Table I

C	(1) ^{1}H	(1) ^{13}C[a]	(2) ^{1}H	(2) ^{13}C[a]	(3) ^{1}H	(3) ^{13}C[a]
C_1	2.05 (s)	14.1 (q)	2.25 (s)	16.6 (q)	2.25 (s)	15.1 (q)
C_2	3.15 (d)	36.7 (t)	3.15 (d of d)	40.3 (t)	3.2–2.9 (m)	49.1 (d)
C_3	6.1–5.6 (m)	133.9 (d)	4.5–4.15 (m)	50.5 (d)	3.75 (d of d)	33.9 (t)
C_4	5.25–5.0 (m)	116.7 (t)	4.0–3.7 (m)	36.0 (t)		

[a] Multiplicity (s, d, t, q) as determined from off-resonance decoupled spectra.

Table II

C	(7) ^{1}H	(7) ^{13}C[a]	(8) ^{1}H	(8) ^{13}C[a]
C_1	2.90 (s)	38.7 (q)	3.1 (s)	42.8 (q)
C_2	3.80 (d)	58.7 (t)	4.1–3.4 (m)	60.0 (t)
C_3	6.2–5.75 (m)	124.9	4.8–4.5 (m)	41.9 (d)
C_4	5.6–5.4 (m)	124.3	4.1–3.4 (m)	35.9 (t)

[a] Multiplicity (s, d, t, q) as determined from off-resonance decoupled spectra.

monium ion such as **4** is readily susceptible to intramolecular attack by an adjacent sulfur atom. Thus, careful analysis (preferably by ^{13}C NMR) of the halogenation products formed from allylic sulfides is warranted in order to confirm the formation of the "expected" products.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million(s) relative to internal tetramethylsilane.

Materials. Allyl methyl sulfide was obtained from Aldrich Chemical Co. and used without further purification. Bromine was procured from J.T. Baker and was distilled from P_2O_5 prior to use.

1,3-Dibromo-2-(methylthio)propane (3). To a solution of 1.00 g (11.3 mmol) of allyl methyl sulfide in 10 mL of CCl_4 cooled to −10 °C in an CCl_4/CO_2 bath was added dropwise a solution of 1.80 g (11.3 mmol) of Br_2 in 5 mL of CCl_4, keeping the temperature below −10 °C. A yellow precipitate formed, which dissolved on warming to room temperature, giving a colorless solution. The CCl_4 was removed in vacuo to give 2.80 g (100%) of **3** as a colorless liquid.

1,2-Dibromo-3-(methylthio)propane (2). A $CDCl_3$ (1 M) solution of **3** was heated at reflux for 5 h or **3** was heated without solvent for 1 h at 115 °C to give a mixture of **2** and **3** in an 82:18 ratio, as shown by ^{13}C NMR. Distillation via Kugelrohr at 98–102 °C (0.2 mmHg) gave a colorless liquid in 68% yield having a **2/3** ratio of 78:22.

Allyl Methyl Sulfone (7). An ice cold solution of 7.28 g (34.0 mmol) of $NaIO_4$ in 70 mL of H_2O containing 1.00 g (11.3 mmol) of allyl methyl sulfide stood at room temperature for 30 h and then at 5 °C for 2 days. The aqueous solution was decanted from the inorganic crystals and extracted with CH_2Cl_2 (4 × 15 mL). The combined organic phase was washed with 10 mL of H_2O and dried ($MgSO_4$), filtered, and concentrated in vacuo to give 0.77 g (56%) of a colorless liquid that was shown to be 93% sulfone and 7% sulfoxide by ^{13}C NMR.

2,3-Dibromo-1-propyl Methyl Sulfone (8). To a solution of 0.51 g (4.3 mmol) of **7** in 3 mL of $CDCl_3$, cooled to −60 °C, was added a solution of 0.68 g (4.3 mmol) of Br_2 in 2 mL of $CDCl_3$. After 10 min at room temperature, ^{13}C NMR showed 100% **8**, and concentration in vacuo gave 1.19 g (100%) of **8** as a light yellow liquid.

Anal. Calcd for $C_4H_8SO_2Br_2$: C, 17.16; H, 2.88; S, 11.45. Found: C, 17.37; H, 2.93; S, 11.34.

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Registry No. 1, 10152-76-8; 2, 86823-45-2; 3, 86823-46-3.

Cation Exchange Resin (Hydrogen Form) Assisted Decomposition of 1-Aryl-3,3-dialkyltriazenes. A Mild and Efficient Method for the Synthesis of Aryl Iodides

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The wide use of aromatic radioiodinated compounds in medicinal diagnostic procedures[1] has warranted the development of a mild and efficient method for the regiospecific incorporation of iodine into an aromatic nucleus. Access to these compounds commonly involve electrophilic halogenations by the in situ generation of radiohalonium ions, which generally require highly activated aromatic rings[2] and result in the formation of a mixture of isomers.[3] Recent work involving the cleavage of aryl–silicon[4] or aryl–boron[5] bonds with electrophilic halonium ions has been directed toward developing more selective methods for this reaction.

On the other hand, nucleophilic substitutions by the Sandmeyer reaction, and its subsequent modifications,[6]

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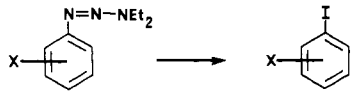
Table I. Yields of Aryl Iodides[a]



1 2

compd	X	isolated yield,[b] %
a	H	85 (49)
b	OCH_3	72
c	p-CH_3	90 (56)
d	p-OCH_3	85 (40)
e	p-CN	92
f	p-$COCH_3$	95
g	p-Cl	80
h	p-Br	85
i	m-NO_2	83 (11)
j	p-NO_2	80 (51)

[a] Purity and identity of aromatic iodides were confirmed by comparison of melting point or boiling point, GC, HPLC retention times, and IR spectra with authentic samples. [b] Yields in the parentheses represent those obtained by the Sandmeyer method (ref 9).

may not be suitable for radiohalogenation because this reaction is plagued by numerous competing side reactions.[7,8] Similarly, the decomposition of diazonium ion equivalents (e.g., 1-aryl-3,3-dialkyltriazenes) in aqueous acid in the presence of potassium iodide give poor yields with strongly deactivated aromatic triazenes.[9] As an alternative method we recently reported the decomposition of aromatic triazenes with trimethylsilyl chloride in the presence of metal halides in acetonitrile.[10]

We now report an efficient, regioselective synthesis of aryl iodides that is suitable for preparing isotopically labeled material. Ion-exchange resins have been widely used as catalysts in organic synthesis.[11] The substitution of cation-exchange resins (H^+ form) for mineral acids in several organic reactions[12] prompted us to study the reaction of a cation exchange resin (H^+ form) with 1-aryl-3,3-dialkyltriazenes in the presence of iodide ion as a nucleophile. The treatment of triazenes **1a–j** with a well-dried sample of NaI and a sulfonic acid cation exchange resin (H^+ form, Bio-Rad AG 50W-X12) in dry acetonitrile at 75 °C for 5 min gave excellent yields of the corresponding aryl iodides **2a–j** (Table I).

In connection with the synthetic features of this procedure several points are noteworthy: (a) the starting triazenes are stable and readily prepared in high yields from commercially available aromatic amines,[13–15] (b) the technique is mild and effective with a wide range of aromatic substrates and is regiospecific, (c) yields are excellent, and the method is rapid and, hence, can easily be adapted to radioiodination of aromatic compounds with short-lived radioiodine (e.g., ^{123}I, half-life: 13.0 h) isotopes, (d) the products are isolated by simple filtration and solvent evaporation, and (e) the resin catalyst can be recycled after regeneration.

Table II. Product Composition of the Reaction of Selected Triazenes with Acids in the Presence of NaI[a]

triazene	acid	ArI, %	ArH, %	total unidentified products, %
1a	CF_3CO_2H	68.6	9.8	21.6
	CH_3SO_3H	75.3	2.6	22.1
	acid resin	>99		
1d	CF_3CO_2H	74.8	6.2	19.0
	CH_3SO_3H	82.1	6.4	11.5
	acid resin	96.0	4.0	
1f	CF_3CO_2H	81.5	10.5	8.0
	CH_3SO_3H	85.2	10.0	4.8
	acid resin	94.0	6.0	

[a] Yields measured by HPLC.

In our hands, this procedure is the most efficient and reproducible scheme to arrive at aromatic iodides. The results in Table I indicate that the reaction proceeds in excellent yields, and show that reaction yields are essentially independent of the electronic character of the aromatic moiety.

Actually the reaction was tested under a variety of conditions with selected 1-aryl-3,3-dialkyltriazenes (Table II), obtaining in every case a mixture of products. For example, in all cases regiospecific protodediazoniation products, namely, benzene, anisole, and acetophenone, were detected from triazenes **1a**, **1d**, and **1f**, respectively, the formation of which could be due to the homolytic cleavage of the aryl–nitrogen bond of the triazene.[16] With trifluoroacetic acid and methanesulfonic acid, byproducts that are not identified constituted about 5–20% of the total yield, whereas such byproducts are not detected with the acid resin reactions. In the light of these facts, it is highly probable that the acid resin plays a striking role in these reactions, by protonating and consequently immobilizing the basic aromatic triazene on the resin surface, facilitating the nucleophilic attack by the iodide ion.

Perhaps the greatest potential utility of the present method lies in the applicability of the technique to the preparation of aryl radioiodides, where rapidity of the synthetic procedure and high yields are required.

Experimental Section

Melting and boiling points reported are uncorrected. The IR spectra were determined on a Perkin-Elmer Model 710B infrared spectrometer. ^1H NMR spectra were recorded on a Bruker WP-200 Fourier transform spectrometer at 200 MHz and the chemical shifts are expressed as ppm (δ) from Me_4Si internal standard. High-pressure liquid chromatography (HPLC) was carried out on Water M-45 instrument (Ultrasphere ODS column, 5 μm, 4.6 × 150 mm, 75% MeOH and 25% water, flow rate 1.0 mL/min; 254-nm UV detector). The gas chromatograms were obtained on a Varian Aerograph Model 940 instrument employing a 3% OV-17 column (6 ft × $^1/_8$ in.), FID detection, and a helium flow rate of 40 mL/min. Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without further purification.

Sulfonic acid resin (AG 50W-X12) was purchased from Bio-Rad Laboratories and regenerated as follows: 100 g of the resin was

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stirred with 10% sulfuric acid (500 mL) for 30 min, filtered, and washed with deionized water until the washings were free of acid. The resin was then washed with THF, acetone, or absolute alcohol (3 × 30 mL), dried in an oven at 75–80 °C for 12 h, and kept over P_2O_5 in a vacuum desiccator for a week. Acetonitrile was distilled from P_2O_5.

General Procedure for the Preparation of Aromatic Dialkyltriazenes (1). The procedure developed by Wallach[13] was used for the preparation of the triazenes. A solution of arylamine (0.10 mol) in 1:1 HCl (50 mL) was cooled to 0 °C and a solution of sodium nitrite (0.11 mol) in water (25 mL) was added dropwise, keeping the temperature of the solution below 0 °C during the addition. The reaction mixture was stirred at 0 °C for an additional period of 30 min. The diazonium salt solution was then added to an ice cold solution of K_2CO_3 (0.15 mol) and diethylamine (0.15 mol) in water (200 mL). The reaction mixture was extracted with ether (2 × 100 mL), and the ether extracts were combined, washed with water (3 × 50 mL), and dried (Na_2SO_4). Removal of ether in a rotary evaporator and distillation or recrystallization of the residue gave the pure triazenes 1. Infrared, ^1H NMR, and mass spectrometry data for aromatic triazenes **1a**,[15] **1b**,[10] **1c**,[10] **1e**,[10] **1f**,[10] and **1g–j**[16] were consistent with the structures.

1-(4-Methoxyphenyl)-3,3-diethyl-1-triazene (1d): yield 93%; bp 104–105 °C (0.3 mm); IR (neat) 2980, 2940, 2840, 1600, 1580, 1500, 1450, 1410, 1350, 1240, 1200, 1160, 1100, 1040, 840, 750 cm^{-1}; NMR ($DCCl_3$) 1.24 (t, 6 H, J = 7.1 Hz), 3.72 (q, 4 H, J = 7.2 Hz), 3.80 (s, 3 H), 6.86 (d, 2 H, J = 9.0 Hz), 7.36 (d, 2 H, J = 9.0 Hz). Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.72; H, 8.27; N, 20.28. Found: C, 63.87; H, 8.35; N, 20.60.

General Procedure for the Preparation of Aryl Iodides. To a suspension of NaI (1.1 mmol), dry sulfonic acid resin (H^+ form, Bio-Rad AG 50W-X12, 0.6–1.0 g, 3–5 mequiv), and dry acetonitrile (4 mL) at 75 °C was added dropwise over a period of 3 min a solution of the triazene (1.0 mmol) in dry acetonitrile (0.5 mL), and the mixture was stirred for an additional 5 min, cooled to room temperature, and filtered. The residue was washed with boiling dichloromethane (5 × 2 mL) and then with boiling methanol (2 × 2 mL). The filtrate and the washings were combined, the solvents were evaporated, and the crude residue was chromatographed on a silica gel column using a 5% pentane–ether mixture as eluent to give the pure aryl iodide (Table I).

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Registry No. **1a**, 13056-98-9; **1b**, 36719-44-5; **1c**, 36719-51-4; **1d**, 36719-69-4; **1e**, 79664-67-8; **1f**, 86452-55-3; **1g**, 52010-59-0; **1h**, 52010-62-5; **1i**, 20942-49-8; **1j**, 10125-39-0; **2a**, 591-50-4; **2b**, 615-37-2; **2c**, 624-31-7; **2d**, 696-62-8; **2e**, 3058-39-7; **2f**, 13329-40-3; **2g**, 637-87-6; **2h**, 589-87-7; **2i**, 645-00-1; **2j**, 636-98-6; benzene, 71-43-2; methoxybenzene, 100-66-3; acetylbenzene, 98-86-2; aniline, 62-53-3; *o*-methylaniline, 95-53-4; *p*-methylaniline, 106-49-0; *p*-methoxyaniline, 104-94-9; *p*-cyanoaniline, 873-74-5; *p*-acetylaniline, 99-92-3; *p*-chloroaniline, 106-47-8; *p*-bromoaniline, 106-40-1; *m*-nitroaniline, 99-09-2; *p*-nitroaniline, 100-01-6; diethylamine, 109-89-7; Bio-Rad AG 50W-X12, 50922-25-3.

Efficient Hydrodehalogenation of Halo Aromatic Compounds on Sulfided $CoO/MoO_3/Al_2O_3$ and $NiO/MoO_3/Al_2O_3$ Catalysts

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Halo aromatic compounds are produced industrially in very large quantities and are widely used. Consequently, they are found in numerous industrial wastes and in the environment. Hydrodehalogenation reactions have great potential for the detoxification of these compounds. For such reactions, transitions metals, in particular palladium, have been used as catalysts.[1-3] Nonetheless, for hydrodehalogenation of a number of industrial wastes (polychlorinated biphenyl and chloroanilines), it would be interesting to use cheaper, effective catalysts, which are less sensitive to interfering materials.

In our studies on the hydrodesulfurization of halogenated benzo[*b*]thiophenes using sulfided $CoMo/MoO_3/Al_2O_3$ as the catalyst, we noticed that dehalogenation occurred prior to either hydrogenation or desulfurization.[4-6] From these studies, we concluded that inexpensive and common industrial hydrodesulfurization catalysts could be used for selective dehalogenation.

In the present study we report on the hydrodehalogenation of various aromatic halides: benzyl, phenyl, naphtyl, benzo[*b*]thiophene derivatives, using the same experimental conditions as for the hydrodesulfurization (HDS) process.

Results and Discussion

All reactions were found to be first order. The half-life values ($t_{1/2}$ are listed in Table I at $P(H_2)$ = 50 atm and 250 °C. The product of the dehalogenation reaction was obtained in very good yield for most of the reactants studied: for **1–7** only one product, the corresponding hydrocarbon, was formed; we observed no hydrogenation. For phenacyl bromide (**8**), under the reaction conditions 250 °C and 50 atm, ethylbenzene was obtained very rapidly. Lowering the experimental conditions to 100 °C and 30 atm, it was possible to obtain a good yield of acetophenone with only traces of ethylbenzene and 1-phenylethanol. For the halobenzothiophenes **9–14**, dehalogenation occurred before hydrogenation or hydrogenolysis of the C–S bond.[6] Once all the starting material had been dehalogenated, the observed products were benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, and ethylbenzene, 95:5:traces for **9–11** and 65:25:15 for **12** and **13**. For the sulfone **14**, decomposition of the reactant occurred, whereas at 190 °C and 50 atm the observed products were benzothiophene *S,S*-dioxide and 2,3-dihydrobenzo[*b*]thiophene *S,S*-dioxide. In all these cases (**9–14**), if the reaction was allowed to proceed further, ethylbenzene was obtained.

It should be noted that the bromo derivatives reacted faster than the chloro analogues. This difference in reactivity was lower for benzene and naphthalene than for the benzo[*b*]thiophenes. In the latter case, this was probably due to the electrophilic character of the sulfur atom.[8] Benzyl bromide reacted faster than (2-bromoethyl)benzene as expected on the basis of previous studies concerning the vinylic character of the benzyl derivatives.[9] The reactivity of the α-naphthyl bromide was studied in

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