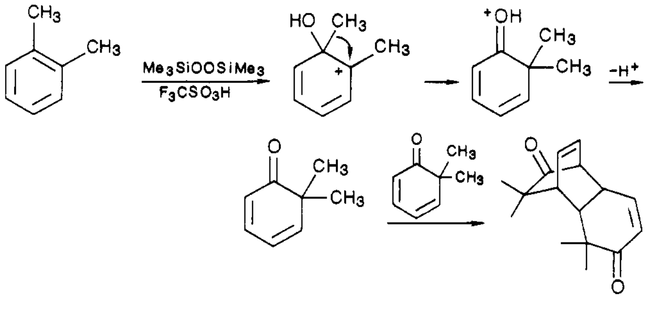
2,3; 22% 2,6 30% 3,4) clearly reveals the occurrence of methyl shifts. Similar observations were reported earlier in related superacid-catalyzed hydroxylations using H_2O_2.[5,7,11] Furthermore, we succeeded in isolating from the reaction mixture 21% of a nonphenolic additional oxygen-containing compound (based on the peroxide). The compound was identified by its analytical and spectral properties as the dimer of 6,6-dimethyl-2,4-cyclohexadien-1-one and was found in all regard identical with the earlier reported compound by Mazur et al.[14] obtained in the reaction of dimethylbenzenes with O(^{3}P) atoms on adsorbed phases. Taking this into account, the yield of the hydroxylation of o-xylene thus is also very high.



A reasonable mechanistic path for the formation of this dimethyl ketone involves ipso attack followed by a methyl shift and cycloadditive dimerization of the intermediate 6,6-dimethyl-2,4-cyclohexadien-1-one catalyzed by the acid.

In conclusion, bis(trimethylsilyl) peroxide/triflic acid is a highly effective hydroxylating reagent for aromatics, providing the corresponding phenols in high yields. The method is safe and more effective than the previously developed ones and should find general use for electrophilic hydroxylation of aromatic substrates.

Experimental Section

Materials. All solvents and aromatic substrates were high purity ($\geqslant$99%) commercial products or distilled before use. Hydrogen peroxide (31%) was purchased from Mallinckrodt. DABCO ($\sim$97%) and chlorotrimethylsilane (98%) were Aldrich products. NMR spectroscopy: spectra were obtained on a Varian VXR-200 spectrometer. GC analysis: Isomeric distributions were determined after silylation by N,O-bis(trimethylsilyl)trifluoroacetamide (Pierce) on a Varian 3700 gas chromatograph equipped with a DB-1 column (column temperature, 100 °C). GC-MS: a Finnigan INCOS-50 mass spectrometer was used in combination with a Varian 3400 gas chromatograph.

Preparation of Bis(trimethylsilyl) Peroxide. The preparation was carried out according to Ricca's procedure.[13] The purity of the peroxide was determined by GC analysis and ^{1}H NMR. The peroxide generally had a purity of 90%. The main impurity was hexamethylsiloxane.

General Procedure for the Hydroxylation of Aromatics. The aromatic substrate (40 mL) was added into a three-necked, 100-mL round-bottomed flask, equipped with magnetic stirrer, thermometer, and dropping funnel, which was kept under nitrogen. Triflic acid (10 mL, 0.11 mol) was then added while the solution was cooled to the adequate reaction temperature (see Table I). Subsequently 1.5 g ($\sim$90%, 7.6 mmol) of bis(trimethylsilyl) peroxide in 15 mL of the aromatic substrate was slowly introduced through the dropping funnel. The solution was usually stirred for 30 min after the addition and then quenched with ice water (25 mL). The organic material was extracted with dichloromethane (3 × 100 mL). It was washed with 10% sodium bicarbonate solution to remove any acid and then extracted with 10% sodium hydroxide solution. This solution was neutralized with 37% hydrochloric acid until a pH of about 1 was reached. Phenolic products were then extracted with dichloromethane, dried, and filtered. After evaporation of the solvent they were characterized by GC and GC-MS analyses and thin layer chromatography (silica gel, dichloromethane eluent).

In case of solid aromatics, such as naphthalene, 0.1 mol of the aromatic substrate was dissolved in 35 mL of dichloromethane and the peroxide was diluted in 15 mL dichloromethane. Otherwise, the above procedure was unchanged. All yields are based on the amount of peroxide used.

Identification of 6,6-dimethyl-2,4-cyclohexadien-1-one dimer in accord with Mazur[14] showed the following: IR (neat) ν 2968, 2926, 2870, 1723, 1666, 1633, 1561, 1471, 1385, 1293, 1253, 1129, 1098 cm^{-1}; GC-MS, m/e 122 ($C_8H_{10}O$, $M^{\bullet+}$ monomer, 50), 107 (8), 94 (9), 93 (12), 91 (13), 79 (100), 77 (45).

Acknowledgment. This work was generously supported by the National Science Foundation. Thomas D. Ernst is grateful for a fellowship of the Swiss National Science Foundation.

Registry No. Benzene, 71-43-2; phenol, 108-95-2; toluene, 108-88-3; o-methylphenol, 95-48-7; m-methylphenol, 108-39-4; p-methylphenol, 106-44-5; mesitylene, 108-67-8; 2,4,6-trimethylphenol, 527-60-6; o-xylene, 95-47-6; 2,3-dimethylphenol, 526-75-0; 2,6-dimethylphenol, 576-26-1; 3,4-dimethylphenol, 95-65-8; naphthalene, 91-20-3; α-naphthalenol, 90-15-3; β-naphthalenol, 135-19-3; chlorobenzene, 108-90-7; o-chlorophenol, 95-57-8; m-chlorophenol, 108-43-0; p-chlorophenol, 106-48-9; (trimethylsiloxy)benzene, 1529-17-5; (trimethylsiloxy)mesitylene, 18052-51-2; 6,6-dimethyl-2,4-cyclohexadien-1-one, 21428-63-7; α-(trimethylsiloxy)naphthalene, 6202-48-8; β-(trimethylsiloxy)naphthalene, 18081-08-8; bis(trimethylsilyl) peroxide, 5796-98-5; triflic acid, 1493-13-6.

Electrophilic Aromatic Substitution. 11.[1] A Kinetic Study of the BF_3-Catalyzed Benzylation Reaction in Nonpolar Solvents. Kinetic Evidence for BF_3 Catalytic Activity Involving a Fluorine-Bridged BF_3 Dimer

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Received August 10, 1988

In aromatic substitution of toluene and benzene the statistically limiting rate ratio is governed by the number of possible substitution positions, i.e., k_T/k_B should be 5/6 or 0.83 at a minimum. However, values less than this have been reported. In an earlier study[2] we suggested Nakane's k_T/k_B of $\sim$0.6 for ethylation in nonpolar solvents[3] was caused by side reactions, particularly disproportionation, which became important after phase separation had occurred. More recently Nakane carried out a series of competitively determined benzylations of toluene and benzene catalyzed by boron trifluoride hydrate in hexane where k_T/k_B values for chlorobenzyl chlorides and benzyl chloride were found again to be below 0.83, this time 0.7.[4] Interestingly, similar k_T/k_B ratios (and product toluene isomer percentages) were determined for reactions in *solvent* boron trifluoride hydrate. However when boron

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(1) Electrophilic Aromatic Substitution. 10. DeHaan, F. P.; Chan, W. H.; Chang, J.; Ferrara, D. M.; Wainschel, L. A. *J. Org. Chem.* **1986**, *51*, 1591-1593.

(2) Carter, B. J.; Covey, W. D.; DeHaan, F. P. *J. Am. Chem. Soc.* **1975**, *97*, 4783-4784.

(3) Nakane, R.; Kurihara, O.; Natsubori, A. *J. Am. Chem. Soc.* **1969**, *91*, 4528-4532.

(4) Takematsu, A.; Sugita, K.; Nakane, R. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2082-2085.

Table I. Competitively Determined Rate Constant Ratios and Product Isomer Percentages for the BF_3-Catalyzed Reaction between Benzyl Chloride and Benzene and Toluene in Cyclohexane or Dodecane

temp, °C	reactants, M				H_2O added, µL	k_T/k_B	% ortho	% meta	% para	b[a]
	$[C_6H_6]$	$[C_6H_5CH_3]$	[BzCl]	$[BF_3]$						
25[b]	0.2880	0.2398	0.0367	0.0442		2.66 ± 0.33[c]	34.2 ± 1.0[c]	2.9 ± 0.1[c]	62.9 ± 1.0[c]	0.61 ± 0.05[d]
25[b]	0.2750	0.2337	0.0393	0.0435	1	4.09 ± 0.09	33.8 ± 0.1	3.5 ± 0.2	62.7 ± 0.2	0.77 ± 0.02
25[b]	0.2750	0.2337	0.0393	0.0435	10	0.62 ± 0.17	41.5 ± 2.3	5.2 ± 0.9	53.3 ± 2.0	0.23 ± 0.17
25[b]	0.2750	0.2337	0.0393	0.0435	100	0.73 ± 0.09	35.3 ± 1.2	7.2 ± 0.7	57.5 ± 0.5	0.33 ± 0.06
65[e]	0.2951	0.2453	0.0365	0.0176		4.2 ± 1.2	39.6 ± 1.9	2.2 ± 0.5	58.2 ± 2.2	0.90 ± 0.05
140[e]	0.2208	0.1919	0.0366	0.0046		4.08 ± 0.14	43.6 ± 8.0	2.7 ± 0.7	53.7 ± 6.9	0.88 ± 0.19
140[e]	0.0501	0.4126	0.0215	0.0045		3.92 ± 0.11	41.3 ± 0.5	8.2 ± 0.6	50.6 ± 1.0	0.99 ± 0.05

[a] Calculated slope for the Brown selectivity relationship. [b] Cyclohexane as solvent. [c] ± Standard deviation. [d] ± 95% confidence limit. [e] Dodecane as solvent.

trifluoride rather than the hydrate was used as catalyst in solvent nitromethane, k_T/k_B values increase for benzyl chloride and all substituted benzyl chlorides (the lowest ratio now being 2.8), *but* the product isomer percentages are unchanged. In nitromethane all results in fact agree closely with those reported by our group[5] and others.[6]

Nakane's results are particularly intriguing in that he found all reactions to proceed homogeneously and with little or no isomerization or disproportionation.

Since the role of water seems critical here and is best assessed through noncompetitive kinetics, we decided to examine the boron trifluoride catalyzed benzylation reaction, with and without water, competitively and noncompetitively, using our usual vacuum line techniques.

Experimental Section

Materials. Vacuum line, drying, and analysis procedures for reagents benzene, benzyl chloride, toluene, and internal standard *o*-dichlorobenzene have been described.[7,8] Solvents cyclohexane (purity 99.97%) and dodecane (purity 99.7%, GC analyses with 25-m OV101 glass capillary column) were thoroughly dried over CaH_2 and then vacuum distilled and finally poured under vacuum into individual storage ampoules.[9] Boron trifluoride (99.5% pure from Matheson) was admitted into a thoroughly flamed evaluated chamber, frozen at −197 °C via liquid nitrogen, thoroughly degassed, and transferred to large storage bulbs on the vacuum line. Quantitative transfer of BF_3 was achieved by using either grease-free valves or valves greased with Halocarbon 25-5S.

Kinetic Procedure. Except for the following three minor modifications, earlier procedures[7,8] were followed. Because of its modest volatility, dodecane was transferred to the reaction chamber by tipping the manifold and pouring after first securing the magnetic breakers with magnets. The last portion of the dodecane was flamed into the reaction chamber. To lessen the attack of BF_3 on the rubber septum during slow 25 °C runs, another septum with a Teflon surface was inserted below the first septum. After a day or two both septa showed signs of BF_3 attack. Lastly, distilled water proved to be an effective quench of each aliquot.

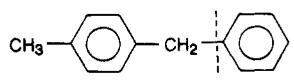
Analysis. Concentrations of reagents were corrected for vapor concentrations. Calculated solution concentrations were consistent with experimentally determined vapor concentrations and consistent with BF_3 solubilities extrapolated from solubility data of BF_3 in pentane.[10] Analyses were carried out with an HP 5880 gas chromatograph and a 25-m glass capillary OV101 column. Retention times were given in an earlier paper.[5] With an oven temperature programmed for 18 min at 150 °C and then increased to 190 °C at a rate of 30°/min, secondary product (when they appeared) retention times were found in the range of 23–73 min.

Results and Discussion

In contrast to its reported speed in boron trifluoride hydrate solution,[4] the boron trifluoride catalyzed reaction of benzyl chloride with benzene or toluene in cyclohexane is very slow at 25 °C, with or without added (controlled) amounts of water. Without water, product diphenyl methane (benzene) and methyl diphenyl methanes (toluene) GC peaks were integrable only after 2 days reaction time (first competitive run, Table I). Small amounts of secondary products were also observed (GC peak area ratios of ca. 1:10 secondary/primary product).

In a second competitive run, the addition of approximately 1 µL of water (to 10.8 mL of solution) had no effect on reaction speed and almost no effect on k_T/k_B or toluene product isomer percentages. With the addition of 10 µL and later 100 µL of water, both benzene and toluene product GC peaks increased at a much more rapid rate, with relative growth rate clearly favoring benzene. The effect of added water on relative rates and product percentages is seen in Table I.

A 25 °C toluene reaction proved to be extremely slow; it took 6 days before product peaks were ever integrable. However, a diphenylmethane (*benzene* product) peak equal in size to the *o*- and half the size of the *p*-methyldiphenylmethane (toluene product) peak was observed in the early stages of reaction. Since there was less than 0.03% benzene impurity in the toluene and since the cyclohexane was benzene free (GC analysis), the most likely source of diphenylmethane is disproportionation of toluene product through migration of the relatively stable *p*-xylyl carbocation, thus leading to "secondary products" and benzene—which is subsequently attacked and converted to diphenylmethane.



Even though diphenylmethane was seen only occasionally in toluene reactions, it may well be the key to an explanation of the anomalously low k_T/k_B ratios observed by Nakane and us when water is present. In reactions as slow as these benzylations, slow but significant disproportionation catalyzed from $BF_3{\cdot}H_2O$ by the strong acids $H_3O{-}BF_3^+$ or H_3O^+ could degrade toluene products into benzene products, thus lowering the measured k_T/k_B below one and also raising the toluene product percent meta/

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[5] DeHaan, F. P.; Delker, G. L.; Covey, W. D.; Ahn, J.; Anisman, M. S.; Brehm, E. C.; Chang, J.; Chicz, R. M.; Cowan, R. L.; Ferrara, D. M.; Fong, C. H.; Harper, J. D.; Irani, C. D.; Kim, J. Y.; Meinhold, R. W.; Miller, K. D.; Roberts, M. P.; Stoler, E. M.; Suh, Y. J.; Tang, M.; Williams, E. L. *J. Am. Chem. Soc.* **1984**, *106*, 7038–7046.

[6] Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448–7461.

[7] DeHaan, F. P.; Covey, W. D.; Ezell, R. L.; Margetan, J. E.; Pace, S. A.; Sollenberger, M. J.; Wolf, D. S. *J. Org. Chem.* **1984**, *49*, 3954–3958.

[8] DeHaan, F. P.; Delker, G. L.; Covey, W. D.; Bellomo, A. F.; Brown, J. A.; Ferrara, D. M.; Haubrich, R. H.; Lander, E. B.; MacArthur, C. J.; Meinhold, R. W.; Neddenriep, D.; Schubert, D. M.; Stewart, R. G. *J. Org. Chem.* **1984**, *49*, 3963–3966.

[9] Reference 7, Figure 3, insert.

[10] Cade, G. N.; Dunn, R. E.; Hepp, H. J. *J. Am. Chem. Soc.* **1946**, *68*, 2454–2455.

Table II. Initial Rates and Rate Constants for the BF_3-Catalyzed Reaction of Benzyl Chloride with Benzene and Toluene in Dodecane at 140 °C

reactants, M				initial rate × 10^8, M s^{-1}	$10i$ rate/ $[BzCl]_0[BF_3]_0^2$, M^{-2} s^{-1}	10^6k_1, s^{-1}	10^4k_1/ $[BF_3]_0$, M^{-1} s^{-1}	10^1k_1/ $[BF_3]_0^2$, M^{-2} s^{-1}	10^3k_1/ $[Arom][BF_3]_0$, M^{-2} s^{-1}	10^1k_1/ $[Arom][BF_3]_0^2$, M^{-3} s^{-1}
$[C_6H_6]$	$[C_6H_5CH_3]$	[BzCl]	$[BF_3]$							
0.5605		0.0208	0.0044	3.56 ± 0.07[a]	0.88 ± 0.02[a]	1.9 ± 0.1[a]	4.3 ± 0.2[a]	0.98 ± 0.05[a]	0.77 ± 0.04[a]	1.75 ± 0.09[a]
0.2995		0.0209	0.0045	5.49 ± 0.33	1.30 ± 0.08	2.4 ± 0.1	5.3 ± 0.2	1.19 ± 0.05	1.78 ± 0.07	3.96 ± 0.16
0.5422		0.0204	0.0021	1.01 ± 0.04	1.12 ± 0.04	0.51 ± 0.02	2.4 ± 0.1	1.16 ± 0.05	0.45 ± 0.02	2.13 ± 0.08
				av	1.1 ± 0.2[b]		4.0 ± 1.5[b]	1.1 ± 0.1[b]	1.0 ± 0.7[b]	2.6 ± 1.25
	0.3892	0.0356	0.0044	10.9 ± 0.4	1.60 ± 0.06	3.16 ± 0.14	7.2 ± 0.3	1.65 ± 0.07	1.86 ± 0.08	4.2 ± 0.2
	0.4306	0.0192	0.0027	2.7 ± 1.0	1.93 ± 0.71	1.42 ± 0.15	5.3 ± 0.6	1.95 ± 0.21	1.22 ± 0.13	4.5 ± 0.5
	0.2476	0.0071	0.0044	2.1 ± 0.1	1.56 ± 0.07	2.82 ± 0.09	6.5 ± 0.2	1.48 ± 0.05	2.61 ± 0.03	6.0 ± 0.5
				av	1.7 ± 0.2[b]		6.3 ± 1.0[b]	1.7 ± 0.2[b]	1.9 ± 0.7[b]	4.9 ± 1.0[b]

[a] ± 95% confidence limit. [b] ± Standard deviation.

percent para ratio (Table I) to Nakane's values, which were determined in hexane "which had been saturated with water".[4] This is consistent with the higher stability and presumably higher rate of intermolecular movement of the *p*-xylyl cation relative to the *m*-xylyl cation.

In order to establish the rate law, a series of noncompetitive reactions was run in solvent dodecane at 140 °C after a 65 °C reaction temperature proved to be too low. At 140 °C reaction speeds were more convenient, typically 1% reaction in 1–2 h, and secondary products were much less in evidence provided water was rigorously excluded from the reaction. At this temperature a modest amount of product isomerization was evident. For example, the percentage of *m*-methyldiphenylmethane in the first toluene reaction (Table II) slowly increased from 4.7% after 4 h (when the GC peak first became integrable) to 6.2% after 21 h. During that time the para product percentage dropped a corresponding amount from an initial value of 56.8%; the ortho product percentage typically did not change appreciably.

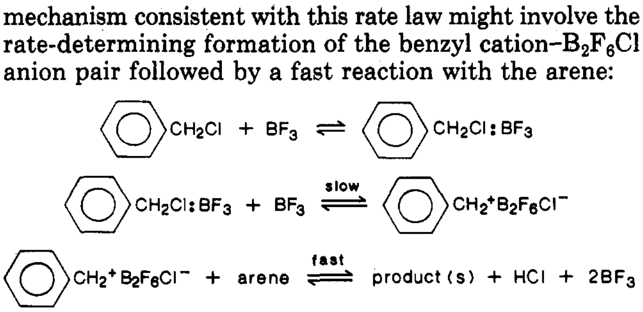
It is clear from the data that boron trifluoride is active as a catalyst. For example, the first benzene reaction was followed through 72% reaction, well past the 21% possible if boron trifluoride were a limiting reagent.

Although the reaction was slow but followable at 140 °C, our useful BF_3 concentration range was severely limited. The upper end, 0.0044 M, was governed by the solubility of 1 atm of BF_3 at 140 °C; the lower end turned out to be half that value. At still lower BF_3 concentrations, BF_3 reaction with the rubber septum interfered.

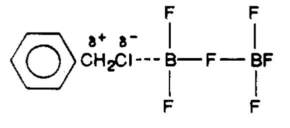
In spite of these limitations, the rate data, Table II, are consistent with a rate law that is first order in benzyl chloride, second order in BF_3 and zero order in arene. A

$$\text{rate} = k_1[\text{RCl}][\text{BF}_3]_0^2$$

mechanism consistent with this rate law might involve the rate-determining formation of the benzyl cation–B_2F_6Cl anion pair followed by a fast reaction with the arene:



Alternatively the formation of a polarized 1:2 benzyl halide–catalyst complex might be rate-determining.



However, one would than expect an S_N2 displacement by arene and first order dependence for benzene or toluene.

Low-temperature conductivity measurements of alkyl floride–boron trifluoride complexes seem to indicate polarized adduct bonds in the case of methyl and ethyl complexes and (based on a 1000-fold increase in conductance) a more ionic character for *n*-propyl, isopropyl, *tert*-butyl, and cyclohexyl complexes.[11] Although benzyl complexes were not examined, their ease of ionization would probably put them in the latter category. Thus the supporting evidence, although indirect, is seen as supportive of a $C_6H_5CH_2^+B_2F_6Cl^-$ ion pair intermediate.

Since the reaction rates are independent of aromatic hydrocarbon concentration it follows that the ratio k_T/k_B, calculated from k_T and k_B each determined noncompetitively, should be close to one; experimentally the value is 1.5 ± 0.4. Although not 1.0, this value is similar to noncompetitively determined k_T/k_B values for benzylation reactions in nitromethane, which are also zero order in aromatic hydrocarbon[5] and may reflect the slightly better solvating property of toluene relative to benzene.[5]

It should be noted that boron trifluoride catalyzed benzylation in cyclohexane and dodecane does not fit Brown's relationship even in the absence of water. As reported in Table I, calculated slopes, *b*, in Brown's selectivity relationship equation, $\log p_f = bS_f$, are all below the least-squares value of 1.31 ± 0.20 (95% confidence limits). While these results are similar to benzyl chloride benzylation in nitromethane and sulfolane (also zero order in arene and found not to fit Brown's relationship), it *is* surprising to find rate-determining formation of the electrophile in a noncoordinating solvent such as dodecane.[12]

Finally, the second-order boron trifluoride rate dependence is most significant in that *it clearly implies a fluorine bridge between boron atoms* in the 1:2 complex, regardless of degree of polarization/ionic character. This is of particular interest because this is so common in other group III halides and halide adducts and almost never seen in boron halides and their complexes. To our knowledge BX_3 dimerization has not been observed[13] (although halogen exchange readily occurs[14]). Low-temperature studies do occasionally indicate the existance of relatively unstable 1:2 addition compounds: $Et_3N \cdot 2BX_3$ (X = F, Cl, Br), pyr·$2BX_3$ (X = F, Br),[15] $C_2H_5Cl \cdot 2BCl_3$,[16] and ether·$2BF_3$

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[11] Olah, G. A.; Kuhn, S. J.; Olah, J. A. *J. Chem. Soc.* **1957**, 2174–2176.

[12] For a discussion of alternative explanations of exceptions to Brown's relationship, the reader is referred to ref 5.

[13] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed; John Wiley & Sons: New York, 1980; p 290.

[14] Greenwood, N. N.; Thomas, B. S. *Comprehensive Inorganic Chemistry*; Trotman-Dickenson, A. F., Exec. Ed.; Pergamon Press: Oxford, 1973; p 969.

(ether = methyl, ethyl, methyl *n*-propyl, methyl isopropyl).[17] A 1:3 complex, $(C_2H_5)_2O{\cdot}3BF_3$, has also been reported.[17] In all these cases the structure of the complex was not established. The only kinetic study that might be seen as supportive of fluorine bridges between boron atoms is that of Clayton & Eastham, who found BF_3–methanol catalysis in the isomerization of *cis*- and *trans*-2-butenes to be first order in free BF_3 in solution as well as first order in BF_3 CH_3OH.[18]

Acknowledgment. This work was supported by a Penta Corporation Grant of Research Corp. and by the National Science Foundation (Grant CHE 79-15122).

Registry No. BF_3, 7637-07-2; H_2O, 7732-18-5; benzyl chloride, 100-44-7; benzene, 71-43-2; toluene, 108-88-3.

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(15) Brown, H. C.; Stehle, P. F.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020–2021.

(16) Martin, D. R.; Hicks, W. B. *J. Phys. Chem.* **1946**, *50*, 422–427.

(17) Wirth, H. E.; Jackson, M. J.; Griffiths, H. W. *J. Phys. Chem.* **1958**, *62*, 871–872.

(18) Clayton, J. M.; Eastham, A. M. *Can. J. Chem.* **1961**, *39*, 138–143. See also Clayton, J. M.; Eastham, A. M. *J. Chem. Soc.* **1963**, 1636–1643.

Photochemical Transformations. 47. Direct Irradiation in Acetic Acid of 1-(Bromomethyl)dibenzosemibullvalene [1-(Bromomethyl)-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene][1]

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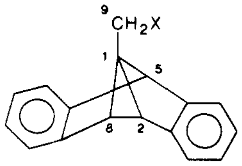
Treatment of 1-Br with silver acetate in acetic acid or deamination of 1-NH_2 in acetic acid has been shown[2] to lead to the hydrocarbon 3,4-benzofluorene (**2**), in addition to a mixture of acetates. Paquette and Meehan earlier reported[3] that base-induced decomposition of the *p*-toluenesulfonylhydrazone of dibenzosemibullvalene-1-carboxaldehyde (**3**) also gave **2**, and they also reported a mechanistic interpretation of that result, on the basis of deuterium-labeling experiments. More recently,[4] we noted that direct irradiation of 4-Cl in acetic acid led to a mixture of acetates and to about 15% of **2**, along with some 1-methylfluoroanthene.



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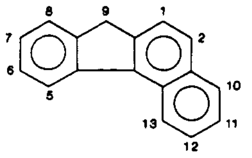

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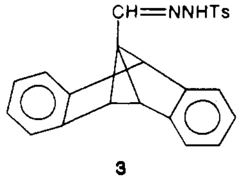
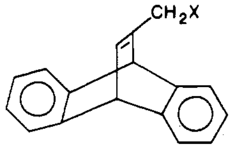


3

As it is known[4] that 4-OAc gives 1-OAc upon irradiation in acetic acid or in benzene (via a di-π-methane process), it seemed likely that 4-Cl might similarly give 1-Cl and that 1-Cl might be the source of **2** in the irradiation. As preliminary attempts to prepare 1-Cl from 1-OH failed, rearranged chlorides being obtained instead, and as 1-Br is readily prepared,[2] we decided to study its photoreactions.

Compound 1-Br is inert to triplet acetone photosensitization.[4] Direct irradiation of 1-Br in acetic acid with 254-nm light gave **2** as sole product, consistent with the idea suggested above. It is of interest that no acetates were formed, although they are the major products of the ground-state reactions with silver acetate of 1-Br and of the homoallylic isomers (**5**) of **1** and are also products of ground- and excited-state reactions of 4-Cl, 4-Br, and their allylic isomers **6**. It is similarly of interest that **2** arises, although in much poorer yields, from the ground-state reactions[2] of **1** species and not from the isomeric **4**, **5**, or **6** species. It was assumed that the acetate mixture arose from rearrangement (migration of the C-1, C-2 bond to C-9) in 1^+, or in a process concerted with loss of nucleofuge from 1-X, to give the benzylic cation 5^+ (cyclopropylcarbinyl to homoallyl cation rearrangement). Cation 5^+ is known[2] to equilibrate rapidly with its Wagner–Meerwein rearrangement allylic isomer $4^+ \leftrightarrow 6^+$; failure to see products from 1^+ in the reactions of **4**, **5**, and **6** species suggests that 1^+ is much less stable than 5^+.



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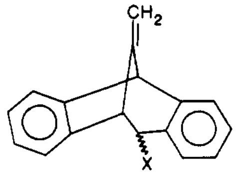

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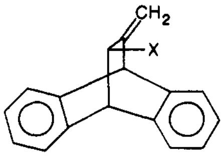
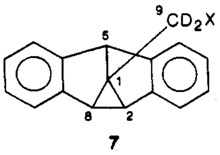


6

Three reaction paths were suggested[2] for the formation of **2**. One involved migration (note the projection **7** of dideuterio-**1**) of C-2 or C-8 from C-1 to C-9, which would give the cyclobutyl cation **8**. (In this discussion, we assume labeling at C-9 of **1**.) Cyclobutyl–homoallyl interconversion leads to ion **9**, which has the correct carbon skeleton but requires hydride shifts followed by proton loss (or proton loss followed by double-bond isomerization) for aromatization to benzofluorene. The key initial step is a 1,2-Wagner–Meerwein shift. A second possible pathway involves migration of C-2 from C-8 to C-9 (a 1,3-shift) to give **10**, the cyclopropylcarbinyl isomer of **8** and **9**. The third path proposed involves migration of the benzo ring from C-8 to C-9 (also a 1,3-migration) to give the cyclopropyl



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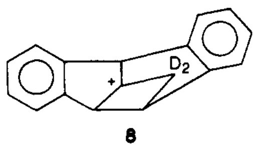

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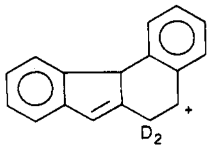

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(1) Previous paper in series: Cristol, S. J.; Aeling, E. O.; Strickler, S. J.; Ito, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 7101.

(2) Cristol, S. J.; Schloemer, G. C.; James, D. R.; Paquette, L. A. *J. Org. Chem.* **1972**, *37*, 3852.

(3) Paquette, L. A.; Meehan, G. V. *J. Am. Chem. Soc.* **1970**. *92*, 3039.

(4) Cristol, S. J.; Braun, D.; Schloemer, G. C.; Vanden Plas, B. J. *Can. J. Chem.* **1986**, *64*, 1081.

0022-3263/89/1954-1209$01.50/0