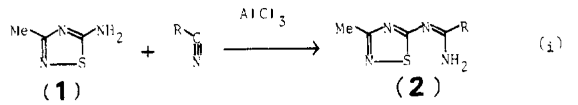
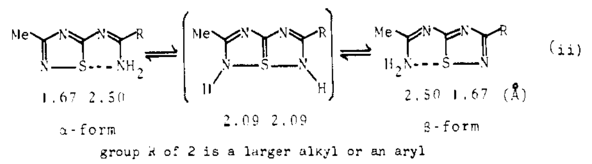
Table I. Some 1,2,4-Thiadiazoles (**2**) and Their Two Forms at Equilibrium[a]

2	R	Me[a] α form	Me[a] β form	R[a] α form	R[a] β form	β/α at equilibrium	mp, °C	yield, %
a	Me	2.51		2.22		1.00	109.5–111.5	34
b	CH_2Cl	2.55	2.22	4.30	4.61	2.14	103.5–104.2	45
c	CH_2Me	2.52	2.21	1.28(t)	1.34 (t)[b]	1.68	visc oil	59
d	$CHMe_2$	2.52	2.21	1.27(d)	1.34 (d)[c]	2.53	93.1–94.0	49
e	CMe_3	2.50	2.21	1.32	1.40	8.57	91.5–92.2	42
f	p-MeC_6H_4	2.55	2.23			5.99	146.0–147.5	41
g	C_6H_5	2.57	2.23			14.5	148.0–148.7	50
h	p-ClC_6H_4	2.58	2.26			~50	121.0–122.0	55

[a] ^1H NMR data: δ values in $CDCl_3$ at 34 °C, Me_4Si as internal standard. [b] CH_2*Me*, $J = 7.2$ Hz. [c] CH*Me*$_2$, $J = 6.6$ Hz.

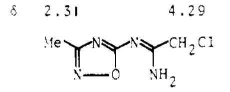
lowed by purification by dry column chromatography (Merck, Al_2O_3, $CHCl_3$) and recrystallization of the eluted adduct from benzene–hexane (eq i).



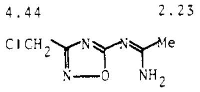


The ^1H NMR spectrum of 5-(1-aminoethylimino)-3-methyl-1,2,4-thiadizole (**2a**) shows two singlets at δ 2.51 (3-Me) and 2.22 (Me of the amidino group). However, to our surprise, the spectrum of the chloromethyl compound (**2b**), shows two pairs of singlets (Table I): one pair at δ 2.55 and 4.30 (α form) and the other at 2.22 and 4.61 (β form), the ratio (β/α) being 2.14 ($CDCl_3$, at 34 °C). A series of compounds (**2**) show the same phenomenon (Table I). This fact can be rationalized only by assuming the occurrence of ring transformation according to eq ii, the bond switch being facilitated by participation of π-hypervalent sulfur.

In order to confirm this rationalization, the corresponding oxygen analogues (**3a** and **3b**) were prepared from 5-amino-1,2,4-oxadiazoles[8] according to eq i. **3a** (mp 126–128 °C) and **3b** (mp 155.0–155.7 °C) show single methyl and chloromethyl signals as shown below, thus confirming the rationalization.



(**3a**)



(**3b**)

group R of 2 is a larger alkyl

The β form is more favored when the group R of **2** is a larger alkyl group or a phenyl group with an electron-withdrawing substituent. This fact is consistent with the increase in steric hindrance encountered by the group R when it is attached to the amidino group than when it is on the thiadiazole ring and also with the conjugation of the benzene ring with the heterocycle. In **2b**, the electron-withdrawing effect of the chlorine atom may be operative, because the van der Waals radius of a chlorine atom is smaller than that of a methyl group (cf. **2c**).[9]

The equilibrium was measured for **2b** at 34 °C in several solvents and it is shown that the β form is more favored in solvents with lone-pair electrons; β/α ratios in different solvents are 2.23 (PhH), 2.08 (PhCl), 4.47 (Me_2CO-d_6), 5.74 (Me_2SO-d_6), and 6.53 ($MeOH$-d_4). The temperature dependence of the equilibrium was measured for the *tert*-butyl compound **2e** in chlorobenzene; β/α ratios at different temperatures are 7.66 (54), 6.78 (69), 6.14 (85), and 5.49 (116). The α form is more favored at higher temperatures and the resulting thermodynamic parameters are ΔH −1.21 kcal/mol and ΔS 0.25 eu.

These facts indicate that the sulfur atom moves back and forth ~0.8 Å along the N—S- - -N line during the ring transformation, the rate of which is slow enough to be detected by NMR (34–120 °C) and is fast enough for normal handling of the sample solution.[10]

Acknowledgment. Partial support of this work by the Kurata Foundation is acknowledged.

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(10) Exact structure determination of **2** by the X-ray method has not been carried out yet, but the N—S- - -N distance was taken from that of an analogous compound in ref 6.
(11) All compounds except **2c**, which gave approximate but acceptable data, gave satisfactory elemental analysis.

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Structure of (3-Chloro-2-hydroxy-5-nitrophenyl)-(2′-chlorophenyl)iodonium Hydroxide Inner Salt

Sir:

The reaction of phenols with phenyliodine diacetates, in general, leads to the formation of mixtures of products including acetoxyphenols and benzoquinones.[1] A notable exception was the report by Fox and Pausacker[2] that on treatment of 4-nitrophenol with phenyliodine diacetate they obtained in 85% yield a yellow crystalline compound, to which they assigned structure **1**. On heating **1**, the *o*-iododiphenyl ether **2** was obtained. In a synthesis of specific chlorinated dibenzofurans,[3] we have used the oxidation of chlorinated 4-nitrophenols with chlorinated phenyliodine diacetates to yield the *o*-iododiphenyl ethers, with subsequent ring closure to the dibenzofurans through the pheniodoxin-5-ium iodide. In the course of this synthetic work,[4] we examined the structure of one of the compounds analogous to **1**. We report the structure of this compound to be (3-chloro-2-hydroxy-5-nitrophenyl)-(2′-chlorophenyl)iodonium hydroxide inner salt (**3**), based on chemical, spectral, and X-ray crystallographic data. This is the first reported example of a phenoxide-iodonium betaine.

Reaction of 2-chloro-4-nitrophenol (4.9 g, 28.2 mmol) with 2-chlorophenyliodine diacetate (10 g, 28.1 mmol) in 200 mL of glacial acetic acid for 48 h gave a yellow crystalline precipitate. This was collected by filtration, washed with anhydrous ether, and dried under vacuum over silica gel at room temperature to yield a substance, mp 133–134 °C, with satisfactory spectral and elemental analyses for $C_{14}H_{10}NO_5Cl_2I$. However, after the material was thoroughly pulverized and dried over KOH under vacuum for 72 h, a compound having the molecular formula (analysis for C, H, N, Cl, I) $C_{12}H_6NO_3Cl_2I$ was obtained: ^1H NMR (Me_2SO-d_6) δ 7.42 (ddd, J = 7.8, 7.1, and 1.9 Hz, H(5′)), 7.65 (ddd, J = 7.9, 7.1, and 1.7 Hz, H(4′)), 7.81 (dd, J = 7.9 and 1.9 Hz, H(3′)), 8.10 (d, J = 2.8 Hz, H(4)), 8.32 (dd, J = 7.8 and 1.7 Hz, H(6′)), and 8.44 (d, J = 2.8 Hz, H(6)); IR (KBr) 1571, 1504, 1358, 1310, 1134, 918, 761, 699 cm^{-1}; mass spectrum m/e (rel intensity) 409 (69), 328 (19), 236 (80), 173 (100); UV (95% EtOH) λ_{max} 206 and 369 nm (glacial acetic acid), λ_{max} 249 and 358 nm. When **3** was heated, the diphenyl ether, **4**, was obtained essentially quantitatively. **4** ($C_{12}H_6NO_3Cl_2I$): ^1H NMR ($CDCl_3$) δ 8.44 (d, J = 3.0 Hz, H(2)), 8.12 (d, J = 3.0 Hz, H(6)), 7.27 (m, H(3′)), 6.82 (m, H(4′) and H(5′)), and 6.15 (m, H(6′)).

Single crystals of **3** suitable for X-ray crystallographic analyses were obtained as transparent yellow needles from 88% formic acid. The crystal data from the precession photographs and diffractometer data are as follows. $C_{12}H_6NO_3Cl_2I$: mol wt, 409.98; monoclinic, $P2_1/n$ (γ unique); a = 15.928 (9), b = 18.271 (6), c = 4.623 (2) Å; γ = 105.58°; Z = 4; ρ_{calcd} = 2.106, ρ_{obsd} = 2.11 g cm^{-3} (flotation). Diffraction intensities were measured in the θ–2θ scan mode using graphite monochromated Mo Kα radiation on a diffractometer. The intensities were corrected for Lorentz-polarization effects. The iodine and chlorine atoms were located from a three-dimensional Patterson map. The structure was solved by conventional heavy-atom methods and was refined by a full-matrix least-squares program.[5] The standard R value at convergence was 0.060 (1787 observed reflections with $I > 3\sigma_I$).

An analysis of the difference map showed peaks of electron density whose maximum values were equivalent to about two electrons. The positions of these peaks around the iodine atom suggest that they arise from errors in scattering and absorption corrections. Further refinement is planned. The picture (as drawn by ref 6) of the molecule and the atom labeling are shown in Figure 1. Existence of an inner salt (with a positive charge on iodine and a negative charge on oxygen) is deduced from certain bond distances, angles, and intramolecular distances. First, the C(2)–O distance of 1.26 Å is shorter than the average value of 1.36 Å obtained from a random sample of phenolic C–OH bonds.[7] This short distance indicates the existence of an increased bond order that may be attributed to added bonding electrons. This evidence indicates that oxygen has a negative charge that results from the complete loss of the hydroxy hydrogen atom. Second, the I–C(1) distance of 2.08, the I–C(1′) distance of 2.11, and the C(1)–I–C(1′) angle of 97.8° are in agreement with the values obtained for diphenyliodonium compounds. This evidence indicates that the iodine atom exhibits a positive charge. Third, the I–C(1)–C(2) bond angle of 104.2 (7)° is significantly more acute than in the ordinary salt of diphenyliodonium chloride (120.5 and 117.5°).[8] This evidence indicates that there is an ionic attraction between iodine and oxygen. In fact, the intramolecular I⋯O distance of 2.768 Å agrees with the minimum distance reported[9] for the ionic attraction between iodine of the diphenyliodonium and an oxygen atom of a nitrate group.

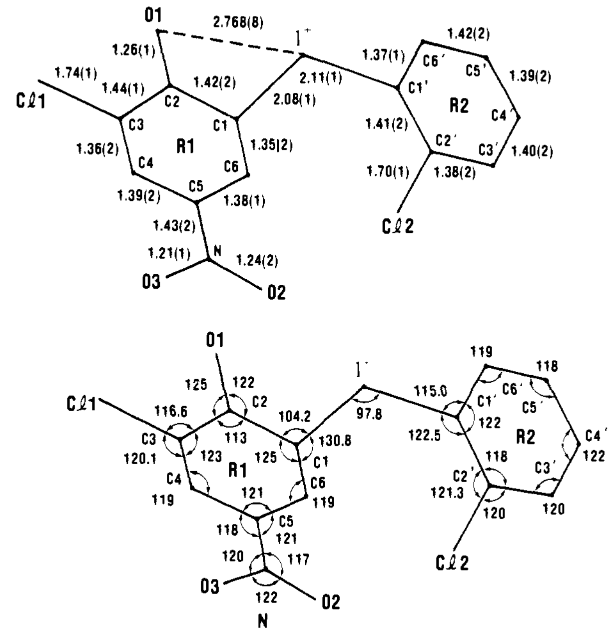

Figure 1. Bond distances (ångstroms) and angles (degrees). Estimated standard deviations (esd) in bond distances are given in parentheses. The esd in bond angles range from 0.8° for bond angles with terminal I or Cl to 1.0° for bond angles with only C, N, or O. The esd for C–I–C bond angle was 0.4°.

On reexamination of the reaction of 4-nitrophenol and phenyliodine diacetate, the product, on washing with ethyl ether and air drying, gave analytical data in agreement with those reported.[3] However, on drying under vacuum over KOH for 72 h, the inner salt **5** was obtained: $C_{12}H_8NO_3I$; mol wt, 341.10; mp 127–128 °C; ^1H NMR (Me_2SO-d_6) δ 8.32 (d, J = 2.9 Hz, H(6)), 8.11 (m, H(2′) and H(6′)), 7.92 (dd, J = 9.5 and 2.9 Hz, H(4)), 7.50 (m, H(3′), H(4′), and H(5′)), and 6.31 (J = 9.5 Hz, H(3)).

^{13}C NMR data were obtained for compounds **2**, **3**, **4**, and **5** and are presented in Table I. Assignment of spectral lines due to carbon atoms bearing the iodine, oxygen, and nitro groups in the inner salt **3** (C(1), C(1′), C(2), C(5), respectively) was made by a single-frequency off-resonance decoupling experiment and was quite straightforward.[10] The resonance at 100.1 ppm was assigned to C(1) and that at 114.9 ppm to C(1′) on

Table I. ^{13}C NMR Data

	diphenyl ethers			inner salts	
position	**2**[a]	**4**[a]	position	**5**[b]	**3**[b]
1	142.8	145.4	5	143.9	144.0
2	134.7 (d)	133.6 (d)	6	133.4	132.4 (d)
3	87.7	92.1	1	100.6	100.1
4	162.0	156.1	2	162.5	158.2
5	116.1 (d)	123.3	3	118.6 (d)	124.4
6	125.5 (d)	126.4 (d)	4	132.8 (d)	132.6 (d)
1′	154.6	151.1	1′	111.9	114.9
2′	119.9 (d)	128.9	2′	138.0 (d)	139.7
3′	130.5 (d)	124.3 (d)	3′	134.8 (d)	132.6 (d)
4′	125.5 (d)	127.7 (d)[c]	4′	136.0 (d)	138.1 (d)
5′	130.5 (d)	131.2[c]	5′	134.8 (d)	133.4 (d)
6′	119.9 (d)	114.7 (d)	6′	138.0 (d)	140.7 (d)

[a] In Me_2SO-d_6, parts per million from Me_4Si. [b] In TFA-d, parts per million from Me_4Si. [c] These resonances may be interchanged.

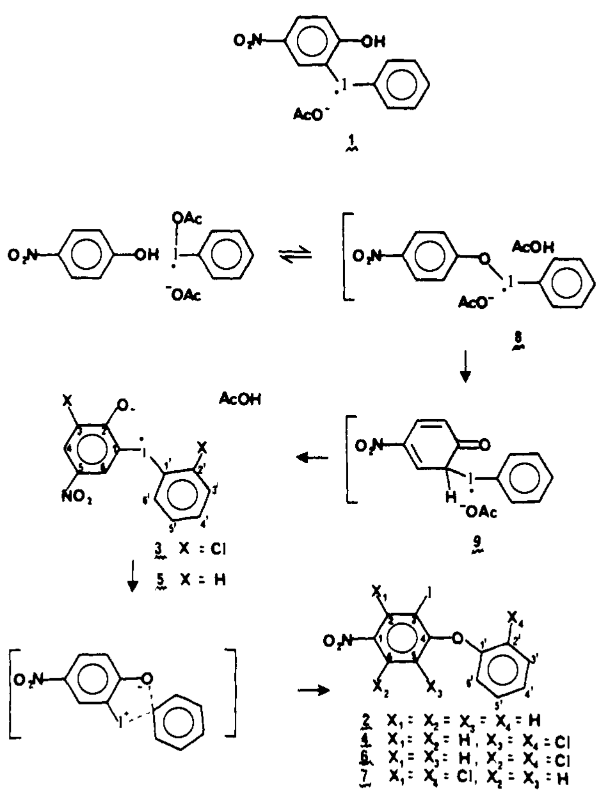

Figure 2. Mechanism for the formation of (3-chloro-2-hydroxy-5-nitrophenyl)(2′-chlorophenyl)iodonium hydroxide inner salt.

the basis of (i) substantial observed shielding of ortho carbons in phenolic systems[10] and (ii) the less extensively coupled signal for C(1) in the fully coupled spectrum. The latter consideration also suggested that the less extensively coupled resonance line at 144.0 ppm was due to C(5) whereas that at 139.7 ppm was due to C(2′). The remaining quaternary signals due to chlorine-bearing carbons were assigned by comparison with resonance lines of corresponding methine carbons (C(3), C(2′), and C(6′)) in the inner salt **5**. Essentially all of the signals due to methine carbons in each of the four compounds listed in Table I could be assigned by proton homonuclear spin decoupling experiments together with a series of four proton decoupler-stepped off-resonance decoupling experiments.[11,12]

Some preliminary observations on the nature of this reaction have been noted. Under the same experimental conditions, no reaction occurred between 4-nitroanisole and phenyliodine diacetate. Reaction of 2,6-dichloro-4-nitrophenol with phenyliodine diacetate at 45 °C for 50 days was reported to give 2,6-dichloro-1,4-benzoquinone (47%).[2] In all cases examined in the chlorinated dibenzofuran syntheses, no unexpected rearrangements were observed (i.e., for the chlorinated phenyliodine diacetates, ipso displacement of the iodine occurred) and rearrangement of the iodine was always ortho to the original phenol carbon. In the reaction of 3-chloro-4-nitrophenol with 2-chlorophenyliodine diacetate, a 3:1 mixture of **6** and **7**, respectively, resulted.

With the demonstrated stability of the inner salt in cases where the nitrophenol contains no electron-donating functionality, the mechanism originally proposed,[2] with revision of the structure of the intermediate salt (see Figure 2), is supported. The reported[2] formation of 5-iodo-2-methoxy-4-phenoxy-nitrobenzene from 3-methoxy-4-nitrophenol under identical conditions with the formation of the inner salt from 4-nitrophenol suggests that, for nitrophenols with electron-donating substituents, either a concerted rearrangement of **9** (from **8**) or a rapid rearrangement of the inner salt (analogous to **5**) occurs.

The mechanism and general synthetic utility of this reaction are under investgation.[13]

Acknowledgment. We thank Dr. A. Perloff for his work on precession photographs and Mr. Douglas W. Phillipson for the mass spectral analyses. The X-ray structure determination was supported by the Food and Drug Administration, FDA-NBS Interagency Agreement 224758253.

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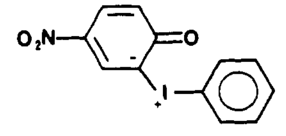

A

phenyliodine diacetate: P. B. Kokil and P. M. Nair, *Tetrahedron Lett.*, 4113 (1977). This assignment was based on the upfield shift of the ring A protons in trifluoroacetic acid (TFA) relative to their shifts in Me_2SO. However, our studies have shown that very similar shifts are observed for 4-nitrophenol: 4-nitrophenol Na salt, Me_2SO-d_6, δ 6.10 (2-H), 7.83 (3-H); 4-nitrophenol, TFA-*d*, 7.08 (2-H), 8.27 (3-H); **5**, Me_2SO (Kokil and Nair), 6.35 (3-H), 7.97 (4-H); **5**, TFA (Kokil and Nair), 7.46 (3-H); 8.52 (4-H). While this ylide structure is undoubtedly a contributing resonance form, our data indicate that the primary charge localizations are on the oxygen and iodine atoms with an oxygen-iodine ionic bond.

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Aluminum Atom–Benzene Molecular Complex: Matrix Isolation Electron Spin Resonance Study

Sir:

Recently we have shown that the Al atom ($3s^2\ 3p^1$) forms a π-coordination complex with ethylene and that the complex results from the dative interaction between the vacant antibonding π orbital of ethylene and the semifilled p orbital of Al parallel to the double bond.[1] We report in this communication the generation and the detection by ESR of the Al atom–benzene molecular complex stabilized in neon matrices. The lowest, vacant π orbitals of benzene belong to the irreducible representation e_2 (doubly degenerate) of the C_{6v} symmetry group. The semifilled p orbital of Al located along the symmetry axis of benzene would belong to either a_1 (p_z) or e_1 (p_x and p_y), and hence cannot effect the dative interaction with

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