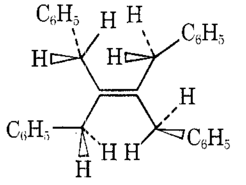
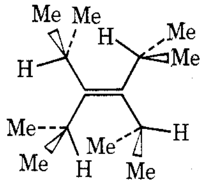
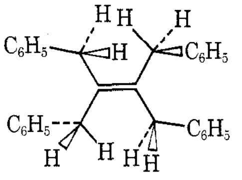


1a



2

spectrum of 1 was measured from approximately 30 to −30 °C in carbon tetrachloride solution. Over this temperature range, the benzyl protons of 1 remained as a singlet. This suggests that the "cogwheel" effect is inoperative with 1. Instead, it seems most reasonable that a rapid equilibrium may occur between conformations **1a** and **1b** such that unique protons are not detected over this temperature range.



1b

In summary, the bromination rate of 1 dramatically demonstrates the importance of steric effects in addition reactions of olefins.[9] Without a consideration of steric effects, the experimental rate is slower by a factor of about 5 × 10^5-fold. However, an excellent correlation[11] by eq 2 results when steric effects are included. It is apparent that the mere proximity of phenyl groups to the olefin bond is sufficient to cause slow rates of addition reactions. Lastly, ^{1}H NMR data suggest that a "cogwheel" effect is not operative with 1.

Experimental Section[12]

2,3-Dibenzyl-1,4-diphenyl-2,3-butanediol (3). A mixture of 9.95 g (47.3) mmol) of dibenzyl ketone (MCB, recrystallized from cyclohexane), 0.540 g (20.0 mg-atoms) of aluminum foil (Reynolds Wrap, sanded prior to use), 0.10 g (0.368 mmol) of mercuric chloride, and 150 ml of benzene (reagent grade, distilled from calcium hydride) was stirred and heated at 60–70 °C for 24 h under a nitrogen atmosphere. The reaction mixture was then cooled in an ice bath while 100 ml of 5% hydrochloric acid was added over a 2.0-h period. The organic layer was separated and the aqueous phase was extracted with carbon. tetrachloride. The combined organic phases were washed with water, dried over anhydrous potassium carbonate, and concentrated on a rotary evaporator to give 9.34 g of a viscous yellow oil. NMR analysis of this oil, relative to a measured amount of methylene chloride, indicated a 48% yield of pinacol **3**. Chromatography of the oil (9.3 g) on silica gel (70 g) with 10% benzene–90% *n*-hexane eluent gave 4.23 g (42.3% yield) of **3**: mp 118–120 °C (lit.[13] mp 120 °C); ir 3560, 3090, 3060, 3030, and 2940 cm^{-1}; NMR OH (1.77, s, 1.94), $C_6H_5CH_2$ [2.92, AB (J = 14 Hz), 8.0], and C_6H_5 (7.08, s, 19.6).

Tetrabenzylethylene (1). A solution of 9.09 g (21.5 mmol) of pinacol **3**, 15.0 ml (13.5 g, 90.9 mmol) of ethyl orthoformate (dried over calcium sulfate and distilled at 146 °C), and 0.10 g (0.82 mmol) of benzoic acid was stirred and heated at 148–155 °C (internal temperature) for 9.0 h under a nitrogen atmosphere. During this period 2.0 ml (ca. 80% of theory) of ethanol was distilled from the reaction solution. The excess ethyl orthoformate was distilled and the residual oil was heated with 0.20 g (1.6 mmol) of benzoic acid for 16 h. The reaction mixture was then dissolved in 25 ml of carbon tetrachloride and this solution was washed with 0.2 M potassium carbonate and with water. The organic solution was dried over calcium sulfate and rotary evaporated to 8.31 g of a yellow, oily solid. Recrystallization from *n*-hexane gave 6.60 g (82.8% yield) of white needles of **1**: mp 119.7–120.7 °C (lit.[14] mp 119.5–120.5 °C); ir 3080, 3060, 3025, 2960, 2920, and 2850 cm^{-1}; NMR CH_2 (3.47, s, 8.00), C_6H_5 (7.10, s, 20.0); mass spectrum, P *m/e* 388 (12), P − $C_6H_5CH_2$ 297 (9.0), P − ($C_6H_5CH_2$, C_6H_5, and H) 219 (12), P − [2($C_6H_5CH_2$) and H] 205 (13), P − [2($C_6H_5CH_2$), H, and C] 193 (3.9), and $C_7H_7^+$ 91 (100).

Kinetics of Bromination. An acetic acid solution of 1 and bromine (each 7.63 × 10^{-3} M) were placed in an aluminum foil wrapped vessel under a nitrogen atmosphere, which was thermostated at 24.0 °C. Aliquots were periodically withdrawn and titrated by an iodometric procedure.[5] The second-order rate coefficients were obtained by a least-squares fit.

Acknowledgment. We thank the U.S. Army Research Office (Durham) for support of this research.

Registry No.—1, 19754-02-0; **3**, 33574-71-9; dibenzyl ketone, 102-04-5.

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Remote Substituent Effects on Carbon-13 Shieldings in Some Bicyclo[2.2.2]octyl Systems

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Fluorine-19 chemical shifts of certain dibenzobicyclo[2.2.2]octyl derivatives, e.g., adducts of 10-substituted 9-fluoroanthracenes with maleic anhydride (I) and dimethyl acetylenedicarboxylate (II), have been studied in anticipation that these ^{19}F substituent chemical shifts (^{19}F SCS) might approximate to the field component of the overall ^{19}F SCS in aromatic fluorides where direct partitioning of components is impossible.[2] Although structural deformations in some bicyclic tertiary fluorides are apparently to blame for worrying fluctuations in chemical shift, Anderson and Stock reasoned

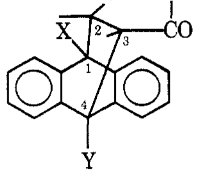
Table I. Carbon-13 Chemical Shifts[a] of Some Bicyclo[2.2.2]octyl Systems

System		Carbon number[b]				Substituent effects at carbon			
		1	2	3	4	1	2	3	4
III[c]	X = H	23.99	26.11	26.11	23.99				
	Br	62.88	37.61	29.14	22.78	38.89	11.50	3.03	−1.21
	F	92.47	31.30	27.38	24.26	68.48	5.19	1.27	0.27
		(185.3)	(18.4)	(9.4)	(3.3)				
IV[d]	X = H[e]	45.5	48.6	48.6	45.5				
	Br[e]	nl	55.94	50.49	45.0		7.34	1.89	−0.5
	F	95.0	51.87	49.56	44.24	49.5	3.27	0.94	−1.26
		(212)	(18.31)	(6.10)	(3.0)				
	CN[e]	47.2	51.52	48.77	44.67	1.7	2.92	0.17	−0.83
	CH_3	nl	52.33	50.00	45.4		3.73	1.4	−0.1
	$COCH_3$	61.07	50.17	49.85	45.96	15.57	1.57	1.25	+0.46
V[f]	X = H	52.60	147.06	147.06	52.6				
	Br	66.73	(142.63	140.58)	49.90	14.13			−2.7
	CN	nl	(143.88	142.25)	50.28				−2.32
	NO_2	nl	(142.5	143.3)	50.60				−2.00
	CH_3	nl	(155.58	142.15)	50.28				−2.32
	$C(CH_3)_3$	68.84	(155.47	145.49)	51.41	16.24			−1.19
VI	X = H	24.58	26.59	32.18	34.13				
	OCH_3	73.60	29.71	33.09	34.13	49.02	3.12	0.91	0.0
	OH	69.57	34.26[g]	33.48[g]	34.26	44.99	7.67	1.30	0.13
	$OCOCH_3$	80.62	30.23	33.09	34.20	56.04	3.64	0.91	0.07
	F	94.50	31.50	33.52	34.20	69.92	4.91	1.34	0.07
		(183.8)	(19.1)	(10.3)	(2.9)				
	Cl	67.42	36.61	33.35	34.20	52.84	10.02	1.17	0.07

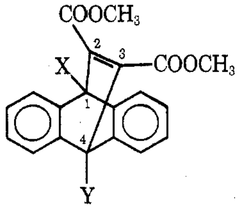
[a] In ppm with respect to internal Me_4Si unless otherwise indicated. Positive shifts correspond to lower shieldings. [b] Numbering system for convenience only. [c] From ref 9 and for CCl_4 solutions referenced to internal cyclohexane. These have been referenced to Me_4Si by assuming δ_c (cyclohexane) is 27.00 ppm. [d] For solvent DMF–$CDCl_3$ (3:1). [e] Confirmed by deuterium substitution. [f] $CDCl_3$ solvent. Assignments for bridging carbons (i.e., C_2, C_3) unproven and β, γ effects therefore not listed. [g] Assignments may require reversal.

that dibenzo fusion should essentially eliminate substituent-induced skeletal changes.[2] These authors suggested, in particular that the ^{19}F SCS data for series II below "portray the polar interactions that would be realised in a rigid molecule such as benzene".

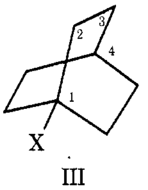
Carbon-13 chemical shifts also seem to provide a useful measure of substituent effects in aromatic systems,[3–8] and again the problem of assessing the field component of the overall ^{13}C SCS arises. Recourse, again, to bicyclic molecules would seem logical but in the study of Maciel and Dorn[9] with 1-substituted bicyclo[2.2.2]octanes (III) it was not clear that the response of C_4 could provide a useful platform from which to develop an understanding of long-range electronic (i.e., δ) effects at carbon. Nevertheless, the proposal of Anderson and Stock[2] regarding the beneficial effects of dibenzofusion seemed to warrant study in respect of carbon-13 shifts. In this note we present our findings for systems IV, V, and VI, and the somewhat melancholy conclusions regarding substituent effects that seem to follow.



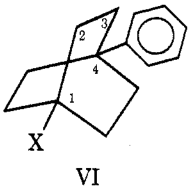
I, Y = F
IV, Y = H



II, Y = F
V, Y = H



III



VI

In this note, we are primarily concerned with the chemical shift of C_4 in series III–VI and spectral assignments have been arrived at by standard techniques. For series IV, C_4 was assigned on the basis of deuterium substitution in the starting anthracenes, consideration of ^{19}F–^{13}C couplings for the fluoroanthracene adduct,[10] and chemical shift trends. For V the closeness of the signals of C_4 and $COOCH_3$ required application of the partially relaxed Fourier transform spectral technique (PRFT),[11] depending on the different relaxation times of such carbons. These assignments for the parent (X = Y = H) of system V were confirmed by a fully proton-coupled spectrum.[10,12] For series VI, C_4 was assigned on the basis of intensities and chemical shifts. The results for C_1–C_4 are presented in Table I. The chemical shifts for other carbons in these systems have generally been obtained, but assignments have not been made, and hence the data are not tabulated.

Regarding the δ effects (i.e., at C_4) it is clear that these are a function of the particular bicyclo[2.2.2]octyl system under scrutiny, although changes in the C_1–C_4 distances are small and not capable of rationalizing these trends through the distance term in the field theory treatment. As suggested by Anderson and Stock,[2] for systems III and IV in particular, structural disturbances are probably significant and may be associated with the quite large variations in some of the α and β effects as well. Nevertheless, in system IV the C_4 SCS are to higher field (except for $COCH_3$), a movement traditionally associated with increased electron density and nuclear shielding.[3–8] For system V, regarded[2] as most resistant to structural unruliness, all C_4 SCS are to higher field by not inconsiderable amounts. The methyl group, which exerts an extremely feeble dipolar effect, is comparable to cyano, nitro, and bromo. The bulky *tert*-butyl group was examined to explore the effect of sterically induced distortions, and in this case the C_4 SCS is the smallest in an absolute sense. "Peri-type" hydrogen interactions are severe in this system as judged

Table II. Analytical and Spectroscopic Data for Certain Adducts

Series IV				Series V			
	Mp, °C	C	H		Mp, °C	C	H
X = H	257–258	(lit. 258–260)[21]		X = H	160–161	(lit. 160–161)[24]	
Br	252–253	(lit. 253–254)[21]		Br	178–179	60.19	3.76
F	239–240	73.20	3.87			(60.15)	(3.76)
		(73.46)	(3.74)	CN	174–175	72.58	4.44
CN	227–228	75.78	3.81			(73.04)	(4.34)
		(75.78)	(3.66)	NO_2	182–183	66.61	4.19
CH_3	269–270	77.96	4.80			(65.75)	(4.10)
		(78.62)	(4.82)	CH_3	184–185	75.39	5.40
$COCH_3$	259–260	75.30	4.51			(75.45)	(5.39)
		(75.47)	(4.40)	$C(CH_3)_3$	177–178	76.40	6.45
						(76.59)	(6.38)

^1H NMR Data

Series V

X =	$-COOCH_3$	CH	Aromatics	Other
H	3.75	5.45	6.85–7.5	
Br	3.77, 3.85	5.70	7.00–7.85	
CN	3.80, 3.91	5.67	7.05–7.85	
NO_2	3.77, 3.84	5.63	7.00–7.65	
CH_3	3.73, 3.80	5.62	6.85–7.5	2.16
$C(CH_3)_3$	3.70, 3.73	5.52	6.96 (m, 4 H) 7.30 (m, 2 H); 7.75 (m, 2 H)	1.82 (6 H); 1.94 (3 H)

Series IV

X =	H_1	H_2	H_3	H_4	Aromatics	Other
H[a]	4.94	3.62	3.62	4.94	7.16–7.60	
$COCH_3$		4.24 ($J_{H_2\text{-}H_3}$ = 10 Hz)	3.64 ($J_{H_2\text{-}H_3}$ = 10 Hz; $J_{H_3\text{-}H_4}$ = 3.5 Hz)	4.90 ($J_{H_3\text{-}H_4}$ = 3.35 Hz)	7.2–7.70	2.94
F[a]		3.72	3.66	4.80	7.16–7.68	

[a] Poorly soluble and coupling constants poorly defined.

by the duality of sharp signals in the ^1H and ^{13}C spectra for the methyl groups of the arrested *tert*-butyl group.[13] In system V, the upfield C_4 SCS may be due in part, for the bromo, cyano, and nitro groups, to polarization of the C_4–H σ bond, but "through-space" effects in bicyclo[2.2.2]octyl systems are apparently of secondary importance to "through-bond" effects.[14,15] The reverse may be the situation for the bicyclo[2.2.1]heptyl framework.[16] In system V, through-bond hyperconjugative transfer of electron density induced by the substituent may occur, but it is not clear what effects on the C_4 chemical shifts it might have.

For system VII, Anderson and Stock[2] observed low-field (i.e., positive) ^{19}F SCS but the correspondence among the substituents for the ^{13}C and ^{19}F SCS is poor. The ^1H chemical shifts of H_4 in system V (these appear as singlets at ca. δ 5.60) are all to lower field from the parent (X = H), with the bromo compound showing the largest shift (+0.25 ppm) and the *tert*-butyl the smallest (+0.07 ppm). Somewhat surprisingly, in system VI, C_4 responds very feebly to 1 substitution and tentatively we associate this with the inability of the substituent to polarize the C_4–phenyl bond, in a direction disfavored on electronegativity grounds. Other poorly understood factors may also be involved.

What are the implications of these results for the idea that SCS data from bicyclic systems approximate to the field component of the overall SCS in substituted aromatics? A number of points warrant emphasis.

(a) For ^{13}C shifts, apparently in systems (e.g., V) regarded as quite rigid, a number of factors, not necessarily related to the electronic capabilities of the substituent, contribute to the overall screening term and vary with the substituent.

(b) While system V may minimize these effects, the presence of highly polar groups in the bridge systems of IV and V may promote varying interactions when the substituents are powerfully dipolar and lead to additional complications. The π nature of the bridging group in V may also sustain certain polarizations.

(c) The recent conclusions[14–16] that in certain bicyclo[2.2.2]octyl systems through-bond transfer of charge, involving the bridging 2,3 bond is important, creates a mechanism for affecting both ^{13}C and ^{19}F SCS in these systems, that is not a complication in benzenoid frameworks. Relating data from the two systems must therefore be somewhat dangerous.

(d) While the results of Anderson and Stock[2] for system II are in the anticipated low-field direction (e.g., when X = NO_2 SCS = 1.68 ppm for DMF) this figure conceivably could be the result of deshielding and shielding contributions, the latter varying in some way with the substituent. The characteristics of the "molecular cavities" in bicyclic and aromatic systems are also different and could seriously affect transmission. See c above.

(e) A crucial assumption for both ^{13}C SCS and ^{19}F SCS would be required that, for example, the response of sp^3-bound fluorine (in system II) to remote dipolar substituents would be similar to the response of sp^2-bound (i.e., aromatic) fluorine. Considering that C–F π-polarization is extremely important in regulating the ^{19}F chemical shift,[17] the above assumption seems to us to be very tenuous.

(f) Surely the logical approach for magnetic resonance investigation of the field component of the total SCS observed in an aromatic system (whether ^{19}F or ^{13}C) is to examine a system in which the probe nucleus is still in the aromatic environment, but the substituent is contained in an attached, desirably strain-free system, so constructed that resonance and related effects are prohibited. We have seen above that in system V, dipolar substituents actually shield C_4 but in aromatic systems, the whole π system is polarized, and leads to a deshielding of the carbon probe.[18]

The data in Table I indicate wide variations for the α, β, and γ effects as a function of substituent and molecular system.[19] For the α effect there appears to be a basic correlation with substituent electronegativity within a system, but substantial differences between systems for the same substituent, e.g., for the sterically small fluoro, α effects of +68.48 (III), +49.5 (IV), and +69.92 (VI) are noted. The β effects are again positive, i.e., deshielding in nature, but the dependence on substituent electronegativity is not obvious. It would seem in fact, that more electronegative substituents may be associated in part with increased shielding at C_β, a result in accord with some theoretical work predicting alternation of charge in a σ-bonded framework.[20] Other factors, such as degree of substitution and strain, may be important, the latter particularly at the α position. Small but significant deshielding effects at C_γ are also observed, and these C_γ positions are anti to the substituent. It is not clear how well the alternating polarization hypothesis accommodates these data, but a number of factors are almost certainly operating in this region.

Experimental Section

Compounds. The maleic anhydride adducts (series IV) were prepared in the standard way by refluxing the 9-substituted anthracene with slightly more than 1 equiv of maleic anhydride in the minimum amount of *o*-xylene for 3–12 h, depending on the 9-substituent.[21] On cooling crystals of the adducts separated, in quite pure form, and one further crystallization from xylene provided analytically pure compounds.

9,10-Dideuterioanthracene was obtained by the *p*-toluenesulfonic acid catalyzed H–D exchange with anthracene. Specifically 9-deuterated anthracene resulted from lithium aluminum deuteride reduction of anthrone followed by acid (3 N HCl) induced dehydration. ^{1}H NMR analysis indicated ~95% deuterium incorporation. 9-Bromo-10-deuterioanthracene was synthesized by bromine addition and hydrogen bromide elimination in the reported manner.[22] Careful ^{1}H NMR measurements revealed ca. 50% deuterium at the 10 position indicating the absence of a significant isotope effect in the elimination. 9-Cyano-10-deuterioanthracene was obtained from the 9-bromo compound on treatment with copper(I) cyanide in *N,N*-dimethylformamide.[23]

The dimethyl acetylenedicarboxylate adducts (series V)[24] were prepared by refluxing equimolar amounts of the reagents in benzene and monitoring the reaction by ^{1}H NMR analysis of the $COOCH_3$ region. The benzene solvent was removed and the adducts were recrystallized from methanol. The structures of the adducts were confirmed by elemental analyses, ^{1}H NMR spectra (where solubility was adequate), and of course the ^{13}C spectra.

Compounds in series I, II, and III have been reported elsewhere,[2,9] while those in series VI will be described in detail in another connection.[25]

^{13}C spectra were recorded with a Bruker HX-90 spectrometer operating in the FT mode, and chemical shifts are relative to internal Me_4Si and accurate to ±0.05 ppm.

The analytical data for new compounds are assembled in Table II, and the ^{1}H NMR data for series V also. These adducts are generally quite soluble, and the chemical shifts ($CDCl_3$, internal Me_4Si) pertain to 5% weight/volume solutions. The maleic anhydride adducts are far less soluble, and chemical shift data for series IV, X = H, F, and $COCH_3$, only, are tabulated.

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Registry No.—III (X = H), 280-33-1; III (X = Br), 7697-09-8; III (X = F), 20277-22-9; IV (X = H), 5443-16-3; IV (X = Br), 58802-01-0; IV (X = F), 26306-24-1; IV (X = CN), 58802-02-1; IV (X = Me), 58802-03-2; IV (X = $COCH_3$), 17478-86-3; V (X = H), 1625-82-7; V (X = Br), 58802-04-3; V (X = CN), 58802-05-4; V (X = NO_2), 58802-06-5; V (X = CH_3), 58802-07-6; V (X = $C(CH_3)_3$), 33740-56-6; VI (X = H), 23062-62-6; VI (X = OMe), 6555-88-0; VI (X = OH), 2001-62-9; VI (X = OCOMe), 54986-35-5; VI (X = F), 22947-58-6; VI (X = Cl), 33732-68-2.

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(1) Direct enquiries to this author.

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A Method for Relating Esterification Rates and Structures of Alkyl-Substituted Acetic Acids

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The relationship between the esterification rate and structure of aliphatic acids has been investigated since the latter part of the 19th century.[1] The collection of data by Loening, Garrett, and Newman[2] for hydrogen chloride catalyzed esterifications in methanol is commonly used in relating structure and rate. By including additional data, some recent studies have suggested that there are relationships between rate and structure not previously disclosed.[3] The purpose of the present study is to further examine the problem of rate and structure by the use of an expanded collection of comparable esterification data.

In the original method the determination of rate coefficients of slow-reacting acids was seriously limited since during the extended esterification time a substantial amount of the hydrogen chloride catalyst reacted with the methanol.[2] In the present study, pairs of acids are allowed to react together and the ratios of the rate coefficients are determined by gas–liquid