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(27) A referee suggests that the comparison to an isopropyl cation is oversimplified. Both electron density and bond order contribute heavily to the paramagnetic term of the ^{13}C screening constant. The downfield shifts of C_2 must be due not only to decreased electron density but also to decreased π bond order.

Nuclear Magnetic Resonance Studies. IV.[1] The Carbon and Phosphorus Nuclear Magnetic Resonance of Phosphine Oxides and Related Compounds

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The ^{13}C and ^{31}P NMR of 16 phosphine oxides and sulfides are examined. Changes in the ^{13}C and ^{31}P NMR of triphenylphosphine oxide, sulfide, and selenide with respect to changes in the P–X bond are discussed. Perturbations on the ^{13}C–^{31}P nuclear spin coupling are examined for this series of compounds and various alkyl-substituted diphenylphosphine oxides. Support is given for the theory of competitive $d\pi$–$p\pi$ overlap with the PO bond for phenyl and vinyl substituted phosphine oxides.

Phosphorus, a second row atom, possesses empty d orbitals which may overlap with filled p orbitals on an adjacent atom. Thus the following resonance structures may be considered.

$$\overset{+}{R_3P}-\overset{-}{X} \longleftrightarrow R_3P=X$$

1a   1b

X = O, S, Se
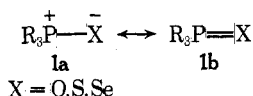
The formal PX double bond in **1b** is expected to be quite different from a normal $p\pi$–$p\pi$ double bond of, for example, a carbonyl group. The d orbitals are diffuse and more directional than 3p orbitals and most of the electron density in a $p\pi$–$d\pi$ bond is expected to lie in the vicinity of the X atom.[2] The physical evidence which has been used to imply $d\pi$–$p\pi$ overlap in the phosphoryl bond is quite persuasive and includes X-ray fluorescence,[3] basicity data,[4] ^{13}C–H nuclear spin coupling,[5] bond dissociation energies,[2,6] bond lengths,[7] dipole moments,[8] NQR measurements,[4] and photoelectron spectra.[10] This is further corroborated by semiempirical[11] and ab initio[12] molecular orbital calculations. There is less evidence of multiple PX bonding for phosphine sulfides and selenides. The general view, however, seems to be that the P–S (and analogously, P–Se) bond is weaker and there is less π bonding than in the PO bond. Bond dissociation energies,[13] ir force constant calculations,[14] and semiempirical molecular orbital calculations[11] lend support for this notion.

It has been considered that an important consequence of a strong, multiple PX bond is that competitive π bonding from an additional, weaker π donor is diminished (e.g., a vinyl or phenyl group). Various physical techniques, especially ^{19}F NMR, have given support for this notion.[15] Thus, in a vinyl phosphine oxide the $d\pi$–$p\pi$ contribution from the PO bond will decrease $d\pi$–$p\pi$ bonding from the vinyl group to phosphorus. In vinyl phosphonium salts the ^{13}C and ^{31}P NMR data strongly suggest $d\pi$–$p\pi$ overlap between the vinyl group and phosphorus.[16] These differences will be examined in this context.
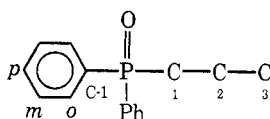
Results and Discussion

The values of the ^{13}C chemical shifts, ^{31}P–^{13}C coupling constants, and ^{31}P chemical shifts are given in Tables I and

II. The ^{13}C chemical shifts previously reported[17] for tri-*n*-butylphosphine oxide and sulfide agree with the values reported in Table I. The ^{13}C chemical shifts and couplings reported for triphenylphosphine oxide also agree with those previously reported by Gray.[18] The values of the ^{31}P chemical shift and ^{31}P–^{77}Se coupling agree with those given by Stec and coworkers.[19]

Quin noted[17] that the close proximity of the ^{13}C resonances for carbons 2 and 3 in tri-*n*-butylphosphine oxide and sulfide are difficult to assign and are subject to adjustment. We have reexamined this problem and make our assignments based on spectra determined at two different field strengths. Additionally, in the case of tri-n-butylphosphine oxide, T_1 values were determined by the inversion-recovery technique.[20] The T_1 values for a $CDCl_3$ solution (not degassed) of the four carbons are found to be 1.2, 1.7, 2.4, and 3.0 ± 0.6 sec, respectively, for carbons 1–4. This is the normal sequence for saturated alkyl chains.[21] Moreover, the closely spaced inner lines of the four-line pattern due to C-2 and C-3 in tri-*n*-butylphosphine oxide were readily assigned by careful adjustment of the delay time in the inversion–recovery sequence so that the two low-field lines due to C-3 where inverted while the two high-field lines were upright.[22] On this basis the assignments given by Quin[17] were confirmed, but a value of $^2J_{P-C}$ = 3.9 ± 0.1 Hz was found instead of the reported $^2J_{P-C}$ = 5 Hz.

The ^{31}P chemical shift of triphenylphosphine sulfide (3) is deshielded by 13.9 ppm from triphenylphosphine oxide (2). This is consistent with an expected smaller contribution of resonance structure **1b** for the sulfide. Likewise, the ^{31}P resonance of **2** is shielded by 27.9 ppm from its phosphonium salt analog 16, while the ^{31}P resonance of **3** is virtually unaffected upon protonation to 17.[23] However, in triphenylphosphine selenide (4), the ^{31}P chemical shift is deshielded by only 6.5 ppm from the oxide 2 and is shielded by 7.4 ppm with respect to the sulfide 3. This irregularity in the ^{31}P chemical shift of the selenide is not in accord with the expected changes in the P–Se bond as compared to the P–S and P–O bonds. For example, an ir force constant study gave the strengths of the P–X bond, and hence the order of contribution of resonance structure **1b**, as P–O > P–S ≫ P–Se.[25] Therefore, a straightforward interpreta-

Table I
Carbon and Phosphorus Chemical Shifts[a]

Compd	Registry no.	Compd no.	Carbon, ppm								^{31}P, ppm
			1	2	3	4	C-1	o	m	p	
Ph$_3$P=O	791-28-6	2					132.8	132.1	128.5	131.8	29.3
Ph$_3$P=S	3878-45-3	3					133.0	132.2	128.5	131.5	43.2
Ph$_3$P=Se	3878-44-2	4					131.9	132.7	128.5	131.5	35.8
Ph$_2$P(=O)Me	2129-89-7	5	16.5				134.3	130.4	128.5	131.6	28.7
PhP(=O)Me$_2$	10311-08-7	6	18.0				135.0	129.6	128.6	131.5	32.5
Me$_3$P=O	676-96-0	7	18.6[b]								41.0[d]
Ph$_2$P(=O)—Et	1733-57-9	8	22.7	5.5			133.1	130.8	128.6	131.6	32.8
Ph$_2$P(=O)-i-Pr	2959-75-3	9	26.9	15.2			132.4	130.8	128.5	131.4	36.2
Ph$_2$P(=O)-t-Bu	56598-35-7	10	33.8	25.1			131.3	132.0	128.2	131.3	38.8
PhP(=O)Cl$_2$	824-72-6	11					134.2	130.1	129.7	134.7	34.9
(n-Bu)$_3$P=O	814-29-9	12	27.9	23.9	24.3	13.7					46.9
(n-Bu)$_3$P=S	3084-50-2	13	30.8	24.5	23.9	13.6					48.1
Ph$_2$P(=O)—CH=CH$_2$	2096-78-8	14	131.3	134.4			132.4	131.1	128.5	131.8	22.4
Ph$_2$P(=O)—C≡CH[c]	6104-48-9	15	77.9	95.3							
Ph$_3$$\overset{+}{P}$—OH HSO$_4^-$	56648-89-6 56598-36-8	16					120.0	131.1	129.0	132.8	57.2
Ph$_3$$\overset{+}{P}$—SH HSO$_4^-$	56598-38-0 56598-39-1	17					119.3	132.6	129.8	135.2	42.6
Ph$_3$$\overset{+}{P}$—CH=CH$_2$ Br$^-$	5044-520	18	119.2	145.2			117.2	133.9	130.7	135.5	19.3
Ph$_2$$\overset{+}{P}$(Me)(CH=CH$_2$) I$^-$	56598-40-4	19	119.3	143.7	9.9		118.1	132.9	130.2	135.0	17.3

[a] All compounds were run in CDCl$_3$ solution and are referenced with respect to Me$_4$Si in the carbon NMR. The ^{31}P NMR are referenced with respect to external 85% H$_3$PO$_4$ with resonances deshielded from H$_3$PO$_4$ being reported as positive values. Compounds 16 and 17 were run in 3:1 concentrated sulfuric acid–glacial acetic acid solutions using external Me$_2$SO-d_6 as a deuterium lock and Me$_4$Si as the reference. [b] Values taken from G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 37, 3458 (1972). [c] Values taken from R. M. Lequan, M. J. Pouet, and M. P. Simonnin, *J. Chem. Soc., Chem. Commun.*, 475 (1974). [d] Value taken from H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, 106, 1251 (1973).

tion of the ^{31}P chemical shifts of these compounds is not possible at this time.

The two phosphonium salts of triphenylphosphine oxide and sulfide (16 and 17) exhibit C-1 phenyl carbon resonances that are shielded by 15.6 and 14.7 ppm, respectively, from their precursors, 2 and 3. A similar effect has been noted for the C-1 phenyl carbons in P–C and P–N ylides with respect to their phosphonium salts.[1] In addition, the carbon α to the carbon or nitrogen bearing the formal negative charge in these compounds is also deshielded, compared to their phosphonium salts.[1] A similar situation occurs with carbons α to a sulfoxide group.[26] The anisotropy of the sulfoxide group has been studied by ^{1}H NMR;[27] however, anisotropy is expected to contribute no more than 4–5 ppm to the ^{13}C chemical shift.[28] It is possible that these shifts may be due in part to an electric field effect, since the PX bond is polar.[29] However, the important fact is that this effect is always observed in compounds capable of resonance interactions such as 1a and 1b.

In Table II, it is seen that $^1J_{P-C}$ for the C-1 phenyl carbons decreases regularly in the order 2 > 3 > 4. The corresponding couplings in the phosphonium salts 16 and 17 are also larger than those in the respective parent compounds, 2 and 3. This is consistent with the idea that the electro-

negativity of the X substituent determines, in part, the magnitude of P–C coupling to the C-1 phenyl carbon. The alkyl carbon 1 couplings of tri-n-butylphosphine oxide and sulfide (12 and 13) also follow this trend. Furthermore, replacement of two phenyl groups with electronegative chlorine atoms in phenylphosphoryl chloride (11) dramatically increases the C-1 phenyl coupling to 158.7 Hz. This phenomenon has been found to be a common feature in the one-bonded P–C couplings in phosphonium salts.[16]

Various studies[3b,30] have revealed that phosphorus becomes more positively charged and, hence, more electronegative when methyl or other alkyl groups are replaced by phenyl groups. In Table I and the ^{13}C chemical shifts of the methyl carbons in going from methyl diphenylphosphine oxide (5) to dimethyl phenylphosphine oxide (6) and trimethylphosphine (7) are increasingly deshielded. Furthermore, these methyl carbons are all deshielded with respect to a methyl carbon directly bonded to a phosphonium group (e.g., carbon 3 in 19). If one assumes the argument that increased charge withdrawal by α substituents results in deshielding the ^{13}C chemical shifts, then the shifts of the methyl carbons in this series are not in accord with changes of the charge on phosphorus. Effects, other than electronic in origin, as discussed previously, and steric factors may be

Table II
$^{13}C-^{31}P$ Coupling Constants[a]

Compd	No.			Carbon, Hz					
		1	2	3	4	C-1	o	m	p
$Ph_3P{=}O$	2					103.5	9.8	17.7	2.4
$Ph_3P{=}S$	3					85.0	10.6	12.7	2.8
$Ph_3P{=}Se$	4		$(J_{P-Se} = 732.4)$			70.8	9.8	12.2	3.7
$Ph_2P({=}O)-Me$	5	73.5	$(J_{C-H} = 127.4)$			100.9	9.7	11.8	2.8
$PhP({=}O)Me_2$	6	70.8	$(J_{C-H} = 128.0)$			98.0	9.6	11.6	2.8
$Me_3P{=}O$	7	68.3[b]	$(J_{C-H} = 129)$[c]						
$Ph_2P({=}O)Et$	8	73.0	4.7			98.4	9.0	11.5	2.7
$Ph_2P({=}O)-i-Pr$	9	72.8	2.7			94.3	8.5	11.3	2.7
$Ph_2P({=}O)-t-Bu$	10	70.8	*			89.9	8.1	10.8	2.6
$PhP({=}O)Cl_2$	11					158.7	13.8	18.4	3.8
$(n-Bu)_3P{=}O$	12	65.1	3.9	13.9	*				
$(n-Bu)_3P{=}S$		50.5	3.8	15.4	*				
$Ph_2P({=}O)-CH{=}CH_2$	14	97.8	*			104.6	10.0	12.0	2.9
$Ph_2P({=}O)-C{\equiv}CH$[b]	15	164.6	29						
$Ph_3\overset{+}{P}-OH\ HSO_4^-$	16					107.4	9.8	12.2	*
$Ph_3\overset{+}{P}-SH\ HSO_4^-$	17					85.4	11.0	14.6	*
$Ph_3\overset{+}{P}-CH{=}CH_2\ Br^-$	18	80.3	*			90.3	10.5	12.9	3.2
$Ph_2\overset{+}{P}\overset{Me}{\underset{CH{=}CH_2}{<}}\ I^-$	19	80.6	*	56.2		89.4	11.2	12.7	*

[a] The numbering system used is the same as in Table I. The digital resolution was ±0.1 Hz, except for compounds 16 and 17, where the high viscosity of the solution prohibited resolution beyond ±2.4 Hz. The digital resolution used in the determination of the C–H coupling was ±0.6 Hz. An asterisk indicates unresolved coupling. [b] Values taken from references listed in Table I. [c] Value taken from P. Haake, W. B. Miller, and D. A. Tyssee, *J. Am. Chem. Soc.*, 86, 3577 (1964).

operative in this case. The same situation is also present for the C-1 phenyl chemical shifts.

The phosphorus–methyl carbon couplings decrease regularly in **5, 6,** and **7**; also, the P–C couplings to the C-1 phenyl carbons decrease in the order 2 > 5 > 6. It might be argued that changes in the effective nuclear charge on phosphorus are consistent with this trend, if the nuclear charge on 2 is greater than on 7. However, the C–H couplings of the methyl groups in **5, 6,** and **7** are nearly identical. In **4** the C–H coupling has been reported to be 129 Hz.[30] We have found the C–H coupling for the methyl groups in **5** and **6** to be 127.4 and 128.0 ± 0.6 Hz, respectively, whereas the C–H coupling for the tetramethylphosphonium salt has been given as 134 Hz.[30] If the C–H coupling can be taken as a reflection of the electronegativity of the substituent on the methyl group,[28] then our data suggest than there is little change in the amount of positive charge on phosphorus for **2, 5, 6,** and **7**. There may be changes in bond lengths and/or bond angles as the number of phenyl groups around phosphorus is increased, so that it is not possible at this time to effect a quantitative separation of the factors responsible for the changes of J_{P-C} in this series of compounds.

The replacement of hydrogen atoms with methyl groups in going from methyl to *tert*-butyldiphenylphosphine oxide (compounds **5, 8, 9,** and **10**) causes a decrease in the P–C coupling to the carbon 1 of the alkyl group concomitantly with a decrease in the coupling to the C-1 phenyl carbon. This effect has also been found for an analogous series of alkyl-substituted triphenylphosphonium salts.[16] The reduction of $^1J_{PC}$ for the alkyl carbon 1 in **10** compared to **5** is consistent with the notion that the C–C–C bond angles in **10** increase as a result of nonbonded interactions between

the methyl C–H bonds. Therefore, the percent s character in the central carbon hybrid orbitals comprising the C–C (or C–H) bonds must increase in **10** compared to **5** at the expense of decreasing the percent s character of the carbon hybrid making up the P–C bond. Alternatively, the P–C bond distance may increase in **10** compared to **5** as a result of steric interactions between the methyl and phenyl groups. Both rationales lead to the same conclusion, namely, a decrease in the $^1J_{P-C}$ coupling for the alkyl carbon in **10** compared to **5**. Similarly, as the percent s character of the carbon hybrid comprising the P–C bond decreases or as the P–C bond length increases, the electronegativity of this substituent decreases[31] causing the $^1J_{P-C}$ for the C-1 phenyl carbon to decrease.

In Figure 1 the ^{31}P chemical shifts of a series of alkyl-substituted diphenylphosphine oxides [Ph₂P(O)R] are plotted against the ^{13}C chemical shifts of the methyl carbons in an analogous series of alkanes (Me–R). Similar relationships have been found for the ^{31}P chemical shifts in alkyl-substituted phosphonium salts[16] and ^{15}N chemical shifts in aliphatic amines.[32] This has been assumed to mean that the same factors influencing ^{13}C chemical shifts are also present in the ^{31}P and ^{15}N chemical shifts for these two series of compounds. In the present case this relationship also implies that there is little change in the nature of the PO bond among the alkyldiphenylphosphine oxides.

In Figure 1 it is apparent that triphenylphosphine oxide (**2**) and vinyldiphenylphosphine oxide (**14**) are shielded by 6.7 and 11.6 ppm, respectively, from what would be expected if the relationship between ^{13}C and ^{31}P chemical shifts was linear. The transfer of charge from a π donor onto phosphorus, presumably via d orbitals, has previously been shown to cause the ^{31}P resonance to become more

shielded.[16,33] This factor may contribute in the present case. However, inspection of the ^{13}C chemical shifts for carbon 2 in 14 and 18 reveals that the β vinyl carbon for the phosphine oxide 14 is shielded by 10.8 ppm from the β vinyl carbon of the phosphonium salt 18. Likewise, replacement of the methyl group in methylvinyldiphenylphosphonium iodide (19) with an oxygen atom (14) results in the β vinyl carbon becoming shielded by 9.3 ppm. The para phenyl carbons of the phosphine oxides in Table I are also shielded in comparison to their phosphonium salt analogs[16,18] (compounds 18 and 19 are typical examples). If the ^{13}C chemical shifts for these vinyl carbons are taken as being at least in part exemplary of the differences in the electronic distribution for these carbons, then a model can be proposed for these phosphine oxides, in which there is diminished interaction between the vinyl or phenyl groups and phosphorus. Thus, this model is consistent with competitive $d\pi$–$p\pi$ overlap as developed by other physical methods and discussed in the introduction. Carbon 2 for ethynyldiphenylphosphine oxide (15) is also shielded compared to its phosphonium salt analog.[16] The fact that carbon 1 for the vinyl and ethynyl carbons in 14 and 15 are deshielded with respect to most substituted ethylenes and acetylenes[28] is taken to be a consequence of the previously noted effect of carbons α to the PO bond. Therefore, the shielding of the ^{31}P resonances for 2 and 14 in Figure 1 are
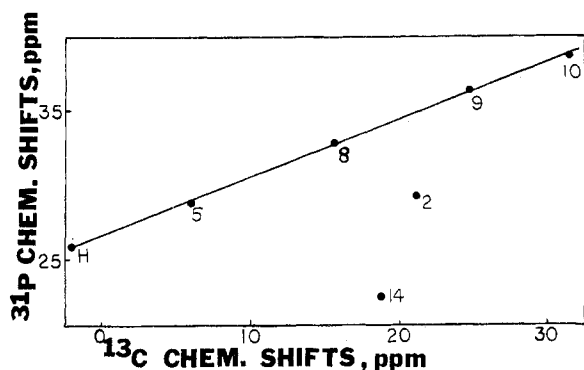

Figure 1. Comparison of the ^{31}P chemical shifts of Ph$_2$P(O)R vs. the ^{13}C chemical shifts of **Me–R**. The numbers refer to compounds listed in Table I. The point labeled H refers to R = H; the ^{31}P chemical shift was taken from ref 34. The correlation coefficient for this data was 0.9996, not including 2 and 14.

probably not simply a result of $d\pi$–$p\pi$ interactions between the vinyl and phenyl groups and phosphorus. Another factor of importance is that these two groups are more electronegative than an alkyl group[31] and, therefore, the contraction of the d orbitals on phosphorus is facilitated along with increased $d\pi$–$p\pi$ overlap between the oxygen atom and phosphorus.[2] Thus, a portion of the shielding of the ^{31}P resonance for 2 and 14 can be ascribed to increased multiple bonding in the PO fragment.

In Table II $^1J_{PC}$ for carbon 1 of the substituent increases from 73.0 Hz for 8 to 97.8 and 164.6 Hz for 14 and 15, respectively. This phenomenon has also been observed for phosphonium salts[16] and phosphonates.[34] This is probably a reflection of increased s character of the substituent (assuming the Fermi contact term to be dominant). It also should be noted that the coupling of phosphorus to the C-1 phenyl carbon is larger in vinyldiphenylphosphine and triphenylphosphine oxides (14 and 2) compared to any of the other alkyldiphenylphosphine oxides, which is consistent with the notion previously developed for the dependence of $^1J_{PC}$ for the C-1 phenyl carbon and the electronegativity of the other substituents.

Conclusions

A unified description of the factors influencing ^{13}C, ^{31}P, and P–C couplings for the phosphine oxides is likely to be quite complex. Part of the difficulty is by a lack of quantitative information on how the PO (or PS) bond is perturbed upon changing the other substituents around phosphorus. Reliable theoretical techniques may shed light on this situation. It does appear that the changes of the ^{13}C chemical shifts for phosphine oxides are compatible with competitive $d\pi$–$p\pi$ overlap. Electronegative and steric effects are reflected in the P–C couplings. It should be possible to relate the factors responsible for ^{31}P chemical shifts of alkyl-substituted phosphine oxides to the ^{13}C chemical shifts of analogs. Finally, the data presented here for replacement of alkyl with phenyl groups in the phosphine oxides cast doubt on the interpretation by others that the phosphorus is becoming more positively charged. It appears that the situation is much more complex. Other physical information, such as the energy of the PO bond for this series, would be most useful.

Experimental Section

The spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system as previously described.[16] The ^{31}P and ^{13}C data were taken at operating frequencies of 36.43 and 22.63 MHz, respectively. ^{13}C NMR data were also obtained for 12 and 13 on a Varian CFT-20 at 20.0 MHz. The ^{31}P chemical shifts are reported as referenced to external 85% H$_3$PO$_4$ with resonances deshielded from the reference being reported as positive. The ^{13}C chemical shifts are reported with respect to internal Me$_4$Si. All samples were run as 0.25–0.50 M solutions of CDCl$_3$, except as noted in Table I, with broad band ^{1}H decoupling. Spectral assignments were made with comparisons of the ^{13}C chemical shifts and the magnitudes of P–C coupling constants to previously reported compounds.[16–18] The phosphine oxides and sulfides were prepared by standard methods[35] and triphenylphosphine selenide was purchased from Aldrich Chemicals. *tert*-Butyldiphenylphosphine oxide (10) was prepared by heating 5.0 g (0.0112 mol) of *tert*-butyltriphenylphosphonium iodide[36] at 80°C with 100 ml of 20% NaOH–H$_2$O solution overnight. The mixture was extracted with chloroform and dried over anhydrous magnesium sulfate. Recrystallization gave 2.3 g (80% yield) of 10: mp 131–132°C; ^{1}H NMR δ 1.2 (d,[2] J_{P-H} = 15.0 Hz, 9 H), 7.25–8.3 (m, 10 H). An exact mass determination by mass spectrometry gave mass 258.11734 (calcd, 258.11599).

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Thallium in Organic Synthesis. XXXIX. A Convenient Synthesis of Nitroaryl Iodides[1,2]

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A method is described for the conversion of aromatic substrates to nitroaryl iodides by (1) thallation with thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA), (2) nitration of the isolated arylthallium ditrifluoroacetate with acetyl nitrate, and (3) treatment of the resulting nitroarylthallium intermediate with iodine in chloroform. Nitration occurs meta to the thallium substituent, and iodine enters the ring at the position formerly occupied by thallium.

The classic route to nitroaryl iodides from aromatic substrates comprises a sequence of reactions involving nitration or dinitration, selective reduction of one of the nitro groups to an amine, diazotization, and subsequent replacement of the diazonium group with iodine utilizing potassium iodide.[3] Alternatively, nitroarenes can be iodinated with molecular iodine in various media.[4–6] The drawbacks of the former approach are the multiple reaction steps required and the frequently observed iodine atom migration which occurs under acidic conditions;[7] a disadvantage of the latter synthesis is the occasional occurrence of polyiodination when 20% oleum–iodine is employed.[4]

We describe a facile conversion of aromatic substrates to nitroaryl iodides via arylthallium ditrifluoroacetates. The appropriate arene is first thallated with thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA).[8] The *isolated* arylthallium ditrifluoroacetate is then nitrated with acetyl nitrate[9] (conveniently generated in situ by adding 70% nitric acid to an excess of acetic anhydride) in the presence of concentrated sulfuric acid, and the intermediate nitroarylthallium derivative is then refluxed with molecular iodine in chloroform. In the resulting nitroaryl iodide, the iodine atom enters the ring at the position formerly occupied by thallium; i.e., the position which is generally most reactive to electrophilic substitution. The nitro substituent is almost invariably meta to the iodine atom. Since nitration and iodination of the arylthallium ditrifluoroacetate can be achieved without isolation of the intermediate nitroarylthallium species, this overall procedure constitutes a two-step synthesis of nitroaryl iodides from arenes. Furthermore, the requisite arylthallium ditrifluoroacetate intermediates are readily prepared from the precursor arenes utilizing TTFA in TFA,[8] and are stable, crystalline solids which can be kept indefinitely.

Representative yields of nitroaryl iodides prepared by this technique are listed in Table I.

Varying amounts of sulfuric acid were employed to promote the nitration of the above arylthallium ditrifluoroacetates, the amount of sulfuric acid being determined by the reactivity of the latter intermediates to electrophilic substitution.[9] Arylthallium ditrifluoroacetates substituted with electron-withdrawing groups are not nitrated satisfactorily under the above conditions. For example, 4-chlorophenylthallium ditrifluoroacetate gives only very small amounts of ring nitration with acetyl nitrate, even in the presence of a large excess of concentrated sulfuric acid.[15]