reochemical assignments being made on the basis of difference NOE experiments on **6a** and **7a**[8] and a corroborative X-ray structure determination of **6c**.[9]

The nitrone reactions are regiospecific as indicated and proceed in high yield. They are moreover well-behaved, second-order kinetic processes, showing the expected[10] moderate decrease in rate as one increases the polarity of the solvent. (C_6D_6, E_T = 34.5; $CDCl_3$, E_T = 39.1; CD_3OD, E_T = 55.5 kcal/mol; relative rates of 16, 5.4, and 1.0, respectively, for the reaction of MFA with **5a**.)

The observed remarkable preference for syn addition of nitrones to MFA is in dramatic contrast to similar additions to methoxy and phenoxyallene wherein anti products were formed to large excess, likely due to steric effects.[11] Since a fluorine substituent should exert little if any steric effect, the observed stereochemical preferences must derive from other subtle influences. The fluorine substituent of MFA may indeed provide a unique probe of such subtle effects.

The results may be related to the observation of preferential syn addition of 1,3-dipoles to *cis*-3,4-dichlorocyclobutene[12] although it should be noted that its Diels-Alder reactions exhibited no similar syn selectivity.[13] Moreover, the syn selectivity exhibited in the dichlorocyclobutene system is not reflected in similar studies on the *cis*-3,5-dichlorocyclopentene system.[14] The present work indeed constitutes the first example of the stereochemical directing effect of an allylic fluorine substituent on a cycloaddition.[15]

Distinction between a number of possible explanations for these results cannot yet unambiguously be made. It would appear, however, that an explanation involving direct interaction of the 1,3-dipole with fluorine's lone pairs is unlikely, inasmuch as the basicity as reflected by the proton affinity of a carbon-bound fluorine substituent is seemingly low.[16,17] Further studies are under way to clearly distinguish such an explanation involving direct fluorine lone-pair interaction from other potential sources of influence such as transition-state dipole-dipole interactions or orbital distortion of the C_2-C_3 π-bond by its proximate, eclipsed allylic fluorine substituent.[18,19]

Acknowledgment. We acknowledge with thanks the support of this research in part by the National Science Foundation.

Registry No. 1, 75372-17-7; **2**, 75372-20-2; **3**, 75372-19-9; **4**, 75372-22-4; **5a**, 3376-23-6; **5b**, 1137-96-8; **5c**, 31928-56-0; **6a**, 98857-92-2; **6b**, 98857-93-3; **6c**, 98857-94-4; **7a**, 98857-95-5; **7b**, 98857-96-6; **7c**, 98857-97-7; fluoroallene, 51584-22-6; cyclopentadiene, 542-92-7; butadiene, 106-99-0.

Supplementary Material Available: IR, NMR, and mass spectral determinations of **1-4**, **8**, **6a-c**, and **7a-c**, X-ray structure determination of **6c**, and tables of bond lengths and angles of **6c** (9 pages). Ordering information is given on any current masthead page.

(6) The reaction mixtures were probed by ^{19}F NMR and TLC indicating only **6** and **7** to be products along with two unidentified possible products for the R = CH_3 case, each present in 3% yield. The products were fully characterized.[7]

(7) Salient spectroscopic features of stereochemical importance were (for the R = 2-naphthyl case—others analogous): (a) Greater deshielding of cis-allylic protons by F; ^1H NMR (300 MHz) δ **6c** 5.65 (br s, 1 H, CHPh), 4.61 (m, 2 H, CH_2); **7c** 5.22 (br s, 1 H, CHPh), 4.88 (m, 2 H, CH_2). (b) Larger transoid allylic J_{HH}; ^1H NMR δ **6c** 6.49 (ddt, J_{HF} = 81.55, J_{HHcis} = 1.70, $J_{HHtrans}$ = 1.86 Hz by decoupling experiments, 1 H, CHF); **7c** 6.47 (ddt, J_{HF} = 80.68, $J_{HHtrans}$ = 2.19, J_{HHcis} = 1.34 Hz, 1 H, CHF). (c) Larger transoid allylic J_{CF}; ^{13}C NMR (75 MHz) δ **6c** 69.6 (s, CHPh), 65.8 (d, $J_{FCtrans}$ = 5.9 Hz, CH_2); **7c** 69.5 (d, $J_{FCtrans}$ = 4.9 Hz, CHPh), 66.1 (s, CH_2).

(8) For the irradiation of the PhCH and CH_2 in the ^1H NMR, the CHF NOE enhancements were 1.9% and 4.2%, respectively, for **6a**. For the analogous irradiations in **7a**, the enhancements were 1.9% and <1%.

(9) The crystal was grown from slow evaporation of solvent from an ethanolic solution of **6c** in an uncapped NMR tube. Crystal data: monoclinic, $P2_1/c$, a = 5.940 (1) Å, b = 23.685 (3) Å, c = 22.672 (4) Å, β = 91.69 (1)°, V = 3188.4 (8) Å^3, Z = 8. Intensity data: Nicolet R3m diffractometer; Mo Kα radiation, graphite monochromator; ω-2θ scan to 2θ = 50.0°; 5439 unique reflections; 3545 reflections $I \geq 3\sigma(I)$. Structure solution and refinement: SHELXTL programs; direct methods and Fourier synthesis; least-squares refinement; R(usual) = 0.073, R(weighted) = 0.078; goodness of fit = 1.61.

(10) Huisgen, R.; Seidl, H.; Bruning, I. *Chem. Ber.* **1969**, *102*, 1102.

(11) Battioni, P.; Vo Quang, F.; Vo Quang, Y. *Bull. Soc. Chim. Fr.* **1978**, 401, 415.

(12) Gandolfi, R.; Ratti, M.; Toma, L. *Heterocycles* **1979**, *12*, 897 and references therein.

(13) Warrener, R. N.; Johnson, R. P.; Jefford, C. W.; Ralph, D. A. *Tetrahedron Lett.* **1979**, *20*, 2939 and references therein.

(14) Caramella, P.; Albini, F. M.; Vitali, D.; Rondan, N. G.; Wu, Y.-D.; Schwartz, T. R.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 1875.

(15) See however: Franck-Newmann, M.; Sedrati, M. *Tetrahedron Lett.* **1983**, *24*, 1387.

(16) The proton affinities, defined as the enthalpies for the gas-phase reactions $BH^+ \rightarrow B + H^+$, of ethane, CH_3F, CH_3Cl, H_2O, and NH_3 are, for example, 142, approx. 151, 160, 170, and 205 kcal/mol, respectively.[17]

(17) Hartman, K. N.; Lias, S.; Ausloos, P.; Rosenstock, H. M.; Schroyer, S. S. "A Compendium of Gas Phase Basicity and Proton Affinity Measurements"; NBS: Washington, D.C., 1979; NBSIR 79-1777, 545 pp.

(18) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703.

(19) Houk has suggested that "pyramidalization of the alkene carbons" of the 3,4-disubstituted cyclobutenes may contribute to their syn selectivity.[14]

Stereoselective Total Synthesis of (±)-8-Deoxyanisatin

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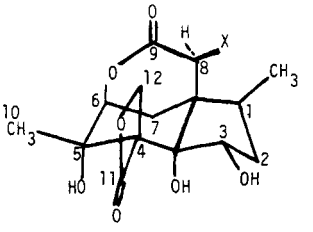
The convulsant principle of the seeds of Japanese star anise (*Illicium anisatum*, L.) was first characterized by Lane et al. in 1952,[1] and the full structure and stereochemistry of this potent $C_{15}H_{20}O_8$ toxin were established in a masterful 1968 paper by Yamada's group at Nagoya.[2] The structure of anisatin was shown to be the highly functionalized dilactone **1** on the basis of extensive



1 X = OH, **2** X = H

degradative and spectroscopic data as well as by elucidation of its facile rearrangement reactions in base or upon heating.[3]

In 1982 Woodward et al.[4] reported model studies to construct the bridging α-hydroxy δ-lactone unit of this challenging synthetic target, and recently Lindner[5] continued this approach in an imaginative yet so far unsuccessful attack on the anisatin system. We now report a stereoselective sequence that comprises the first total synthesis of (±)-8-deoxyanisatin (**2**).

Conjugate addition of $LiMe_2Cu$ to 2-allyl-2-cyclopentenone,[6] with stereoselective trapping of the resulting enolate by 2-(trimethylsilyl)-1-buten-3-one followed by aldol cyclization[7] gave the methylhydrindenone **3**.[8] Stiles carboxylation of **3** followed by

(1) Lane, J. F.; Koch, W. T.; Leeds, N. S.; Gorin, G. F. *J. Am. Chem. Soc.* **1952**, *74*, 3211.

(2) Yamada, K.; Takada, S.; Nakamura, S.; Hirata, Y. *Tetrahedron* **1968**, *24*, 199. The LD_{50} in mice for **1** is noted here as 1 mg/kg.

(3) Yamada, K.; Takada, S.; Hirata, Y. *Tetrahedron* **1968**, *24*, 1255.

(4) Lindner, D. L.; Doherty, J. B.; Shoham, G.; Woodward, R. B. *Tetrahedron Lett.* **1982**, *23*, 5111. See also: Doherty, J. B. Ph.D. Thesis, Harvard University, Cambridge, MA, 1975.

(5) Lindner, D. L. Ph.D. Thesis, Harvard University, Cambridge, MA, 1982. We are indebted to Dr. Lindner for a copy of his thesis prior to its formal publication.

(6) Novak, L.; Baan, G.; Marosfalvi, J.; Szantay, C. *Chem. Ber.* **1980**, *113*, 2939.

(7) Cf.: Boeckman, R. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6867.

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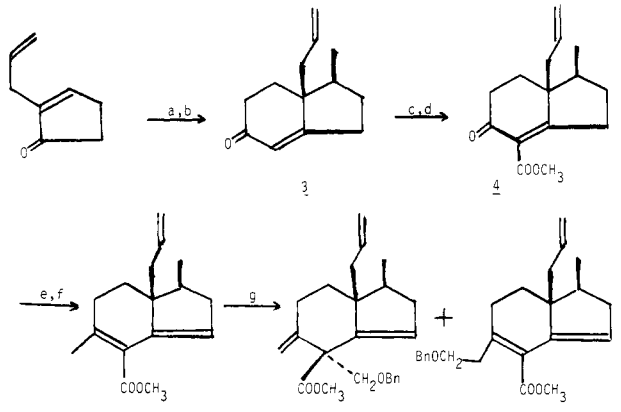
Scheme I[a]



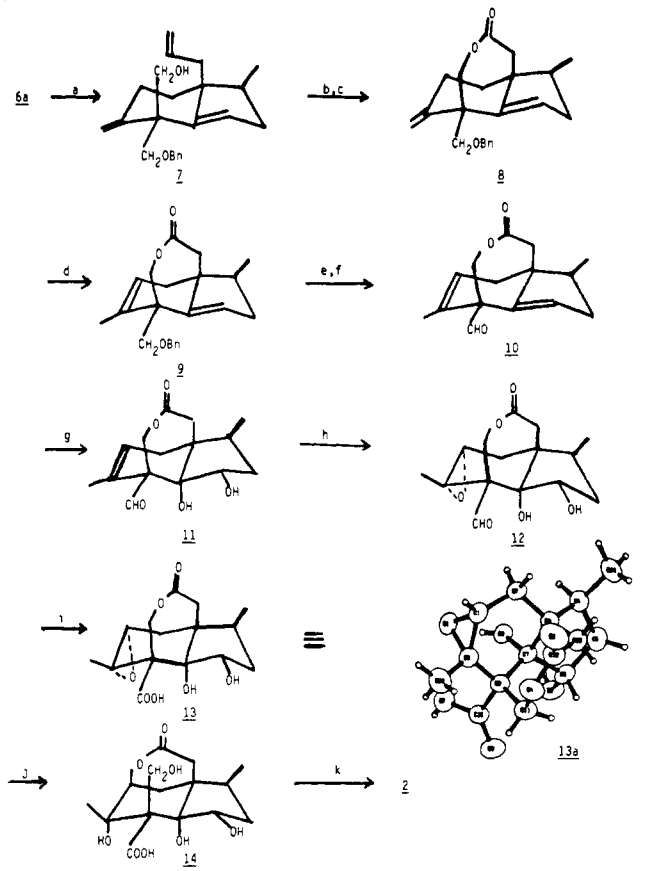
[a] $Me_2LiCu{\cdot}SMe_2$ in Et_2O, −30 °C, then Me_3Si-MVK; (b) 10% KOH in EtOH, reflux 40 min; (c) 2.0 M MMC in DMF, 130 °C, 2 h; (d) CH_2N_2, 10 min, 0 °C; (e) CH_3MgBr in Et_2O, −78 °C, 1 h; (f) MeOH, catalytic concentrated HCl, 25 °C, 2 h; (g) 1.2 equiv of LDA in THF, −78 °C, HMPA, then $BnOCH_2Cl$, to 25 °C.

CH_2N_2 gave keto ester **4** in 41% overall yield. Addition of CH_3MgBr and subsequent dehydration gave 60% of the single triene ester **5**.[9] Attempted deconjugative alkylation of this ester gave unexpected results. Under optimum conditions (1.2 equiv of LDA, THF, HMPA), the enolate of ester **5** reacted with $BnOCH_2Cl$ (1.2 equiv) to give a 5:4 ratio of α- vs. γ-alkylation products **6a** and **6b**[10] in 87% yield. This appears to be the first example of substantial γ-alkylation of the Li enolate of a simple α,β-unsaturated ester and may represent the 1,3-diaxial interaction destabilizing the development of the transition state for the normal α-alkylation process.[11]

The readily separable major ester **6a** was reduced to the carbinol **7** which on Lemieux–von Rudloff oxidation[12] followed by mild lactonization gave ϵ-lactone **8** in 33% overall yield. Isomerization (CH_3SO_3H, CH_2Cl_2, reflux, 46 h) gave 75% of the lactone **9**, thus completing the task of masking the 4β-hydroxymethyl chain for release at a subsequent point in our strategy. Debenzylation of **9** with BBr_3 followed by PDC oxidation gave 70% of the lactone aldehyde **10**. With the β-face of the molecule blocked by the secondary methyl as well as the ϵ-lactone, OsO_4 now reacted stereoselectively at the cyclopentene site to give the α-diol **11**, mp 222–224 °C, as the sole isolable product in 37% yield.

Reaction of the remaining double bond with CF_3CO_3H gave in quantitative yield the acid-stable epoxy aldehyde **12** (mp 187–189 °C)[13] which was converted by $NaClO_2$ oxidation[14] in 76% yield to the crystalline epoxy acid **13**, mp 195–196 °C. The structure and stereochemistry of acid **13** were confirmed by single-crystal X-ray analysis (cf. **13a**).[15] Reaction of acid **13** with 15% LiOH in MeOH at 0 °C for 4 h followed by gentle acidification to pH 2 in a two-phase (EtOAc–H_2O) system gave directly 68% of the desired δ-lactone **14**.[16] The facile formation of this δ-lactone from the acid-stable epoxide must represent bridging carboxyl participation in diaxial opening of the protonated epoxide.[17]

Scheme II[a]



[a] (a) $LiAlH_4$, Et_2O, 25 °C, 15 min; (b) KIO_4, K_2CO_3, catalytic $KMnO_4$ in aqueous *t*-BuOH, 25 °C, 60 h; (c) catalytic *p*-TsOH, C_6H_6, reflux, 20 min; (d) catalytic CH_3SO_3H, CH_2Cl_2, reflux, 46 h; (e) 4 equiv of BBr_3, CH_2Cl_2, −78 °C, 3 min; (f) 1.4 equiv of PDC, CH_2Cl_2, 25 °C, 24 h; (g) 1.1 equiv of OsO_4, C_5H_5N, 25 °C, 30 min; (h) 6 equiv of CF_3CO_3H, CH_2Cl_2, 0 °C, 15 min; (i) 3 equiv of $NaClO_2$, NH_2SO_2OH, 1:1 aqueous dioxane, 25 °C, 30 min; (j) 15% LiOH, MeOH, 0 °C, 4 h, then to pH 2 in EtOAc–H_2O; (k) 1.0 equiv of $PhSO_2Cl$, C_5H_5N–CH_2Cl_2, 0 °C, 3 h.

As already noted by Doherty,[4] steric constraints preclude lactonization of the COOH in **14** with all but the primary hydroxyl group. The crude δ-lactone reacted with $PhSO_2Cl$ (1 equiv in CH_2Cl_2–py, 0 °C, 3 h) to give ca. 90% of racemic 8-deoxyanisatin (**2**) (mp 112–114 °C from hexane–CH_2Cl_2). The IR of synthetic **2** showed strong β- and δ-lactone absorptions at 1830 and 1734 cm^{-1}, respectively (cf. **1**: 1826 and 1739 cm^{-1}). The MS showed a small molecular ion and a large $(M - H_2O)^+$ at m/z 294.1098. The coupled 400-MHz ^1H NMR of **2**[18] showed δ and J values appropriately comparable to those reported for natural anisatin,[3]

(8) All new compounds gave satisfactory CH or mass spectrometric analyses plus IR and proton NMR spectra. Hydrindenone **3** was obtained in 20:1 stereoselectivity and showed the secondary methyl as a doublet at δ 1.05 (J = 7 Hz).

(9) **5**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (1 H, m), 5.54 (1 H, br s), 5.09 (1 H, d, J = 17 Hz), 5.01 (1 H, d, J = 10 Hz), 3.80 (3 H, s), 2.34 (2 H, m), 2.21–1.85 (6 H, m), 1.84 (3 H, s), 1.34 (1 H, td, J = 6,13), 1.09 (3 H, d, J = 7).

(10) The minor γ-alkylation product **6b** showed clearly the $BnOCH_2CH_2$ signals as coupled triplets centered at δ 3.49 (J = 6 Hz) and δ 2.50 (J = 6 Hz), as well as all other signals required for **6b**.

(11) For a discussion of α- vs. γ-alkylation of extended enolates, see: Albaugh-Robertson, P.; Katzenellenbogen, J. A. *J. Org. Chem.* **1983**, *48*, 5288. Also: Majewski, M.; Mpango, G. B.; Thomas, M. T.; Wu, A.; Snieckus, V. *Ibid.* **1981**, *46*, 2029 and references therein. When the electrophile was CH_3I, alkylation of the enolate of **5** gave 2:1 γ-alkylation product.

(12) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701, 1710, 1714.

(13) **12**: ^1H NMR (400 MHz, $CDCl_3$, partial) δ 10.0 (1 H, s), 4.51 (1 H, m), 3.2 (1 H, d, J = 4.8 Hz), 1.40 (3 H, s), 0.87 (3 H, d, J = 7 Hz).

(14) Lindgren, B. O.; Nilsson, T. *Acta Chem. Scand.* **1973**, *27*, 888.

(15) We are deeply grateful to Dr. Henry R. Luss (Eastman Kodak Research Laboratories) for the X-ray analysis.

(16) **14**: IR ($CHCl_3$) 3408, 1729, 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 (1 H, m), 4.40 (1 H, br s), 3.93 (1 H, br d, J = 12 Hz), 3.83 (1 H, br d, J = 12 Hz), 2.63 (1 H, d, J = 2.0 Hz), 2.50–2.23 (3 H, m), 1.85–1.65 (3 H, m), 1.63 (3 H, s), 0.88 (3 H, d, J = 7 Hz).

(17) Conformational control in the diaxial opening of steroid secondary–tertiary epoxides by acids has been well established by: Mihina, J. S. *J. Org. Chem.* **1962**, *27*, 2807. Bowers, A.; Denot, E.; Urquiza, R.; Sanchez-Hidalgo, L. M. *Tetrahedron* **1960**, *8*, 116.

(18) **2**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (3a-OH, s), 4.73 (5-OH, s), 4.63 (C-3 H, ddd, J = 9.2, 5.3, 4.6 Hz), 4.38 (C-6 H, dd, J = 3.4, 1.8 Hz), 4.23 and 4.19 (AB quartet for C-12 CH_2, J = 6.9 Hz), 2.65 (C-1 H, m), 2.55 (C-8α H, d, J = 19.1 Hz), 2.47 (C-7β H, ddd, J = 14.4, 2.9, 1.8 Hz), 2.41 (3-OH, d, J = 5.3 Hz), 2.08 (C-8β H, dd, J = 19.1, 2.9 Hz), 1.86 (C-2 CH_2, m), 1.85 (C-7α H, dd, J = 14.4, 3.4 Hz), 1.59 (C-10 CH_3, s), 0.89 (C-13 CH_3, d, J = 7.2 Hz).

anisatin triacetate,[2] and noranisatin[19] and in particular established the integrity of the tertiary hydroxyls at C-3a and C-5 (singlets at δ 5.18, 4.73) and the lone secondary hydroxyl at C-3 (δ 2.41, d, J = 5.3 Hz); the latter collapses to a singlet upon irradiation of C-3 H at δ 4.63. The above sequence thus completes a stereocontrolled 18-step route to (±)-8-deoxyanisatin from 2-allyl-2-cyclopentenone and represents the first synthesis of any member of this intricate tetracyclic series.[20]

Supplementary Material Available: Tables of atomic coordinates, temperature factors, bond lengths, and bond angles for **13a** and NMR data for compounds **6a**, **9**, and **11** (9 pages). Ordering information is given on any current masthead page.

(19) Since 8-deoxyanisatin is a new compound not readily available from natural anisatin, diagnostic δ and J values were compiled from the 60-MHz spectra of Yamada for (a) anisatin in CF_3COOH,[3] (b) anisatin triacetate in $CDCl_3$[2] or (c) the closest analogue, the corresponding γ-lactone noranisatin in $CDCl_3$.[2] These data are tabulated by proton position and source below.

C-3	H	4.60	dd	J = 8.5, 5.5 Hz	(c)
C-6	H	4.31	d	J = 5.0 Hz	(c)
		[4.59	dd	J = 4.2 Hz	(a)]
C-12	CH_2	4.21, 4.13	ABq	J = 7.0 Hz	(b)
C-7β	H	2.74	d	J = 13.5 Hz	(c)
C-7α	H	2.21	dd	J = 13.5, 5.0 Hz	(c)
C-10	CH_3	1.50	s		(c)
C-13	CH_3	0.87	d	J = 7.0 Hz	(b)

(20) Partial support of this research by grant CA-18846, awarded by the National Cancer Institute (USPHS), is gratefully acknowledged.

NMR Isotope Shifts as a Probe of Electronic Structure

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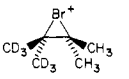
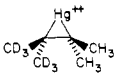
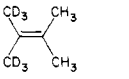
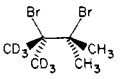
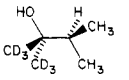
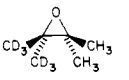
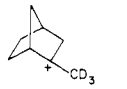
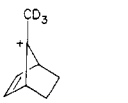
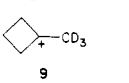
Deuterium isotope effects on carbon-13 chemical shifts have been used for the study of degenerate rearrangements,[1] for conformational analysis,[2] for spectral assignments,[3] and for probing charge distribution.[4] The two-bond isotope effects appear to be particularly revealing of the electronic distribution in the molecule.[4,5] The sign and magnitude of the two-bond deuterium isotope effect at the positively charged carbon atom in β-deuterated carbocations has been shown to depend on the electron demand and the charge delocalization mechanism.[4a]

For classical carbocations, the positive (downfield) β-isotope shifts are related to the demand for hyperconjugative stabilization by the C–H (or D) bonds.[4,5] In other cases in which the C–H (or D) bond is adjacent to an electron-deficient sp^2 hybridized carbon, the smaller positive shifts can be similarly explained.[6] For σ-delocalized carbocations, the negative (upfield) β-isotope shifts have been attributed to an isotopic perturbation of resonance.[4a] This perturbation results from averaging a vibrational motion over an anharmonic potential well and produces a change in the averaged electron distribution for different isotopomers.[7]

Table I. Deuterium Isotope Effects on the Carbon-13 NMR Chemical Shifts of 2,3-Dimethyl-2-butene Derivatives

compd	$^2\Delta C(D)^a$	$^3\Delta C(D)^a$
 1	+1.51	−0.30
 2	−1.59	+1.49
 3	−0.194	+0.032
 4	−0.404	−0.062
 5	−0.280	−0.089
 6	−0.253	−0.114
 7	−2.2	+0.4 (C1)[b]
 8	−0.8	0.0[b]
 9	−1.1	0.0[b]

[a] The two- and three-bond deuterium isotope effects (in ppm) at C2 and C3 of the 2,3-dimethyl-2-butene derivatives were determined at 67.9 MHz. [b] Reference 4a.

Although the energy surfaces for deuterated and nondeuterated materials should exactly coincide, small changes in bond lengths and angles which result from averaging a vibrational motion in an anharmonic potential well can be expected to occur. The increased electron density at an sp^3 hybridized carbon as a result of the lower zero-point vibrational energy of deuterium and a reduced C–D bond length is conveniently referred to as an inductive effect. For a C–D bond adjacent to an empty p orbital, the lower zero-point vibrational energy leads to a reduced electron delocalization to the p orbital and a reduced electron density at that carbon. This effect at a carbon β to the site of substitution is termed a hyperconjugative isotope effect.[7] Numerous examples of these effects are known, but in only a few cases have NMR isotope shifts been used to probe the mechanism of electron delocalization in moleules.[4a] We present here studies that suggest important new insights into the electronic structure of the bromonium ion **1** and the mercurinium ion **2** derived from 2,3-dimethylbutene.

The deuterium isotope effects on the carbon-13 chemical shifts were determined from the NMR spectra of samples containing a mixture of the nondeuterated and the gem-d_6 isotopomer of **1**[8,9]

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