to different extents and in different ways, on window and cell materials, and then combining to provide product.

Conclusion

At total pressures between 2 and 7 atm and temperatures between 283 and 313 K, the gaseous isomeric (*Z*)- and (*E*)-2-butenes react with hydrogen chloride gas to produce gaseous 2-chlorobutane. The addition of hydrogen chloride to the alkene, monitored by infrared spectroscopy, appears to be independent of the geometry of the alkene, mostly antarafacial across the double bond, and a surface-catalyzed process.

Registry No. (*E*)-2-Butene, 624-64-6; (*Z*)-2-butene, 590-18-1; 2-chlorobutane, 78-86-4; D_2, 7782-39-0.

Aryl Arylazo Sulfones Chemistry. 2. Reactivity toward Alkaline Alkane- and Areneselenolate and Alkane- and Arenetellurolate Anions

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Tolyl arylazo sulfones react with various alkyl- and arylseleno reagents to produce substituted alkyl aryl and unsymmetrical diaryl selenides. The corresponding tellurides can also be obtained. Isolated yields in both cases are good. This procedure is an interesting alternative to the classical Sandmeyer reaction.

Aryl arylazo sulfones have been studied from the point of view of their thermal and photochemical stability.[1] Only a few reports have been published about their chemical reactivity.[2]

Very recently, we described the reaction of various arylazo *p*-tolyl sulfones toward the iodide anion, leading, in acetonitrile solution, to the corresponding iodoarenes.[3] That method competes effectively with the one using iodine and arene diazonium tetrafluoroborates[4] or the other conventional methods using potassium iodide aqueous solutions.

The synthesis of alkyl (or aryl) phenyl selenides as well as their corresponding telluro derivatives is of increasing interest.[5]

Recently, Petrillo et al.[6] reported an easy preparation of symmetrical and unsymmetrical diaryl sulfides from arenethiolates and arenediazonium tetrafluoroborates.

Here, we want to disclose new information about the reactivity of arylazo *p*-tolyl sulfones toward alkaline alkane- and areneselenolate or alkane- and arenetellurolate anions.

Results and Discussion

The addition of sodium or lithium methaneselenolate anion (1 equiv), at room temperature to a solution in acetonitrile, of various arylazo *p*-tolyl sulfones **2a–h** in the presence of a catalytic amount of 18-crown-6 (method C), leads to the formation of the corresponding aryl methyl selenides **3a–h** with isolated yields ranging from 38% to 59% (Scheme I; Table I, entries 6–13).

Table I. Reaction of Alkaline Alkane- and Areneselenolate Anion with Aryl *p*-Tolylazo Sulfones 2a–m

	aryl *p*-tolylazo sulfones		nucleophilic species	exptl cond[a,b]	yield of **3**, **4**, or **5**[c] from **2**, %
entry	2	Y			
1	**a**	2-$COOCH_3$	CH_3SeLi	A	0[d]
2	**a**	2-$COOCH_3$	CH_3SeLi	B	5
3	**a**	2-$COOCH_3$	CH_3SeLi	C	52 (28)
4	**a**	2-$COOCH_3$	CH_3SeLi	D	38
5	**a**	2-$COOCH_3$	CH_3SeNa	D	25
6	**a**	2-$COOCH_3$	CH_3SeNa	C	54
7	**b**	H	CH_3SeNa	C	56 (32)
8	**c**	3-$COOC_2H_5$	CH_3SeNa	C	58 (30)
9	**d**	4-$COOC_2H_5$	CH_3SeNa	C	59 (48)
10	**e**	3-Cl	CH_3SeNa	C	54 (22)
11	**f**	3,5-Cl_2	CH_3SeNa	C	48 (38)
12	**g**	4-NO_2	CH_3SeNa	C	56 (32)
13	**h**	3,5-$(OCH_3)_2$	CH_3SeNa	C	52 (35)
14	**a**	2-$COOCH_3$	*n*-C_4H_9SeLi	A	0
15	**a**	2-$COOCH_3$	*n*-C_4H_9SeLi	C	55 (51)
16	**b**	H	*n*-C_4H_9SeLi	C	50 (38)
17	**e**	3-Cl	*n*-C_4H_9SeLi	C	43 (32)
18	**g**	4-NO_2	*n*-C_4H_9SeLi	C	46 (29)
19	**h**	3,5-$(OCH_3)_2$	*n*-C_4H_9SeLi	C	46 (26)
20	**i**	2-Cl	*n*-C_4H_9SeLi	C	42 (37)
21	**j**	2-CN	*n*-C_4H_9SeLi	C	48 (43)
22	**k**	2-OCH_3	*n*-C_4H_9SeLi	C	42 (37)
23	**b**	H	C_6H_5SeLi	C	70
24	**e**	3-Cl	C_6H_5SeLi	C	37
25	**g**	4-NO_2	C_6H_5SeLi	C	53
26	**l**	2-NO_2	C_6H_5SeLi	C	48
27	**m**	4-I	C_6H_5SeLi	C	10[e]

[a] All experiments are realized in the presence of a catalytic amount of 18-crown-6. [b] A: in tetrahydrofuran solution, room temperature or reflux, 1 equiv of nucleophile. B: in tetrahydrofuran–CH_3CN (50:50) solution, room temperature, 1 equiv of nucleophile. C: in CH_3CN solution, room temperature, 1 equiv of nucleophile. D: same as in C but with 2 equiv of nucleophile. [c] Isolated. The corresponding yield is given in parentheses when the tetrafluoroborate method is used. [d] When heating, methyl benzoate is obtained (35%). [e] 1,4-$(C_6H_5Se)_2C_6H_4$ is isolated (21%) as the major product.

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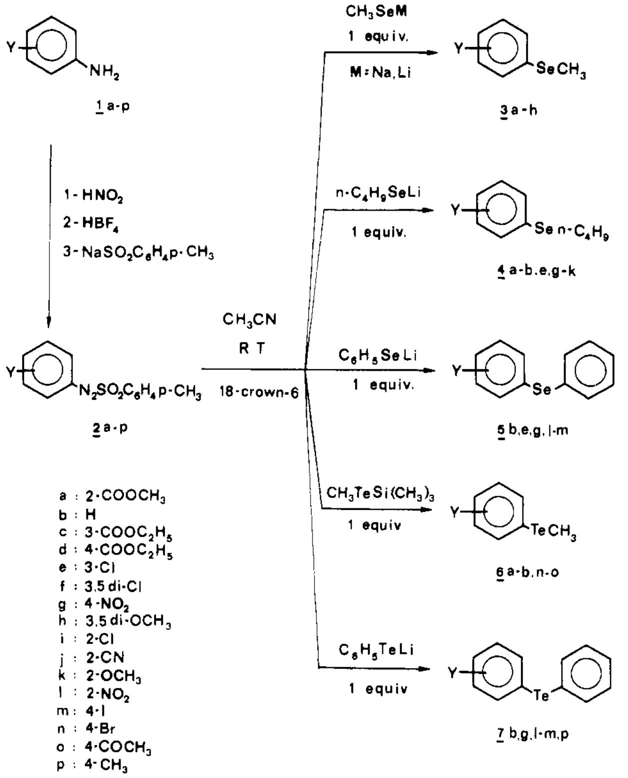
0022-3263/86/1951-5196$01.50/0

Scheme I



In preliminary experiments with **2a,b,h**, we have observed the drastic influence of the solvent on the reaction. When tetrahydrofuran is used, the starting arylazo *p*-tolyl sulfones **2a,b,h** are recovered unchanged at room temperature and only tars are obtained under prolonged refluxing conditions. Replacing THF by dimethylformamide leads to the already published deazosulfonation of **2a,b,h**.[3] If acetonitrile is used without 18-crown-6, yields are lower (typically 10–30%).

The use of sodium or lithium salts seems to make no difference and give nearly the same yields (Table I, entries 3–6). When an excess of methaneselenolate anion is employed, yields in isolated products are lower, due to the difficulties encountered during the purification procedures.[7]

The replacement of sodium methaneselenolate by lithium *n*-butaneselenolate furnishes the corresponding *n*-butyl aryl selenides **4a,b,e,g,h** (Scheme I; Table I, entries 14–22).

The case of the (3,5-dimethoxyphenyl)azo *p*-tolyl sulfone (**2h**) (Table I, entry 19) constitutes a new synthesis of the dimethyl ether of 1′-selenaolivetol, an important intermediate for the synthesis of 3-selena cannabinoids.

The use of sodium benzeneselenolate in place of alkaneselenolates affords a new synthesis of asymmetric aryl phenyl selenides **5b,e,g,l,m** (Scheme I; Table I, entries 23–27). Particularly noteworthy is the case of (4-iodophenyl)azo *p*-tolyl sulfone (**2m**), which furnishes predominantly 1,4-bis(phenylseleno)benzene (Table I, entry 27).

All the aryl *p*-tolyl sulfones **2a–m** are obtained from the corresponding arenediazonium tetrafluoroborates.[8] Those are found to react with dialkyl diselenides and dialkyl ditellurides to give compounds **3**, **4**, or **6**.[9] Compared to the tetrafluoroborate procedure, our yields are at least competitive or better, without using an excess of organoselenium reagent.

Table II. Reaction of Telluro Nucleophiles with Aryl *p*-Tolyl Sulfones 2a

entry	aryl *p*-tolylazo sulfones 2		nucleophilic species	exptl cond[a,b]	yield[c] of 6 or 7 from 2, %
	2	Y			
1	**a**	2-COOCH$_3$	CH$_3$TeSi(CH$_3$)$_3$	E	48
2	**b**	H	CH$_3$TeSi(CH$_3$)$_3$	E	62
3	**n**	4-Br	CH$_3$TeSi(CH$_3$)$_3$	E	36
4	**o**	4-COCH$_3$	CH$_3$TeSi(CH$_3$)$_3$	E	53
5	**b**	H	C$_6$H$_5$TeLi	C	41
6	**g**	4-NO$_2$	C$_6$H$_5$TeLi	C	26
7	**l**	2-NO$_2$	C$_6$H$_5$TeLi	C	32
8	**m**	4-I	C$_6$H$_5$TeLi	C	36
9	**p**	4-CH$_3$	C$_6$H$_5$TeLi	C	38

[a] All experiments are performed in the presence of a catalytic amount of 18-crown-6. [b] C: in CH_3CN solution, room temperature, 1 equiv of nucleophile. E: in CH_3CN solution, room temperature, 1 equiv of $CH_3TeSi(CH_3)_3$ generated in situ. [c] Isolated.

Furthermore, we have successfully extended the above reaction to the methyltellurodeazosulfonation of aryl *p*-tolyl sulfones **2a,b,n,o** using (methyltelluro)trimethylsilane generated "in situ"[10] as the source of the methyltelluro function (Scheme I; Table II, entries 1–4). This affords a new synthesis of substituted telluroanisoles **6a,b,n,o**. Yields are good compared to those obtained with the tetrafluoroborate procedure (typically 30–50%).

The direct use of lithium methanetellurolate (generated in THF from methyllithium and elemental tellurium) was unsuccessful because, during the absolutely necessary change of THF to acetonitrile, a mixture of dimethyl telluride and dimethyl ditelluride is formed to the detriment of the methanetellurolate anion, and we have observed that those species are inert toward arylazo *p*-tolyl sulfones.

Interestingly, unsymmetrical diaryl monotellurides **7b,g,l,m,p** are obtained when lithium benzenetellurolate is mixed with arylazo *p*-tolyl sulfones (Table II, entries 5–9). This constitutes an important improvement of the reaction between the corresponding arenediazonium tetrafluoroborate and telluroanisole or tellurophenetole, which leads, because of the radical nature of the mechanism of this last reaction, to a mixture of diphenyl telluride, diaryl telluride, and diaryl ditelluride, laboriously separated.

Finally, we have studied the reactivity of aryl *p*-tolyl sulfones toward other nucleophilic species of group VIB (16),[13] such as potassium selenocyanate, sodium methoxide, sodium ethanethiolate, and sodium acetate (condition C). This furnishes mixtures of deazosulfonation products and starting material **2**. These last results and particularly the one with sodium methoxide parallel the observations of Bunnett et al.[11] who found that (2-halogenoarylazo aryl

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(7) In fact, an important amount of dimethyl diselenide is produced under those experimental conditions.

(8) Ahern, M. F.; Leopold, A.; Beadle, J. P.; Gokel, G. W. *J. Am. Chem. Soc.* **1982**, *104*, 548.

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(10) (Methyltelluro)trimethylsilane is generated in situ in THF solution from lithium methanetellurolate and trimethylsilyl chloride. THF has to be completely replaced by acetonitrile before adding the azo sulfone otherwise reagents are recovered unchanged.

(11) Bunnett, J. F.; Happer, D. A. R. *J. Org. Chem.* **1967**, *32*, 2701.

(12) Characterizing data for new tolyl arylazo sulfones are given as follows. Compound number: melting point (corrected); IR (KBr); ^{1}H NMR data (δ, $CDCl_3$/HMDSO). **2a**: 112–114 °C; $\nu_{C=O}$ 1730 cm^{-1}; δ 2.40 (s, ArCH_3), 3.65 (s, OCH_3), 7.40–8.30 (m, H_{Ar}). **2c**; 106–108 °C; $\nu_{C=O}$ 1710 cm^{-1}; δ 1.26 (t, CH$_2$CH_3, J = 7 Hz), 2.39 (s, ArCH_3), 4.25 (q, CH_2CH$_3$, J = 7 Hz), 7.00–8.30 (m, H_{Ar}). **2d**: 106–108 °C; $\nu_{C=O}$ 1715 cm^{-1}; δ 1.26 (t, CH$_2$CH_3, J = 7.5 Hz), 2.33 (s, ArCH_3), 4.35 (q, CH_2CH$_3$, J = 7.5 Hz), 7.05–8.06 (m, H_{Ar}). **2f**: 136 °C; δ 2.43 (s, ArCH_3), 7.30–8.35 (m, H_{Ar}). **2h**: 129 °C; δ 2.38 (s, ArCH_3), 3.78 (s, (OCH_3)$_2$), 6.29–7.80 (m, H_{Ar}). **2j**: 131–132 °C; $\nu/_{C\equiv N}$ 2240 cm^{-1}; δ 2.33 (s, ArCH_3), 7.00–7.74 (m, H_{Ar}). **2k**: 99–100 °C; δ 2.30 (s, ArCH_3), 3.68 (s, OCH_3), 6.55–7.80 (m, H_{Ar}). **2m**: 106 °C; δ 2.48 (s, ArCH_3), 6.48–7.86 (m, H_{Ar}). **2o**: 116–118 °C; $\nu_{C=O}$ 1690 cm^{-1}; δ 2.30 (s, ArCH_3), 2.45 (s, COCH$_3$), 7.25–8.45 (m, H_{Ar}).

sulfones are deazosulfonated under nearly identical conditions.

Work is now in progress to study the reactivity of nucleophiles derived from the fourth and the fifth families of the periodic chart.

Experimental Section

General Method. All the known compounds cited in this paper have been fully characterized through melting point, ^{1}H NMR, MS, and thin-layer chromatography. Tolyl arylazo sulfones have been synthesized according to Ahern.[8] New tolyl arylazo sulfones **2a,c,d,f,j,k,m,o** gave satisfactory elemental analysis (C, ± 0.27; H, ± 0.25) and significant characterization data are given below.[12] Sodium methaneselenolate was obtained from methaneselenol and sodium methoxide in methanol solution. Dry sodium methaneselenolate was obtained after elimination of the methanol under reduced pressure. The lithium salt of methane-, butane- and benzeneselenol were prepared from commercial methyl-, butyl-, or phenyllithium in hexane solution and elemental selenium in tetrahydrofuran suspension. After elimination of the solvents under reduced pressure, the residual solids were dissolved in acetonitrile. The trimethylsilyl derivative of methanetellurol was generated in situ from commercial methyllithium in ether, elemental tellurium in tetrahydrofuran suspension, and trimethylsilyl chloride. The following procedures are representative.

Synthesis of *o*-(Methoxycarbonyl)selenoanisole (3a). A mixture of 3.18 g (10 mmol) of **2a**, 50 mg of 18-crown-6, 1.18 g (10 mmol) of sodium methaneselenolate, and 150 mL of acetonitrile was stirred for 8 h at room temperature. The reaction mixture was poured into water (300 mL) and extracted with ether (3 × 100 mL). The mixed organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography using a mixture of $CHCl_3$–C_6H_6 (15:85) as eluent.

Synthesis of 4-Bromotelluroanisole (6n). To a suspension of 1.27 g (10 mmol) of elemental tellurium in 60 mL of THF was added 11 mmol of methyllithium in ether solution in 10 min at room temperature. The excess of methyllithium was destroyed by adding 1 mL of propanone. Trimethylsilyl chloride (1.09 g, 1.27 mL) was added in one portion and the mixture allowed to stand for 10 min. Volatile materials were eliminated under reduced pressure before redissolving the solid residue obtained in 120 mL of acetonitrile. After addition of 50 mg of 18-crown-6 and 3.49 g of **2n** and being stirred during 8 h at room temperature, the reaction mixture was poured into water (300 mL) and extracted with ether (3 × 100 mL). The mixed organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography using a mixture of $CHCl_3$–C_6H_6 (15:85) as eluent.

Registry No. **2a**, 105230-44-2; **2b**, 26788-89-6; **2c**, 105230-45-3; **2d**, 105230-46-4; **2e**, 105230-47-5; **2f**, 105230-48-6; **2g**, 38568-60-4; **2h**, 105230-49-7; **2i**, 60095-84-3; **2j**, 105230-50-0; **2k**, 95765-82-5; **2l**, 60095-87-6; **2m**, 105230-51-1; **2n**, 33604-66-9; **2o**, 105230-52-2; **2p**, 33604-67-0; **3a**, 78377-06-7; **3b**, 4346-64-9; **3c**, 105230-53-3; **3d**, 3757-99-1; **3e**, 1694-00-4; **3f**, 105230-54-4; **3g**, 43022-52-2; **3h**, 105230-55-5; **4a**, 105230-56-6; **4b**, 28622-61-9; **4e**, 10520-57-7; **4g**, 105230-58-8; **4h**, 86297-09-8; **4i**, 105230-59-9; **4j**, 105230-60-2; **4k**, 105230-61-3; **5b**, 1132-39-4; **5e**, 105230-62-4; **5g**, 6343-83-5; **5l**, 65848-40-0; **5m**, 105230-63-5; **6a**, 105230-64-6; **6b**, 872-89-9; **6n**, 28192-39-4; **6o**, 32294-61-4; **7b**, 1202-36-4; **7g**, 79424-71-8; **7l**, 79424-69-4; **7m**, 105230-65-7; **7d**, 56950-00-6; CH_3SeLi, 50491-55-9; CH_3SeNa, 37773-10-7; BuSeLi, 55163-69-4; PhSeLi, 52251-58-8; $Me_3SiTeCH_3$, 34117-12-9; PhTeLi, 52251-60-2; Te, 13494-80-9; CH_3Li, 917-54-4; Me_3SiCl, 75-77-4; 1,4-bis(phenylselenyl)benzene, 71672-72-5.

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(13) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Group IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Thioimidate *N*-Oxides: Nitrones of Thio Esters

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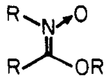
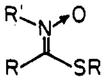
A group of three *C*-phenyl and three *C*-alkyl thioimidate *N*-oxides (nitrones of thio esters) was prepared by S-alkylation of *N*-alkylthiohydroxamic acids with methyl or ethyl iodide followed by basification of the resulting hydriodide salts. An X-ray crystallographic analysis of *S*-methyl *N*-methylthiobenzimidate *N*-oxide (**9Z**) established the *Z* stereochemistry for the more stable isomer. The ^{1}H NMR, ^{13}C NMR, IR, and UV spectral properties of the thio ester nitrones are reported. The *E*/*Z* stereochemistry of the *C*-alkyl derivatives is tentatively assigned on the basis of NOE measurements, long-range coupling, and chemical shift correlations. Thermal equilibration in bromobenzene-d_5 at 80 °C gave the following *E*/*Z* ratios: *C*-phenyl, 5:95; *C*-methyl, 46:54; *C*-ethyl, 53:47; *C*-isopropyl, 83:17. The equilibrium values are rationalized in terms of a balance between electronic stabilization and steric destabilization of the *Z* isomers. Hydrolysis of **9Z** in aqueous acid at 100 °C gave *S*-methyl thiobenzoate and *N*-methylhydroxylamine, whereas basic hydrolysis at 100 °C afforded *N*-methylbenzohydroxamic acid as the principal initial product.

The chemistry of nitrones derived from aldehydes and ketones has been extensively explored(1) since the first members of this family of dipolar compounds were reported.(2) In contrast, nitrones of esters (imidate *N*-oxides, A) and thio esters (thioimidate *N*-oxides, B) have appeared only infrequently in the recent literature. The preparation and dipolar cycloaddition reactions of the cyclic analogues, oxazoline and oxazine *N*-oxides, have been described,(3) and



A



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