a Government of Iran, Minister of Science and Higher Education Scholarship to S.Y. are also very much appreciated.

Registry No.—**1**, 931-59-9; **2**, 933-01-7; **3**, 463-49-0; **4**, 590-19-2; **5**, 591-96-8; **6**, 598-25-4; **7**, 3043-33-2; **8**, 1000-87-9; (*E*)-(2*RS*,5*RS*)-5-chloro-3-hexen-2-yl 4′-chlorophenyl sulfide, 67145-79-3; (*E*)-(2*RS*,5*SR*)-5-chloro-3-hexen-2-yl 4′-chlorophenyl sulfide, 67145-80-6.

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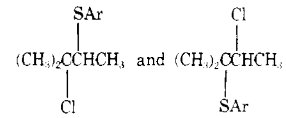

$(CH_3)_2C(Cl)CH(SAr)CH_3$ and $(CH_3)_2C(SAr)CH(Cl)CH_3$

are δ 1.46 and 1.67, respectively.[13]

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9-Substituted Fluorenes. Evaluation of Substituent Effects via Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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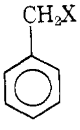
The carbon-13 NMR shielding effects for a series of 9-substituted fluorenes and 9-substituted 1-methylfluorenes, where the substituents are OH, Cl, Br, and I, have been determined. Shift data for several other fluorenyl systems are also presented. The substituent effects are discussed in terms of the transmission of electronic interactions. The substituent shifts at the meta and para carbon centers are analyzed using the Swain–Lupton parameters. Qualitatively, this analysis suggests that π-inductive effects are twice as important as hyperconjugative interactions. The first instances of downfield substituent shifts for γ-syn disposed carbons are observed, while upfield shifts are seen for the resonances of γ-anti carbons.

There has been considerable controversy concerning the transmission of the electronic properties of substituents to aromatic systems through potentially insulating centers such as in **1**.[2,3] Three types of substituent effects are generally considered to participate in systems like **1**: (1) σ-inductive effects; (2) π-inductive effects; and (3) resonance effects, in this case hyperconjugative interactions. Often the discussion of the mechanism for the transmission of the substituent effect is clouded by a lack of understanding or agreement of the terminology involved. So that this is not a problem here, the terms pertinent to the discussion (although available in the literature) will be reviewed.[2g,f,4]



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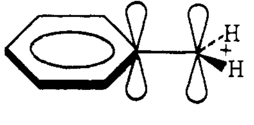
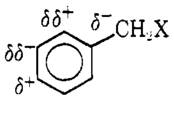
The *σ-inductive effect* requires a net charge transfer between the substituent and the σ framework, resulting in reorganization of the σ charge at various positions leading to *successive* polarization of the σ electrons. This interaction is most probably important only for the α and β carbons in these systems.[5]

Resonance effects result in a net transfer of charge between the aromatic π system and the substituent. In the context of the present discussion, hyperconjugation accounts for the resonance properties. Hyperconjugation requires specific stereochemical orientation and is most favorable when the dihedral angle of the potential hyperconjugative moiety is 0° with the aromatic π bonds.[6] This σ–π bond interaction is shown schematically below.



There are two mechanisms which fall under the heading of *π-inductive effects*:[2,4] (1) a process which causes reorganization of the aromatic π electrons by an *alternating* polarization of the π electrons,



(2) a polarization of the π electrons toward the ipso carbon. This second mechanism is often called a π-polarization effect.

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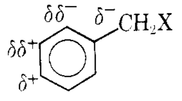
Table I. Chemical Shifts and Substituent Chemical Shifts (ppm) for the 9-Substituted Fluorene Systems (2)[a]

X	$C_{1,8}$	$C_{2,7}$	$C_{3,6}$	$C_{4,5}$	$C_{10(10')}$	$C_{11(11')}$	C_9
H	124.8	126.5	126.5	119.7	143.1	141.6	36.7
I	126.6	127.8	129.0	120.4	145.8	139.9	22.3
	(1.8)	(1.3)	(2.5)	(0.7)	(2.7)	(−1.7)	(−14.4)
Br	126.4	128.1	129.2	120.3	144.2	139.9	46.0
	(1.6)	(1.6)	(2.7)	(0.6)	(1.1)	(−1.7)	(9.3)
Cl	125.7	127.9	129.2	120.0	143.8	140.0	57.5
	(0.9)	(1.4)	(2.7)	(0.3)	(0.7)	(−1.6)	(20.8)
OH	125.1	127.8	129.0	119.9	145.7	140.0	74.9
	(0.3)	(1.3)	(2.5)	(0.2)	(2.6)	(−1.6)	(38.2)

[a] The substituent chemical shifts are in parentheses.

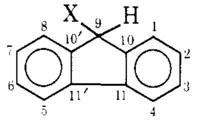
The basic difference between the two π-inductive effects is represented by the magnitude of charge density reorganization at the ortho and meta positions.



The close relationship between charge density changes and carbon-13 NMR shifts[7] should allow for the dissection of the various mechanisms involved in the transmission of substituent effects. Unfortunately, it is sometimes difficult to distinguish between the π-inductive effects by simple inspection of carbon-13 chemical shift data. This problem arises because ortho carbon shifts are subject to steric and compressional effects, while meta carbon chemical shifts often vary over a very narrow range and thus are marginally influenced by electronic effects.

Separation of inductive–field effects from resonance or hyperconjugative contributions can be readily accomplished by using the dual substituent parameter equation (DSP).[8,9] By confining the study to a closely related series of compounds, the relative importance of the various mechanisms can be determined.

Previous work in this laboratory using the DSP analysis has shown that the transmission of substituent effects in α-substituted toluenes operates via a π-inductive mechanism.[3b] However, the structural features inherent in these molecules, the freely rotating CH_2X moiety, may preclude the availability of hyperconjugative interactions by the CX σ bond. In order to further investigate the transmission of substituent electronic effects through a fully saturated center, a series of stereochemically well-defined systems **2** and **3**, where the α substituent is held rigid, was studied. These compounds are interesting because the X group at the "sp^3" carbon atom is constrained with respect to the planar aromatic π system. The incorporation of a methyl moiety in one ring destroys the inherent symmetry of this system and allows comparisons between two slightly different aromatic centers.



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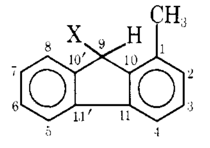


3

Chemical Shift Assignments. The chemical shift (and substituent shift) data for the 9-substituted fluorenyl and 1-methyl-9-substituted fluorenyl compounds are given in Tables I and II, respectively.

Since the discussion of the data depends largely upon correct carbon assignments, substantial care was taken for the parent system. The task of making assignments was facilitated by inspection of the proton-coupled spectrum as well as by consideration of substituent effects observed in some model systems. Using the proton-coupled spectrum "fingerprint",[10] the C_2 and C_3 resonances were readily distinguished from the C_1 and C_4 resonances. Since the chemical shifts for C_2 and C_3 are equivalent, this leaves only C_1 and C_4 to be assigned. The C_4 resonance is expected to be at higher field than C_1 due to steric compression effects. Additional information is derived from the coupled spectrum, where the C_1 resonance is seen to be more highly coupled than is C_4. The C_{10} and C_{11} shift assignments have been made previously by Johnson and Jankowsky.[11] These latter assignments were presumably made by consideration of intensity effects. In the decoupled spectrum the C_{10} resonance is seen to be more intense than the C_{11} resonance owing to the greater number of adjacent hydrogens, and thus a slightly greater NOE effect is obtained.[12] The correctness of these shift assignments can be judged by the good correlation between the observed and calculated chemical shifts in the 1-OH, 1-CH_3, 2-I, and 2-NO_2 fluorenyl systems (Table III).

The shift assignments for the 1-methyl substituted fluorenyl systems were somewhat more difficult to make owing to the increased number of carbon signals. However, this task was facilitated by using the fingerprint method and substituent effects. A reasonable assumption was also employed to make these assignments. That is, the carbon chemical shifts in the unsubstituted ring would remain relatively unchanged. With the aid of the proton-coupled spectrum, the assignments of the protonated carbons will now be described.

By analogy with the unmethylated material, C_4 and C_5 are assigned to the two highest field resonances. The assignment of C_4 to the higher field resonance is consistent with the substituent shift induced by a para methyl group.[7] The coupling

Table II. Chemical Shifts and Substituent Chemical Shifts (ppm) for the 1-Methyl-9-Fluorene Systems (3)

X	H	I	Br	Cl	OH
1	134.1	135.4 (1.3)	136.2 (2.1)	136.4 (2.3)	136.6 (2.5)
2	127.6 (1.1)[a]	128.4 (0.8)	129.0 (1.4)	129.2 (1.6)	129.2 (1.6)
3	127.0	129.4 (2.4)	129.6 (2.6)	129.7 (2.7)	129.7 (2.7)
4	117.4 (−2.3)	118.0 (0.6)	117.8 (0.4)	117.7 (0.3)	117.6 (0.2)
5	120.0	120.5 (0.5)	120.2 (0.2)	120.1 (0.1)	120.2 (0.2)
6	126.5*	129.0 (2.5)	129.6 (3.1)	129.7 (3.2)	129.6 (3.0)
7	126.6*	127.8 (1.2)	127.9 (1.3)	127.9 (1.3)	127.9 (1.3)
8	124.9	126.4 (1.5)	126.1 (1.2)	125.7 (0.8)	125.3 (0.4)
9	35.7	21.7 (−14.0)	46.1 (10.4)	51.4 (21.7)	75.0 (39.3)
10	141.4 (−1.9)	142.9 (1.5)	141.3 (−0.1)	141.1 (−0.3)	143.9 (2.1)
11	142.1* (0.5)	138.7* (−3.4)	139.7 (−2.4)	140.1 (−2.0)	140.3* (−1.8)
10′	143.1 (0.0)	145.4 (2.3)	143.2 (0.1)	143.9 (0.8)	145.9 (2.8)
11′	142.0* (0.4)	139.0* (−3.0)	139.7 (−2.3)	140.1 (−1.9)	140.5* (−1.5)
CH_3	18.7	19.4 (0.7)	18.8 (0.1)	18.6 (−0.1)	18.1 (−0.6)

[a] Substituent shift vs. nonmethylated material; an asterisk indicates that reversal of assignments may be possible.

Table III. Chemical Shifts and Calculated Chemical Shifts (ppm) for Some Fluorenyl Derivatives[a]

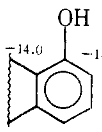
	1-OH	1-CH_3	2-I	2-NO_2
1	152.1 (152.0)[b]	134.1 (133.8)	134.1 (133.9)	121.2 (119.8)
2	113.5 (113.4)	127.6 (127.0)	91.8 (91.8)	146.8 (144.5)
3	126.9 (127.4)	127.0 (126.2)	135.7 (135.6)	123.0 (121.6)
4	113.0 (112.1)	117.4 (116.5)	121.4 (119.0)	120.4 (120.7)
5	120.2	120.0 (119.7)	119.9 (119.9)	119.8 (120.1)
6	126.7	126.5 (126.5)	127.3 (127.0)	127.4 (126.9)
7	128.5	126.6 (126.5)	126.9 (126.7)	128.8 (128.2)
8	125.1	124.9 (124.8)	124.9 (125.0)	125.3 (125.2)
9	33.5	35.7	36.5	36.9
10	128.5 (130.0)	141.4 (143.6)	145.4 (145.3)	144.8 (144.1)
10′	141.6	143.1	142.6 (142.9)	139.4 (139.6)
11	142.8 (142.7)	142.1 (142.1)	140.7 (141.0)	148.0 (148.0)
11′	144.0	142.0	141.2 (141.2)	143.9 (144.0)

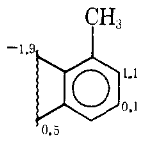
[a] Registry No.: 1-OH, 6344-62-2; 2-I, 2523-42-4; 2-NO_2, 607-57-8. [b] Calculated values are in parentheses.

pattern of the next resonance indicates that this carbon is an ortho-type carbon, and therefore it is assigned to C_8. The fingerprint method was also used to assign the next three signals, all being meta-type carbons.[10] These must arise from C_2, C_6, and C_7. Assuming a minimal effect of the methyl at C_6 and C_7, the assignments were made as shown in the table. The assignment of C_3 is obvious from the coupled spectrum because of its lack of long range couplings.

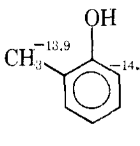
The assignments of the nonprotonated carbons were based primarily upon substituent shifts as well as on peak intensity considerations. Thus, C_1 is assigned to the highest field nonprotonated carbon shift. Intensity considerations separate the C_{10},$C_{10'}$ signals from the C_{11},$C_{11'}$ signals. This is also consistent with the upfield shift of the C_{11},$C_{11'}$ signals observed by comparison with the parent compound. The C_{10} assignment is made by consideration of substituent effects.

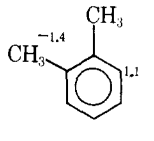
Substituent Effects. Before proceeding with the discussion of substituent effects in the 9-substituted fluorenyl systems, it may prove worthwhile to look at the unusual substituent effects observed for the 1-OH and 1-CH_3 systems. The substituent shifts are shown below.



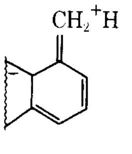


Similar effects are observed in the substituent shifts in *o*-cresol and *o*-xylene,[13] as well as in some 1-substituted naphthalenes.[14]





Possible explanations for the observed shifts include participation of canonical forms such as shown.



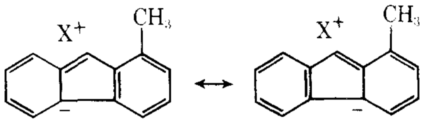
An alternative explanation involves deformation of the C_1–C_{10}–C_9 bond angle to diminish steric interactions. In analogy with the 1-substituted naphthalenes, this would lead to shielding of C_{10} and deshielding of the C_2 resonances.[14] The actual picture is probably a blend of these two situations. In any case, the incorporation of the methyl group at C_1 should affect the ease and nature of the transmission of substituent effects to the substituted ring.

The substituent shifts at C_9 in both systems compare well with the analogous values obtained for the α-substituted toluenes.[3b] The substituent shifts at $C_{10(10')}$ do not correlate with the toluene data, and in **3** it is apparent that the shifts are not symmetric with respect to the substituent. The $C_{10'}$ substituent shifts in **3** compare well with those in **2**, but the C_{10} shifts are somewhat smaller in magnitude. This may be a consequence of the opening of the C_9–C_{10}–C_1 bond angle mentioned earlier. If the bond angle opening mechanism is important, then the substituent shift of the methyl group should be to higher field as X becomes larger. The substituent shifts observed at C_{10} obtained by comparing **2** and **3** are −1.9 (H), −2.2 (OH), −2.7 (Cl), −2.8 (Br), and −2.9 (I) ppm, and thus they are in agreement with the proposed mechanism.

The substituent shifts observed at the carbons in the γ position are interesting owing to the inherent assymmetry in these compounds. In **2** there are two different γ carbons, and in **3** there are four different γ carbons. Because of this assymmetry, these systems should prove useful in assessing the mechanism by which the γ shift is transmitted to aromatic centers. Since the γ carbons are virtually equidistant, albiet differently disposed geometrically from the substituent, as measured from molecular models, the differences in the γ shifts should reflect electronic interactions. In 1-substituted naphthalenes the γ shift of the peri carbon to higher field was interpreted as a steric interaction.[15] In the present instance, C_1 and C_8 are seen to be in a somewhat similar orientation to the substituent. However, these carbon resonances are invariably shifted to low field while the resonances for the anti carbons C_{11} and $C_{11'}$ are shifted to higher field. It was found that in α-substituted toluenes the ortho carbon (to the CH_2X moiety) resonances were shifted to higher fields.

A simplistic approach to explain the fluorene shift trends would be to consider that in the toluene system the methylene moiety is freely rotating and on a time averaged basis one ortho carbon will be syn and the other anti to the substituent. The observed shift would reflect the sum of the syn and anti interactions. Based on this notion, the sum of the substituent shifts for $C_{1(8)}$ and $C_{11(11')}$ observed in the fluorene systems **2** and **3** should be equal to that found in the α-substituted toluenes. In the instance of **2** the values compare favorably with the toluene data given in parentheses: X = Br, −0.1 (−0.3); X = Cl, −0.7 (−0.7); and X = OH, −1.3 (−2.0) ppm. For system **3**, the correlation is poor.

In **3** the substituent shifts for the $C_{11(11')}$ resonances are generally much larger than those found in **2** and seem to indicate a greater degree of negative charge on this carbon in **3**. A possible explanation which would account for the upfield shift involves a hyperconjugative electron release mechanism.



For system **3**, the hyperconjugative electron release is favored to a greater degree owing to relief of steric interactions between the methyl and the 9 substituent. The parallelism between substituent shift and substituent size is in accord with this possibility. A similar hyperconjugative electron release in aliphatic systems has been invoked to explain the upfield substituent shifts of γ-anti carbons.[16]

There are other interesting trends observed for the γ carbons C_1 and C_8. In **2** and **3**, the substituent shifts are to lower field. This is somewhat surprising since these carbons are

γ-syn to the substituent. In 1-substituted naphthalenes, a somewhat similar system at least as far as steric interactions are concerned, upfield shifts are observed. These upfield shifts were purposed to be due to steric interactions. The observations here suggest that the shifts in the fluorenes, as well as in the naphthalenes, are electronic in nature. It is also noticed for C_8 in **2** and **3** that the magnitude of the substituent shift follows an inverse order with respect to substituent electronegativity. However, for the C_1 resonance in **3** the opposite trend prevails. This appears to be due to the interaction of the substituent and the methyl group at C_1. As the substituent shift at the methyl becomes more negative, the substituent shift at C_1 becomes more positive. It is interesting that the sum of the C_1 and C_8 substituent effects stays relatively constant.

The analysis of the substituent shifts at δ carbons $C_{2,7}$ and $C_{4,5}$ also indicates differences in the electronic transmission of charge density as a function of relative position to the substituent. The anti carbons C_4 and C_5 are less affected by the substituent than are C_2 and C_7. The $C_{2,7}$ shifts are also larger than those observed in the α-substituted toluene series. The methyl carbon is also δ disposed to the substituent, and it is believed that these shifts are through space in origin.[17] The substituent effects observed at $C_{2,7}$ in **2** and at C_7 in **3** were analyzed by the DSP equation (C_2 in **3** did not give good correlation, presumably due to the ortho effect of the methyl group). The results are as follows.[18] For **2** $C_{2,7}$: $\rho F = 1.77$, $\rho R = -0.82$, $\bar{r}$ 0.985. For **3** C_7: $\rho F = 1.62$, $\rho R = -0.79$, $\bar{r}$ 0.997. This observation suggests that inductive-type interactions are twice as important for the substituent shifts as are resonance effects.

The remaining substituent effects to be discussed are those observed at C_3 and C_6. In all instances downfield shifts are observed, and they indicate a decrease of electron density at these carbons. The DSP analysis of these shifts indicates that the inductive term F is about twice as important as the resonance term R. For **2** $C_{3,6}$: $\rho F = 3.16$, $\rho R = -1.65$, $\bar{r} = 0.991$. For **3** C_3: $\rho F = 3.78$, $\rho R = -1.78$, $\bar{r} = 0.983$. For **3** C_6: $\rho F = 3.49$, $\rho R = -0.76$, $\bar{r} = 0.996$.

The shifts observed at the para position here are about twice as large as those observed at the meta position (C_2, C_7). This result is consistent with the observations made on para-substituted benzenes.[19]

Conclusions

It has been shown that substitution at the 9 position of a fluorenyl ring induces substantial changes in the chemical shifts of the aryl ring system. It is clear that the magnitude of the substituent shift is very dependent upon the relative orientation of the interacting nuclei. From the DSP treatment of the data at C_2, C_3, C_6, and C_7, both resonance (hyperconjugative) and π-inductive effects are important. Judging from the pattern of the substituent shifts, π-bond polarization toward the ipso carbon is the dominant π-inductive mechanism.

Experimental Section

Fluorene, 9-chlorofluorene, 9-hydroxyfluorene, 9-bromofluorene, 1-methylfluorene, 1-hydroxyfluorene, 2-iodofluorene, and 2-nitrofluorene were commercially available and were used as received. 1-Methyl-9-fluorenone was received from Professor P. D. Bartlett, Texas Christian University. The proton NMR spectra were recorded on a Jeol MH100 spectrometer system. The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a Jeol FX-60 spectrometer system equipped with a Texas Instruments computer with a 24K memory. The spectra were obtained at an observing frequency of 15.03 MHz. Sample concentrations were ca. 10% w/v in deuteriochloroform of the proton-decoupled spectra and ca. 50% w/v for the proton-coupled spectra in 10 mm o.d. sample tubes. General NMR spectral and instrumental parameters that were employed are the following: internal deuterium lock to the solvent; spectral width of 2500 Hz (166.6 ppm); a pulse width of 5 μs, corresponding to a 45° pulse angle; and a pulse repetition time of 1.8 s. For all spectra, 8K time-domain data points were used. All shifts reported are referenced to internal Me_4Si and are estimated to be accurate to ±0.05 ppm.

High-resolution mass spectra were recorded by Mr. G. Gabel of the Biochemistry Department at Texas A&M University, College Station, Tex., on a Consolidated Electronics mass spectrometer system.

9-Iodofluorene. A methylene chloride solution of 1.8 g (0.01 mol) of 9-fluorenol and 48% hydroiodic acid was stirred at room temperature for 1 h. The organic layer was separated, neutralized by a saturated solution of sodium bicarbonate, and washed three times with 50-mL portions of water. After removing the solvent at reduced pressure, the crude material was dissolved in petroleum ether and placed in the freezer. After about 1 h, 1.6 g (53% yield) of light yellow crystals was deposited: mp 148–149 °C dec; NMR ($CDCl_3$) δ 6.42 (1 H), 7.40 (m, 4 H), 7.70 (m, 4 H). This compound was found to be quite unstable, liberating iodine readily. An accurate analysis therefore could not be obtained.

9-Hydroxy-1-methylfluorene. This compound was prepared by the addition of an excess of sodium borohydride to an ethanol solution containing 4.0 g (0.022 mol) of 1-methylfluorenone. The reaction mixture was stirred for 0.5 h and quenched with water, and the organic material was extracted into methylene chloride. After drying the organic layer with magnesium sulfate, removing the solvent in vacuo, and recrystallization from hexane, 3.9 g (91% yield) of colorless cotton-like crystals was isolated: mp 162–162.5 °C; NMR ($CDCl_3$) δ 2.56 (3 H), 5.54 (1 H), 7.20–7.70 (m, 7 H). Anal. Calcd for $C_{14}H_{12}O$: 196.0888. Found: 196.0883.

9-Bromo-1-methylfluorene. To a cooled methylene chloride solution (0 °C) containing 2.0 g (10 mmol) of 9-hydroxy-1-methylfluorene was added 5.4 g (20 mmol) of phosphorus tribromide. The reaction mixture immediately turned brown. After careful quenching of the reaction mixture with 100 mL of ice water and neutralization by a saturated aqueous solution of bicarbonate, the organic layer was collected. After drying the solvent and removal in vacuo, 2.1 g (86%) of light brown crystals was deposited. Recrystallization from hexane afforded colorless crystals: mp 98–99.5 °C; NMR ($CDCl_3$) δ 2.50 (3 H), 5.92 (1 H), 7.12–7.68 (m, 7 H). Anal. Calcd for $C_{14}H_{11}Br$: 258.0044. Found: 258.0031.

9-Chloro-1-methylfluorene. A procedure similar to that used to prepare the bromo derivative was used here, starting with 2.0 g (10 mmol) of the alcohol and 7.5 g of phosphorus pentachloride. Recrystallization from hexane yielded 1.7 g (85%) of slightly yellow crystals: mp 78–80 °C; NMR ($CDCl_3$) δ 2.58 (3 H), 5.82 (1 H), 7.20–7.23 (m, 7 H). Anal. Calcd for $C_{14}H_{11}Cl$: 216.0510. Found: 216.0526.

9-IodO-1-methylfluorene. This compound was prepared by the same method used to prepare 9-iodofluorene: 35% yield of pale brown crystals; mp 104–105 °C dec; NMR ($CDCl_3$) δ 2.42 (3 H), 6.36 (1 H), 7.16–7.75 (m, 7 H). This compound liberated iodine readily and thus did not analyze properly.

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Registry No.—**2** (X = H), 86-73-7; **2** (X = I), 64421-01-8; **2** (X = Br), 1940-57-4; **2** (X = Cl), 6630-65-5; **2** (X = OH), 1689-64-1; **3** (X = H), 1730-37-6; **3** (X = I), 67145-88-4; **3** (X = Br), 36804-48-5; **3** (X = Cl), 67145-89-5; **3** (X = OH), 36804-47-4; hydroiodic acid, 10034-85-2; sodium borohydride, 16940-66-2; 1-methylfluorenone, 5501-37-1; phosphorus tribromide, 7789-60-8; phosphorus pentachloride, 10026-13-8.

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$$\delta = \rho_F F + \rho_R R + \delta o$$

δo is the intercept of the equation, and ρ_F and ρ_R are the regression coefficients. F and R are contributions arising from field and inductive effects, taken together, and resonance effects, respectively.[9]
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Notes

Thallium in Organic Synthesis. 51. Oxidation of Enolizable Ketones to α-Nitrato Ketones by Thallium(III) Nitrate in Acetonitrile[1]

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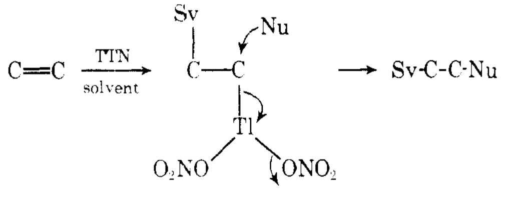
Thallium(III) nitrate (TTN) is a versatile reagent for the oxidation of a wide variety of olefinic and enolic groups, and in almost all cases the exclusive or predominant reaction pathway is oxidative rearrangement.[2] Occasionally, however, nucleophilic displacement of the thallium substituent in the intermediate oxythallation adduct leads to unrearranged products (eq 1). This latter type of reaction appears to occur most frequently when water or methanol is used as solvent (i.e., Nu = H_2O or CH_3OH), but we[3] and others[4–7] have noted instances where nitrate ion participates as the nucleophile to give nitrate esters, usually in low yield. Recently, however, Ouellette and Bertsch have shown that certain olefins and cyclopropanes can be converted into diol dinitrates in moderate to excellent yield by treatment with TTN in pentane,[8] and this report prompts us to describe some related studies.

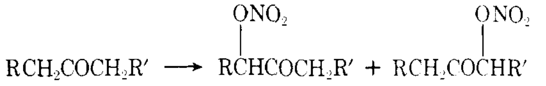


(1)

In the course of our systematic study of the utility of TTN as an oxidant, we have examined the reactions of various types of functional groups with TTN in aprotic, poorly or nonnucleophilic solvents. We describe now one aspect of these studies, namely the smooth conversion of enolizable ketones into the corresponding α-nitrato ketones[9] by treatment with TTN in either dimethyl or diethyl carbonate or, preferably, acetonitrile.

Addition of TTN to an equimolar amount of acetophenone dissolved in dimethyl or diethyl carbonate resulted in the immediate formation of a dark brown color as the TTN dissolved. When the mixture was heated to 60–80 °C, however, the brown color rapidly discharged and thallium(I) nitrate precipitated. NMR spectroscopic examination of the product obtained after workup showed that it consisted of approximately equal amounts of unreacted acetophenone and its α-nitrato derivative, $C_6H_5COCH_2ONO_2$. Similar results were obtained with a variety of substituted acetophenones and with propiophenone. When 2 equiv of TTN[10] were used, however, acetophenone was converted into the α-nitrato ketone in 84–87% yield; propiophenone was similarly converted into $C_6H_5COCH(ONO_2)CH_3$ in 86–89% yield.

Use of dimethyl and diethyl carbonate for the oxidation of substituted acetophenones was not entirely satisfactory. In certain cases, most notably with 3-methoxyacetophenone, the α-nitrato ketone was obtained in poor yield (10–15%); in other cases the reactions proceeded exothermically, and NMR examination of the crude products revealed the presence of variable amounts of decomposition products. Fortunately, these problems were readily eliminated by the use of acetonitrile as solvent; 2 equiv of TTN were again necessary.[10] Oxidations were carried out at 60–80 °C for 12 h and led to excellent yields of the α-nitrato ketones. Yield data for the various conversions are listed in Table I. Unsymmetrical dialkyl ketones of the type $RCH_2COCH_2R^1$ (butan-2-one, pentan-2-one) were also smoothly oxidized in high yield, but as anticipated, approximately equal amounts of isomeric α-nitrato ketones were obtained (eq 2).



$$RCH_2COCH_2R' \longrightarrow \underset{\displaystyle RCHCOCH_2R'}{\overset{ONO_2}{|}} + \underset{\displaystyle RCH_2COCHR'}{\overset{ONO_2}{|}} \qquad (2)$$

It is now well established[11] that oxidation of acetophenones by TTN in methanol results in initial methoxythallation of the enol C=C bond and that a subsequent 1,2-aryl migration

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