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Aromatic Arylation with Aryl Radicals. IV. The Kinetic Hydrogen Isotope Effect in the Aromatic Phenylation with Phenyl Radical

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Anisole-4*d*, chlorobenzene-4*d*, chlorobenzene-d_5, nitrobenzene-d_5, *m*-dinitrobenzene-d_4, and 1,3,5-tri-*t*-butylbenzene-d_3 were phenylated with phenyl radical generated from PhN_2BF_4–$NaNO_2$, *N*-nitrosoacetanilide or phenylazotriphenylmethane(PAT), and the isotope effect in these phenylations was determined. The values of k_H/k_D in the phenylations of chlorobenzene and 1,3,5-tri-*t*-butylbenzene are not so larger than unity, whereas that in the phenylation at the 2-position of *m*-dinitrobenzene with PAT was very large (~11).

Large isotope effect was observed in the phenylation of arenes with the phenyl radical generated from benzoyl peroxide (BPO) in highly diluted solutions ($k_H/k_D=6.6$),[1] whereas no isotope effect was observed in the phenylations with *N*-nitrosoacetanilide (NNA) or phenylazotriphenylmethane.[2] It has been proposed that in highly diluted solutions of BPO the hydrogen-abstraction from the cyclohexadienyl radicals produced proceeds slowly by disproportionation between the cyclohexadienyl radicals themselves since benzoyloxy radical is ineffective due to its low concentration,[1] whereas in the phenylations with NNA or PAT no isotope effect is observed since the hydrogen-abstraction from the cyclohexadienyl radicals proceeds quickly by the presence of efficient hydrogen abstractors in rather high concentrations.[2]

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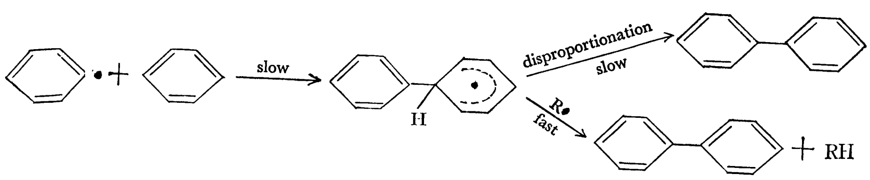
[1] E. L. Eliel, Z. Welvart, and S. H. Wilen, *J. Org. Chem.*, **23**, 1821 (1958); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Amer. Chem. Soc.*, **82**, 2936 (1960).

[2] E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Lett.*, **1962**, 749; E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, **30**, 2451 (1965).



A previous paper from our laboratories described the generation of phenyl radical from PhN_2BF_4–$NaNO_2$ in DMSO according to the following scheme, and an isotope effect was observed in the phenylation of arenes with this system.[3]

$$PhN_2BF_4 + NaNO_2 \longrightarrow PhN{=}N{-}O{-}N{=}O + NaBF_4$$

$$PhN{=}N{-}O{-}N{=}O \longrightarrow Ph\cdot + N_2 + NO_2$$

or

$$2PhN{=}N{-}O{-}N{=}O \longrightarrow PhN{=}N{-}O{-}N{=}NPh + N_2O_3$$

$$PhN{=}N{-}O{-}N{=}NPh \longrightarrow Ph\cdot + N_2 + \cdot ON{=}NPh$$

In this system, abstraction of the hydrogen atom from the cyclohexadienyl radicals is efficiently carried out either by NO_2 or $PhN{=}NO\cdot$, the latter radical being the hydrogen abstractor in the phenylation with NNA.[4] Existence of isotope effect in the phenylation in the presence of an efficient hydrogen-abstractor contradicts with the interpretation proposed by Eliel *et al.*[2] In an attempt to gain further understanding in this problem, various deuterated arenes have been phenylated with phenyl radicals produced from PhN_2BF_4–$NaNO_2$, BPO, NNA and PAT, and the results will be described in this paper.

Table 1. Isomer distributions and partial rate factors in the phenylation of PhX and deuterated PhX with PhN_2BF_4–$NaNO_2$ in DMSO at 20°C[a]

Substrate	Isomer distributions (%)			Partial rate factors		
	o-,	m-,	p-,	k_o/k	k_m/k	k_p/k
$PhOCH_3$	72.4	14.2	13.4			
$PhOCH_3$-4*d*	71.6	14.3	14.1			
PhCl	56.5	23.5	20.0	3.45	1.44	2.44
PhCl-4*d*	55.3	24.2	20.5			
PhCl-d_5	58.2	23.4	18.4	3.13	1.26	1.98
$PhNO_2$	77.4	5.9	16.7	19.8	1.51	8.55
$PhNO_2$-d_5	73.4	6.8	19.8	12.3	1.14	6.62

a) The average values of two experiments.

Results and Discussion

Table 1 shows the isomer distributions and partial rate factors in the phenylation of arenes and deuterated arenes. The isomer distributions in phenylated $PhOCH_3$-4*d* and PhCl-4*d* are not too much different from those in the corresponding methyldiphenyls and chlorodiphenyls. From the partial rate factors in the phenylations of PhCl-d_5, PhCl, $PhNO_2$-d_5, and $PhNO_2$, the values of k_H/k_D at the *ortho*, *meta* and *para* positions were calculated. The results are shown in Table 2.

Table 2. Kinetic isotope effect in the phenylation with phenyl radical

Substrate	k_H/k_D in the formation of substituted diphenyls[a]		
	2-,	3-,	4-,
PhCl-d_5	1.10	1.14	1.23
$PhNO_2$-d_5	1.61	1.32	1.29

a) These values were calculated from the partial rate factors listed in Table 1. Experimental errors were ±0.10

Isotope effect is fairly small in the case of chlorobenzene ($k_H/k_D = 1.10 \sim 1.23$), whereas it is considerably large in the case of nitrobenzene ($k_H/k_D = 1.29 \sim 1.61$). It is interesting that the k_H/k_D values are different at different positions of these arenes.

The fact that isotope effect was observed in the presence of an efficient hydrogen-abstractor ($PhN{=}NO\cdot$ or NO_2) contradicts with the explanation proposed by Eliel *et al.*[2] In order to determine isotope effect more directly and in greater details, competitive phenylations of an arene and the corresponding deuterated arene were carried out by use of the phenyl radicals generated from PhN_2BF_4–$NaNO_2$, *N*-nitrosoacetanilide and phenylazotriphenylmethane. The results are shown in Table 3.

In the phenylation of $C_6D_5NO_2$–$C_6H_5NO_2$, the k_H/k_D values at *para* position were nearly unity regardless of the phenyl radical source, whereas those at *ortho* position were fairly large in the cases of PhN_2BF_4–$NaNO_2$ and NNA ($k_H/k_D = 2.36$ and 2.02). It appears strange that no isotope effect was observed at *ortho* position of nitrobenzene when PAT was used as the radical source.

In the phenylation of *m*-$C_6D_4(NO_2)_2$–*m*-$C_6H_4(NO_2)_2$, isotope effects were observed both at 4 and 2 positions with the phenyl radicals generated from all the sources. In the case of the phenylation with PAT, the k_H/k_D value at the more crowded 2 position was greater than that expected from the zero-point energies of the C–H and C–D bonds ($k_H/k_D \fallingdotseq 11$).

Bromberg, Muszkat, and Fischer observed an unusually large isotope effect ($k_H/k_D = 95$) in the initiation step of the reaction of 4a,4b-dihydrophenanthrene with oxygen.[5] They stated that the large kinetic isotope effect is due to both a considerable loss of zero-point energy of stretching and bending vibration in the transition state and a large contribution from quantum-mechanical tunnelling.

Shih, Hey, and Williams reported absence of isotope effect in the phenylation of tritiated benzene with benzoyl peroxide,[6] and Price and Convery also reported absence of isotope effect in the phenylation of 2,4-

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[3] M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, This Bulletin, **43**, 1131 (1970).

[4] C. Rüchardt and B. Freudenberg, *Tetrahedron Lett.*, **1964**, 3623.

[5] A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Commun.*, **1968**, 1352.

[6] C. Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, **1959**, 1871.

TABLE 3. KINETIC HYDROGEN ISOTOPE EFFECT IN THE COMPETITIVE PHENYLATION OF ARENES WITH PHENYL RADICAL

Substrate	Radical source	Temperature (°C)	k_H/k_D in the formation of substituted diphenyls[a]		
			2-,	3-,	4-,
$C_6D_5NO_2+C_6H_5NO_2$	PhN_2BF_4–$NaNO_2$	20±3	2.36	b	1.06
$C_6D_5NO_2+C_6H_5NO_2$	PhN(NO)$COCH_3$	20±0.1	2.02	b	1.03
$C_6D_5NO_2+C_6H_5NO_2$	PhN=$NCPh_3$	55±0.1	1.01	b	1.00
				2, 4, 6-	
1,3,5-C_6D_3*t*-Bu_3+1,3,5-C_6H_3*t*-Bu_3	PhN(NO)$COCH_3$	20±0.1		1.06	
1,3,5-C_6D_3*t*-Bu_3+1,3,5-C_6H_3*t*-Bu_3	PhN=$NCPh_3$	55±0.1		1.01	
			2,4-,		2,6-,
m-$C_6D_4(NO_2)_2$+*m*-$C_6H_4(NO_2)_2$	PhN_2BF_4–$NaNO_2$	20±3	1.54		1.55
m-$C_6D_4(NO_2)_2$+*m*-$C_6H_4(NO_2)_2$	PhN(NO)$COCH_3$	20±0.1	1.45		1.77
m-$C_6D_4(NO_2)_2$+*m*-$C_6H_4(NO_2)_2$	PhN=$NCPh_3$	55±0.1	1.76		~11
m-$C_6D_4(NO_2)_2$+*m*-$C_6H_4(NO_2)_2$	BPO[c]	90—100	2.03		e
m-$C_6D_4(NO_2)_2$+*m*-$C_6H_5(NO_2)_2$	BPO[d]	80±0.1	2.53		e

a) The average values of two experiments; experimental errors were ±0.10.
b) Yields of the meta isomer were low, and isolation was not possible.
c) Without solvent. d) In acetonitrile. e) Yields of 2,6-isomers were low, and they were not isolated.

dinitrotritiobenzene with benzoyl peroxide.[7] Both of these groups used benzoyl peroxide in rather large concentrations, and it is conceivable that many benzoyloxy radicals (a highly active hydrogen-abstractor) are present in the media and effectively abstract hydrogens of the intermediate cyclohexadienyl radicals. In an attempt to establish whether or not isotope effect exists under such conditions, the experiment of Price and Convery was repeated with benzoyl peroxide in a *m*-$C_6H_4(NO_2)_2$–*m*-$C_6D_4(NO_2)_2$ mixture. As shown in Table 3, k_H/k_D was found to be 2.03. Since the conditions of this experiment are somewhat drastic (a solid mixture of benzoyl peroxide and *m*-dinitrobenzene is heated up over 90°C for melting and decomposition), a similar mixture was dissolved in acetonitrile and the homogeneous solution was let to decompose at 80°C. Again, isotope effect was observed (k_H/k_D=2.53). In the experiment with a solid mixture of BPO and *m*-dinitrobenzene, some decomposition of BPO must have taken place in solid phase before melting, and therefore the result is somewhat ambiguous. In the experiment with an acetonitrile solution, however, the result clearly shows that isotope effect exists in phenylation of *m*-dinitrobenzene with BPO.

It has been said that there is no isotope effect in nitration of arenes. However, recently Myhre, Beug, and James have observed kinetic isotope effects in nitrodeprotonation of a series of 1-X-2,4,6-tri-*t*-butylbenzenes and reported that the k_H/k_D values changed from 1.0 to 3.8 as X is varied from H to CH_3.[8] Such a correlation between isotope effect and the size of the substituent may exist in our systems too, since 1) almost no isotope effect at the *para* positions and greater isotope effect was observed at *ortho* positions, and 2) a very large isotope effect (~11) was observed with the phenylation of *m*-dinitrobenzene at its 2-position with the phenyl radical produced from PAT (the hydrogen abstractor is bulky trityl radical).

In order to clarify the relationship between isotope effect and the size of the substituents, 1,3,5-tri-*t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene-2,4,6-d_3 were competitively phenylated with the phenyl radicals generated from NNA and PAT. However, the k_H/k_D values obtained were 1.06 and 1.01, and thus there is no definite correlation between isotope effect and the size of the substituents in free-radical phenylation of arenes.

TABLE 4. ISOMER DISTRIBUTIONS IN THE PHENYLATION OF *m*-DINITROBENZENE AND *m*-DINITROBENZENE-d_4

Substrate	Radical source	Temperature (°C)	Yields of dinitrodiphenyls (%)	
			2,6-	2,4-
m-$C_6H_4(NO_2)_2$	PhN_2BF_4–$NaNO_2$	20±3	67.1	32.9
m-$C_6H_4(NO_2)_2$	PhN=$NCPh_3$	60±0.1	36.5	63.5
m-$C_6D_4(NO_2)_2$	PhN=$NCPh_3$	60±0.1	14.5	85.5

In an attempt to gain further understanding on this problem, *m*-dinitrobenzene and *m*-dinitrobenzene-d_4 were phenylated with the phenyl radicals produced from PhN_2BF_4–$NaNO_2$ and PAT, and the isomer distributions of the dinitrodiphenyls were determined. The results are shown in Table 4. In the case of *m*-$C_6H_4(NO_2)_2$–PhN_2BF_4–$NaNO_2$, the amount of 2,6-dinitrodiphenyl produced was 67%, whereas in the case of *m*-$C_6H_4(NO_2)_2$–PAT it decreased to 36.5%. This finding can be rationalized by assuming that very bulky trityl radical abstracts the hydrogen at the crowded 2 position of the 1,3-dinitro-2-phenylcyclohexadienyl radical much more slowly than that at the less crowded 4 position of the 1,3-dinitro-4-phenylcyclo-

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[7] C. C. Price and R. J. Convery, *J. Amer. Chem. Soc.*, **79**, 2941 (1957); **80**, 4101 (1958).

[8] P. C. Myhre, M. Beug, and L. L. James, *ibid.*, **90**, 2105 (1968).

hexadienyl radical. The amount of 2,6-dinitrodiphenyl produced further decreased to 14.5% in the case of m-$C_6D_4(NO_2)_2$–PAT. These data are consistent with the abnormally large k_H/k_D value ($\sim$11) observed in the case of m-$C_6H_4(NO_2)_2$–m-$C_6D_4(NO_2)_2$–PAT (Table 3).

Thus, a very large isotope effect was observed in free-radical phenylation at the crowded 2-position of m-dinitrobenzene, and not at the crowded 2-position of 1,3,5-tri-*t*-butylbenzene. Resonance stabilization of the intermediate cyclohexadienyl radical must be taken into consideration in addition to the bulkiness of the substituents. The more resonance-stabilized is the cyclohexadienyl radical, the more slowly proceeds the following hydrogen-abstraction step. If this is so, it is reasonable that no isotope effect was shown by *t*-butyl group which is bulky but possesses no ability of resonance-stabilization.

The k_H/k_D value observed for phenylation at the 2-position of m-dinitrobenzene ($\sim$11) was greater than the value expected from the zero-point energy of the C–H bond (6~7). This finding can be rationalized only by assuming a large contribution from quantum-mechanical tunnelling effect or assuming that in the free-radical substitution at such an overcrowded position the activation entropy factor varies with isotopes.

Experimental

Materials. Benzenediazonium tetrafluoroborate was prepared according to the directions described previously.[9] *N*-Nitrosoacetanilide was prepared by the method reported in the literature[10] and dried in a desiccator which was kept in a refrigerator; mp 75°C (decomp.). Phenylazotriphenylmethane (PAT) was prepared by the bromine-water oxidation of phenylhydrazotriphenylmethane,[11] which was synthesized from phenylhydrazine and triphenylmethyl chloride in ether.[12] Crude PAT was recrystallized from benzene-ethanol; mp 111—112°C (decomp.). Dimethyl sulfoxide was dried with calcium hydride and distilled; bp 86°C/25 mmHg. Benzene and chlorobenzene were washed with concentrated sulfuric acid and water successively, dried over calcium chloride, and distilled; bp 80 and 131°C, respectively. Anisole was washed with an aqueous sodium hydroxide solution and water, dried over calcium chloride, and distilled; bp 153°C. Nitrobenzene was washed repeatedly with a potassium dichromate solution, dried over calcium chloride, and distilled; bp 95.5°C/18 mmHg.

Authentic samples of substituted diphenyls were prepared by the methods described previously.[13] Anisole-4*d* was prepared by the hydrolysis of *p*-methoxyphenylmagnesium bromide in D_2O (isotopic purity, 99.75%, E. Merck AG, Darmstadt); bp 58°C/15 mmHg. Its isotopic purity was determined to be 92% by mass spectrometry. Chlorobenzene-4*d* was prepared in a similar manner from *p*-bromochlorobenzene; bp 131°C. Its isotopic purity was 90%. Chlorobenzene-d_5 and nitrobenzene-d_5 of CIBA Limited were used without further purification. Isotopic purity was 98.5% and 99%, respectively. m-Dinitrobenzene-d_4 was prepared by the nitration of benzene-d_6 (isotopic purity>99 atom % D, E. Merck AG, Darmstadt) with anhydrous potassium nitrate and sulfuric acid-d_2, which was produced from sulfuric anhydride and deuterium oxide-d_2 (isotopic purity, 99.75%, E. Merck AG, Darmstadt). Crude m-dinitrobenzene-d_4 was recrystallized from ethanol; mp 89°C. Its isotopic purity was determined to be 97.5% by mass spectrometry. 1,3,5-tri-*t*-butylbenzene was prepared by the method described in the literature;[14] mp 72—73°C (from methanol). 1,3,5-tri-*t*-butylbenzene-2,4,6-d_3 was obtained by hydrogen-deuterium exchange (six times was needed) from 1,3,5-tri-*t*-butylbenzene and trifluoroacetic acid-d_1 which was prepared from trifluoroacetic anhydride (Aldrich Chemical Co., Inc.) and deuterium oxide-d_2 (E. Merck AG, Darmstadt, isotopic purity: 99.75%) in carbon tetrachloride according to the method described in the literature.[8] After the exchange reaction was repeated for six times, exchange was shown to be 98% complete by its NMR spectrum (comparison of its integrated signal with that of the known amount of ferrocene as an internal standard).

*Phenylation of Anisole, Anisole-4*d*, Chlorobenzene or Chlorobenzene-4*d *with Benzenediazonium Tetrafluoroborate-Sodium Nitrite.* Under a nitrogen atmosphere a solution of 0.25 g (1.3 mmol) of benzenediazonium tetrafluoroborate dissolved in DMSO (2.0 g) was added drop by drop at 20°C into a vigorously stirred solution of sodium nitrite (3 mol/mol of PhN_2BF_4) and an aromatic substrate (anisole, anisole-4*d*, chlorobenzene or chlorobenzene-4*d*; 50 mol/mol of PhN_2BF_4) in 10 g of DMSO. Evolution of nitrogen was instantaneous upon addition of each drop of the diazonium salt solution, and the addition was completed in about five minutes. Treatment of the reaction mixtures and the quantitative determination of the diphenyl isomers produced were made according to the method reported previously.[3]

Competitive Phenylation of Chlorobenzene–Benzene and Chlorobenzene-d_5*–Benzene.* Under a nitrogen atmosphere a solution of 0.2 g of benzenediazonium tetrafluoroborate in DMSO (2.0 g) was added drop by drop at 20°C into a vigorously stirred solution of sodium nitrite (3 mol/mol of PhN_2BF_4) in 6.0 g of DMSO and an equimolar mixture of benzene and chlorobenzene (or benzene and chlorobenzene-d_5; 50 mol/mol of PhN_2BF_4). The reaction mixture was treated according to the method described previously.[3]

Competitive Phenylation of Nitrobenzene–Chlorobenzene and Nitrobenzene-d_5*–Chlorobenzene.* Competitive phenylation of nitrobenzene-chlorobenzene (or nitrobenzene-d_5–chlorobenzene) with benzenediazonium tetrafluoroborate-sodium nitrite were carried out in a manner similar to that described above, and the diphenyl isomers produced were determined by glc.

Partial rate factors in the phenylation at each position of an arene were calculated by using the following equation.

$$k_x/k = (k_x/k_{o-\mathrm{Cl}}) \times (k_{o-\mathrm{Cl}}/k)$$

where,

k_x/k: the partial rate factor in the phenylation of PhX at the x (o-, m-, or p-) position

$k_x/k_{o-\mathrm{Cl}}$: the ratio of the phenylation rate at the x position of PhX *versus* that at the *ortho* position of chlorobenzene

$k_{o-\mathrm{Cl}}/k$: the partial rate factor in the phenylation at the *ortho* position of chlorobenzene

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[9] E. B. Starkey, "Organic Syntheses," Coll. Vol. 2, p. 225, Wiley, New York, N. Y. (1943).

[10] H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, **1940**, 369.

[11] M. Gomberg and H. W. Berger, *Ber.*, **36**, 1088 (1903).

[12] C. R. Hauser and B. E. Hudson, Jr., "Organic Syntheses," Coll. Vol. 3, p. 842, Wiley, New York, N. Y. (1955).

[13] M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, This Bulletin, **43**, 215 (1970).

[14] J. M. A. Baas, H. V. Bekkum, M. A. Hoefnagel, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **88**, 1110 (1969).

Competitive Phenylation of Nitrobenzene–Nitrobenzene-d$_5$. An equimolar mixture of nitrobenzene (40 mmol) and nitrobenzene-d_5 (40 mmol) was phenylated by using 8 mmol of a phenylating agent (PhN_2BF_4–$NaNO_2$–DMSO (150 g) or *N*-Nitrosoacetanilide or PAT) under a nitrogen atmosphere. The reaction mixture was dissolved in ether and washed with water. The solvent was removed under reduced pressure, and elution chromatography of the residue on alumina yielded an *o*-nitrodiphenyl–*o*-nitrodiphenyl-d_4 mixture and a *p*-nitrodiphenyl–*p*-nitrodiphenyl-d_4 mixture. The *m*-isomer mixture could not be isolated because of its low yield. The kinetic isotope effect was calculated from the parent peak ratio (I_{199}/I_{203}) of the mass spectrum of each mixture (Hitachi Mass Spectrometer RM-60).

$$\frac{\text{yield of } PhC_6H_4NO_2}{\text{yield of } PhC_6D_4NO_2} = \frac{k_H}{k_D} \times \frac{[C_6H_5NO_2]}{[C_6D_5NO_2]}$$

Competitive Phenylation of m-*Dinitrobenzene*–m-*Dinitrobenzene*-d$_4$. *m*-Dinitrobenzene (25 mmol) and *m*-dinitrobenzene-d_4 (25 mmol) were phenylated by using 5 mmol of a phenylating agent (PhN_2BF_4–$NaNO_2$, *N*-nitrosoacetanilide or PAT) in DMSO (150 g) under a nitrogen atmosphere. The reaction mixture was dissolved in chloroform and washed with water to remove DMSO. Evaporation under reduced pressure removed chloroform and then unreacted *m*-dinitrobenzene and *m*-dinitrobenzene-d_4. Elution chromatography of the residue on alumina gave a 2,4-dinitrodiphenyl–2,4-dinitrodiphenyl-d_3 mixture and a 2,6-dinitrodiphenyl–2,6-dinitrodiphenyl-d_3 mixture. The kinetic isotope effect was calculated from the parent peak ratio (I_{244}/I_{247}). It was ascertained that the parent peak ratio did not change when ionization potential was changed from 15 to 70 eV.

Competitive Phenylation of 1,3,5-tri-t-*butylbenzene–1,3,5-tri*-t-*butylbenzene-2,4,6*-d$_3$. 1,3,5-tri-*t*-butylbenzene (7.0 mmol) and 1,3,5-tri-*t*-butylbenzene-2,4,6-d_3 (7.0 mmol) were phenylated under nitrogen either by NNA (2 mmol) in acetonitrile (20 g) or by PAT (2 mmol) in benzene (18 g). The reaction mixture was dissolved in ether and washed with water. After the ether was removed, most of the unreacted 1,3,5-tri-*t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene-2,4,6-d_3 was removed by chromatography on alumina. The substituted diphenyl fraction was subjected to a Hitachi glc K-53 (column: Apiezon L, 1 m) which is connected with a Hitachi Mass Spectrometer RM-60. The k_H/k_D value was calculated from the parent peak ratio (I_{322}/I_{324}) of 2,4,6-tri-*t*-butyldiphenyl and 2,4,6-tri-*t*-butyldiphenyl-3,5-d_2.

Phenylation of m-*Dinitrobenzene and* m-*Dinitrobenzene*-d$_4$ *with PAT or* PhN_2BF_4–$NaNO_2$. Ten mmol of *m*-dinitrobenzene (or *m*-dinitrobenzene-d_4) was phenylated with 1 mmol of PAT (or PhN_2BF_4–$NaNO_2$) in 50 g of DMSO under a nitrogen atmosphere. The reaction mixture was diluted with ether, washed with water, and dried over anhydrous magnesium sulfate. The ether and about 70% of the unreacted *m*-dinitrobenzene (or *m*-dinitrobenzene-d_4) was distilled off under reduced pressure. The residual *m*-dinitrodiphenyl isomers were analyzed by a Hitachi glc K-53 (column: Apiezon L, 10%, 1 m on Chromosorb W).

Phenylation of m-$C_6H_4(NO_2)_2$–m-$C_6D_4(NO_2)_2$ *with BPO.* 1) A solid mixture of BPO (3 mmol), *m*-$C_6H_4(NO_2)_2$ (17 mmol) and *m*-$C_6D_4(NO_2)_2$ (17 mmol) was placed in an oil bath at 90°C, and then heated up to and kept at 100°C for one day.

2) An acetonitrile solution (60 g) of BPO (2 mmol), *m*-$C_6H_4(NO_2)_2$ (26 mmol) and *m*-$C_6D_4(NO_2)_2$ (26 mmol) was let to decompose at 80±0.1°C under nitrogen for one day.

The two reaction mixtures were subjected to distillation under reduced pressure for removal of *m*-dinitrobenzenes (and acetonitrile). Elution chromatography of the residue gave a mixture of 2,4-dinitrodiphenyl and 2,4-dinitrodiphenyl-d_3. Isotope effect was calculated from the ratio of the parent peaks (I_{244}/I_{247}).

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