135457-92-0; (–)-22, 4835-96-5; 23a, 135457-93-1; 24a, 135558-14-4; 25a, 135557-56-1; 26a, 135557-57-2; (–)-27, 96303-89-8; 28a, 135481-27-5; 29a, 135558-15-5; (–)-32, 94594-91-9; (+)-32, 119944-89-7; 33a, 127470-56-8; 33b, 127420-42-2; 33d, 127381-63-9; 33e, 127381-65-1; 35a, 127381-61-7; ent-38b, 127381-62-8; 38d, 127381-64-0; 38e, 127470-57-9; 41a, 127381-66-2; 41e, 127381-68-4; 43e, 127420-41-1; maleic anhydride, 108-31-6.

Supplementary Material Available: Tables of data collection details, fractional atomic coordinates, bond distances, bond and torsional angles, as well as anisotropic and isotropic thermal parameters associated with the X-ray structure determination of 35a; ^{1}H NMR spectra for all new compounds; UV spectra for compounds 10a, 12, (–)-32, and 33a (46 pages). Ordering information is given on any current masthead page.

Direct Polyiodination of Benzenesulfonic Acid

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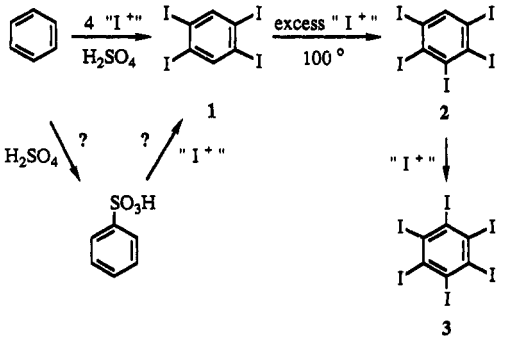
Direct aromatic polyiodination of benzenesulfonic acid (using I_2 and H_5IO_6 in H_2SO_4 at room temperature) was performed to test the possible intermediacy of $C_6H_5SO_3H$ in the corresponding direct polyiodination of benzene to $C_6H_2I_4$. The major product from $C_6H_5SO_3H$ was 3,4,5-triiodobenzenesulfonic acid (4). In contrast, no 4 was formed in the C_6H_6 reaction, showing that no significant sulfonation of C_6H_6 to $C_6H_5SO_3H$ occurred during benzene iodination. Compound 4 itself was shown to be inert under the reaction conditions. A pathway is proposed from $C_6H_5SO_3H$ to the other reaction products (C_6I_6, C_6I_5H, two $C_6I_4H_2$ isomers, and 3,4,5-triiodophenol), which therefore avoids the intermediacy of 4.

We have recently described a powerful system for the direct polyiodination and periodination of a variety of unactivated aromatic substrates.[1,2] This mixture, 3:1 iodine:periodic acid in concentrated sulfuric acid, may be thought of as producing iodonium ion, I^+, although the actual electrophilic species may be more complex.[3] Thus, 4 equiv of "I^+" at room temperature convert benzene to 1,2,4,5-tetraiodobenzene (1) in good yield, whereas forcing conditions (2-fold excess of "I^+" at 100 °C) produce hexaiodobenzene (3) in moderate yield. The presumed intermediate pentaiodobenzene (2) is not observed in substantial yield in either case.[2]



Since aromatics can undergo sulfonation in concentrated sulfuric acid,[4] the question arises whether the substrates become sulfonated during the course of direct polyiodinations. Such sulfonated intermediates would be deactivated toward subsequent iodination but would not be expected to be inert, since iodination can proceed on deactivated substrates such as nitrobenzene and benzoic acid.[2] We did not observe sulfonated products in our earlier studies, but sulfonated intermediates could escape detection by undergoing subsequent iododesulfonation[5,6] during the reaction or protiodesulfonation[5] during the aqueous isolation of products.

To test this possibility, we studied the polyiodination reaction of the prototypical aromatic substrate, benzene. Benzene is more apt to be sulfonated than any of the deactivated substrates (including iodinated benzenes),[4] and in fact is known to form benzenesulfonic acid, $C_6H_5SO_3H$, in concentrated H_2SO_4.[7] We subjected benzene and its sulfonation product, $C_6H_5SO_3H$, to the same iodination conditions and examined the product mixtures. If sulfonation of benzene is an initial step during benzene's polyiodination to 1, then the room-temperature reaction starting with $C_6H_5SO_3H$ should also give the product 1. In the event, the two substrates gave quite different product mixtures, prompting us to propose separate pathways for their polyiodination.

Results and Discussion

Iodination Conditions. Iodinations were performed with the appropriate quantities of 3:1 I_2/H_5IO_6 in concentrated H_2SO_4 to provide the relative equivalents of "I^+" shown in Table I. After cooling this reagent mixture on ice, the substrate was added with stirring; $C_6H_5SO_3H$ was supplied as its sodium salt. Reactions were allowed to stir at room temperature for 2 days or were heated to 55 °C for 1 day as shown in Table I. Benzene reactions typically produced voluminous precipitates; in contrast, no precipitates were apparent in the $C_6H_5SO_3H$ reactions.

Each completed reaction mixture was poured onto ice, and any precipitate was collected by filtration. The aqueous filtrate was concentrated; any resulting pearly paste was collected by centrifugation and purified by the HCl precipitation method of Boyle.[8] This paste was identified by its NMR and mass spectra as 3,4,5-triiodobenzenesulfonic acid (4); it was the only arenesulfonic acid

(1) Mattern, D. L. *J. Org. Chem.* **1983**, *48*, 4772.
(2) Mattern, D. L. *J. Org. Chem.* **1984**, *49*, 3051.
(3) Garrett, R. A.; Gillespie, R. J.; Senior, J. B. *Inorg. Chem.* **1965**, *4*, 563.
(4) Sutter, C. M.; Weston, A. W. *Org. React.* **1946**, *3*, 141.
(5) Cerfontain, H. *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*; Wiley-Interscience: New York, 1968; pp 185–198.
(6) Boyle, M. *J. Chem. Soc.* **1911**, *99*, 325.
(7) Gold, V.; Satchell, D. P. N. *J. Chem. Soc.* **1956**, 1635.
(8) Boyle, M. *J. Chem. Soc.* **1909**, *95*, 1683.

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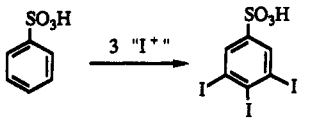
that we isolated. The original precipitate was triturated



4

several times with hot THF; orange **3** was insoluble and easily isolated. The THF-soluble products were quantified by the ^1H NMR spectrum of the crude mixture. Included were major products **1** and **2**, which were isolated and identified by their spectra and melting points. In addition, a number of minor NMR signals were present. In order to assign these signals, we decided to synthesize a number of likely candidates; these were known compounds, but their NMR spectra were generally unavailable.

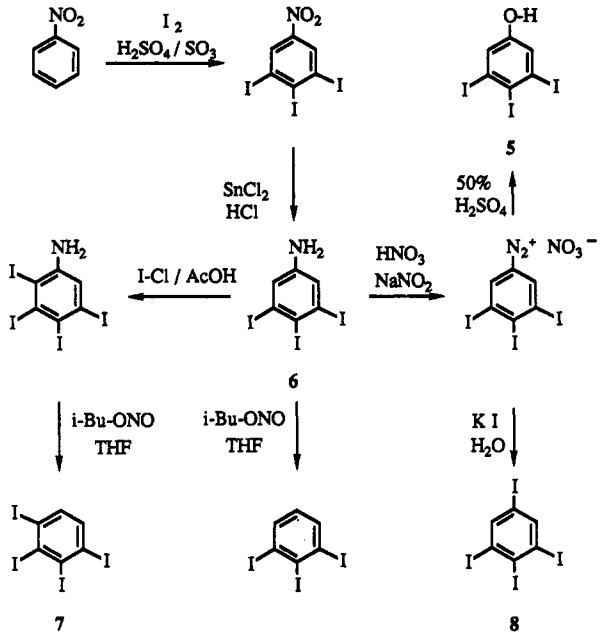
Synthesis. The four candidates were prepared from 3,4,5-triiodoaniline (**6**) as shown in Scheme I, following a diazonium salt strategy devised[9] (but incorrectly executed[10]) by Willgerodt and Arnold. Compound **6** was prepared by reduction[10] of 3,4,5-triiodonitrobenzene, which was in turn obtained by iodination of nitrobenzene with I_2 in oleum.[11] Conversion of **6** to its nitrate diazonium salt[10] followed by treatment with aqueous iodide[9] gave 1,2,3,5-tetraiodobenzene (**8**); the salt also was decomposed in hot aqueous H_2SO_4[12] to give 3,4,5-triiodophenol (**5**). (The candidacy of a triiodophenol was suggested by a mass spectrum of a crude iodination product mixture.) Deamination of **6** with isobutylnitrite in THF[13] gave 1,2,3-triiodobenzene, which was not observed in any of our polyiodination product mixtures. Finally, **6** was iodinated with ICl[9] and deaminated[13] to give the third and final $C_6H_2I_4$ isomer, 1,2,3,4-tetraiodobenzene (**7**).

Each of the possible products displayed an aromatic singlet in the ^1H NMR (Me_2SO-d_6) at a distinctive chemical shift (δ) as follows: **2**, 8.46; **1**, 8.32; **8**, 8.19; **4**, 7.99; **7**, 7.62; and **5**, 6.87. Phenol **5** also gave an OH signal at a characteristic shift (δ 6.67). We have assigned the minor peaks in the NMR of the crude polyiodination product mixtures, as shown in Table I, based on their correspondence to these values.

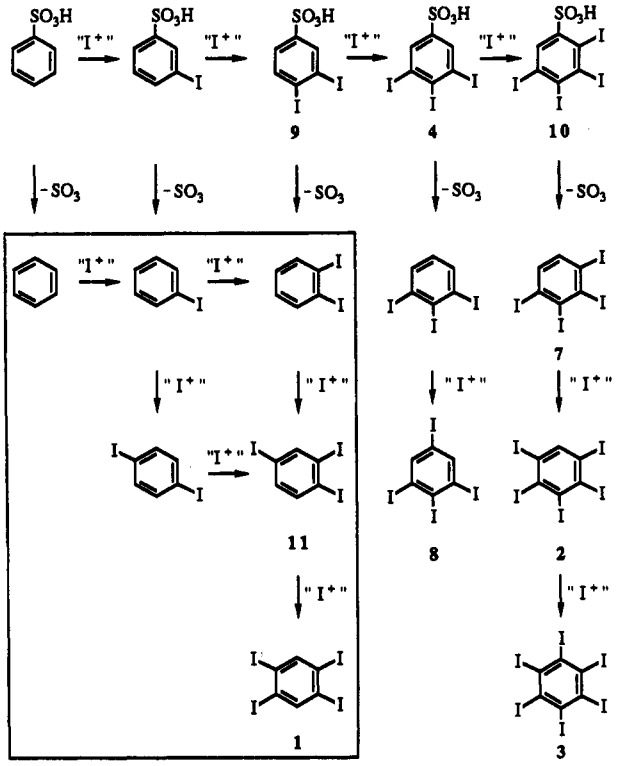
Polyiodination Products. The results of polyiodinations of benzene and $C_6H_5SO_3H$ under various conditions are shown in Table I. With 4 equiv of "I^+" at room temperature, benzene yields predominantly **1**, with traces of other products (entry 1). In contrast, $C_6H_5SO_3H$ yields **4** as the major product, along with some **1** and **2** and smaller amounts of **3**, **5**, and **8**, under the same conditions (entry 4). No sulfonation product **4** is observed when benzene is the substrate. This makes it clear that benzene is not sulfonated to any significant extent during the room-temperature polyiodination reaction: any $C_6H_5SO_3H$ formed would be detected by its substantial conversion to **4**. Sulfonation of iodinated benzene intermediates therefore also seems unlikely, since they are deactivated toward electrophilic attack.[4] At 55 °C the situation is less clear, as there is a trace of **4** product (entry 3); sulfonation apparently can compete better at the higher temperature.

Conversely, it is clear from Table I that desulfonation occurs, at some stage, for over half of the $C_6H_5SO_3H$ substrate. Product **1** could be the end result of desulfonation of $C_6H_5SO_3H$ itself or of mono-, di-, or triiodinated derivatives. More perplexing is the appearance of highly iodinated **2** and **3** in much *greater* amounts than are formed from the *more* activated substrate benzene. This suggests that a pathway for the formation of **2** and **3**, separate from the benzene pathway, is operating.

Scheme I



Scheme II



Pentaiodobenzene. Although pentaiodobenzene **2** can be prepared using a mercuration/iododemercuration sequence,[14] and by diazonium salt substitution,[9] its formation in substantial amounts from $C_6H_5SO_3H$ suggested this reaction as a less tedious preparative route. At 55 °C with 5 equiv of "I^+", $C_6H_5SO_3H$ formed **2** in 34% yield within

(9) Willgerodt, C.; Arnold, E. *Chem. Ber.* **1901**, *34*, 3343.
(10) Kalb, L.; Schweizer, F.; Zellner, H.; Berthold, E. *Chem. Ber.* **1926**, *59*, 1860.
(11) Arotsky, J.; Butler, R.; Darby, A. C. *J. Chem. Soc. C* **1970**, 1480.
(12) Cassebaum, H. *Arch. Pharm.* **1959**, *292*, 565; *Beil. E4 6*, 1088.
(13) Cadogen, J. I. G.; Molina, G. A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 541.
(14) Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1977**, *30*, 1701.

Table I. Polyiodination of Benzene and Benzenesulfonic Acid

entry	substrate	relative equiv of "I+"	temp (°C)	molar % yield of products						
				1	2	3	4	5	7	8
1	C_6H_6	4	rt	66	1	0	0	1	2	0
2	C_6H_6	5	rt	65	12	0	0	6	0	0
3	C_6H_6	6	55	25	36	10	1	17	0	0
4	$C_6H_5SO_3H$	4	rt	14	15	4	32	4	0	2
5	$C_6H_5SO_3H$	5	rt	16	18	10	20	2	0	0
6	$C_6H_5SO_3H$	4	55	14	22	1	32	3	0	0
7	$C_6H_5SO_3H$	5	55	10	34	8	21	3	0	0
8	$C_6H_5SO_3H$	6	55	3	28	12	5	28	0	0

the THF-soluble fraction (entry 7), somewhat better than reactions with 4 equiv (entry 6) or 6 equiv (entry 8). Two crystallizations from 2-methoxyethanol gave bright yellow **2**, free of 1 according to ^1H NMR assay, in 26% yield. Benzene can give a similar crude yield of **2** (entry 3), but the presence of additional 1 makes the purification more difficult.

Proposed Pathways. Scheme II shows our initial hypothetical pathway for the course of $C_6H_5SO_3H$ polyiodination. The SO_3H group directs the first iodine to a meta position; the second incoming iodine avoids the hindered positions ortho to the SO_3H group to give 3,4-diiodobenzenesulfonic acid (**9**). Desulfonation of any of these three compounds would lead into the benzene pathway box in Scheme II. In the box, 1,2-diiodobenzene iodinates in the 4-position to avoid having three bulky iodines adjacent; for the same reason, the resulting triiodobenzene 11 iodinates to give 1,2,4,5-tetraiodobenzene (**1**) rather than the 1,2,3,5 isomer **8**.

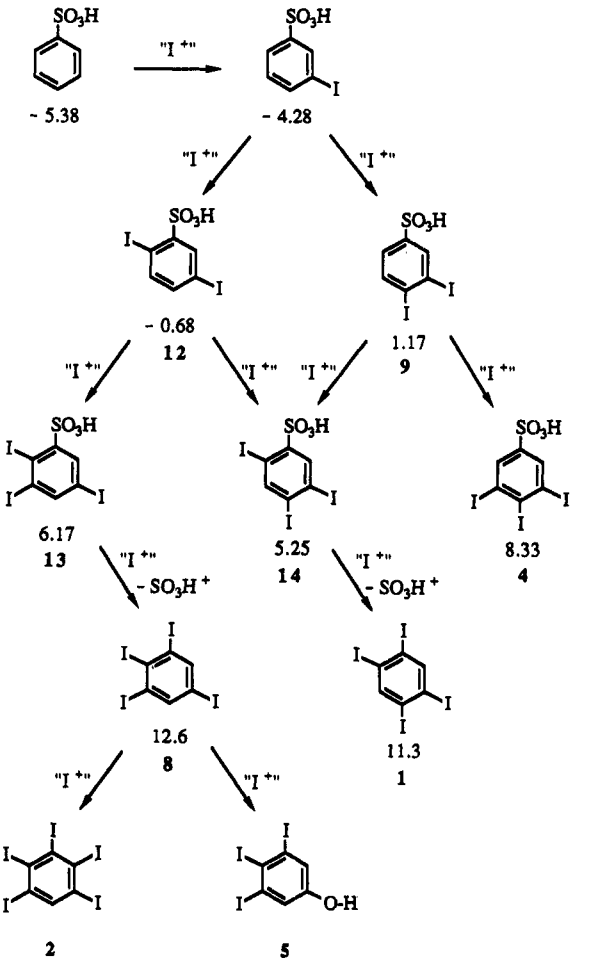
Major product **4** results from iodination in the position nonadjacent to the bulky SO_3H group of **9**. No unhindered iodination possibilities are left. However, **4** can iododesulfonate,[5,6] in one or (as shown) two steps to give **8** (observed in trace amounts) or can iodinate in the ortho position to give hindered **10**, which again can iododesulfonate in one or two steps to give the observed **2**. Occasional iodination of **2** gives some **3**. This scheme accounts for the formation of **2** and **3** outside of the benzene pathway, for the appearance of **4** and **1** as major products, and for the trace of **8**.

To test Scheme II, we treated compound **4**, which we had already isolated, to the iodination conditions. We expected that **4** would be converted to **2** and **3**, with perhaps some **8**, but would not form **1** (which has a different substitution pattern). However, when **4** was treated with 1 equiv of "I^+" for 2 days at room temperature, only unreacted **4** was isolated (80% recovery)—that is, **4** is stable to these iodination conditions. Not only are the two branches of Scheme II that lead from **4** to **8** and **3** therefore untenable, but the fact that **4** does not desulfonate makes it most unlikely that *any* of the first four compounds in Scheme II will desulfonate, thus leaving no pathway to product **1**.

A final difficulty with Scheme II is that it does not address the presence of triiodophenol **5**. It is tempting to speculate that **5** arises directly from **4**. Although there is some precedence for such hydroxydesulfonations, the conditions (such as strong base[15] or photolysis[16]) do not resemble those involved here. Further, **5** is formed even in the benzene iodinations (Table I), where **4** is absent or scarce.

An alternative pathway, which avoids the difficulties of Scheme II, is given in Scheme III. A major difference is

Scheme III[a]



[a] Numbers are MM2 steric energies in kcal/mol.

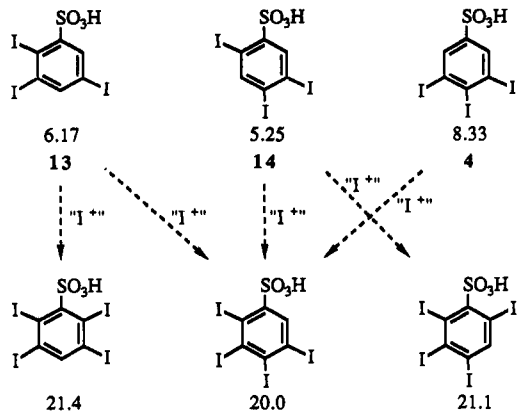
that iodine is allowed to substitute ortho to the sterically demanding sulfonic acid group. To judge the reasonableness of this approach, we performed MM2 molecular mechanics calculations on the proposed intermediates; the resulting steric energies are given in Scheme III.

The MM2 steric energies suggest that there is in fact no great steric advantage of 3,4-diiodobenzenesulfonic acid (**9**) over the 2,5 isomer **12**. That is, we allow the second incoming iodine to attack adjacent to either SO_3H or I (but not between the two bulky groups). Similarly, the third iodine may attack any position (except the one between two substituents) to give the triiodo isomers **13**, **14**, and **4**, all with similar steric energies.

Further normal substitution by iodine is stymied at this point. Each iodine addition so far, placing an iodine ortho to a single existing substituent, has cost about 6 kcal/mol in steric energy. As shown in Scheme IV, normal electrophilic substitution by a fourth iodine would cost about 14 kcal/mol, making those reactions prohibitive.

(15) Buzbee, L. R. *J. Org. Chem.* **1966**, *31*, 3289.
(16) Izawa, Y.; Suzuki, N.; Inoue, A.; Ito, K.; Ito, T. *J. Org. Chem.* **1979**, *44*, 4581.

Scheme IV[a]



[a] Numbers are MM2 steric energies in kcal/mol.

Table II. Iodination of Tetraiodobenzene Isomers with 1 equiv of "I+" at Room Temperature for 2 Days. Recovery of Starting Material Is in Italics

	molar % yield of products				
substrate	1	2	5	7	8
1	*79*	6	9	0	0
7	0	30	0	*48*	0
8	0	49	34	0	*5*

Instead, we propose that those triiodo isomers whose SO_3H groups are crowded by an adjacent iodine, namely 13 and 14, *iododesulfonate*[5,6] at a steric cost of only 6 kcal/mol (Scheme III). We prefer iododesulfonation to a two-step process, since initial desulfonation would give 11; 11 is an intermediate in the "benzene box" pathway in Scheme II, thus yielding 1, but providing no credible source for 2, 5, and 8. In contrast, iododesulfonation of 14 provides 1 directly, and iododesulfonation of 13 gives 8. As noted above, the third triiodo isomer 4 is stable to the reaction conditions; possibly its less crowded environment protects the SO_3H group from desulfonation, allowing 4 to survive as the major product.

Finally, we propose that 8 converts to the two remaining products, 2 and 5, based on separate treatment of each of the isolated tetraiodobenzene isomers with 1 equiv of "I+" (Table II). Each of the isomers can add a fifth iodine to make pentaiodobenzene 2, but 8 is the most extensively converted. Further, 8 makes substantial amounts of 5 under these low-"I+" conditions. Both 2 and 5 are products of the $C_6H_5SO_3H$ iodination; Scheme III thus accounts for all of the observed products.

It is interesting to note that the steric energies of tetraiodobenzene isomers 1 and 8 are quite close. Therefore, the iodination of 11 (box in Scheme II) apparently yields the 1 isomer not for steric reasons, but because the 5 position (leading to 1) is activated by two iodines in ortho/para positions; attack at the 6 position (leading to 8) gives a σ complex stabilized by only a single ortho iodine. The all-adjacent isomer 7 has notably higher strain (steric energy 19.7 kcal/mol).

There remains the puzzle of the formation of phenol 5 and tetraiodobenzene isomer 7 in small amounts during the polyiodination of benzene, since the pattern of three adjacent iodines does not appear in the predominant benzene pathway (box, Scheme II). We propose that occasional iodination of 11 in the 3- or 6-positions gives small amounts of 7 and 8; as discussed above, 8 rapidly reacts further to give the observed 2 and 5.

Interestingly, even 1 stirred by itself in H_2SO_4 for two days yields some 5 (13%) along with 75% recovery of 1. This scrambling of iodines suggests a Jacobsen[17] "type 3"[18] rearrangement, wherein a polyiodoaromatic deiodinates upon heating in strong acid, with the released electrophilic iodine reattaching at a new position.[19,20] Thus, 1 could deiodinate to 11, and 11 could reiodinate to 8; 8, under conditions of low "I+", would convert to 5 rather than 2. The mechanism for the formation of 5 from 8 is not obvious[21] and will be the object of future studies.

Conclusions

Benzene and benzenesulfonic acid do not share reaction pathways during room-temperature direct polyiodination. Benzene is not sulfonated, since products shown to arise from $C_6H_5SO_3H$ are not observed; we propose that benzene follows the straightforward boxed pathway in Scheme II. The inertness of triiodobenzenesulfonic acid 4 in this system argues that simple desulfonation of arenesulfonic acids does not occur; we propose instead that benzenesulfonic acid follows the pathway in Scheme III by triiodinating to three $C_6H_2I_3SO_3H$ isomers. One of these, 4, is stable and a major product. In contrast, isomers 13 and 14 have congested ortho-substituted SO_3H groups and iododesulfonate to tetraiodobenzene isomers 1 (a major product) and 8 (an intermediate); 8 was shown in a separate experiment to convert to the other two observed products, pentaiodobenzene 2 and phenol 5, thus completing the pathway.

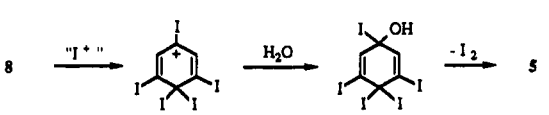
Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed with silica gel on polyester sheets (Aldrich or Sigma) and visualized under UV light. ^1H NMR and ^{13}C NMR spectra were determined with a JEOL-FX60Q or a Bruker AC-E 300 spectrometer in Me_2SO-d_6. Mass spectra were determined with a Hewlett-Packard 5985 GC/MS instrument (heated probe). IR spectra (KBr pellet) were determined with a Perkin-Elmer 1600 FT-IR spectrometer. The microanalysis was performed by Desert Analytics, Tucson, AZ.

MMP2 calculations[24] were performed on a MicroVAX II computer. Some parameters involving I[25] and SO_3H[26] were estimated; details are in the supplementary material.

General Iodination Procedures. Periodic acid (G.F. Smith Co.; 0.522 g, 2.29 mmol) was dissolved with stirring in concd H_2SO_4 (40 mL). Iodine (Fisher; 1.74 g, 6.86 mmol) was crushed and added to the clear solution. (These quantities give 16 mmol (4 equiv) of "I+".) After 15 min of stirring, the dark mixture was placed in an ice bath. Benzene (MC&B; 0.357 mL, 4.00 mmol) or sodium benzenesulfonate (MC&B; 0.721 g, 4.00 mmol) was then added

(17) Smith, L. I. *Org. React.* **1942**, *1*, 370.
(18) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1642.
(19) Suzuki, H.; Goto, R. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 389.
(20) When 2 was stirred in H_2SO_4 for 2 days at 55 °C, we saw no evidence of a Jacobsen-type disproportionation to 1 and 3.
(21) One possibility is ipso attack[22] of "I+" on 8 to form the σ complex shown; nucleophilic attack[23] by water would give a cyclohexadiene that could undergo 1,4-elimination[23] to yield 5.



(22) Traynham, J. G. *J. Chem. Educ.* **1983**, *60*, 937.
(23) Banwell, T.; Morse, C. S.; Myhre, P. C.; Vollmar, A. *J. Am. Chem. Soc.* **1977**, *99*, 3042.
(24) The 1987 MM2 parameter set was obtained from Prof. N. L. Allinger, University of Georgia.
(25) Bowen, J. P.; Reddy, V. V.; Patterson, D. G.; Allinger, N. L. *J. Org. Chem.* **1988**, *53*, 5471.
(26) Garduño-Juarez, R.; Ocampo-Garcia, E. *Comput. Chem.* **1989**, *13*, 117.

slowly. The mixture was allowed to stir at room temperature for 2 days or was heated at 55 °C for 1 day. Benzene reactions turned lavender or tan; $C_6H_5SO_3H$ reactions ended deep brown. The mixture was poured into 100 mL of an ice/water mixture. Any resulting solid was collected by suction filtration on a sintered glass filter and washed with portions of CCl_4 (50 mL total) and MeOH (50 mL total) to remove iodine. This solid was triturated several times with hot THF, leaving an orange powder with the NMR and IR spectra of C_6I_6 (3).[2] Rotary evaporation of the THF gave mixtures of tetraiodobenzene isomers 1, 7, and 8, C_6HI_5 (2), and triiodophenol 5 as shown in Table I. The identity and relative amounts of these products were determined by ^1H NMR analysis of the crude THF extract. 1 could be isolated from the crude mixture as described previously.[2]

3,4,5-Triiodobenzenesulfonic Acid (4). The above aqueous filtrate was concentrated to about 75 mL by flowing air over its surface at room temperature for several days. Concentrates from $C_6H_5SO_3H$ reactions precipitated a pearly paste, which was separated from the supernatant by centrifugation. 4 was purified by Boyle's procedure of dissolving the crude paste in 12 parts of water, heating while adding 25 parts of concentrated HCl, and then cooling;[8] the new precipitate was isolated by centrifugation, transferred in MeOH solution, and dried by rotary evaporation of a toluene suspension to give a white solid (38% from room temperature reaction with 4 equiv of "I^+"). The product was probably hydrated;[8] its mp varied depending on the extent of drying: mp 151–157 °C (lit.[8] mp 158 °C); TLC (MeOH) R_f 0.89; ^1H NMR δ 7.99 (s); ^{13}C NMR δ 150.4 (CS), 135.2 (d, CH), 122.2 (C_4I), 108.2 ($C_{3,5}I$); MS m/e 535.7 (M^+, 100), 409.0 ($M^+ - I$, 27); IR 3350 (br) cm^{-1}.

Pentaiodobenzene (2). $C_6H_5SO_3H$ was treated with 5 equiv of "I^+" for 1 day at 25 °C followed by 1 day at 55 °C and worked up as described above. Two crystallizations of the THF-soluble portion from 2-methoxyethanol gave a 26% yield of bright yellow needles, mp 231.5–235 °C (lit.[14] mp 228–230 °C), with no evidence of 1 remaining in the ^1H NMR spectrum: TLC (3:1 hexane/CH_2Cl_2) R_f 0.60; ^1H NMR δ 8.46 (s); ^{13}C NMR δ 109.6 ($C_{1,5}I$), 122.1 ($C_{2,4}I$), 123.5 (C_3I), 145.8 (CH); MS m/e 707.5 (M^+, 100), 580 ($M^+ - I$, 36), 454 ($M^+ - I_2$, 58), 327 ($M^+ - I_3$, 54), 200 ($M^+ - I_4$, 76); IR 3080 cm^{-1}.

3,4,5-Triiodonitrobenzene was prepared by a literature procedure[11] in 8% yield: mp 159–162 °C (lit.[11] mp 166–167 °C); ^1H NMR δ 8.53 (s); ^{13}C NMR δ 145.0 (CNO_2), 132.3 (C_p), 131.6 (CH), 109.2 (C_m); MS m/e 500.8 (M^+, 100), 455 ($M^+ - NO_2$, 31); IR 3090 cm^{-1}.

3,4,5-Triiodoaniline (6) was prepared by $SnCl_2$ reduction[10] of triiodonitrobenzene in 80% yield: mp 162–164 °C (lit.[10] mp 174.5 °C); TLC (1:1 hexane/CH_2Cl_2) R_f 0.36; ^1H NMR δ 7.18 (2 H, s, ArH), 5.55 (2 H, s, NH_2).

3,4,5-Triiodobenzenediazonium nitrate was prepared by diazotization[10] of triiodoaniline in 85% yield: mp 120 °C (no lit.[10] mp); ^1H NMR δ 9.06.

3,4,5-Triiodophenol (5). A solution of 203 mg (0.37 mmol) of the above diazonium salt in 20 mL of 50% H_2SO_4 was heated to 75 °C with stirring for 45 min. The resulting precipitate was collected by centrifugation and dried by rotary evaporation of a toluene suspension. 5 was isolated by column chromatography (silica gel, THF in CH_2Cl_2) to give 27 mg (15%): mp 175 °C (lit.[12] mp 177–178 °C); TLC (MeOH) R_f 0.86; ^1H NMR δ 6.87 (2 H, s, ArH), 6.67 (1 H, s, OH); ^{13}C NMR δ 151.5 (COH), 139.2 (CI), 128.0 (CI), 125.0 (CH); MS m/e 472 (M^+, 26), 345 ($M^+ - I$, 10), 219 ($M^+ - I_2$, 100); IR 3421 cm^{-1}. The ^1H NMR indicated contamination by about 5% of 7.

1,2,3,5-Tetraiodobenzene (8). To 350 mg (0.642 mmol) of the above diazonium salt in 30 mL of H_2O was added 114 mg (0.69 mmol) of KI; the mixture was heated at 65 °C for 1 h. Two crystallizations of the resulting crude solid from AcOH gave yellow crystals (40%): mp 162–165 °C (lit.[9] mp 148 °C); TLC (1:1 hexane/CH_2Cl_2) R_f 0.84; ^1H NMR δ 8.19 (s); ^{13}C NMR δ 97.0 (C_5I), 110.5 ($C_{1,3}I$), 122.2 (C_2I), 145.4 (CH); MS m/e 581.5 (M^+, 100); IR 3090 cm^{-1}.

2,3,4,5-Tetraiodoaniline. To 471 mg (1.00 mmol) of 3,4,5-triiodoaniline in 60 mL of AcOH was added 10 g of NaOAc, followed by dropwise addition of 162 mg (1.00 mmol) of ICl in 5 mL of AcOH. The mixture was heated at 75 °C for 2.5 h, cooled, and decanted into 300 mL of H_2O. The resulting precipitate was crystallized twice from EtOH to give light yellow crystals (52%): mp 143–144 °C; TLC (1:1 hexane/CH_2Cl_2) R_f 0.49; ^1H NMR δ 7.44 (1 H, s, Ar-H), 5.76 (2 H, s, NH_2); ^{13}C NMR δ 151.1 (CNH_2), 123.2 (C_3), 122.5 (CH), 108.0 (C_5), 102.8 (C_4, $^3J_{C-H}$ = 8.7 Hz), 96.6 (C_2); MS m/e 596.7 (M^+, 61), 343 ($M^+ - I$, 100), 216 ($M^+ - I_2$, 80); IR 3406, 3334 cm^{-1}. Anal. Calcd for $C_6H_3NI_4$: C, 12.08; H, 0.51; N, 2.35; I, 85.07. Found: C, 12.37; H, 0.54; N, 2.21; I, 84.93.

1,2,3,4-Tetraiodobenzene (7). To a refluxing solution of isoamyl nitrite[27] (117 mg, 1.00 mmol) in 10 mL of THF[13] was added dropwise 597 mg (0.500 mmol) of tetraiodoaniline in 5 mL of THF. After 3 h, the solvent was removed by rotary evaporation, and the residue was eluted from an alumina chromatography column with hexane to give 6 as a yellow solid (56%): mp 128–129 °C (lit.[28] mp 136 °C); TLC (hexane) R_f 0.58; ^1H NMR δ 7.62 (s); ^{13}C NMR δ 107.7 ($C_{1,4}I$), 123.0 ($C_{2,3}I$), 139.8 (CH); MS m/e 581.5 (M^+, 100).

1,2,3-Triiodobenzene was prepared in a similar fashion from 3,4,5-triiodoaniline in 34% yield: mp 104–106 °C (lit.[29] mp 110–113 °C); TLC (1:1 hexane/CH_2Cl_2) R_f 0.80; ^1H NMR δ 7.92 (2 H, d, $C_{4,6}H$), 6.81 (1 H, t, C_5H). The ^1H NMR spectrum indicated contamination by about 10% of 8.

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Registry No. 1, 636-31-7; 2, 608-96-8; 3, 608-74-2; 4, 135598-04-8; 5, 116434-91-4; 6, 108673-30-9; 7, 634-68-4; 8, 634-92-4; 3,4,5-triiodonitrobenzene, 53663-23-3; periodic acid, 13444-71-8; sodium benzenesulfonate, 515-42-4; 3,4,5-triiodobenzenediazonium nitrate, 68596-99-6; 2,3,4,5-tetraiodoaniline, 135598-05-9; 3,4,5-triiodoaniline, 108673-30-9; 1,2,3-triiodobenzene, 608-29-7; benzene, 71-43-2.

Supplementary Material Available: Estimated MMP2 parameters, additional IR data, and experimental procedures for literature syntheses (2 pages). Ordering information is given on any current masthead page.

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