(58), 91 (32), 80 (23), 79 (80), 77 (44), 67 (30).

3,9-Dimethyl-3-azabicyclo[4.3.0]non-9-en-8-one (14c). This was prepared from **7c** in a manner similar to that used for **14a:** 60% yield; bp (0.02 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.66 (br s, 3 H), 2.30 (s, 3 H), 0.8–3.1 (m, 7 H), 3.27 (br s, 1 H), 3.60 (br s, 1 H); IR (CCl_4) 1708, 1665 cm^{-1}; mass spectrum (70 eV), *m/e* 165 (M^+, 62), 164 (54), 137 (58), 122 (100), 94 (32), 79 (39), 77 (20), 53 (21), 44 (47), 42 (69), 41 (24), 39 (21).

General Procedure for the Alkylation of Doubly Activated Esters and Nitriles. To a refluxing suspension of 6 mmol of NaH (hexane washed) in 25 mL of THF was slowly added 5 mmol of active methylene compound. After hydrogen evolution was complete, 6 mmol of **3** was added and the refluxing was continued for 14 h. Upon cooling, the reaction mixture was acidified with dilute aqueous HCl, stirred for 15 min to hydrolyze the enol ether, and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by bulb-to-bulb distillation. Analytical samples were obtained by preparative GC (OV17). The following alkylated products were obtained.

Diethyl 2-Ethyl-2-(1-methyl-2-oxopropyl)malonate (16a):[15] 71% yield; bp (0.05 torr) 118 °C (bath); ^{1}H NMR (220 MHz, $CDCl_3$) δ 0.90 (t, 3 H), 1.20 (t, 6 H), 1.24 (d, 3 H), 2.02 (q, 2 H), 2.24 (s, 3 H), 3.21 (q, 1 H), 4.21 (q, 4 H); IR ($CHCl_3$) 1715 cm^{-1}; mass spectrum (70 eV), *m/e* 258 (M^+, absent), 213 (25), 187 (72), 170 (35), 142 (43), 141 (77), 139 (46), 115 (29), 114 (22), 97 (23), 69 (25), 43 (100), 29 (53).

Diethyl 2-Ethyl-2-(2-oxobutyl)malonate (17a): 14% yield; bp (0.05 torr) 118 °C (bath); ^{1}H NMR (220 MHz, $CDCl_3$) δ 0.64 (t, 3 H), 0.84 (t, 3 H), 1.02 (t, 6 H), 1.82 (q, 2 H), 2.20 (q, 2 H), 2.84 (s, 2 H), 3.98 (q, 4 H); IR (neat) 1710 cm^{-1}; mass spectrum (70 eV), *m/e* 258 (M^+, absent), 187 (24), 141 (36), 139 (34), 127 (22), 83 (20), 57 (73), 55 (31), 29 (100), 27 (21).

Dimethyl 2-Methyl-2-(1-methyl-2-oxopropyl)malonate (16b): 76% yield; bp (0.05 torr) 120 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3 H), 1.52 (s, 3 H), 2.21 (s, 3 H), 3.41 (q, 1 H), 3.71 (s, 6 H); IR (neat) 1730 cm^{-1}; mass spectrum (70 eV), *m/e* 216 (M^+, 1), 185 (20), 174 (27), 145 (32), 142 (71), 125 (50), 115 (48), 114 (84), 113 (23), 83 (39), 59 (47), 55 (37), 43 (100).

Methyl 2-(1-Methyl-2-oxopropyl)-2-cyanoacetate (19):[16] 48% yield; bp (0.05 torr) 110 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.44 (dd, 3 H), 2.29 (d, 3 H), 3.30 (m, 1 H), 3.83 (s, 3 H), 3.95 (m, 1 H); IR (neat) 2250, 1750, 1720 cm^{-1}; mass spectrum (70 eV), *m/e* 169 (M^+, 3), 68 (7), 43 (100), 28 (6), 15 (9).

Methyl 2-(2-Oxobutyl)-2-cyanoacetate (20): 13% yield; bp (0.05 torr) 110 °C (bath); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, 3 H), 2.50 (q, 2 H), 3.1 (d, 2 H), 3.85 (s, 3 H), 4.1 (t, 1 H); IR (CCl_4) 2261, 1752, 1720 cm^{-1}; mass spectrum (70 eV), *m/e* 169 (M^+, 5), 140 (7), 138 (9), 112 (27), 80 (7), 59 (6), 57 (100), 29 (17).

1-Carbomethoxy-1-(1-methyl-2-oxopropyl)cyclohexane (22). To a solution of 2.6 mmol of LDA (generated in situ) in 10 mL of THF at 0 °C was added 351 mg (2.47 mmol) of carbomethoxycyclohexane. After 0.5 h, 0.50 mL (3.0 mmol) of **3** was added and the mixture was slowly allowed to warm to room temperature. After 12 h, 5 mL of 3 M aqueous acetic acid was added. After an additional 12 h, the reaction mixture was diluted with ether and water. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo; bulb-to-bulb distillation afforded 456 mg (2.15 mmol, 87%) of the alkylated product **22:** bp (0.02 torr) 130 °C (bath); ^{1}H NMR (CCl_4) δ 1.04 (d, 3 H), 0.9–1.8 (m, 10 H), 2.05 (s, 3 H), 2.69 (q, 1 H), 3.66 (s, 3 H); IR (CCl_4) 1734 cm^{-1}; mass spectrum (70 eV), *m/e* 212 (M^+, 1), 141 (100), 109 (44), 81 (44), 72 (29), 43 (60).

3-Methyl-4-cyano-2-hexanone (24). To a solution of 2.4 mmol of LDA (generated in situ) in 5 mL of THF at −78 °C was added 0.16 mL (2.0 mmol) of butyronitrile. After 0.5 h, 0.33 mL (2.0 mmol) of **3** in 3 mL of HMPA was added and stirring was continued for an additional 0.5 h. The reaction mixture was slowly warmed to room temperature over the course of 6 h, acidified with dilute aqueous HCl, stirred for 15 min to hydrolyze the enol ether, and diluted with ether and water. The organic layer was separated, washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude alkylated product was purified by bulb-to-bulb distillation to afford 0.17 g (1.2 mmol, 61%) of products **24,** that GC analysis (OV17 at 100 °C) and NMR, IR, and mass spectra showed were diastereoisomers, in a ratio of 52:48.

24a: bp (5 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.15 (t, 3 H), 1.30 (d, 3 H), 1.55 (q, 2 H), 2.20 (s, 3 H), 2.6–2.9 (m, 2 H); IR ($CHCl_3$) 2220, 1712 cm^{-1}; mass spectrum (70 eV), *m/e* 139 (M^+, 1), 72 (12), 68 (10), 43 (100).

24b: bp (5 torr) 100 °C (bath); ^{1}H NMR (CCl_4) δ 1.15 (t, 3 H), 1.30 (d, 3 H), 1.55 (q, 2 H), 2.20 (s, 3 H), 2.6–2.9 (m, 2 H); IR ($CHCl_3$) 2220, 1712 cm^{-1}; mass spectrum (70 eV), *m/e* 139 (M^+, 1), 82 (5), 72 (19), 70 (16), 68 (13), 55 (8), 43 (100), 42 (5), 41 (8).

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Registry No.—**1,** 67722-23-0; **3,** 67722-24-1; **4a,** 10468-40-3; **4b,** 6114-69-8; **4c,** 67722-22-9; **7a,** 67722-25-2; **7b,** 67722-26-3; **7c,** 67722-27-4; **8a,** 29943-11-1; **8b,** 59574-62-8; **9,** 67722-28-5; **14a,** 24730-98-1; **14b,** 67722-29-6; **14c,** 67722-30-9; **15a,** 133-13-1; **15b,** 609-02-9; **16a,** 67722-31-0; **16b,** 67722-32-1; **17a,** 67722-33-2; **18,** 105-34-0; **19,** 67722-34-3; **20,** 67722-35-4; **21,** 4630-82-4; **22,** 67722-36-5; **23,** 109-74-0; **24** isomer 1, 67722-37-6; **24** isomer 2, 67722-38-7.

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Concerning the Electronic Effects of Substituted Methyl Groups

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The nature of the substituent effect(s) exerted by substituted methyl groups attached to aromatic or other unsaturated systems continues to be an area of considerable interest.[1] This contribution was prompted by the recent work of Shapiro[2] which purported to demonstrate that in a series of para-substituted benzyl systems, hyperconjugative interactions at the para position were of minor importance. This conclusion contrasted with persuasive evidence to the contrary, particularly that from systems in which the C–X bond was geometrically defined with respect to the π system[1] and from PES studies of benzyl systems.[3]

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Table I. ^{13}C and ^{19}F Substituent Chemical Shifts (SCS, ppm)[a] in α-Substituted 2-Methylnaphthalenes

CH_2X, X =	registry no.	C-6[b]	C-7[b]	C-10[b]	6-F[c]	registry no.	7-F[d]	registry no.
SCH_3	13183-61-4	−0.05	−0.38	−0.85	−0.29	66922-58-5	0.22	66922-62-1
OCH_3	42101-92-8	0.06	0.30	−0.36	−0.25	66922-59-6	0.14	66922-63-2
$N(CH_3)_2$	2018-89-5	−0.23	0.13	−0.63	−0.67	66922-60-9	0.11	66922-64-3
Br	939-26-4	0.79	0.71	−0.30	1.07	581-72-6	0.73	64168-12-3
Cl	2506-41-4	0.72	0.72	−0.15	*e*		*e*	
CN	7498-57-9	0.69	0.99	−0.85	+0.79	66922-61-0	1.16	66922-65-4

[a] Referred to the chemical shift of the appropriate carbon or fluorine in naphthalene. Positive signs indicate shifts to lower field. [b] For dilute solution in $CDCl_3$. [c] Solvent, benzene. 6β disposition. [d] Solvent, benzene. 7β disposition. [e] Not measured.

We consider there are certain unsatisfactory features in Shapiro's approach. First, the electronic effect of CH_2X was dissected by Taft's multiparameter treatment (DSP) with an inadequate basis of substituents. (The recommendations on a basis set of substituents have been outlined by Taft.[4]) Second, a worrying aspect of the analysis is that it is unclear whether Shapiro has used resonance constants (σ_R°)[4] for CH_2X (as he should have) or for X. If the latter is the case, the analysis is invalid. Third, we feel it is necessary to comment on Shapiro's assertion that π-inductive phenomena will be manifested in ρ_I. It is important to note that the π-inductive term[5] embraces two distinct electronic mechanisms: (a) inductomesomeric effect[6] and (b) field induced π polarization.[7,8] The latter will emerge in ρ_I, as it is completely a function of σ_I. However, the inductomesomeric effect is not necessarily a function of σ_I and is generally more dependent on the electronegativity of X.[9] In addition, it is generally considered indistinguishable from mesomeric phenomena.[6] Hence it is unclear in what term this effect will be manifested.

Our approach is based on the recent observation[8] that the substituent chemical shift (SCS) of C-10 in 2-substituted naphthalenes is described by the following (eq 1):

$$\text{SCS} = 0.41\sigma_I + 11.23\sigma_R^\circ(\text{C-10; DCCl}_3) \quad (1)$$

Clearly the C-10 SCS is dominated heavily by resonance.[16] We successfully employed this equation for determining the σ_R° constants of metalloidalmethyl groups.[10]

We have prepared and examined the ^{13}C spectra of α-substituted 2-methylnaphthalenes ($C_{10}H_7CH_2X$) where X = H, Cl, Br, OCH_3, $N(CH_3)_2$, and CN, for dilute solutions (5–10% wt/v) in $CDCl_3$. Assignments have been made by standard procedures and assisted by the "fluoro-substitution" technique[8] with certain 6- and 7-fluoro derivatives. (Under the appropriate conditions, quaternary carbons, of which C-10 is one of three in $C_{10}H_7CH_2X$, can be distinguished from tertiary, i.e., protonated carbons by the contrasting signal intensities.)

The substituent chemical shifts (SCS) for C-6, C-7, and C-10 in the series are located in Table I.

The following equations (eq 2 and 3) describe the dependence of the C-6 and C-7 SCS on substituent constants[8] and have been employed to calculate σ_I and σ_R° values for these substituted methyl groups.

$$\text{SCS} = 4.01\sigma_I + 7.74\sigma_R^\circ(\text{C-6; DCCl}_3) \quad (2)$$

Table II. σ_I Values

substituent	source: ^{19}F phenyl[a]	^{19}F naphthyl(6β,7β)[b,c]	^{13}C naphthyl(6β,7β)[c]	Hine[d]	Charton[e]
CH_2SCH_3		+0.08	+0.14		
CH_2OCH_3	−0.01	+0.06	+0.11 (0.13)[f] (0.09)[g]	+0.01 (CH_2OH)	+0.07 (CH_2OH: 0.05; 0.09)
$CH_2N(CH_3)_2$		+0.07	+0.05		(CH_2NH_2: 0.08)
CH_2Br	+0.16	+0.17	+0.25		+0.18
CH_2Cl	+0.16 (0.19)[h]		+0.26 (0.23)[i]	+0.17	+0.15 (0.17; 0.11)[j]
CH_2CN	+0.26	+0.31	+0.36 (0.31)[k]	+0.23	

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Table III. σ_R° Values

substituent	source: ^{19}F phenyl tag[a]	^{19}F naphthyl(6β,7β)[b]	IR technique[c]	^{13}C naphthyl(C6,C7)	^{13}C naphthyl(C10)
CH_2SCH_3		−0.07	(±)0.10	−0.08	−0.08
CH_2OCH_3	−0.06	−0.05	(±)0.04	−0.05	−0.04
$CH_2N(CH_3)_2$		−0.10	(±)0.10	−0.06	−0.06
CH_2Br	−0.02	−0.01	−0.02	−0.03	−0.03
CH_2Cl	−0.03		−0.03	−0.04	−0.02
CH_2CN	−0.08	−0.12	(±)0.09	−0.10	−0.09

[a] Footnote *a* from Table II. [b] The correlative equations employed are described in W. Adcock, J. Alste, S. Q. A. Rizvi, and M. Aurangzeb, *J. Am. Chem. Soc.*, **98**, 1701 (1976). [c] See ref 15.

Table IV

substituent	polar contribution	resonance contribution	net	obsd[a]
CH_2SCH_3	0.66	−1.68	−1.02	−1.51
CH_2OCH_3	0.52	−0.84	−0.32	−0.86[b]
$CH_2N(CH_3)_2$	0.24	−1.26	−1.02	−1.19
CH_2Br	1.18	−0.63	+0.55	+0.70
CH_2Cl	1.23	−0.63	+0.60	+0.33
CH_2CN	1.47	−1.89	−0.42	−0.43
CH_3[c]	−0.19	−2.73	−2.92	−3.05

[a] Measured for dilute solutions (5–10% w/v) in $CDCl_3$ containing internal benzene. [b] Measured for OCH_2CH_3. [c] $\sigma_I(CH_3) = -0.04$; $\sigma_R°(CH_3) = -0.13$ (private communication, professor R. W. Taft).

$$SCS = 2.85\sigma_I + 0.37\sigma_R°(C\text{-}7; DCCl_3) \quad (3)$$

In Table II, an assembly of σ_I values from the present work, and literature reports, is presented.

In Table III, a similar compilation of available $\sigma_R°$ values together with those based on the C-6, C-7, and C-10 chemical shift data is presented. The best σ_I values in Table II were employed in the C-10 SCS equation to calculate $\sigma_R°$ values. The agreement between the $\sigma_R°$ values based on different techniques is impressive.

With the availability now of σ_I and $\sigma_R°$ values in which high confidence can reside, it is possible to calculate the polar and resonance contributions to the C-4 SCS in a series of benzyl derivatives ($C_6H_5CH_2X$) and then the calculated SCS by using the appropriate DSP equation (eq 4).[11] The calculated and experimental SCS can then be compared (Table IV).

$$SCS = 4.73\sigma_I + 20.98\sigma_R°(para; DCCl_3) \quad (4)$$

It is clear (Table IV) that for all groups the resonance effect is comparable to or greater than the polar contribution. It should be further noted that the calculated net effect is in good agreement with the observed. This analysis negates Shapiro's conclusion[2] that resonance contributions for these groups is unimportant (with respect to the polar effect).

The question naturally arises as to why the resonance contribution of all the CH_2X groups is less than that for CH_3 (Table IV). This could be associated with a reduction in C–H hyperconjugation resulting from a localizing of the π-type orbitals of the CH_2X group due to the electronegativity of X.[12] However, the present data do not allow dismissal of the idea of C–X hyperconjugative electron withdrawal. Indeed, there is strong evidence from several approaches that this is a significant, if not substantial, contributing interaction.[1,3,13] Comparison of the $\sigma_R°$ values of CH_2CN (−0.10) and CH_2Cl (−0.03) is of interest considering that $\sigma_I(Cl) < \sigma_I(CN)$, although the halogen electronegativity is greater. We associate this result with the special nature of the C≡N grouping, with polarization of the cyanomethyl substituent thus $-CH_2^{\delta\delta-}—C^{\delta+}\equiv N^{\delta-}$.[14] It is gratifying to note the good agreement (in absolute terms) of our $\sigma_R°(CH_2X)$ values with those (of largely undetermined sign) based on the IR technique.[15] The signs of $\sigma_R°$ are established by our work.

Experimental Section

Compounds. The substituted 2-methylnaphthalenes were prepared by standard routes from 2-methylnaphthalene. The 2-bromomethyl- or 2-chloromethylnaphthalenes served as the immediate precursors of the other members of the series. The 6-fluoro and 7-fluoro analogues of the parent series were obtained by the same sequences from the 6-fluoro- or 7-fluoro-2-methylnaphthalenes. These latter compounds were obtained in high yield by the cyclization route recently reported.[10] All compounds exhibited appropriate ^1H and ^{13}C spectra and had other physical properties in agreement with literature values.

Spectra. Proton decoupled ^{13}C spectra were obtained at 67.89 MHz in the FT mode for dilute solutions (5% w/v) in $CDCl_3$, and referenced to internal Me_4Si. The ^{19}F NMR spectra were obtained at 84.66 MHz on a Bruker WH-90 Fourier transform NMR spectrometer operating under proton decoupled conditions using benzene solutions containing 5% wt/wt of the substituted fluoronaphthalene and 2% wt/wt of 2-fluoronaphthalene.

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1,8-Bishomocubane[1]

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Recently, we required substantial amounts of 1,8-bishomocubane (**1**)[1] in connection with our continuing studies of the chemistry of highly strained ring systems. Two synthetic routes have previously been described in the literature.[2,3] Both syntheses start with the reasonably expensive cyclooctatetraene and both involve steps which occur in low yield. We wish to report here an alternate route to 1,8-bishomocubane which utilizes benzoquinone (**2**) and 1,3-cyclohexadiene (**3**) as starting materials (Scheme I).

As shown above, *p*-benzoquinone (**2**) was readily converted into 2,5-dibromobenzoquinone (**4**) according to the literature procedure.[4] Diels–Alder addition of **4** to 1,3-cyclohexadiene (**3**) in refluxing benzene gave 2,5-dibromotricyclo[6.2.2.0^{2,7}]-dodeca-4,9-diene-3,6-dione (**5**) in 81% yield.[5] Irradiation of **5** for 20 min in Pyrex with a 450 W Hanovia high-pressure

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