7.19; N, 9.99. Found: C, 76.95; H, 7.31; N, 10.15.

4-Amino-5-*tert*-butyl-4'-(dimethylamino)biphenyl-3-carbonitrile (8c) was prepared from 0.17 g (0.49 mmol) of 13 in 25 mL of CH_3CN by addition of 1 mL of HBF_4 (40% in ether). After being stirred for 45 min, the solution was treated with lu until an aqueous extract was no longer acidic. The solvent was evaporated, and the residue was several times extracted with ether. The resulting colorless material was recyrstallized from methanol and yielded 70 mg (51%) of 8c: mp 137-138 °C; MS *m/z* 293 (100, M^+), 278 (28), 263 (10); ^1H NMR (90 MHz, CCl_4) δ 1.44 (s, 9 H, *tert*-butyl), 2.95 (s, 6 H, $N(CH_3)_2$), 4.49 (s, 2 H, NH_2), 6.5-7.6 (m, 6 H, aromatic protons); IR (KBr) 3470/3390 (NH), 2900 (CH), 2205 (CN). Anal. Calcd for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.61; H, 7.71; N, 14.02.

Diethyl 2-[3,5-Di-*tert*-butyl-1-[4-(dimethylamino)-phenyl]-4-imino-2,5-cyclohexadien-1-yl]malonate (12). A 2.55-g (16-mmol) portion of diethyl malonate was treated with 0.12 g (5.2 mmol) of Na dissolved in 20 mL of EtOH. The resulting solution was added to a solution of 4c (from anodic oxidation of 0.28 g (0.86 mmol) of aniline 1c) in acetonitrile. After immediate decolorization, the excess of diethylmalonate was evaporated at 100 °C (0.1 Torr). The product 12 was isolated as an oil (yield, 93%): MS *m/z* 482 (6, M^+), 426 (13), 324 (100), 309 (44), 173 (68); ^1H NMR (90 MHz, $CDCl_3$), δ 1.13 (t, 6 H, J = 7 Hz, OCH_2CH_3), 1.31 (s, 18 H, *tert*-butyl), 2.89 (s, 6 H, $N(CH_3)_2$), 4.02 (q, J = 7 Hz, OCH_2CH_3), 4.17 (s, $CH(COOEt)_2$; the integration of the signals at 4.02 and 4.17 corresponds to 5 H), 6.68 (s, vinylic protons), 6.84 (q, A_2B_2, J = 9 Hz, aromatic protons; the integration of the signals between 6.56 and 7.11 corresponds to 6 H), a signal for the NH proton was not found, in C_6D_6 it was detected at 9.98 (s, broad, 1H); IR (KBr) 3400 (NH), 2960 (CH), 1760/1735 (C=O), 1565 (C=N) cm^{-1}. Anal. Calcd for $C_{29}H_{42}N_2O_4$: C, 72.17; H, 8.77; N, 5.80. Found: C, 71.95; H, 8.61; N, 5.72.

1,5-Di-*tert*-butyl-3-[4-(dimethylamino)phenyl]-6-imino-2,4-cyclohexadiene-1-carbonitrile (13) was obtained after addition of a 7% excess of NBu_4CN to the electrogenerated solution of 4c (from 0.27 g (0.83 mmol) of 1c). It was recrystallized from petroleum ether (30/50), giving yellow crystals (yield, 64%): mp 98 °C dec; MS *m/z* 349 (1, M^+), 324 (2), 293 (100), 278 (36); ^1H NMR (90 MHz, CCl_4) δ 1.06 (s, 9 H, *tert*-butyl), 1.33 (s, 9 H, *tert*-butyl), 2.99 (s, 6 H, $N(CH_3)_2$), 5.97 (d, 1 H, J = 2 Hz), 6.60 (d, J = 2 Hz, vinylic protons), 6.91 (q, A_2B_2, J = 9 Hz, aromatic protons, the integration of the signals between 6.50 and 7.50 corresponds to 5 H), 10.69 (s, broad, 1 H, NH); IR (KBr) 3390 (NH), 2890 (CH), 2225 (CN), 1585/1525 (C=N) cm^{-1}. Anal. Calcd for $C_{23}H_{31}N_3$: C, 79.04; H, 8.94; N, 12.02. Found: C, 79.25; H, 9.12; N, 12.23.

Reaction of 4c with Thiophenolate Ion. To a solution of cation 4c (derived from 0.28 g (0.86 mmol) of 1c) in acetonitrile were added 1 g of powdered Na_2CO_3 and 1 g (9.0 mmol) of thiophenol. From the resulting colorless solution the solvent was evaporated. The resulting oil was separated by preparative TLC on silica gel (petroleum ether/acetone (5:2)) to give 60 mg (34%) of diphenyl disulfide and 45 mg (17%) of aniline 1c.

Reaction of 4c with Acetate and *tert*-Butylate Ion. A solution of cation 4c in acetonitrile was treated with an excess of sodium acetate or KO-*t*Bu until decolorization occurred (24 h under reflux and 15 min at room temperature, respectively). From the reaction mixtures only small amounts of 1c could be isolated.

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Registry No. 1a, 65624-10-4; 1b, 86385-58-2; 1c, 86385-59-3; 5a, 65624-04-6; 5b, 134006-25-0; 5c, 134006-26-1; 5d, 86385-64-0; 5e, 134006-27-2; 5f, 134006-28-3; 5g, 86385-65-1; 5h, 134006-29-4; 5i, 134006-30-7; 6, 134006-31-8; 7a, 134006-32-9; 7b, 134054-76-5; 8b, 134006-33-0; 8c, 134006-34-1; 12, 134006-35-2; 13, 134006-36-3; 15a, 65624-05-7; 15b, 65624-06-8; 15c, 65624-08-0; 15d, 65624-07-9; 15e, 134006-37-4.

Positional Reactivity of Dibenzofuran in Electrophilic Substitutions

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Isomer distributions of dibenzofuran (DBF) in Friedel-Crafts acylations, Friedel-Crafts alkylations, and nitrations have been determined. The 2- and 3-positions of DBF represents most of the total reactivity. However, the ratio of 2- to 3-isomers greatly varied, depending on the nature of the electrophile. The positional reactivities have been found to be in the following sequence: 2- > 3- > 1- > 4-positions for Friedel-Crafts acylations, Friedel-Crafts benzylations, and nitrations with alkyl nitrate/Lewis acid or nitronium tetrafluoroborate. The ratios for acylations varied over a range from 13.1 to 2.9, while for benzylations and nitrations from 2.0 to 1.0. In contrast, for nitrations of DBF with nitric acid a different reactivity order was found: 3- > 2- > 1- > 4-, with the ratio varying from 0.8 to 0.03 depending on the nature of solvents used. The selectivity for the 3-substitution increased with increase in nitronium ion-like character of nitrating reagents. In particular, nitration with nitric acid in dichloromethane gave mostly 3-nitro-DBF (95% of the four possible isomeric mixture). The charge-transfer nitration with tetranitromethane under the UV irradiation has shown a similar isomer distribution to that in nitration with nitric acid. The MNDO calculations predicts that the late transition-state model (by σ-complex) favors reactions at the 2-position while the early transition-state model (by HOMO electron density) leads to the 3-substitution.

Dibenzofuran (DBF) is not only a key industrial intermediate but also a compound being investigated in heteroaromatic chemistry. Recently, DBF's chemistry has attracted much attention.[1] Positional reactivity of DBF in electrophilic substitutions is anomalous. Friedel-Crafts acylations,[2] Friedel-Crafts alkylations,[3] sulfonation,[4] and halogenations[5] of DBF give predominantly 2-substituted products. In contrast, nitrations with nitric acid in a

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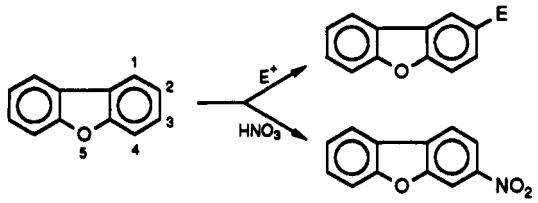
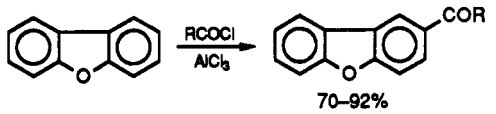
0022-3263/91/1956-4671$02.50/0

Scheme I[a]



[a] E = COR, alkyl, CHO, SO_3H, Cl, Br, I.

Scheme II[a]



70–92%

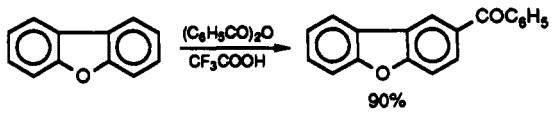
[a] R = CH_3, $C_6H_5CH_2$, C_6H_5, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 3-ClC_6H_4, 4-$CF_3C_6H_4$, 4-$NO_2C_6H_4$, 3,5-$(NO_2)_2C_6H_3$, C_6F_5.

mixed-acid system exclusively occur at the 3-position.[6] Isomer distributions for the all possible positions of DBF in conventional electrophilic substitutions have been examined little so far. Dewar and Urch reported that the nitration of DBF by nitric acid in acetic anhydride gives 40% of 2- and 3- and 20% of 1-nitro products.[7] We recently reported the isomer distributions for Friedel–Crafts benzoylation with benzoyl chloride,[2a,8] Friedel–Crafts benzylation with benzyl chloride,[8] and nitrations with some nitrating systems.[6a,9] The partial rate factors for each position of DBF relative to benzene were given for the protodetritiation and protodetrimethylsilylation by Eaborn.[10,11] The 2-position of DBF represents an average of 87% of the total reactivity of the four positions for the proton-exchange reactions and the Friedel–Crafts benzoylation. In contrast, the nitration with nitric acid in trifluoroacetic acid (TFA) solution occurs at the 3-position predominantly (≥90%).[6a] This anomalous difference in orientation between the nitration and the other reactions has been inexplicable in terms of the concepts that serve to interpret reactivities of monosubstituted benzenes in common electrophilic substitutions (Scheme I).[11] Now, we have systematically reexamined isomer distributions of DBF in Friede–Crafts acylations, Friedel–Crafts alkylations, and nitrations. Using MNDO approximations, we have estimated the positional reactivity of DBF for electrophilic substitutions.[12]

Results and Discussion

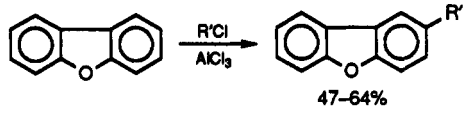
A number of Friedel–Crafts acylations, Friedel–Crafts alkylations, and nitrations of DBF were carried out with excess of DBF under controlled low-conversion conditions (less than 20%). The reaction products were analyzed by GLC to determine the isomer distributions. The results

Scheme III



90%

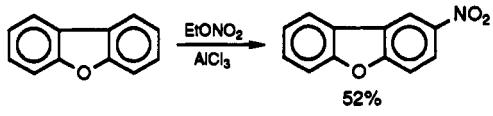
Scheme IV[a]



47–64%

[a] R′ = 4-$CH_3C_6H_4CH_2$, $C_6H_5CH_2$, 4-$ClC_6H_4CH_2$.

Scheme V



52%

are summarized in Table I together with the results of proton-exchange reactions reported by Eaborn.

Isomer Distributions of Friedel–Crafts Acylations. The acylations of DBF were carried out under the usual Friedel–Crafts conditions with acid chlorides. For example, DBF was reacted with 4-methoxybenzoyl chloride in the presence of aluminum trichloride in a dichloromethane solution at 20 °C. The GLC of the resulting crude product indicated four peaks besides those for the starting materials, showing the formation of all four possible acylated isomers of DBF. Following is the retention time sequence for the isomers: 1- < 4- < 2- < 3-. These times were confirmed by coinjection of authentic compounds prepared by independent procedures. Similarly, acetylation, phenacetylation, and substituted benzoylations (with the following substituents: 4-methyl-, 4-chloro-, 3-chloro-, 4-(trifluoromethyl)-, 4-nitro-, 3,5-dinitro-, and pentafluoro groups) were carried out (Scheme II). The positional reactivity order of DBF for Friedel–Crafts acylations has been found to be 2- ≥ 3- ≥ 1- ≳ 4-. This is basically in agreement with that observed for the proton-exchange reactions. A ratio of the 2- to 3-acyl-DBFs changes significantly with the nature of acylating agents, varying from 13.1 to 2.9. The ratio decreases with increase in the electron-withdrawing ability of the substituent on the benzoyl group. The reactions carried out in nitrobenzene showed some increase in 2-isomer than those carried out in dichloromethane. DBF on treatment with benzoic anhydride in boiling TFA gave a product mixture identical with that in benzoylation with benzoyl chloride/aluminum trichloride in dichloromethane (runs 3 and 4). The species responsible for the benzoylation is probably a mixed anhydride of trifluoroacetic acid and benzoic acid (Scheme III).

Isomer Distributions for Friedel–Crafts Alkylations. Friedel–Crafts alkylations of DBF with 4-methylbenzyl, 4-chlorobenzyl, and isopropyl chlorides were conducted in the presence of aluminum trichloride in a nitrohydrocarbon solution. A GLC chart of the crude products obtained showed a pattern similar to that of the benzylation previously reported,[8] i.e., two small peaks followed by two large peaks of the 2- and 3-isomers. In the case of isopropylation, some other peaks were detected with longer retention times than those of the 2- and 3-isopropyl-DBFs. These may be attributed to di- and/or polyalkylated products. The positional reactivity order of DBF for Friedel–Crafts substituted benzylations has been found to be 2- > 3- > 1- > 4-positions (Scheme IV). A ratio of the 2- to 3-isomers varied in a range between

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(12) A portion of this work has been reported in a short communication: Keumi, T.; Hamanaka, K.; Hasegawa, H.; Minamide, N.; Inoue, Y.; Kitajima, H. *Chem. Lett.* **1988**, 1285.

Table I. Isomer Distributions of Dibenzofuran in Electrophilic Substitutions under the Controlled Reaction Conditions[a]

run	reaction type	reagents	solvent	temp (°C)	isomer distributions (%) 1-	2-	3-	4-	ratio of 2-/3-isomers
1	acylation	$C_6H_5COCl/AlCl_3$	$PhNO_2$	20	0.7	92	7	0.4	13.1
2	protodetritiation[10]	TFA	TFA	70	3	86	7	4	12.3
3	acylation	$C_6H_5COCl/AlCl_3$	CH_2Cl_2	20	0.6	90	9	0.2	10.0
4		$(C_6H_5CO)_2O$/TFA	TFA	70	1.0	90	8	1.0	11.3
5		$C_6H_5CH_2COCl/AlCl_3$	$PhNO_2$	20	0.2	90	10	0.1	9.0
6		$4\text{-}CH_3OC_6H_4COCl/AlCl_3$	CH_2Cl_2	20	0.5	89	10	0.5	8.9
7		$4\text{-}CH_3C_6H_4COCl/AlCl_3$	CH_2Cl_2	20	0.8	89	10	0.2	8.9
8		$CH_3COCl/AlCl_3$	CH_2Cl_2	20	0.8	88	10	1.3	8.8
9	protodesilylation[11]	$HClO_4$	MeOH	50	3	83	10	4	8.3
10	acylation	$C_6H_5CH_2COCl/AlCl_3$	CH_2Cl_2	20	0.4	89	11	0.1	8.1
11		$4\text{-}ClC_6H_4COCl/AlCl_3$	CH_2Cl_2	20	0.9	88	11	0.4	8.0
12		$4\text{-}CF_3C_6H_4COCl/AlCl_3$	CH_2Cl_2	20	0.7	87	12	0.3	7.3
13		$3\text{-}ClC_6H_4COCl/AlCl_3$	CH_2Cl_2	20	1.3	85	13	0.7	6.5
14		$4\text{-}NO_2C_6H_4COCl/AlCl_3$	CH_2Cl_2	20	0.8	84	15	0.5	5.6
15		$C_6F_5COCl/AlCl_3$	$PhNO_2$	20	1.6	75	22	1.1	3.4
16		$3,5\text{-}(NO_2)_2C_6H_3COCl/AlCl_3$	CH_2Cl_2	20	8.1	70	22	0.1	3.2
17		$C_6F_5COCl/AlCl_3$	CH_2Cl_2	20	2.1	72	25	1.4	2.9
18	alkylation	$4\text{-}CH_3C_6H_4CH_2Cl/AlCl_3$	$EtNO_2$	20	3	64	32	1	2.0
19			$PhNO_2$	20	5	59	33	3	1.8
20		$C_6H_5CH_2Cl/AlCl_3$	$CHCl_3$	20	12	50	32	6	1.6
21			$PhNO_2$	20	9	50	35	6	1.4
22		$(CH_3)_2CHCl/AlCl_3$	$MeNO_2$	0	20	34	25	21	1.4
23	nitration	$CH_3CH_2ONO_2/AlCl_3$	$EtNO_2$	20	11	52	35	2	1.5
24			$PhNO_2$	20	13	50	35	2	1.4
25		CMN[b]/$TiCl_4$	$MeNO_2$	20	11	50	36	2	1.4
26		CMN[b]/$AlCl_3$	$MeNO_2$	20	10	51	37	2	1.4
27		NO_2BF_4	$EtNO_2$	0	22	43	33	2	1.3
28		$n\text{-}C_4H_9ONO_2/AlCl_3$	$MeNO_2$	20	10	48	40	2	1.2
29	alkylation	$4\text{-}ClC_6H_4CH_2Cl/AlCl_3$	$PhNO_2$	20	7	48	40	5	1.2
30			$EtNO_2$	20	6	47	43	4	1.1
31	nitration	NO_2BF_4	CH_2Cl_2	−50	21	41	36	2	1.1
32		$CH_3CH_2ONO_2/AlCl_3$	$(CH_2Cl)_2$	20	15	44	39	2	1.1
33		CMN[b]/$AlCl_3$	CH_2Cl_2	20	13	43	42	3	1.0
34		99% HNO_3	Ac_2O	20	11	39	48	2	0.81
35		99% HNO_3	$(CF_3CO)_2O$	0	11	39	50	1	0.78
36		99% HNO_3	CF_3SO_3H	−30	10	36	52	2	0.69
37		65% HNO_3	50% H_2SO_4	45–90	15	26	57	2	0.46
38		99% HNO_3	MeCN	45–90	11	26	61	2	0.42
39		99% HNO_3	AcOH	45–90	10	26	62	2	0.42
40		65% HNO_3	65% H_2SO_4	45–95	10	14	75	1	0.19
41		99% HNO_3	$MeNO_2$	20	8	7	84	1	0.08
42		99% HNO_3	TFA/AcOH (2v/3v)	0	7	7	86	1	0.08
43		99% HNO_3	TFA	0	3	4	93	1	0.04
44		99% HNO_3	CH_2Cl_2	−45	2	3	95	1	0.03
45	CT-nitration[c]	$C(NO_2)_4$/light	TFA	0	6	11	83	1	0.13
46			MeCN	0	10	22	63	5	0.35

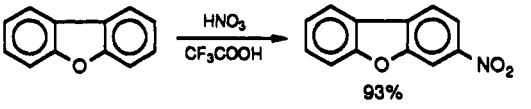
[a] Controlled to keep low conversion (less than 20%). Reproducible accuracy of isomer distributions is within ±1%. [b] 1-Cyano-1-methylethyl nitrate. [c] Irradiated with 100-W high-pressure mercury lamp.

2.0 and 1.1. The selectivity of the 2- over 3-isomers is much lower than that for the acylations, and it decreased successively in the following order: 4-methylbenzylation > benzylation > 4-chlorobenzylation.

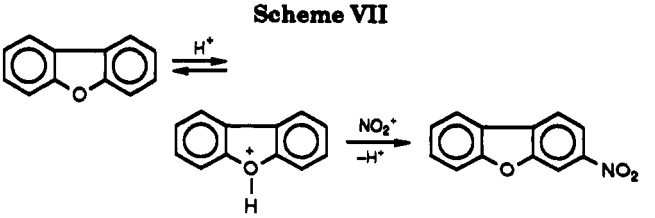
Isomer Distributions for Nitrations. In contrast to the Friedel–Crafts acylations and alkylations, nitrations of DBF show a different behavior. The ratio of 2- to 3-isomer in the nitration of DBF is highly dependent on the nature of the nitrating agent used and varies from 1.5 to 0.03. The reactions can be divided into two groups by the ratio, i.e., one giving a ratio of more than 1 such as Friedel–Crafts-type nitrations by alkyl nitrate/Lewis acid system, and others giving a ratio less than 1 such as nitrations by a nitric acid system.

The positional reactivity in nitrations with alkyl nitrate/Lewis acid systems or nitronium tetrafluoroborate has been found to be in the following order 2- > 3- > 1- > 4-positions, which resembles the order of Friedel–Crafts benzylations (Scheme V). In remarkable contrast, the positional reactivity in nitration of DBF with nitric acid systems follows a different sequence: 3- ≥ 2- > 1- ≥ 4-

Scheme VI



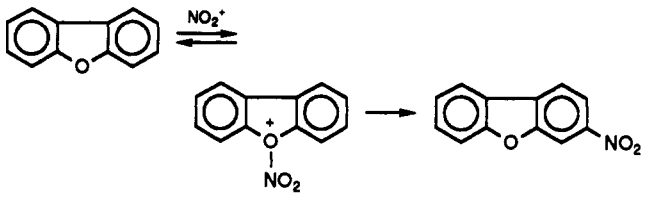
Scheme VII



positions. In particular, the nitration of DBF with nitric acid in TFA or with excess of nitric acid in dichloromethane predominantly gave 3-nitro-DBF (Scheme VI).

The preferential formation of the 3-isomer in these reactions might be explained by initial protonation of the oxygen atom by acids, which leads to a change in the di-

Scheme VIII



recting effect of DBF toward the electrophilic attack (Scheme VII).[10] The results of the Table I, however, indicate no direct relationship between the amount of the 3-isomer formed and the acidity of solvent used. For example, a super strong acid, trifluoromethanesulfonic acid, does not increase the amount of the 3-isomer compared to acetic acid or TFA (runs 36, 39, and 43). Also, benzoylation with benzoic anhydride in boiling TFA (run 4) does not show a significant increase in the yield of the 3-isomer compared to benzoylation with benzoyl chloride/aluminum trichloride in dichloromethane (run 3). In addition, as will be shown later, the initial protonation of the oxygen atom of DBF is unlikely according to the semiempirical calculation. Another possibility is that the nitronium ion might be trapped initially by the oxygen atom of DBF, followed by a rearrangement. However, it is difficult to explain why the rearrangement should give the 3-isomer predominantly (Scheme VIII).

Consequently, we have considered that the change in the isomer ratio in the nitration of DBF is due to the nature of nitrating species itself. The reacting species in nitration by nitric acid in organic solvent has been thought to be the nitronium ion associated with nitrate ion and molecular nitric acid as shown in eq 1.[13] The species in a nitric

$$5HNO_3 \rightleftarrows NO_2^+NO_3^-HNO_3 + H_3O^+NO_2^-HNO_3 \quad (1)$$

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^- \quad (2)$$

acid/sulfuric acid system has been recognized to be a nitronium ion in the equiribrium equation (2).[14] The concentration of a nitronium ion in the eqs 1 and 2 increases with the increase in the dielectric constant of the solvent or in the concentration of nitric acid and sulfuric acid.[15] The amount of 3-nitrodibenzofuran formed in nitration of DBF by nitric acid systems tends to increase with an increase in the dielectric constant of the solvent used in the sequence: dichloromethane (run 44, ϵ = 8.9), TFA (run 43, ϵ = 8.55), acetic acid (run 39, ϵ = 6.15). It also increases with an increase in the concentration of sulfuric acid (runs 37 and 40).

A mixture of fuming nitric acid and excess acetic anhydride has been recognized to afford acetyl nitrate as shown in eq 3.[16] A similar reaction can be considered for

$$(CH_3CO)_2O + HNO_3 \rightarrow CH_3COONO_2 + CH_3COOH \quad (3)$$

a mixture of fuming nitric acid and trifluoroacetic anhydride (eq 4). It has been reported that nitric acid in

$$(CF_3CO)_2O + HNO_3 \rightarrow CF_3COONO_2 + CF_3COOH \quad (4)$$

trifluoromethanesulfonic acid also affords trifluoromethanesulfonyl nitrate as shown in eq 5.[17] Therefore,

$$2CF_3SO_3H + HNO_3 \rightarrow CF_3SO_3NO_2 + H_3O^+CF_3SO_3^- \quad (5)$$

Table II. Positional Reactivity Indices of Dibenzofuran (DBF) Calculated by MNDO Methods

position of DBF	HOMO electron density	spin populatn[a]	total energy of protonated DBF$^+$ (eV)	rel energy of protonated DBF$^+$ (kcal/mol)
1	0.125	+0.425	-1974.554 19	3.23
2	0.061	-0.419	-1974.694 39	0
3	0.301	+0.559	-1974.562 10	3.05
4	0.041	-0.431	-1974.664 32	0.69
5	0.000	-0.003	-1973.910 95	18.07
			-1968.091 91 (free DBF)	

[a] The calculation was performed for the open-shell system of DBF radical cation.

Table III. Total Energies of Substituted Dibenzofuranoium Ions Calculated by MNDO Method

substit E	intermed type	energy of (E)-dibenzofuranonium ion: 2-position ϵ_2 (eV)	3-position ϵ_3 (eV)	rel energy $\epsilon_3 - \epsilon_2$ (kcal/mol)
CH_3CO	σ-complex	-2580.606 90	-2580.472 50	3.10
CH_3	σ-complex	-2131.069 18	-2130.939 85	2.98
Cl	σ-complex	-2314.845 27	-2314.755 52	2.07
NO_2	σ-complex	-2807.272 74	-2807.197 50	1.74
NO_2	π-complex	-2806.155 51	-2806.163 15	-0.18

the nitrating species in the reactions of runs 34–36 can be characterized as the nitrates CH_3COONO_2, CF_3COONO_2, and $CF_3SO_3NO_2$, respectively. Ratios of the 3- over 2-isomer in nitrations by these nitrating systems seem to depend on the leaving-group ability of a gegen ion of the nitronium ion, i.e., $CF_3SO_3^- > CF_3COO^- > CH_3COO^-$.

On the other hand, alkyl nitrates react with Lewis acid to give a polarized coordination complex as shown in eq 6.[18] Nitronium tetrafluoroborate is insoluble in di-

$$RONO_2 + AlCl_3 \longrightarrow \overset{-AlCl_3}{\overset{\vdots}{R\overset{+}{O}NO_2}} \quad (6)$$

chloromethane, but it would form a similar complex in a nitroalkane solution (eq 7). Nitrations by species in eqs

$$CH_3NO_2 + NO_2BF_4 \rightarrow CH_3N(O)ONO_2\text{–}BF_4 \quad (7)$$

3–7 may be classified as a nitration by NO_2X, differing from nitrations by free nitronium ion generated by eqs 1 and 2. The nitrating species NO_2X are of either a tight ion pair of nitronium ion with oxygen anions or nitrates.

The observation of a relationship between the isomer ratios and the nature of nitrating species led us to surmise that the extent of nitronium ion character of the reagents is responsible for the observed isomer distributions. The free nitronium ion-like reagents preferentially give 3-nitrodibenzofuran (runs 37–44). On the other hand, the nitrate-like reagents decrease the regioselectivity in giving the 3-isomer. Friedel–Crafts-type nitrations using an alkyl nitrate/Lewis acid system show similar positional reactivity to the Friedel–Crafts benzylations.

Factors Controlling Positional Reactivities of Dibenzofuran in Electrophilic Substitutions. We performed MNDO calculations to estimate the positional reactivity of DBF toward electrophiles.[19] We limited the

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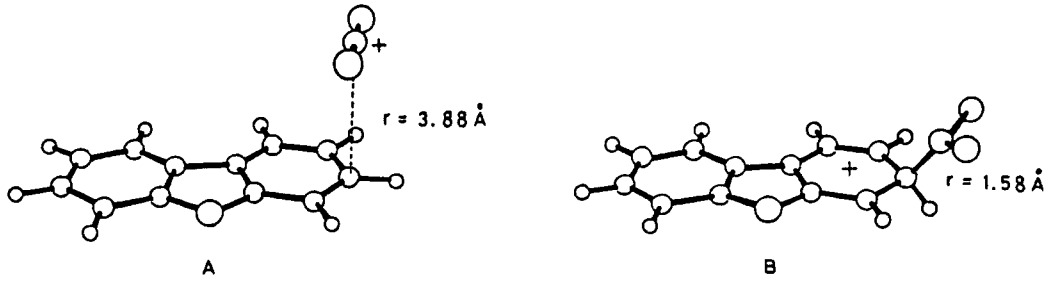
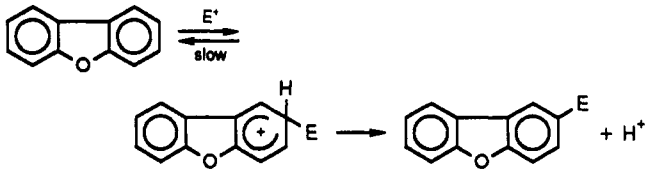


Figure 1. Optimized structures for the nitrated π- (A) and σ-complexes (B) at the 3-position of dibenzofuran.

Scheme IX



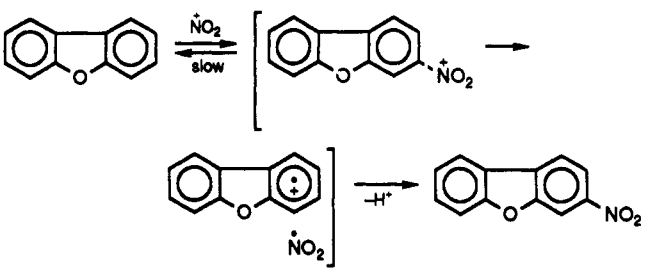
discussion on the reactivity to the 2- and 3-positions, since the both positions represent most of the total reactivity of a DBF molecule for electrophilic substitutions presented in Table I. The calculations with full geometry optimization were carried out on two reactivity indices: (i) HOMO electron density of free DBF or relative stability of oriented π-complexes as a model for the early transition state and (ii) relative stability of the σ-complex intermediate as a model for the late transition state.[20] The results are listed in Tables II and III. The optimized structures for the π- and σ-complexes with nitronium ion at the 3-position are shown in Figure 1.

The relative stability of protonated dibenzofuranonium ion increased in the following order 2- > 4- > 3- > 1- > 5-positions, in contrast to the order of the HOMO electron density, 3- > 1- > 2- > 4- > 5-positions. The calculated sequences for the relative stability of protonated dibenzofuranonium ion are fundamentally in agreement with the order of the positional reactivity observed for the protodetritiation reaction of DBF. The calculation indicates that the O-protonation requires the highest energy of all the positions of DBF. The 2-σ-complexes for acetylation, methylation, nitration, and chlorination are more stable than the corresponding 3-σ-complexes. Therefore, the positional reactivities observed in the Friedel–Crafts reactions including nitration with alkyl nitrate/Lewis acid systems can be explained by the late transition-state mechanism. Without giving detailed isomer distributions, positive halogenation,[5] chloromethylation,[21] formylation,[22] and sulfonation[4] have been reported to give the 2-substituted derivatives as the sole isolable product. These reactions also would follow the late transition-state mechanism (see Scheme IX).

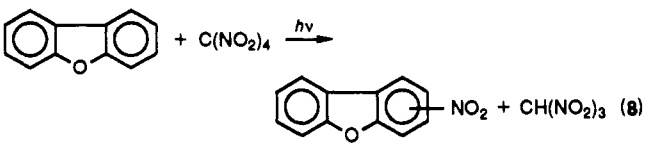
In remarkable contrast, the positional reactivity observed in the nitration of DBF with nitric acid systems is inconsistent with that expected for the late transition mechanism. The reactivity orders seem to be controlled by the early transition-state mechanism because the HOMO electron density is the highest at the 3-position and the oriented π-complex with a nitronium ion is more stable at the 3-position than at the 2-position.

An alternative explanation would be possible for the notable positional reactivity in the nitration. Since nitronium ion has a high electron affinity and, moreover,

Scheme X



DBF is a good electron donor as expected from the calculated ionization potential 8.30 eV (cf. the value of 8.82 eV for toluene[23]), it would be appropriate to consider the possibility of the charge-transfer mechanism in the nitration.[24] To confirm this, we undertook the nitration of DBF with tetranitromethane in TFA under irradiation by high-pressure mercury lamp. Under these conditions, the charge-transfer mechanism should predominate.[25] The product contained a mixture of mononitrated DBFs (99% yield), the composition being similar to that of the thermal nitration with nitric acid in TFA (runs 43 and 45, eq 8).



The charge-transfer nitration carried out in acetonitrile also gave a mixture of the almost same composition as that for the thermal nitration (runs 38 and 46). It is worth noting that the nitration with tetranitromethane did not proceed without irradiation.

These results lead us to suggest that the nitration of DBF with nitric acid may proceed by the pathway of formation of a stable oriented π-complex at the 3-position, followed by charge-transfer from DBF to nitronium ion giving DBF radical cation and NO_2 radical. Recombination of these radicals gives exclusively 3-substituted product (Scheme X). This is partly confirmed by the fact that the spin population of DBF radical cation is the highest at the 3-position.

Thus, the anomalous difference in orientation between the Friedel–Crafts type reactions and the nitrations with nitric acid systems can be explained by the nature of transition-state determining products. The reactions favoring the 2-substitution are subjected to the late tran-

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sition-state-like mechanism, while predominant formation of the 3-isomer follows the early transition-state mechanism.

Experimental Section

Measurements. All melting points are uncorrected. IR spectra were recorded on a Hitachi EPI-S2 Model spectrophotometer as KBr pellets. ^{1}H NMR spectra were recorded on a JEOL-FX 270 FT-NMR (270 MHz) spectrometer in chloroform-*d* solution with tetramethylsilane as an internal standard. GLC analysis was carried out on a Hitachi GC Model 163 gas chromatograph equipped with a hydrogen flame ionization detector and a stainless-steel column (length 5 m, i.d. 3 mm) packed with 3% Dexil 300 GC on Chromosorb W. Isomer distributions were calculated from peak areas obtained by a System Instruments Chromatocorder 11 instrument after calibrating for each authentic compound.

Materials. 1-Acetyl-DBF. To a suspension of cuprous iodide (3.16 g; 16.6 mmol) in ether (100 mL) was added methyllitium (12 mL; 18% ether solution, 17.4 mmol) at 0 °C over 20 min under nitrogen stream. After the mixture was stirred for 20 min at the same temperature and cooled at −78 °C, a solution of 1-(chlorocarbonyl)-DBF[2a] (4.3 mmol) in ether (60 mL) was added dropwise to the reaction mixture at −78 °C. Then, the mixture was stirred further for 20 min at the same temperature, poured into ice–water, and extracted with ether. The organic layer was washed with 5% aqueous sodium hydroxide and water, dried, and evaporated to give the crude product (quantitative yield). Distillation of the product under vacuum gave 1-acetyl-DBF (0.48 g, 48% yield): bp 198 °C (2 mmHg); ^{1}H NMR δ 2.36 (s, 3 H), 7.10–7.60 (m, 6 H), 8.75–8.90 (m, 1 H); IR ν (neat) 3000, 1700, 1208, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.96; H, 4.76.

4-Acetyl-DBF. A similar reaction of 4-(chlorocarbonyl)-DBF[2a] with methyllithium gave 4-acetyl-DBF: 54% yield; mp 67 °C; ^{1}H NMR δ 2.77 (s, 3 H), 7.10–7.80 (m, 5 H), 7.90–7.95 (m, 2 H); IR (KBr) ν 3000, 1690, 1180, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.75; H, 4.63.

The following acyl-DBFs were obtained from Friedel–Crafts reaction of DBF and the corresponding acid chloride. Their structures were determined on the basis of their spectroscopic data according to our previous reports.[26]

2-(4-Methylbenzoyl)-DBF: 27% yield; mp 139–140 °C (EtOH); ^{1}H NMR δ 2.47 (s, 3 H), 7.30–7.40 (m, 3 H), 7.50 (t, 1 H, J = 7.3 Hz), 7.59–7.64 (m, 2 H), 7.76 (d, 1 H, J = 7.8 Hz), 7.94–7.98 (m, 2 H), 8.43 (s, 1 H); IR (KBr) ν 1645, 1610, 1273, 1200, 750 cm^{-1}; UV λ_{max} (log ϵ) 220 (4.47), 246 (4.40) nm. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.68; H, 5.10.

2-Phenacetyl-DBF: 24% yield; mp 118 °C (EtOH); ^{1}H NMR δ 4.40 (s, 2 H), 7.27–7.42 (m, 6 H), 7.47–7.53 (m, 1 H), 7.59 (d, 2 H, J = 3 Hz), 7.80 (d, 1 H, J = 3.6 Hz), 8.16 (d, 1 H, J = 3.9 Hz), 8.65 (s 1 H); IR ν 1686, 1192, 798 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.61; H, 4.92

3-Phenacetyl-DBF: 2% yield; mp 162 °C (cyclohexane); ^{1}H NMR δ 4.39 (s, 2 H), 8.23 (s, 1 H), 8.02–8.04 (m, 2 H), 7.33–7.60 (m, 9 H); IR ν 2900, 1675, 1192, 742 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.69; H, 4.81.

2-[4-(Trifluoromethyl)benzoyl]-DBF: 31% yield; mp 177–178 °C (EtOH); ^{1}H NMR δ 7.37–7.43 (m, 1 H), 7.50–7.56 (m, 1 H), 7.61–7.67 (m, 2 H), 7.79 (d, 2 H, J = 3 Hz), 7.92–8.00 (m, 4 H), 8.44 (d, 1 H, J = 0.5 Hz); IR ν 3055, 1648, 1328, 750 cm^{-1}. Anal. Calcd for $C_{20}H_{11}O_2F_3$: C, 70.59; H, 3.26. Found: C, 70.45; H, 3.18.

3-[4-(Trifluoromethyl)benzoyl]-DBF: 4% yield; mp 188–189 °C (CH_3CN); ^{1}H NMR δ 7.42–7.44 (m, 1 H), 7.53–7.65 (m, 2 H), 7.78–7.96 (m, 4 H), 8.03–8.10 (m, 4 H); IR ν 2920, 1651, 1324, 750 cm^{-1}. Calcd for $C_{20}H_{11}O_2F_3$: C, 70.59; H, 3.26. Found: C, 70.32; H, 3.01.

2-(Pentafluorobenzoyl)-DBF: 23% yield; mp 124–125 °C (EtOH); ^{1}H NMR δ 7.43–7.69 (m, 4 H), 7.90–8.01 (m, 2 H), 8.48 (s, 1 H); IR ν 1677, 1490, 1218, 740 cm^{-1}. Anal. Calcd for $C_{19}H_7O_2F_5$: C, 63.00; H, 1.95. Found: C, 62.69; H, 1.87.

3-(Pentafluorobenzoyl)-DBF: 2% yield; mp 152–153 °C (EtOH); ^{1}H NMR δ 7.39–7.45 (m, 1 H), 7.55–7.65 (m, 2 H), 7.83–7.87 (m, 1 H), 8.02–8.08 (m, 3 H); IR ν 1672, 1488, 1316, 1260, 1207, 983 cm^{-1}. Anal. Calcd for $C_{19}H_7O_2F_5$: C, 63.00; H, 1.95. Found: C, 62.76; H, 1.88.

2-(3,5-Dinitrobenzoyl)-DBF: 32% yield; mp 200–201 °C (AcOH); ^{1}H NMR δ 7.43 (t, 1 H, J = 7.8 Hz), 7.58 (t, 1 H, J = 7.3 Hz), 7.65 (d, 1 H, J = 8.3 Hz). 7.72 (d, 1 H, J = 8.8 Hz), 7.80 (d, 1 H, J = 7.3 Hz), 7.94 (dd, 1 H, J = 2.0, 9.0 Hz), 8.46 (s, 1 H), 8.96 (s, 2 H), 9.26 (s, 1 H); IR ν 1660, 1555, 1350, 1270, 720 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 243 (4.58) nm. Anal. Calcd for $C_{19}H_{10}O_6N_2$: C, 62.99; H, 2.78. Found: C, 62.87; H, 2.90.

3-(3,5-Dinitrobenzoyl)-DBF: 5% yield; mp 219–220 °C (benzene); ^{1}H NMR δ 7.45 (t, 1 H, J = 7.3 Hz), 7.58–7.67 (m, 2 H), 7.81 (d, 1 H, J = 8.3 Hz), 8.05 (s, 1 H), 8.07 (d, 1 H, J = 7.3 Hz), 8.13 (d, 1 H, J = 8.3 Hz), 8.98 (s, 2 H), 9.28 (s, 1 H); IR ν 1670, 1560, 1350, 1300, 720 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 230 (4.47), 316 (4.25) nm. Anal. Calcd for $C_{19}H_{10}O_6N_2$: C, 62.99; H, 2.78. Found: C, 62.90, H, 2.85.

1-(3,5-Dinitrobenzoyl)-DBF: 3% yield; mp 195–196 °C (EtOH); ^{1}H NMR δ 7.32–7.67 (m, 5 H), 7.92 (d, 1 H, J = 8.3 Hz), 8.21 (d, 1 H, J = 7.8 Hz), 9.05 (s, 2 H), 9.23 (s, 1 H); IR ν 1670, 1550, 1350, 1285, 725 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 231 (4.53), 324 (3.97) nm. Anal. Calcd for $C_{19}H_{20}O_6N_2$: C, 62.99; H, 2.78. Found: C, 62.92; H, 2.88.

The following acyl-DBF's were prepared by Friedel–Crafts reaction of arenes with the corresponding (chlorocarbonyl)-DBF following our previous report.[2a]

3-(4-Methylbenzoyl)-DBF: 61% yield; mp 168–169 °C (EtOH); ^{1}H NMR δ 2.46 (s, 3 H), 7.31 (d, 2 H, J = 7.8 Hz), 7.39 (t, 1 H, J = 7.8 Hz), 7.53 (t, 1 H, J = 7.3 Hz), 7.61 (d, 1 H, J = 8.3), 7.77 (d, 2 H, J = 8.3 Hz), 7.82 (d, 1 H, J = 7.3 Hz), 8.01–8.04 (m, 3 H); IR ν 1645, 1615, 1288, 750 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 221 (4.50), 307 (4.47) nm. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.68; H, 5.10.

3-(4-Methoxybenzoyl)-DBF: 60% yield; mp 159 °C (EtOH); ^{1}H NMR δ 3.90 (s, 3 H), 6.99 (d, 2 H, J = 7.8 Hz), 7.38 (t, 1 H, J = 7.3 Hz), 7.52 (t, 1 H, J = 8.3 Hz), 7.61 (d, 1 H, J = 8.3 Hz), 7.79 (d, 1 H, J = 7.8 Hz), 7.87 (d, 2 H, J = 7.8 Hz), 7.98–8.04 (m, 3 H); IR ν 1645, 1613, 1295, 1260, 750 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 219 (4.47), 308 (4.49) nm. Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.70; H, 4.51.

3-(4-Chlorobenzoyl)-DBF: 21% yield; mp 181–182 °C (EtOH); ^{1}H NMR δ 7.28–7.62 (m, 3 H), 7.79–7.83 (m, 3 H), 8.00–8.07 (m, 5 H); IR ν 1648, 1637, 1273, 850, 740 cm^{-1}. Anal. Calcd for $C_{19}H_{11}O_2Cl$: C, 74.40; H, 3.61. Found: C, 74.53; H, 3.99.

1-(4-Methoxybenzoyl)-DBF: 73% yield; mp 66–67 °C (*n*-hexane); IR ν 2900, 1665, 1210, 750 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.65; H, 4.57.

4-(4-Methoxybenzoyl)-DBF: 77% yield; mp 159–160 °C (EtOH); IR ν 2920, 1650, 1203, 747 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 249 (4.21), 252.5 (4.24), 292 (4.38) nm. Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.53; H, 4.33.

The following benzyl-DBFs were prepared by heating a mixture of the corresponding aroyl-DBF, potassium hydroxide, and hydrazine hydrate in diethylene glycol under reflux according to our previous report.[8]

2-(4-Methylbenzyl)-DBF: 52% yield; mp 61–62 °C (MeOH); ^{1}H NMR δ 2.32 (s, 3 H), 4.10 (s, 2 H), 7.12 (s, 4 H), 7.26–7.33 (m, 2 H), 7.39–7.55 (m, 3 H), 7.55 (s, 1 H), 7.88 (d, 1 H, J = 3 Hz); IR ν 2900, 1485, 1455, 1200, 800, 740 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.06; H, 6.08.

3-(4-Methylbenzyl)-DBF: 63% yield; mp 99–100 °C (EtOH); ^{1}H NMR δ 2.32 (s, 3 H), 4.10 (s, 2 H), 7.12 (s, 4 H), 7.17–7.44 (m, 4 H), 7.53 (d, 1 H, J = 4 Hz), 7.84 (d, 1 H, J = 3 Hz), 7.92 (d, 1 H, J = 3 Hz); IR ν 2900, 1460, 1425, 1200, 745 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.93. Found: C, 88.14; H, 5.77.

2-(4-Chlorobenzyl)-DBF: 33% yield; mp 68–69 °C (EtOH); ^{1}H NMR δ 4.10 (s, 2 H), 7.16 (d, 2 H, J = 3 Hz), 7.23–7.34 (m, 4 H), 7.41–7.56 (m, 3 H), 7.72–7.73 (m, 1 H), 7.90 (d, 1 H, J = 3 Hz); IR ν 2920, 1490, 1200, 1090, 800 cm^{-1}. Anal. Calcd for $C_{19}H_{13}OCl$: C, 77.95; H, 4.47. Found: C, 77.69; H, 4.53.

3-(4-Chlorobenzyl)-DBF: 60% yield; mp 123–124 °C (EtOH); ^{1}H NMR δ 4.11 (s, 2 H), 7.14–7.52 (m, 9 H), 7.84–7.87 (m, 2 H); IR ν 2942, 1500, 1465, 1210, 750 cm^{-1}. Anal. Calcd for $C_{19}H_{13}OCl$:

(26) Keumi, T.; Yagi, Y.; Kato, Y.; Taniguchi, R.; Temporin, M.; Kitajima, H. *J. Chem. Soc., Perkin Trans. 2* **1984**, 799.

C, 77.95; H, 4.47. Found: C, 77.71; H, 4.77.

Isopropyl-DBFs were prepared by the reaction of the corresponding acetyl-DBF with methylmagnesium iodide followed by heating with 5% paradium carbon at 200 °C.

2-Isopropyl-DBF: 24% yield from 2-acetyl-DBF; bp 132 °C (3 mmHg); ^{1}H NMR δ 1.34 (d, 6 H, J = 6.8 Hz), 3.08 (h, 1 H, J = 6.8 Hz), 7.20–7.92 (m, 7 H); IR ν 2950, 1480, 1448, 1200, 745 cm^{-1}; MS m/z 210 (M^+, 60), 195 (60), 177 (50), 165 (100). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.95; H, 6.55.

3-Isopropyl-DBF: 30% yield; bp 160 °C (6 mmHg); mp 46–47 °C; ^{1}H NMR δ 1.33 (d, 6 H, J = 6.8 Hz), 3.08 (h, 1 H, J = 6.8 Hz), 7.20–7.92 (m, 7 H); IR ν 2950, 1457, 1428, 1206, 930, 752, 728 cm^{-1}; MS m/z 210 (M^+, 45), 195 (70), 177 (85), 165 (100). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.44; H, 6.65.

Other DBF derivatives used as the authentic compounds for determining isomer distributions were prepared by the procedures reported in the literature. Melting points of compounds were as follows: 2-acetyl-DBF, mp 81–82 °C (lit.[27] mp 80–81 °C); 3-acetyl-DBF, mp 147–148 °C (lit.[28] mp 144 °C); 2-(4-methoxybenzoyl)-DBF, mp 142–143 °C (lit.[29] mp 142–143 °C); 2-(4-chlorobenzoyl)-DBF, mp 156–157 °C (lit.[30] mp 155–156 °C); 2-(3-chlorobenzoyl)-DBF, mp 139–140 °C (lit.[30] mp 138–140 °C); 3-(3-chlorobenzoyl)-DBF, 159–160 °C (lit.[30] mp 159–160 °C); 2-(4-nitrobenzoyl)-DBF, mp 200–201 °C (lit.[29] mp 203 °C); 3-(4-nitrobenzoyl)-DBF, mp 216–219 °C (lit.[29] mp 218–219 °C); 1-nitro-DBF, mp 123 °C (lit.[6b] mp 126–127 °C); 2-nitro-DBF, mp 153–154 °C (lit.[7] mp 151–152 °C); 3-nitro-DBF, mp 181–182 °C (lit.[6b] mp 182–183 °C); 4-nitro-DBF, mp 138–139 °C (lit.[31] mp 138–139 °C).

General Procedure for Friedel–Crafts Acylation of DBF. To a solution of DBF (2.2 mmol) in a given solvent (2 mL), was added a solution of acyl chloride (0.5 mmol) and aluminum trichloride (0.5 mmol) dissolved in the same solvent (2 mL) over 10 min at 20 °C. After being stirred for 2 h at the same temperature, the reaction mixture was hydrolyzed with 1 M hydrochloric acid and extracted with ether. The ether layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the resulting residue was analyzed by GLC.

Benzoylation with Benzoic Anhydride. A mixture of DBF (0.50 g, 3.08 mmol), benzoic anhydride (0.35 g, 1.54 mmol), and trifluoroacetic anhydride (2.59 g, 12.3 mmol) in trifluoroacetic acid (10 mL) was heated under reflux for 10 h. After that, it was poured into ice–water and extracted with ether. The ether layer was washed with water, aqueous hydroxide, and water and dried. After evaporation of the solvent, the resulting residue was analysed by GLC.

Friedel–Crafts Isopropylation of DBF. To a solution of DBF (1.00 g, 6 mmol) and aluminum trichloride (0.20 g, 1.5 mmol) in nitromethane (10 mL) was added a solution of isopropyl chloride (0.12 g, 1.5 mmol) in nitromethane (5 mL) at 0 °C over 10 min under stirring. After being stirred for 2 h at the same temperature, the reaction mixture was poured into ice–water and extracted with ether. The ether layer was analyzed by GLC. In a similar procedure, Friedel–Crafts benzylations of DBF with substituted benzyl chlorides were carried out.

Nitration with Nitric Acid. A typical procedure is described for the nitration in TFA as follows. To a suspension of DBF (0.500 g, 3 mmol) in TFA (10 mL) was a solution of 99% nitric acid (0.057 g, 0.91 mmol) in TFA (2 mL) dropwise at the 0 °C. The reaction mixture was stirred at the same temperature for 0.5 h and poured into ice–water. The resulting precipitate was extracted with ether, and the ether layer was analyzed by GLC.

Nitration with Ethyl Nitrate. To a solution of DBF (0.500 g, 3 mmol) and ethyl nitrate (0.08 g, 0.75 mmol) in nitromethane (3 mL) was added a solution of aluminum trichloride (0.12 g, 0.9 mmol) in nitroethane (2 mL) at 5 °C over 10 min, and then the mixture was stirred at 20 °C for 1 h. After an addition of 0.1 M hydrochloric acid (3 mL), the mixture was extracted with ether and the ether solution was measured by GLC.

Charge-Transfer Nitration. A solution of DBF (0.42 g, 2.5 mmol) and tetranitromethane (3.92 g, 20 mmol) in TFA (50 mL), which is light brown, was irradiated with the 100-W high-pressure mercury lamp filtered through a Pyrex glass at 0 °C for 10 h under nitrogen stream. The reaction mixture was poured into ice–water, and the resulting precipitate was washed with aqueous sodium hydroxide solutions and washed with water to give a light yellow solid (0.53 g, 99% yield). A solution of the solid dissolved in benzene was analyzed by GLC.

MNDO Calculations. The MNDO calculations of DBF and σ-complexes of DBF with an electrophile were made by using the MOPAC-MNDO program of Dewar and collaborators.[19] All geometric parameters (bond length, bond angles, and dihedral angles) were optimized without any specific assumptions. On the other hand, the total energies of the oriented π-complexes of DBF with nitronium ion were calculated under conditions in which only the nitronium structure was optimized.

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