The Dependence of Hyperconjugative Spin–Spin Coupling upon Electron Demand

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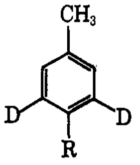
Abstract: It is found that the geminal coupling constants of the methyl protons in a series of *para*-substituted toluenes are quite insensitive to the electron-withdrawing nature of the substituents, which range from an α carbanion to an α carbonium ion. The long-range coupling constants between the methyl and *o*-hydrogens are likewise insensitive to a similar range of substituents. It is concluded that hyperconjugation involving the methyl groups is not strongly dependent upon electron demand, unlike chemical Baker–Nathan effects, though the conclusion must be tempered with the reservation that the exact relationships between the magnitudes of the coupling constants and the magnitude of hyperconjugative stabilization are not yet known.

A common but imperfectly understood chemical observation is the Baker–Nathan reactivity order, in which alkyl groups appear to become better electron-donating groups as the number of α-hydrogens is increased.[1,2] Thus, the Baker–Nathan order of electron release is Me > *t*-Bu, the opposite of the accepted inductive order. It is commonly but by no means universally found that the Baker–Nathan order prevails in situations of large electron demand upon the alkyl group, while the inductive order is found where the electron demand is small.[1,2] The Baker–Nathan effect is frequently explained as due to carbon–hydrogen hyperconjugation, which it is supposed should increase as electron demand increases.[1] Another school of thought holds that the Baker–Nathan effect is a steric effect, usually involving solvent.[2]

An entirely different manifestation of carbon–hydrogen hyperconjugation is found in certain nuclear spin–spin coupling constants. It now seems well established that the long-range coupling constants between an aromatic methyl group and the ring protons arise primarily through a π-coupling mechanism, *i.e.*, through carbon–hydrogen hyperconjugation.[3–11] It is also now evident that the *geminal* coupling constants of methyl or methylene protons are enhanced (*i.e.*, given larger negative values) by adjacent π-electron systems, and that such enhancement has the geometric dependence expected if π hyperconjugation were involved and is opposite in sign to the effect produced by substituents which withdraw electrons inductively.[12–17] A molecular orbital study by Pople and Bothner-By[17] predicts the observed *geminal* coupling effects by inductive and hyperconjugative electron release.

The present paper reports measurements of long-range ($J_{\mathrm{CH_3}\text{-}o}$) and geminal ($J_{gem}$) coupling constants in a series of *para*-substituted toluenes. The purpose of the measurements was to see whether these parameters, known to be related to carbon–hydrogen π hyperconjugation, exhibit the dependence upon electron demand which is associated with the Baker–Nathan effect. In order to measure the desired coupling constants directly, the toluenes (I) were synthesized with the 3 and 5 positions deuterated to obtain the methyl–*ortho*-proton coupling constant and again (II) with one α-deuterium to obtain the geminal coupling constant (using the relationship $J_{\mathrm{HH}} = 6.55 J_{\mathrm{HD}}$). The synthetic methods are described in the Experimental Section, as is the method of measurement. The data for geminal coupling are shown in Tables I–III. Table II gives data on triarylmethyl structures III and IV, which are of the general type II. Table III shows the solvent independence of the geminal coupling constant for one compound. The long-range coupling constants are shown in Tables IV–VI. Table V gives data on triarylmethyl structures of type V. Table VI shows that the coupling constant is again independent of solvent for one compound.



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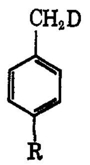

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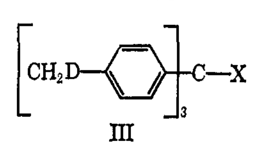

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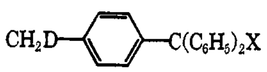

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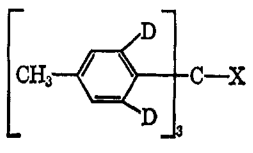

V

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(10) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, 16, 563 (1960).

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Table I. Geminal Coupling Constants for α-Deuterio-*p*-substituted Toluenes (II)

Substituent R	Solvent (concn, %, w/v)	J_{HD}, cps[a]	J_{HH}, cps
H	CS_2 (15)	2.21 ± 0.01 (10)[b]	14.48 ± 0.07
CN	CCl_4 (89)	2.22 ± 0.02 (15)	14.54 ± 0.14
	CS_2 (15)	2.24 ± 0.03 (22)	14.67 ± 0.20
CO_2Et	CCl_4 (78)	2.15 ± 0.02 (14)[c]	14.09 ± 0.14
	CS_2 (15)	2.23 ± 0.03 (32)	14.61 ± 0.21
Cl	Neat	2.20 ± 0.02 (20)	14.41 ± 0.14
	CS_2 (15)	2.22 ± 0.02 (29)	14.54 ± 0.14
NO_2	CS_2 (15)	2.28 ± 0.02 (14)	14.93 ± 0.14

[a] Errors are average deviations. The number in parentheses is the number of measurements. [b] C. G. MacDonald, J. S. Shannon, and S. Sternhell [*Australian J. Chem.*, **17**, 38 (1964)] report 2.24 ± 0.03 cps. [c] MacDonald, Shannon, and Sternhell (footnote *b*) report 2.25 ± 0.05 cps.

The geminal coupling constants do not appear to show any significant variation with electron demand when neutral substituents are on the ring (Table I), but when a very large electron demand is present, as in the carbonium ions in Table II (X = BF_4^- or $CF_3CO_2^-$), the constant seems significantly increased. On the other hand, the carbanion (Table II, X = Li^+) shows a coupling constant essentially like that of methane (J_{HH} = 12.4 cps),[17] noticeably lower than that of all of the other compounds examined. The data might then very well be taken in mild support of the theory that hyperconjugation varies with electron demand.

By contrast, the long-range coupling data (Tables IV and V) certainly show no enhancement of coupling by electron demand, and in fact the smallest constant observed was in the carbonium ion. It was not possible to obtain the carbanion constant because of a persistent line-broadening effect, but the general shape of the signal for V (X = Li^+) suggested a coupling constant like those in Table IV. The insensitivity of the long-range coupling constants to electron de-

Table II. Geminal Coupling Constants in Tris(α-deuterio-*p*-tolyl)methyl (III) and Diphenyltolylmethyl Derivatives (IV)

Type and substituent X	Solvent (concn, %, w/v)	J_{HD}, cps[a]	J_{HH}, cps
III, OH	CS_2 (15)	2.20 ± 0.03 (21)	14.41 ± 0.20
III, BF_4^-	CH_2Cl_2 (26)	2.26 ± 0.01 (18)	14.80 ± 0.07
III, Li^+	THF-d_8 (20)	1.82 ± 0.06 (11)	11.92 ± 0.39
IV, OH	CS_2 (40)	2.18 ± 0.02 (18)	14.28 ± 0.14
IV, $CF_3CO_2^-$	1.5 *M* CF_3CO_2H in $(CF_3CO)_2O$ (10%)	2.31 ± 0.03 (34)	15.13 ± 0.20
IV, $CF_3CO_2^-$	4.5 *M* CF_3CO_2H in $(CF_3CO)_2O$ (8.2%)	2.28 ± 0.03 (21)	14.93 ± 0.20

[a] See footnote *a*, Table I.

Table III. Solvent Effects on Geminal Coupling Constants in α-Deuterio-*p*-nitrotoluene

Solvent (concn, %, w/v)	J_{HD}, cps[a]
CS_2 (15)	2.28 ± 0.02 (14)
$CHCl_3$ (33)	2.28 ± 0.04 (5)
CH_3OH (33)	2.29 ± 0.03 (4)
Acetone (33)	2.31 ± 0.03 (4)
Pyridine (33)	2.30 ± 0.08 (3)

[a] See footnote *a*, Table I.

Table IV. Long-Range Coupling Constants in 3,5-Dideuterio-*p*-substituted Toluenes (I)

Substituent R	Solvent (concn, %, w/v)	$J_{CH_3\text{-}o}$, cps[a]
CN	CS_2 (15)	0.71 ± 0.01 (30)
	Neat	0.73 ± 0.02 (15); 0.70 ± 0.02 (26)
$CO_2C_2H_5$	CS_2 (15)	0.69 ± 0.01 (28)
	Neat	0.68 ± 0.02 (12); 0.71 ± 0.01 (16)
NH_2	CS_2 (10)	0.68 ± 0.01 (28)
	CCl_4 (20)	0.67 ± 0.02 (12)
$NMe_3^+I^-$	D_2O (20)	0.70 ± 0.03 (8)
Cl	CS_2 (15)	0.71 ± 0.02 (29)
	Neat	0.70 ± 0.01 (22)
OH	CS_2 (15)	0.69 ± 0.01 (42)
	Neat	0.68 ± 0.02 (16)

[a] The number in parentheses refers to the number of separate spectra used to obtain the average coupling constant with the indicated average deviation. Where two values are given for the same sample, the measurements were made at widely separated times.

Table V. Long-Range Coupling Constants in Tris(3,5-dideuterio-*p*-tolyl)methyl Derivatives (V)

Substituent X	Solvent (concn, %, w/v)	$J_{CH_3\text{-}o}$, cps[a]
OH	CS_2 (28)	0.66 ± 0.02 (18)
OH	CS_2 (11)	0.68 ± 0.03 (14)
BF_4^-	CH_2Cl_2 (17)	0.53 ± 0.03 (23)

[a] See footnote *a*, Table I.

Table VI. Long-Range Coupling in 3,5-Dideuterio-*p*-cyanotoluene (I, R = CN) as a Function of Solvent

Solvent (concn, %, w/v)	$J_{CH_3\text{-}o}$, cps[a]
CH_3OH (20)	0.71 ± 0.01 (27); 0.74 ± 0.02 (16); 0.72 ± 0.01 (12)
$CHCl_3$ (20)	0.70 ± 0.01 (30); 0.72 ± 0.02 (26); 0.70 ± 0.02 (14)
CCl_4 (20)	0.73 ± 0.02 (15); 0.71 ± 0.02 (31)
Neat	0.73 ± 0.02 (15); 0.70 ± 0.02 (26)
CS_2 (15)	0.71 ± 0.01 (30)

[a] See footnote *a*, Table IV.

mand could be interpreted as contrary to the theory that hyperconjugation varies with electron demand. Certainly neither the long-range nor the geminal coupling constants reported here provide a sensitive correlation with electron demand.

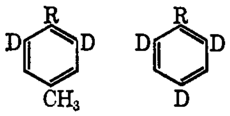
It is quite possible that the observed relative insensitivity of geminal and long-range coupling constants to electron demand is simply the result of a cancellation of two effects.[5,14,17] In the case of the long-range coupling, the constant is dependent upon the bond order between the ring carbons bearing the coupled methyl and proton, and upon the hyperfine interaction constant which reflects the amount of σ–π interaction. The former decreases with increasing electron deficiency while the latter may increase.[18,19] A similar cancellation effect may be present in the case of geminal coupling, where reduction of the "effective number" of π electrons adjacent to the methyl would reduce the coupling constant,[14] while an increase in electron demand, which would accompany this reduction of π electrons, might increase hyperconjugative interaction.

The chemical shift data in Tables VII and VIII show that the various substituents employed in this work do affect the electron density at the methyl protons, but that the methyl has an almost invariant effect on the *ortho* protons as the substituent is varied. The chemical shift effects thus resemble the long-range coupling effects (or lack thereof).

Table VII. Chemical Shift (cps from Tetramethylsilane at 60 Mc) of Methyl Resonance in *para*-Substituted Toluenes

Compound type and substituent (R or X)	Solvent (concn, % w/v)	*J*, cps
I, NH_2	CS_2 (15)	128
I, OH	CS_2 (15)	129
I, H	CS_2 (15)	138
II, H	CS_2 (15)	135
I, Cl	CS_2 (15)	132
II, Cl	CS_2 (15)	135
I, CN	CS_2 (15)	142
II, CN	CS_2 (15)	142
II, NO_2	CS_2 (15)	147
I, $CO_2C_2H_5$	CCl_4 (12)	143
II, $CO_2C_2H_5$	CS_2 (15)	139
III, OH	CS_2 (15)	135
V, OH	CS_2 (15)	136
III BF_4^-	CH_2Cl_2 (20)	163
V, BF_4^-	CH_2Cl_2 (20)	162
III, Li^+	THF-d_8 (20)	123
V, Li^+	THF-d_8 (20)	128

Table VIII. Chemical Shifts of Aromatic Protons in Deuterated Substituted Toluenes (I) and Benzenes[a]



R	ν_{Ar-H}	ν'_{Ar-H}[b]	$\nu - \nu'$
NH_2	+24.9	+14.2	10.7
OH	+23.1	+8.4	14.7
Cl	+15.6	+3.8	11.8
CO_2Et	+7.9	−4.4	12.3
CN	+5.0	−6.3	11.3

[a] Measured on 1.25% (by volume) solutions in cyclohexane with 0.3% benzene added as an internal standard. Shifts are in cps from benzene at 60 Mc. [b] F. Langenbucher, R. Mecke, and E. D. Schmidt, *Amn.*, **669**, 11 (1963).

Experimental Section[20]

2,6-Dideuterio-*p*-methylaniline Hydrochloride.[21] Recrystallized *p*-toluidine hydrochloride (15 g, 0.11 mole) and 99.8% deuterium oxide (20 g, 1.0 mole) were added to a tube which was then flushed with nitrogen and sealed. The tube was heated at 100–110° for 24 hr. After this time the tube was opened, the water was distilled off under vacuum, fresh deuterium oxide (20 g, 1.0 mole) was added, and the mixture was heated in a sealed tube for 24 hr. This procedure was repeated seven times. The product was recrystallized from ethanol–ether solution to give white crystals, mp 242–243° (lit.[21] 243°). An analytical sample of the free amine was prepared by treatment of the deuterated toluidine hydrochloride with 10% aqueous sodium hydroxide to obtain the free amine followed by five recrystallizations of this amine from water in order to equilibrate the amino hydrogens, mp 44–45° (lit.[22] 43.5°).

Anal. Calcd for $C_7H_7D_2N$: C, 77.01; H, 8.31; N, 12.83; D, 22.22 atom %. Found: C, 77.07; H, 8.51; N, 12.56; D, 21.40 atom %.

3,5-Dideuterio-*p*-tolunitrile. The deuterated tolunitrile was prepared *via* the diazonium salt from 2,6-dideuterio-*p*-toluidine hydrochloride (11.2 g, 0.077 mole) by the procedure described by Vogel[23] to yield 3.85 g (42%) of a clear liquid, bp 54.5° (0.81 mm) [lit.[24] 217.6° (760 mm)].

Anal. Calcd for $C_8H_5D_2N$: C, 80.63; H, 5.92; N, 11.76; D, 28.56 atom %. Found: C, 80.69; H, 6.19; N, 11.62; D, 27.45 atom %.

3,5-Dideuterio-*p*-toluic Acid. 3,5-Dideuterio-*p*-tolunitrile (1.85 g, 0.0155 mole) was refluxed with 3.7 ml of aqueous 10% sodium hydroxide and 5.6 ml of ethanol for 2.5 hr. Concentrated hydrochloric acid was added until precipitation of the acid was complete. The white solid was air-dried to yield 1.85 g (87%), mp 178–181° (lit.[25] 176–177°).

Ethyl 3,5-Dideuterio-*p*-toluate. 3,5-Dideuterio-*p*-toluic acid (1.85 g, 13.4 mmoles) and 2.8 ml of redistilled thionyl chloride were refluxed for 1 hr. The excess thionyl chloride was distilled at atmospheric pressure. The residue was distilled under vacuum to yield 2.0 g (95%) of a clear liquid, bp 75° (2.3 mm). Absolute ethanol (4 ml) was added to this liquid and the solution refluxed for 1 hr. Excess ethanol was removed by distillation at atmospheric pressure, and the ester was distilled under vacuum to give 2.0 g (94%), bp 63° (0.55 mm) [(lit.[24] 235.5° (760 mm)].

Anal. Calcd for $C_{10}H_{10}D_2O_2$: C, 72.26; H, 7.28; D, 16.67 atom %. Found: C, 72.30; H, 7.50; D, 16.08 atom %.

3,5-Dideuterio-*p*-chlorotoluene. The deuterated *p*-chlorotoluene was prepared *via* the diazonium salt from 3,5-dideuterio-*p*-toluidine hydrochloride (5.6 g, 0.038 mole) by the procedure described by Vogel[26] to yield 2.46 g (50%) of a colorless liquid, bp 155–157° (lit.[24] 162°).

Anal. Calcd for $C_7H_5D_2Cl$: C, 65.37; H, 5.49; D, 28.56 atom %. Found: C, 65.23; H, 5.26; D, 27.30 atom %.

3,5-Dideuterio-*p*-cresol. The deuterated *p*-cresol was prepared *via* the diazonium salt from 3,5-dideuterio-*p*-toluidine (4.2 g, 38.5 mmoles) by the procedure described by Vogel.[27] The nmr spectrum of this product indicated, by the appearance of an AB

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(19) J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron Suppl.*, **2**, 65 (1963).

(20) All melting points and boiling points are uncorrected. The melting points, boiling points, and procedure references cited in the body of the Experimental Section refer to the undeuterated species (with the exception of the reference to the deuteration of *p*-toluidine hydrochloride). Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer and with a Varian V-4300B spectrometer (with super stabilizer) equipped with a Sanborn recorder and were recorded in part by the staff of the University of Illinois spectroscopic laboratory. Microanalyses and deuterium analyses were performed by Mr. J. Nemeth and associates at the University of Illinois microanalytical laboratory.

(21) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

(22) J. Walker and H. H. Beveridge, *ibid.*, **91**, 1797 (1907).

(23) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., Inc., New York, N. Y., 1956, p 607.

(24) W. H. Perkin, *J. Chem. Soc.*, **69**, 1025 (1896).

(25) H. Y. de Schepper and F. Beilstein, *Ann.*, **137**, 301 (1866).

(26) Reference 23, p 600.

(27) Reference 23, p 614.

pattern of peaks in the aromatic region corresponding to that expected for undeuterated *p*-cresol, that some exchange (5% by nmr integration) had taken place in the reaction. Therefore, the partially deuterated *p*-cresol was treated with 30 ml of 99.5% deuterioacetic acid.[28] This solution was allowed to stand for 30 min before the acetic acid was distilled at atmospheric pressure. This procedure was repeated with a second 30-ml portion of deuterioacetic acid. Distillation of the residue under vacuum gave 2.0 g (48%) of a pale yellow liquid, bp 61° (0.9 mm) [lit.[24] 202° (760 mm)].

Anal. Calcd for $C_7H_5D_3O$: C, 75.63; H, 7.25; D, 37.50 atom %. Found: C, 75.42; H, 7.35; D, 33.80 atom %.

Trimethyl-3,5-dideuterio-*p*-tolylammonium Iodide. 3,5-Dideuterio-*p*-toluidine (1.57 g, 15 mmoles) was added to 5.0 ml of methyl iodide in 10 ml of benzene. The precipitate was recrystallized from ethanol–ether, mp 220° (lit. 202°,[29] 216–218°[30]).

Anal. Calcd for $C_{10}H_{14}D_2N$: C, 43.02; H, 5.78; N, 5.08; D, 12.5 atom %. Found: C, 42.80; H, 5.84; N, 4.71; D, 11.95 atom %.

3,5-Dideuterio-*p*-bromotoluene. The procedure of Vogel[31] was used. Thus, 3,5-dideuterio-*p*-toluidine (5.35 g, 49 mmoles), 40 ml of water, and 9.8 g of concentrated sulfuric acid were cooled to 0°, and 3.5 g of sodium nitrite in 6 ml of water was added until excess sodium nitrite was present as indicated by starch–iodide paper. This solution was then added slowly to a boiling solution of 2.83 g (19.7 mmoles) of freshly prepared cuprous bromide in 50 ml of water. Continuous steam distillation during this addition afforded, after the usual work-up, 4.95 g (58%) of a yellow liquid, bp 183–185° (lit.[32] 185.2°).

Tris(3,5-dideuterio-*p*-tolyl)carbinol. According to the general procedure of Marvel, *et al.*,[33,34] 3,5-dideuterio-*p*-bromotoluene (9.10 g, 53 mmoles) in 25 ml of ether was added to 1.40 g (58 mg-atoms) of magnesium turnings in 20 ml of anhydrous ether over a 2-hr period. The mixture was refluxed an additional 0.5 hr, whereupon a solution of ethyl carbonate (1.57 g, 13 mmoles) in 5 ml of anhydrous ether was added slowly over a 6-hr period. The mixture was stirred overnight and finally refluxed for 1 hr. An ice-cold saturated solution of ammonium chloride (25 ml) was added to quench the reaction. The aqueous layer was extracted several times with ether. The ether layers were combined and dried over anhydrous magnesium sulfate, and the ether, together with some toluene, was distilled. The residue was chromatographed on a Florisil (100–200 mesh) column and eluted with benzene–hexane (1:1). The yellow band was collected. Removal of the solvent on the rotary evaporator left a clear oil which eventually crystallized. Three recrystallizations from hexane gave 3.50 g (87.5%), mp 93–94° (lit.[35] 93–94°).

Anal. Calcd for $C_{22}H_{16}D_6O$: C, 85.67; H, 7.19; D, 27.27 atom %. Found: C, 85.34; H, 7.10; D, 26.95 atom %.

Tris(3,5-dideuterio-*p*-tolyl)methyl Fluoroborate. Tris(3,5-dideuterio-*p*-tolyl)carbinol (102.5 mg, 0.33 mmole) was dissolved in a minimum amount (*ca.* 0.2 ml) of redistilled propionic anhydride. Fluoroboric acid (48%, 0.10 ml) was added. The solution was allowed to stand for 15 min. The solvent was removed under vacuum (0.5 mm). Ice-cold ether (*ca.* 3 ml) was then added and the resulting precipitate centrifuged to the bottom of the tube. The supernatant ether was removed. The orange precipitate was washed with cold ether in this manner until the washes were colorless. The solid was dried at room temperature under vacuum (0.5 mm) to yield 86.5 mg of a granular orange material. This fluoroborate salt was then dissolved in 0.50 ml of methylene chloride and the solution degassed ten times and sealed in an nmr tube. After the solution had stood for a short time, a small amount of insoluble material appeared. It was necessary to remove this to observe the nmr splitting pattern of the methyl group multiplet. This was done by centrifugation of the sealed nmr tube in such a way that the solid material was packed into the upper end of the tube.

Tris(3,5-dideuterio-*p*-tolyl)methane. Using the general procedure of Nystrom and Berger,[36] an ethereal solution of tris(3,5-dideuterio-*p*-tolyl)carbinol (156.7 mg, 0.510 mmole) in 1.5 ml of anhydrous ether was added to a suspension of aluminum trichloride (136 mg, 1.02 mmoles) and lithium aluminum hydride (38 mg, 1.02 mmoles) in 2.0 ml of ether. The mixture was stirred for 12 hr at room temperature. The reaction was quenched with 3 ml of 6 *N* sulfuric acid. The aqueous layer was extracted five times with 1-ml portions of ether. The ether layers were combined and dried over anhydrous magnesium sulfate, and the ether was removed on a rotary evaporator. The residual clear oil was taken up in 1.0 ml of absolute ethanol. Crystals formed after some time. Recrystallization from ethanol gave 90.6 mg (61%), mp 60–62° (lit. 67°,[37] 61–63°[38]).

α-Deuterio-*p*-chlorotoluene. *p*-Chlorobenzylmagnesium chloride was prepared in the usual way by addition of *p*-chlorobenzyl chloride (90 g, 0.56 mole) in 200 ml of sodium-dried ether to 13.6 g of magnesium turnings in 50 ml of ether. The resulting Grignard reagent was quenched with 99.8% deuterium oxide (11 g, 0.61 mole). The mixture was stirred for 0.5 hr. The resulting slurry was extracted several times with ether. The combined ether layers were dried over anhydrous magnesium sulfate, and the ether was removed on a rotary evaporator at room temperature. Distillation of the residue yielded 41.9 g (59%) of a clear liquid, bp 76° (0.48 mm) [lit.[24] 162° (760 mm)].

Anal. Calcd for C_7H_6DCl: C, 65.89; H, 5.53; D, 14.28 atom %. Found: C, 65.91; H, 5.52; D, 14.10 atom %.

α-Deuterio-*p*-toluic Acid. α-Deuterio-*p*-toluic acid was prepared according to the procedure of Vogel[39] for the preparation of *p*-toluic acid from *p*-chlorotoluene. The reaction gave, after two recrystallizations, 20.1 g (48%) of a white solid, mp 177–179° (lit.[25] 176–177°).

Anal. Calcd for $C_8H_7DO_2$: C, 70.06; H, 5.88; D, 12.50 atom %. Found: C, 70.22; H, 5.99; D, 12.20 atom %.

α-Deuterio-*p*-toluamide. α-Deuterio-*p*-toluic acid (17.8 g, 0.13 mole) and 12 ml of redistilled thionyl chloride were refluxed for 1 hr. The excess thionyl chloride was distilled at atmospheric pressure. The residue was distilled under vacuum to yield 19.5 g (97%) of a clear liquid, bp 99.8° (5 mm). A portion of this material (16.7 g) was added dropwise to 62 ml of concentrated ammonium hydroxide at 0°. The resulting white precipitate was filtered, washed repeatedly with water, and dried at 100° (0.5 mm) for 12 hr to yield 13.5 g (93%) of solid, mp 156.5–158.5° (lit.[40] 165°).

Anal. Calcd for C_8H_8DNO: C, 70.56; H, 6.66; D, 11.11 atom %. Found: C, 70.21; H, 6.67; D, 10.80 atom %.

Ethyl α-Deuterio-*p*-toluate. A portion of the acid chloride (1.2 g, 7.72 mmoles) prepared for the above synthesis of the deuterated *p*-toluamide was added dropwise to 1.5 ml of absolute ethanol. The mixture was heated on a steam bath for 45 min. Distillation gave 0.67 g (53%) of a clear liquid, bp 107° (4.2 mm) [lit.[24] 235.5° (760 mm)].

Anal. Calcd for $C_{10}H_{11}DO_2$: C, 72.70; H, 7.32; D, 8.33 atom %. Found: C, 72.74; H, 7.49; D, 7.96 atom %.

α-Deuterio-*p*-tolunitrile. α-Deuterio-*p*-toluamide (2.0 g, 14.7 mmoles) and 4 g of phosphorus pentoxide were thoroughly mixed. The solid mixture was heated under vacuum (100 mm), and the liquid which subsequently distilled was collected. Redistillation yielded 0.98 g (56.5%) of a clear liquid, bp 47° (0.5 mm) [lit.[24] 217.6° (760 mm)].

Anal. Calcd for C_8H_6DN: C, 81.32; H, 5.97; D, 14.29 atom %. Found: C, 81.07; H, 6.19; D, 13.75 atom %.

α-Deuteriotoluene.[41,42] Benzylmagnesium chloride was prepared in the usual manner by addition of 63.2 g (0.50 mole) of redistilled benzyl chloride in 225 ml of ether to 12.2 g of magnesium turnings in 50 ml of ether. Deuterium oxide (30 ml) was then added slowly to the Grignard solution. The normal work-up procedure yielded, after distillation, 26 g (56%) of material, bp 108° (lit.[41] 110°).

Anal. Calcd for C_7H_7D: D, 12.50 atom %. Found: D, 11.88 atom %.

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α-Deuterio-*o*- and *p*-nitrotoluene. An isomeric mixture of deuterated nitrotoluenes was prepared according to the procedure of Vogel[43] for the nitration of benzene. Thus α-deuteriotoluene (15.4 g, 0.166 mole) was added to a mixture of 17.5 ml of concentrated nitric acid and 20 ml of concentrated sulfuric acid. After work-up, distillation afforded 18.4 g (80%), bp 90–130°, of a mixture of two isomers in the ratio 1.27:1.00 (determined by glpc analysis of the distillate through a 10-ft Carbowax 20M column with the following operating parameters: column temperature 120°, flow (He) 60 cc/min, injection port temperature 225°, block temperature 225°; component A had a retention time of 6 min, and component B a retention time of 11 min. The mixture was separated on an Aerograph Autoprep vapor phase chromatograph (Model A-700) through a 20-ft Carbowax 20M preparative column (operating parameters: column temperature 210°, flow 200 cc/min, injection port 250°, detection block 250°).

Component A was identified as the *ortho* isomer by comparison of the aromatic region of its nmr spectrum with that of an authentic sample of *o*-nitrotoluene.

Anal. Calcd for $C_7H_6DNO_2$: C, 60.89; H, 5.11; D, 14.28 atom %. Found: C, 61.01; H, 5.24; D, 14.12 atom %.

Component B was identified as the *para* isomer by a comparison of the aromatic region of its nmr spectrum (which showed the expected AB-type pattern) with that of an authentic sample of *p*-nitrotoluene.

Anal. Calcd for $C_7H_6DNO_2$: C, 60.89; H, 5.11; D, 14.28 atom %. Found: C, 60.98; H, 5.02; D, 14.10 atom %.

α-Deuterio-*p*-tolyldiphenylcarbinol. α-Deuterio-*p*-chlorotoluene (4.0 g, 0.031 mole) in 15 ml of ether (dried over sodium wire) was added dropwise to a mixture of freshly chopped lithium metal (0.65 g, 0.094 g-atom) in 30 ml of ether cooled to 0°. The solution was stirred with a high-speed stirrer. The mixture was stirred an additional 8.5 hr after the addition was complete. Benzophenone (6.28 g, 0.035 mole) in 25 ml of ether was added dropwise. The reaction mixture was stirred for 2 hr at room temperature and then poured into a mixture of 50 g of ice and 50 ml of water. The aqueous layer was acidified to pH 3 and extracted with several portions of ether. The combined ether layers were dried over anhydrous magnesium sulfate and the ether stripped off on the rotary evaporator. Recrystallization of the solid residue from hexane yielded 3.9 g (62%) of white crystals, mp 71–73° (lit.[44] 73–74°).

Anal. Calcd for $C_{18}H_{17}DO$: C, 87.23; H, 6.59. Found: C, 87.23; H, 6.75.

Tris(α-deuterio-*p*-tolyl)carbinol. The procedure used in the synthesis of tris(3,5-dideuterio-*p*-tolyl)carbinol above was repeated using α-deuterio-*p*-chlorotoluene (1.00 g, 7.88 mmoles) and chopped lithium wire (120.4 mg, 17.3 mg-atoms). Ethyl carbonate (250 mg, 2.12 mmoles) was added slowly over 6 hr to the formed lithium reagent. The work-up as outlined in the above procedure yielded 629.4 mg (97%) of white crystals (from hexane), mp 91–92° (lit.[35] 93–94°).

Tris(α-deuterio-*p*-tolyl)methyl Fluoroborate. The procedure used for the preparation of tris(3,5-dideuterio-*p*-tolyl)methyl fluoroborate was followed with 205 mg of tris(α-deuterio-*p*-tolyl)carbinol, 0.3 ml of propionic anhydride, and 0.2 ml of 48% fluoroboric acid. The yield of orange solid was 152.5 mg. This was dissolved in 0.6 ml of methylene chloride, and the nmr sample was prepared as indicated in the above procedure.

Tris(α-deuterio-*p*-tolyl)methane. The procedure outlined above for the preparation of tris(3,5-dideuterio-*p*-tolyl)methane was followed with tris(α-deuterio-*p*-tolyl)carbinol (182.7 mg, 0.6 mmole), aluminum trichloride (164.8 mg, 1.23 mmoles), and lithium aluminum hydride (44.6 mg., 1.18 mmoles). The yield was 128.6 mg (74%) of a white crystalline material (from ethanol), mp 59–60° (lit.[38] 61–63°).

Tris(3,5-dideuterio-*p*-tolyl)methyllithium. Tris(3,5-dideuterio-*p*-tolyl)methane (90 mg, 0.31 mmole) was dissolved in 0.5 ml of octadeuteriotetrahydrofuran which had been allowed to stand over sodium wire overnight. Solid, recrystallized phenyllithium (34.4 mg, 0.41 mmole) was added. The solution immediately turned a bright red. The solution was agitated for 10 min and then, by means of a disposable pipet, was transferred to a precison nmr tube equipped with a stopcock and standard taper joint which could be attached to a vacuum manifold. All of the above operations were carried out in an inert atmosphere enclosure (drybox) which rigorously excluded both oxygen and moisture (an argon atmosphere was used). The nmr tube (with stopcock closed) was removed from the drybox, degassed several times, and sealed under vacuum. The nmr spectrum indicated a mixture of unreacted methane and the corresponding carbanion (in the ratio of 3.0:1.7, respectively, by nmr integration).

Tris(α-deuterio-*p*-tolyl)methyllithium. The above procedure for the preparation of tris(3,5-dideuterio-*p*-tolyl)methyllithium was repeated with tris(α-deuterio-*p*-tolyl)methane (100 mg, 0.346 mmole), 0.5 ml of octadeuteriotetrahydrofuran, and recrystallized phenyllithium (37.8 mg, 0.45 mmole).

Nmr Spectra. To prepare samples for nmr spectral examination, a precision nmr tube was attached to a two-way stopcock which was provided with a standard taper joint at one end. The standard taper joint was of an appropriate size so that it could be attached to the manifold of a vacuum system. The sample, in the chosen solvent, was introduced into the nmr tube with a syringe equipped with a 6-in. needle (the needle projected through the bore of the stopcock to avoid contaminating the sample with stopcock grease). The tube and its contents were cooled to liquid nitrogen temperatures (−196°) and the stopcock was opened to the vacuum system (0.2 mm). After a short time the stopcock was closed and the contents of the tube allowed to warm to room temperature. The tube was again cooled and opened to the vacuum. This procedure was repeated about ten times for each sample. The tube was then sealed off (below the stopcock) under vacuum.

Coupling constants were measured on a Varian A-60 with a 50-cps sweep width. Each time the machine was used, the chart was calibrated with the quartet resonance of neat acetaldehyde, taken as having a peak separation of 2.86 ± 0.01 cps (measured by others[45] and confirmed by us by the wiggle-beat method).

The methyl or deuteriomethyl proton signals were used to measure all coupling constants. The signals were 1:2:1 triplets in the 3,5-dideuteriotoluenes and 1:1:1 triplets with some further fine structure in the α-deuteriotoluenes. The interval $2J$ was measured from the centers of the outermost members of each triplet.

All efforts to employ the wiggle-beat method on the substituted toluenes failed to give a usable train of relaxation wiggles.

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