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

Marc Bonnet, Patrick Geneste,* Alain Guida, and
David Mampouya

Laboratoire de Chimie Organique Physique Appliquée (ERA 954), Ecole Nationale Supérieure de Chimie de Montpellier, 34075 Montpellier Cedex, France

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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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Table I. Half-Life Values for Hydrodehalogenation of Halo Aromatic Products in the Presence of $CoO/MoO_3/Al_2O_3$ Hydrodesulfurization Catalyst[a]

compd	$t_{1/2}$, min	products[b]
1, phenyl chloride	49	benzene
2, phenyl bromide	43	benzene
3, α-naphthyl chloride	38	naphthalene
4, α-naphthyl bromide	29	naphthalene
5, benzyl chloride	2	toluene
6, benzyl bromide	2	toluene
7, (2-bromoethyl)benzene	5	ethylbenzene
8, phenacyl bromide	2	ethylbenzene
9, 2-bromobenzo[*b*]thiophene	6	benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, ethylbenzene
10, 3-bromobenzo[*b*]thiophene	6	benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, ethylbenzene
11, 2,3-dibromobenzo[*b*]thiophene	4	benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, ethylbenzene
12, 3-chlorobenzo[*b*]thiophene	23	benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, ethylbenzene
13, 2,3-dichlorobenzo[*b*]thiophene	18	benzo[*b*]thiophene, 2,3-dihydrobenzo[*b*]thiophene, ethylbenzene
14, 3-bromobenzo[*b*]thiophene *S*,*S*-dioxide[c]	0.6	benzo[*b*]thiophene *S*,*S*-dioxide, 2,3-dihydrobenzo[*b*]thiophene *S*,*S*-dioxide

[a] $P(H_2) = 50$ atm; $t = 250$ °C; wt % of S based on charge = 0.3 in dodecane, decane, or Decalin. [b] For **9-14**, see text for data on the relative percentages of the products formed. [c] This rate was measured by competition with **10** at 190 °C and 50 atm.

Table II. Half-Life Values for Hydrodehalogenation of α-Naphthyl Bromide over Different Catalysts[a]

catalyst	$t_{1/2}$, min
Co-Mo unsulfurized (HR 306)	690
Co-Mo sulfurized (HR 306)	29
Ni-Mo sulfurized (HR 346)	19

[a] $P(H_2) = 50$ atm; $t = 250$ °C; wt % of S based on charge = 0.3 in dodecane.

the presence of different catalysts: sulfided and unsulfided HR 306 (Co–Mo) and sulfided HR 346 (Ni–Mo), under the same conditions as described below. In all cases naphthalene was the only product formed, and all the reactions were first order. The half-life values are listed in Table II.

The unsulfided HR 306 catalyst (Co–Mo) was at least 20 times less active than the sulfided one; in other words, for hydrodehalogenation, the active catalytic species is the sulfurized one as in HDS. The slight difference between the activity of sulfided Co–Mo (HR 346) catalysts is probably due to the better hydrogenating ability of the Ni–Mo catalyst.[10]

Experimental Section

The catalysts were desulfurization catalysts used industrially, HR 306 and HR 346, obtained from Procatalyse, having the following composition $CoO/MoO_3/Al_2O_3$ (3:14:83, w/w) and $NiO/MoO_3/Al_2O_3$ (3:14:83, w/w), respectively; the pressure was 1 atm; the gas flow rate was 100 l/h per 80 g of catalyst, and the initial temperature was 150 °C. It was increased from 150 to 350 °C and maintained at 350 °C for 2 h.

The halo compounds and the catalyst were introduced into the reactor in a dodecane, decane, or Decalin solution. The apparatus used was an agitated autoclave of 0.3-L capacity. This autoclave was equipped with sample inlets, was heated by an external oven, and could be agitated at different speeds. The characteristics of this batch operation have been given by elsewhere.[7] Air was removed by purging with nitrogen at 5-atm pressure. Hydrogen was introduced at 10–15 °C below the working temperature (usually 250 °C). For all the experiments the product content was kept at 0.3 wt % of the charge. All products were analyzed by gas–liquid chromatography and identified by comparison with reference samples (IR, ^1H NMR, and ^{13}C NMR spectra).

Registry No. **1**, 108-90-7; **2**, 108-86-1; **3**, 90-13-1; **4**, 90-11-9; **5**, 100-44-7; **6**, 100-39-0; **7**, 103-63-9; **8**, 70-11-1; **9**, 5394-13-8; **10**, 7342-82-7; **11**, 6287-82-7; **12**, 7342-86-1; **13**, 5323-97-7; **14**, 16957-97-4; CoO, 1307-96-6; MoO_3, 1313-27-5; NiO, 1313-99-1; benzene, 71-43-2; naphthalene, 91-20-3; toluene, 108-88-3; ethylbenzene, 100-41-4; benzo[*b*]thiophene, 95-15-8; 2,3-dihydrobenzo[*b*]thiophene, 4565-32-6; benzo[*b*]thiophene *S*,*S*-dioxide, 825-44-5; 2,3-dihydrobenzo[*b*]thiophene *S*,*S*-dioxide, 14315-13-0.

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Reaction of Various Nucleophiles with 2-Bromo-*p*-xylene and 4-Bromoveratrole via Aryne Reaction

Han Yu Xin and Edward R. Biehl*

Chemistry Department, Southern Methodist University, Dallas, Texas 75275

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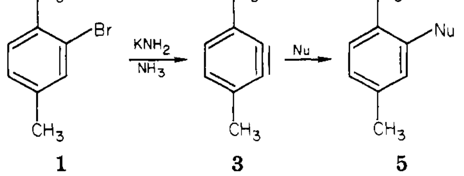
The orientation and reactivity of monosubstituted arynes has been studied extensively;[1] however, little has been reported on such investigations of polysubstituted arynes. By selecting appropriately substituted aryne precursors, high yields of a pure product should be obtained. This paper reports on the aryne reaction of two such compounds, 2-bromo-*p*-xylene, **1**, and 4-bromoveratrole, **2**, with primary and secondary amines, aliphatic nitriles, and potassium amide as base.

Compound **1** will yield the symmetrically substituted aryne 3,6-dimethylbenzyne, **3**, which will yield only 2-substituted *p*-xylenes upon nucleophilic addition. On the other hand, **2** should afford predominately 3,4-dimeth-



1 **3** **5**

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