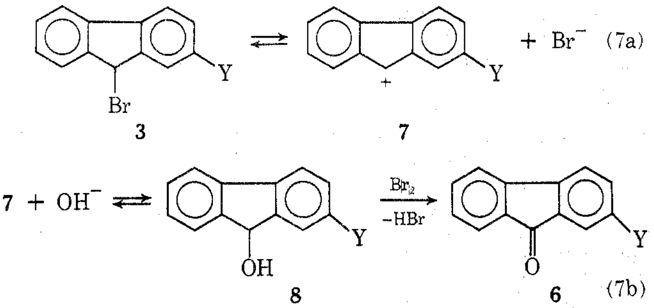
a, Y = NO_2; b, Y = CN; c, Y = Br; d, Y = Ac; e, Y = OMe; f, Y = H

In view of the analogous studies on the reaction of carbanion with hypohalites,[2,3,8] the carbanion **2** from fluorene

Scheme II



Scheme III



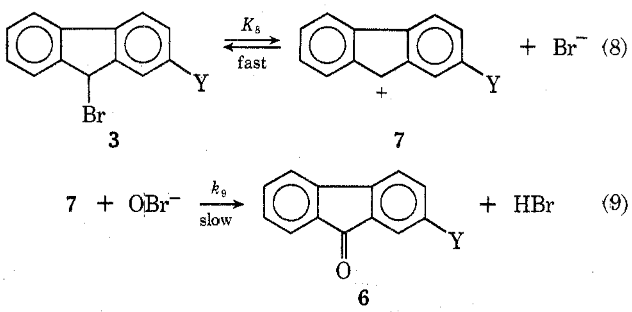
would also react rapidly with hypobromite to give 9-bromofluorene (3). 2,9-Dibromofluorene (3c) yields on treatment of hypobromite in alkaline aqueous dioxane 2-bromofluorenone together with 2,2′-dibromofluorenylidene, but no formation of fluorenylidene but fluorenone was observed at a low concentration of 2,9-dibromofluorene. The change of the rate law (eq 1 and 2) implies that the rate-determining step for 2-bromofluorene changes at 0.4–0.6 *M* NaOH; *i.e.*, at [NaOH] > 0.6 *M*, the formation of carbanion is faster than the oxidation of an intermediate, 2,9-bromofluorene, which was isolated and identified. Furthermore, the k_2 value (12.5×10^{-4} sec^{-1}) of eq 2 agrees with the k_3 value (12.9×10^{-4} sec^{-1}) for the oxidation of **3c** with alkaline hypobromite (eq 3). Hence the intermediacy of 9-bromofluorenes **3** is implied for the formation of fluorenones.

Oxidation of 2,9-Dibromofluorene (Speculation of Subsequent Steps). One of the pathways for the conversion of formed 9-bromofluorene to fluorenone may be Scheme II. 9-Bromofluorene appears to give carbanion **4** more easily than fluorene **1** because of the presence of the electron-attracting 9-bromo group. Since fluorenylidene is obtained by treatment of **3** with alkali, carbanion **4** may exist,[2–4] which may give 9,9-dibromofluorene (**5**) similarly to the conversion of **1** to **3**.[2,3,8] Then dibromide **5** may be hydrolyzed to fluorenone **6**, since α,α-dihalo compounds are hydrolyzed to carbonyl compounds as exemplified in the hydrolysis of benzophenone dichloride[9] and benzal chloride.[10] However, kinetics observed in our hands rule out this scheme, because the rate of **3c** with hypobromite is independent of the concentration of the base (eq 3).

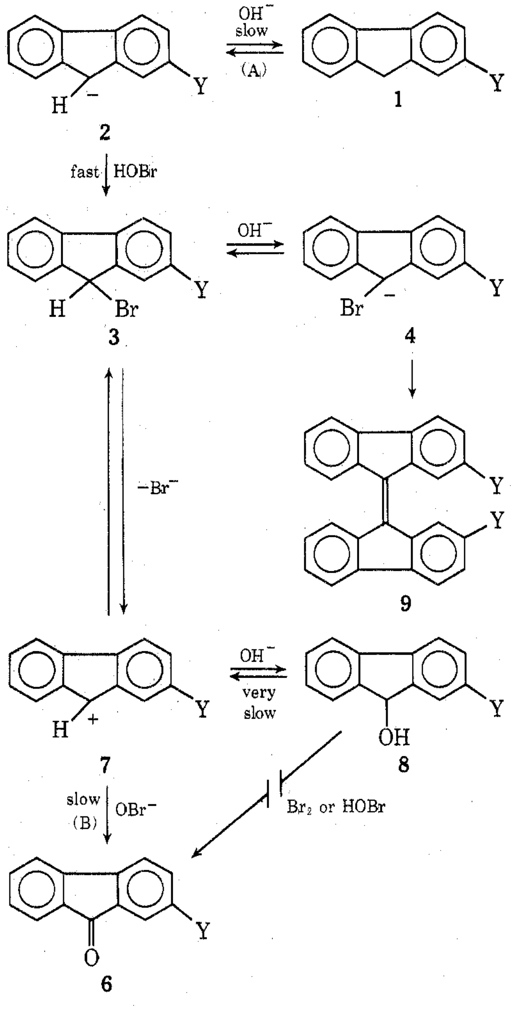
Lovins[11] observed in their study on the solvolysis of 1- and 4-carbomethoxy-9-bromofluorenes the formation of stable 9-fluorenyl cation **7** because of the planarity of **7**. Thus Scheme III is considered; *i.e.*, carbonium ion **7**, which may be formed from **3**, may give fluorenol **8** by an attack of hydroxide ion followed by its oxidation to fluorenone **6** by bromine.

However, no fluorenol **8** but bifluorenylidene **9** alone was obtained by the treatment of **3** with alkali, whereas fluorenone **6** was obtained as a main product by the treatment of **3** with alkaline hypobromite, so that the formation of fluorenol should be slower than the formation of bifluorenylidene and than that of fluorenone. Further, kinetic data are inconsistent with this scheme; *i.e.*, Scheme III cannot lead to the rate equation 3. Hence, the intermediacy of 9-fluorenol **8** is of doubt.

Scheme IV



Scheme V

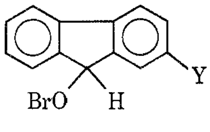


Our kinetic observations can only be explained by Scheme IV.

If eq 9 is rate-determining, the rate should be expressed as

$$v = K_8 k_9[\mathbf{3}][\mathrm{OBr}^-]/[\mathrm{Br}^-] \qquad (10)$$

And this is the case (eq 3). The intermediacy of 9-fluorenyl hypobromite (**10**), which can give fluorenone **6**[12a] in step 9, is probable, because the nucleophilicity of OBr^- should be stronger than that of OH^-.[12b] An alternative process may be a concerted one (11); *i.e.*, fluorenone **6** is formed from **7** by an attack of OBr^- and a simultaneous elimination of HBr.



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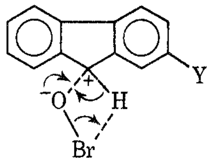

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Overall Mechanism of the Oxidation of Fluorenes. In conclusion, the mechanism of the oxidation of fluorenes by a mixture of bromine and alkali may be as follows in Scheme V. The abstraction of the 9 proton from fluorenes by a base occurs initially to give carbanion **2**, which then gives 9-bromofluorenes **3** by an attack of hypobromite. This scheme is similar to the initial stage of the conversion of benzyl cyanide into dicyanostilbene.[2] However, **3** should give fluorenone but no bifluorenylidene **9**, because (i) carbonium ion **7** may be more stable than carbanion **4**, (ii) the concentration of **3** is very low, (iii) the rate of the formation of **9** is second order in **3**.[2,5d] Carbonium ion **7**, which is formed from **3** by elimination of Br^-, gives directly fluorenone **6** with an attack of hypobromite OBr^- but not through fluorenol **8**. The rate-determining step depends on the concentration of alkali; *i.e.*, step A determines the rate at $[NaOH] < 0.4$ *M* and step B determines the rate at $[NaOH] > 0.6$ *M*.

Experimental Section

Materials. Used fluorene was purified by recrystallization after distillation: mp 116° (lit.[13] 116°). Substituted fluorenes were prepared from fluorene according to the literature. Substituents and mp were as follows: 2-NO_2, 156° (lit.[14] 156–157°); 2-CN, 89–90° (lit.[15] 94°); 2-Br, 110–111° (lit.[16] 113°); 2-Ac, 128° (lit.[17] 128–129°); 2-OMe, 105–106° (lit.[18] 108–109°); 2,9-diBr, 124–125° (lit.[19a] 118–120°, lit.[19b] 127°). The purities of fluorenes were confirmed by glc analysis. A Hitachi K-53 gas chromatograph with a flame ionization detector was used with a 1.0 m × 3.0 mm column packed with Apiezon Grease L (3%) on Celite 545 and/or PEG 20 M (10%) on Chromosorb W at a temperature increasing at 10°/min from 150 to 250°.

Inorganic materials were of commercial guaranteed grade. Dioxane was heated to reflux over sodium and distilled (bp 101°). The solution of hypobromite (1.0 *M*) was prepared by addition of aqueous NaOH (80.0 g in *ca.* 600 ml) to Br_2 (160.0 g) with cooling in a salt–ice bath and then diluted to 1000 ml in a measuring flask. The content of hypobromite was analyzed iodometrically before use. The solution can be stored in a refrigerator for 2 months.

Products. Fluorene (50 mg) was dissolved in 50 ml of dioxane. Water (10 ml), aqueous NaOH (1 *M*, 10 ml), and aqueous NaOBr (1 *M*, 10 ml) were added to the solution which was then stirred at 25° for 5 hr. Aqueous $Na_2S_2O_3$ was poured into the mixture to remove hypobromite and extracted with benzene. Products were isolated, if necessary, with silica gel column chromatography and analyzed by glc and ir to be the expected fluorenones. Substituents, yields, and mp were as follows: 2-NO_2, 100%, 218–220° (lit.[20] 219–221°); 2-CN, 100%, 169–171° (lit.[21] 173–174°); 2-Br, 96%, 149–150° (lit.[21] 149–150°); 2-COOH, 99%, >300° (lit.[6] 310°); 2-OMe, 15%, 76–78° (lit.[21] 78–79°); unsubstituted, 5%, 83° (lit.[13] 85°).

For the preparation of 2,9-dibromofluorene, 2-bromofluorene (200 mg) was added to 200 ml of aqueous dioxane (27% water) containing NaOH (2.1 *M*), NaBr (1.0 *M*), and NaOBr (0.2 *M*) and the heterogeneous reaction mixture was stirred vigorously for 10 hr at 25°. 2,9-Dibromofluorene was obtained in a yield of 73% (by glc analysis): mp 124–125° (lit.[19b] 127°).

The NaOBr oxidation of 2,9-dibromofluorene in the same manner as fluorenes gave 2,2′-dibromobifluorenylidene (0–13%) together with 2-bromofluorenone (100–87%). On the other hand, when 2,9-dibromofluorene (50 mg) was treated with aqueous NaOH alone (10 ml of 1 *M* NaOH) in aqueous dioxane (27% water) at 25° for 5 hr, 2,2′-dibromobifluorenylidene was obtained quantitatively. 2,2′-Dibromobifluorenylidene (the mixture of cis and trans): red crystals; mp 260–280° [lit.[22] 312° (cis), lit.[23] 264° (trans)]; uv (λ_{max}) 253, 264, 282, 292 nm; ir, 810, 770, 720 cm^{-1} (no absorption of carbonyl); glc, only one peak.

Kinetics. 2-Bromofluorene was selected as the most suitable substrate, since it was oxidized at a moderate rate in aqueous dioxane. 2-Nitro- and 2-cyanofluorenes form complexes with alkali so that the rate could not be measured by means of uv spectrophotometry. Fluorene and 2-methoxyfluorene were so slowly oxidized that uv spectrophotometry could not be employed for the rate measurements. Rates of these fluorenes were measured by means of glc as described later. Typical experiments were as follows. The reactions were started by addition of aqueous hypobromite (NaOBr $5\text{–}20 \times 10^{-2}$ *M*) to a mixture of 2-bromofluorene (2×10^{-5} *M*) and aqueous NaOH (0.007–0.7 *M*) in a thermostated 10 mm × 10 mm quartz cell held at constant temperature of 25°. The rate was followed by measuring the concentration of produced 2-bromofluorenone by means of uv spectrophotometry at a wavelength of 264 nm (2-bromofluorenone, λ_{max} 264 nm, ϵ 7.00×10^4; 2-bromofluorene, ϵ_{264} 2.00×10^4).

The plot of ln ([2-bromofluorene]$_0$ − [2-bromofluorenone]) against time gave a satisfactory straight line under these conditions at least up to 80% conversion, where [ ]$_0$ means initial concentration. The pseudo-first-order rate constants (k_{obsd}) were calculated from the slopes.

The rate with 2,9-dibromofluorene (ϵ_{264} 1.15×10^4) was measured in the same way. The formation of bifluorenylidene was negligible under these conditions.

The relative rate of fluorenes were measured by means of glc analysis of substrate and products. The typical experiments were as follows. The reaction was started by addition of a dioxane solution of fluorenes ($2.5\text{–}2.0 \times 10^{-3}$ *M*) to the solution of NaOH (0.0125 *M* or 0.125 *M*) and NaOBr (0.0125 *M* or 0.125 *M*) dipped in a thermostat at 25°. At appropriate time intervals, aliquots were taken out and extracted with benzene. The benzene extract was washed with aqueous $Na_2S_2O_3$ to eliminate hypobromite and concentrated by evaporation of benzene; then the content of fluorenes and fluorenones were measured by glc with a column packed with Apiezon Grease L (3%) as stated above. The plot of ln ([fluorene]/[fluorene]$_0$) is linear up to 60–80% conversion.

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Registry No.—Sodium hypobromite, 13824-96-9.

References and Notes

(1) Contribution No 208.
(2) Y. Ogata and K. Nagura, *J. Org. Chem.*, **39**, 394 (1974).
(3) (a) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966); (b) K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *ibid.*, **37**, 1966 (1972).
(4) (a) L. Chalanay and E. Knoevenagel, *Ber.*, **25**, 285 (1892); (b) E. Knoevenagel, *ibid.*, **21**, 1355 (1888).
(5) (a) E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929); (b) E. Kleuker, *ibid.*, **62**, 2587 (1929); (c) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Amer. Chem. Soc.*, **78**, 1653 (1956); (d) D. Bethell and A. F. Cockerill, *Proc. Chem. Soc., London*, 283 (1964).
(6) R. W. Schiessler and N. R. Eldred, *J. Amer. Chem. Soc.*, **70**, 3958 (1948).
(7) (a) H. F. Koch, D. B. Dahlberg, A. G. Toczko, and R. L. Solsky, *J. Amer. Chem. Soc.*, **95**, 2029 (1973); (b) M. Weizmann and S. Patai, *ibid.*, **71**, 2587 (1949).
(8) (a) K. J. Pederson, *J. Phys. Chem.*, **38**, 559 (1934); (b) R. I. Aylott, A. R. Butler, D. S. B. Grace, and H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 1107 (1973); (c) S. P. Avery and A. R. Butler, *ibid.*, 1110 (1973).
(9) C. S. Marvel and W. M. Sperry, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N.Y., 1932, p 95.
(10) S. C. J. Olivier and A. D. H. Weber, *Recl. Trav. Chim. Pays-Bas*, **53**, 869 (1934).
(11) R. E. Lovins, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **84**, 3959 (1962).
(12) (a) F. D. Chattaway and O. G. Backberg, *J. Chem. Soc.*, **123**, 3000 (1923); (b) J. C. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).
(13) A. Jeanes and R. Adams, *J. Amer. Chem. Soc.*, **59**, 2608 (1937).
(14) W. E. Kuhn, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N.Y., 1943, p 447.
(15) J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 2337 (1959).
(16) J. T. Thurston and R. L. Shriner, *J. Amer. Chem. Soc.*, **57**, 2163 (1935).
(17) F. E. Ray and G. Rieveschl, Jr., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N.Y., 1955, p 23.
(18) G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, 2687 (1955).
(19) K. Suzuki and M. Fujimoto, *Bull. Chem. Soc. Jap.*, **36**, 1654 (1963).
(20) F. J. Moore and E. H. Huntress, *J. Amer. Chem. Soc.*, **49**, 2618 (1927).
(21) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962).
(22) K. Suzuki, *Nippon Kagaku Zasshi*, **75**, 715 (1954).
(23) K. Suzuki, T. Maeda, N. Nawa, and Y. Soda, *Bull. Chem. Soc. Jap.*, **35**, 1299 (1962).