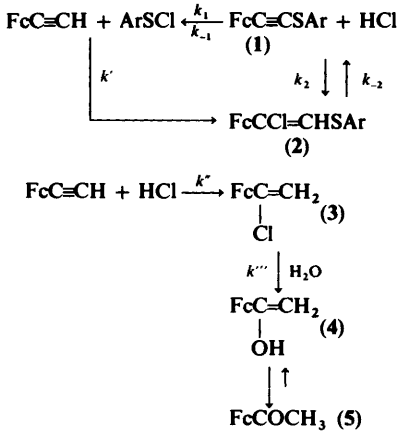
Reaction of Ethynylferrocene with Arenesulphenyl Chlorides[1]

Barbara Floris* and Gabriello Illuminati
Centro C.N.R. di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Università 'La Sapienza,' P. le A. Moro 2, I-00185 Rome

The reaction of ethynylferrocene with arenesulphenyl chlorides [ArSCl; Ar = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$NO_2C_6H_4$, or 2,4-$(NO_2)_2C_6H_3$] follows an unusual pathway; the main outcome is substitution of the acetylenic proton, rather than electrophilic addition to the triple bond. The following compounds were isolated and identified: FcC≡CSAr, FcCCl=CHSAr, and $FcCCl=CH_2$ or $FcCOCH_3$ (Fc = ferrocenyl), depending on the reaction conditions. A mechanistic scheme is proposed.

In the course of our investigation aimed at providing a quantitative basis for the reactivity of the ferrocene system with electrophilic reagents, the kinetics of addition to the double bond of vinylferrocenes were studied.[2–4] The ferrocene derivatives turned out to be more reactive than the corresponding benzene compounds, under comparable conditions, by a factor in the range 22—640. Since we considered that a quantitative comparison of alkene *vs.* alkyne reactivity might be useful in elucidating the mechanism of the addition reactions,[5] we then began to investigate the behaviour of a carbon–carbon triple bond linked to the ferrocenyl moiety.[6] Aside from mercury(II) acetate, arenesulphenyl chlorides (ArSCl) are among the most suitable electrophilic reagents for ferrocene derivatives, because they do not oxidize iron and, moreover, undergo the addition reaction through a bridged intermediate cation.[5,7] We now report the unusual behaviour of ethynylferrocene, when treated with arenesulphenyl chlorides.



Scheme.

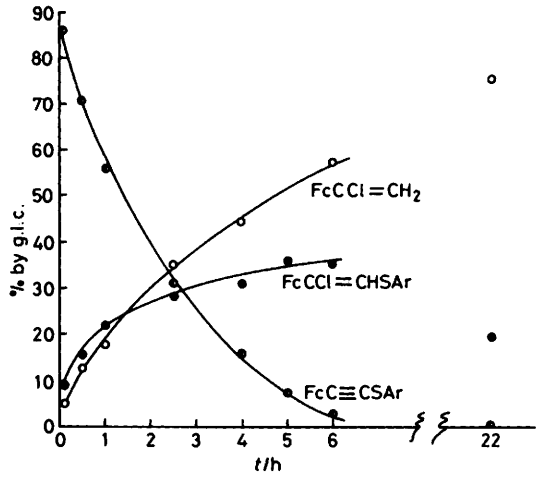
Results and Discussion

The addition of arenesulphenyl chlorides to alkynes is reported to proceed by a mechanism analogous to that for alkenes.[8] However, sometimes high temperatures and/or catalysts are necessary, apparently because the carbon–carbon bond length is shorter in alkynes than in alkenes, resulting in a higher degree of *p* orbital superposition.[8]

Ethynylbenzene adds sulphenyl chlorides at about 1/100 times the rate for styrene (ArSCl = 2,4-dinitrobenzenesulphenyl chloride[9] or *p*-chlorobenzesulphenyl chloride[10]). Apart for some controversy about the regiochemistry of the addition,[11] no anomaly has been observed, ethynylbenzene adding ArSCl with a solvent-dependent orientation[12] and *trans* stereochemistry.[13] Markovnikov and anti-Markovnikov adducts were the only products detected.

Surprisingly, when we treated ethynylferrocene with 2,4-dinitrobenzenesulphenyl chloride in dichloromethane, considerable amounts of acetylferrocene were isolated. On the other hand, the expected addition product was isolated from the reaction between ethynylferrocene and *p*-chlorobenzenesulphenyl chloride, but the reaction appeared to be a complicated one, since the ^1H n.m.r. spectrum, run immediately after mixing equimolar solutions of the reagents, showed complete disappearance of the acetylenic proton, whereas the signals due to the final adduct appeared only after some time. The existence of a process preceding the formation of the expected adduct was confirmed by electronic spectra. The absorbance in the range 550—350 nm changed abruptly after the reagents were mixed, then slowly changed to the spectrum of the adduct or to that of acetylferrocene.

On the basis of the results from g.l.c., mass spectrometry, and preparative experiments, the course of reaction shown in the Scheme may be deduced. Upon mixing equimolar amounts of ethynylferrocene and *p*-chlorobenzenesulphenyl chloride in anhydrous CH_2Cl_2, the reagents disappeared within 5 min (Figure), with formation of *p*-chlorophenylthio(ferrocenyl)-ethyne (**1**) (86% by g.l.c.). Further reaction yielded 1-chloro-1-ferrocenylethene (**3**) and 1-chloro-2-(4-chlorophenylthio)-1-ferrocenylethene (**2**), the latter being formed in larger amounts in the early stages of the reaction, while the former was the main product at the end, *i.e.* when (**1**) was no longer present (Figure).



Gas chromatographic analysis of the reaction between ethynylferrocene and *p*-chlorobenzenesulphenyl chloride in CH_2Cl_2

Such a complex pattern may be explained in terms of a preliminary fast equilibration between the reactants and the initial products, characterized by $k_1 \gg k_{-1}$. The hydrogen chloride formed may react more slowly with the sulphide (1), yielding a product that simulates that of a direct arenesulphenyl chloride addition. On the other hand, if k_{-1} and k_2 are similar, HCl adds to the ethynylferrocene formed through the return reaction (k_{-1}), more rapidly than to (1), *i.e.* if $k'' > k_2$, then it is understandable that 1-chloro-1-ferrocenylethene is the main product. Moreover, the addition of HCl to (1) must be reversible, since on prolonged reaction the proportion of (2) decreased with a corresponding increase in the proportion of (3) (Figure)*.

When water was carefully excluded, as in the experiment represented in the Figure, 1-chloro-1-ferrocenylethene was formed in high yield. (It could be isolated, but quickly decomposed, even in the pure state, with a smell of hydrogen chloride.) If some water was present, (3) was rapidly hydrolysed to the enol (4), which, in turn, tautomerized to acetylferrocene (5).

Some direct addition of arenesulphenyl chloride to ethynylferrocene (*via k'*; see Scheme) may be inferred, since in the early stages of the reaction the proportion of (2) was higher than the proportion of (3). Compounds (1)—(3), as well as acetylferrocene, have been isolated and identified by ^{1}H n.m.r. and mass spectrometry.

When a hindered base, such as triethylamine, was present in the reaction medium, only two compounds were recovered: the substitution product (1), as the main species, and the addition product (2), in small amount. This experiment confirmed that direct addition of arenesulphenyl chloride takes place to some extent, and that hydrogen chloride is responsible for the other results.

When ArSCl is 2,4-dinitrobenzenesulphenyl chloride, a more hindered reagent, the trend of the reaction was analogous, but the ethynylferrocene disappeared more slowly (see Experimental section). Apparently, the steric hindrance of the electrophilic reagent caused a decrease in k_1. On the other hand, whereas k'' is the same as in the case of ArSCl = *p*-chlorobenzenesulphenyl chloride, k_2 is lowered by the electronic effects of the nitro groups on the triple bond of (1). Therefore (3) [and ultimately (5)] is the major product.

The reaction was performed with other ArSCl reagents (benzesulphenyl chloride, *p*-methylbenzenesulphenyl chloride, *p*-methoxybenzenesulphenyl chloride, and *p*-nitrobenzenesulphenyl chloride), with analogous results: compounds (1), (2), and (3) [or (5)] were isolated; (1) was the main product in the presence of Et_3N, with (2) as a side product.

If work-up of the reaction was delayed, some decomposition occurred, thus lowering the yields. However, when immediately purified, the reaction products were isolated quantitatively with respect to the starting materials. Unchanged ArSCl was recovered as the corresponding disulphide, ArSSAr.

A detailed kinetic investigation was not possible, owing to the complexity of the reaction. Nevertheless, the overall reaction, as observed by changes in electronic spectra with time, seems to follow a second-order law. Experiments were performed under pseudo-first-order conditions. Good linear plots were obtained at different wavelengths, both in 1,1,2,2,-tetrachloroethane and in acetic acid, the solvents used in order to allow a comparison with the reactivity of phenylacetylene.

The behaviour of ethynylferrocene with ArSCl is unprecedented. To the best of our knowledge, the previously reported reactions of terminal alkynes with arenesulphenyl chlorides yielded only addition products. Therefore, the unusual reactivity shown by ethynylferrocene must be related to its peculiar structure, and probably to the presence of the iron atom. Dreiding models indicate that an interaction between iron and the electrophilic sulphur atom might occur, but the presence of the benzene ring keeps sulphur in the proximity of the methyne group. This situation might lead to a transition state for the substitution reaction more stable (less hindered) than the bridged transition state of the addition. However, vinylferrocene reacted with ArSCl in the usual way.[4]

Experimental

^{1}H N.m.r. spectra were recorded with a Bruker WP-80 and a Varian EM-360 spectrometer, with $CDCl_3$ or CCl_4 as solvent and Me_4Si as internal standard.

Gas chromatographic analyses were performed with a Hewlett-Packard 5830 instrument, equipped with a 1 m 2% OV 17 Chromosorb GAW-DMCS column, or with a Varian Vista 6000 instrument, equipped with a 0.5 m 5% OV 101 Chromosorb GHP 100—200 column. Gas chromatographic–mass spectrometric analyses were performed with a Kratos MS 80 spectrometer. Both electronic impact and chemical ionization techniques were used, with the same results.

Materials.—Ethynylferrocene was prepared from acetylferrocene, by the method of Rosenblum.[14] 2,4-Dinitrobenzenesulphenyl chloride was obtained by chlorinolysis of benzyl 2,4-dinitrophenyl sulphide,[15] in turn prepared by treating 1-chloro-2,4-dinitrobenzene with phenylmethanethiol.[15] Benzene-, 4-chlorobenzene-, 4-methylbenzene-, 4-methoxybenzene-, and 4-nitrobenzene-sulphenyl chlorides were synthesized by treating the corresponding disulphides with sulphuryl chloride.[16] The disulphides were obtained by oxidizing the corresponding thiols,[17] or by treating 1-chloro-4-nitrobenzene with Na_2S_2.[18]

Commercial reagent grade dichloromethane was used, distilled over P_2O_5 when anhydrous conditions were necessary.

Reaction of Ethynylferrocene with p-*Chlorobenzenesulphenyl Chloride.*—(*a*) Ethynylferrocene (2 mmol) was treated with an equimolar amount of *p*-chlorobenzenesulphenyl chloride in anhydrous CH_2Cl_2 (20 ml) at room temperature under nitrogen. After stirring for 12 h, CH_2Cl_2 was removed with a nitrogen flux and gentle heating with a warm water-bath.

^{1}H N.m.r. in CCl_4 showed that the residue consisted of $FcCCl{=}CH_2$, $FcC{\equiv}CSAr$, and $FcCCl{=}CHSAr$ (Ar = *p*-chlorophenyl) in the ratios 1.1:1:1.1, respectively.

(*b*) The same experiment was carried out with commercial CH_2Cl_2. After 12 h stirring, the mixture was poured into water and extracted with CH_2Cl_2. The organic phase, washed twice with water, dried (Na_2SO_4), and evaporated, afforded $FcCOCH_3$, $FcC{\equiv}CSAr$, and $FcCCl{=}CHSAr$, approximately in the same ratio as in (*a*), with acetylferrocene replacing 1-chloro-1-ferrocenylethene.

(*c*) *Gas chromatographic analysis.* Equimolar amounts (1.06 mmol) of $FcC{\equiv}CH$ and ArSCl (Ar = *p*-chlorophenyl) in anhydrous CH_2Cl_2 (20 ml) were mixed at room temperature under nitrogen. With the inert atmosphere maintained, samples (1 μl) were taken at various time intervals and examined by g.l.c. The results are reported in the Figure. No acetylferrocene was detected under these conditions.

(*d*) *Gas chromatographic–mass spectrometric analysis.*

* A radical mechanism, involving a ferricenium species in the first step, with later formation of HCl, and $FcCCl{=}CH_2$ as the species formed in the last stage, has been suggested by a referee. However, this may be excluded on the following basis: (i) no ferricenium species has ever been detected; (ii) the reaction between $FcC{\equiv}CH$ and ArSCl was unaffected when performed in the presence of radical scavengers; and (iii) $FcCCl{=}CHSAr$ with anhydrous HCl yielded addition products only, with no trace of $FcCCl{=}CH_2$.

Table. Product analyses for the reaction between FcC≡CH and ArSCl in equimolar proportions, at room temperature

	FcC≡CH		FcC≡CSAr		FcCCl=CH_2		FcCCl=CHSAr		$FcCOCH_3$		Reaction
ArSCl	% by g.l.c.	Isolated yield (%)	% by g.l.c.	Isolated yield (%)	% by g.l.c.	Isolated yield (%)	% by g.l.c.	Isolated yield (%)	% by g.l.c.	Isolated yield (%)	time (h)
PhSCl	8		43.5		33		15				3
	1.5		22.5		40.5		35.5				6
	0.5		15.5		49		35				24
	0		15	5.4	44.5	38	40	22			48
p-$CH_3C_6H_4SCl$	10		90								0.02
	0		60 (g.l.c.)				40				22
								55.4		41.2	48
p-$CH_3OC_6H_4SCl$		66.5		2				31.5			24
p-$NO_2C_6H_4SCl$		19.2		24.7		40.3		8.8		6.4	12
PhSCl + Et_3N		38		61.5							24
p-$CH_3C_6H_4SCl$ + Et_3N[a]				91				5			24

[a] When an excess of *p*-$CH_3C_6H_4SCl$ was used, a small amount of FcCCl=$C(SAr)_2$ was observed (M^+ 490/492; *M* 490.89).

FcC≡CH (0.5 ml; 1.06M in CH_2Cl_2) and *p*-ClC_6H_4SCl (0.5 ml; 1.06M in the same solvent) were mixed in a vessel equipped with a Teflon septum. Samples were withdrawn by syringe at intervals and injected into a gas chromatograph. After 4 h, the mixture was analysed by g.l.c.–mass spectrometry. The following compounds were found: 1-chloro-1-ferrocenylethene (M^+ 246/248; *M* 246.52), *p*-chlorophenylthio(ferrocenyl)ethyne (FcC≡CSAr) (M^+ 352/354; *M* 352.66), 1-chloro-2-(4-chlorophenylthio)-1-ferrocenylethene (FcCCl=CHSAr) (M^+ 388/390; *M* 389.12), and the disulphide (ArSSAr) (M^+ 286/288; *M* 287.26). No acetylferrocene (*M* 228.07) was detected, thus confirming that the ketone comes from a side process, extraneous to the investigated reaction.

(*e*) To obtain information about the early stages of the reaction, FcC≡CH (0.5 mmol) was mixed with *p*-ClC_6H_4SCl (0.5 mmol) in anhydrous CH_2Cl_2 (5 ml), under nitrogen. Within 1 min, the mixture was poured over a silica gel column and chromatographed with light petroleum (b.p. 40—70 °C) and diethyl ether as eluants. The following species were eluted: FcC≡CSAr (0.06 mmol, 12%), FcCCl=CH_2 (0.10 mmol, 20%), FcC≡CH (0.24 mmol, 48%), and FcCCl=CHSAr (0.09 mmol, 18%), accounting in all for 98% of the initial mmol of ethynylferrocene.

^1H N.m.r. spectra in CCl_4 showed signals as follows: FcC≡CSAr δ 4.27 [7 H, s and br signal superimposed, unsubstituted cyclopentadienide (cp) ring and β-protons of the substituted cp ring], 4.53 (2 H, complex, α-protons of the substituted ring), and 7.38 (4 H, br s, aromatic); FcCCl=CH_2 δ 4.22 (7 H, s and br signal superimposed, unsubstituted and substituted cp ring), 4.43 (2 H, t, *J* 2.0 Hz, protons of the substituted cp ring), and 5.25 (1 H, d, *J* 1.4 Hz) and 5.47 (1 H, d, *J* 1.4 Hz, vinylic); FcCCl=CHSAr δ 4.26 (5 H, s, cp), 4.35 (2 H, t, *J* 2.0 Hz, β-protons of the substituted cp ring), and 4.87 (2 H, t, *J* 2.0 Hz, α-protons of the substituted cp ring), 6.47 (1 H, s, vinylic), and 7.38 (4 H, br, aromatic).

1-Chloro-1-ferrocenylethene readily decomposed; the n.m.r. spectrum broadened with time.

Another run, performed under the same conditions, but without particular precautions to avoid moisture, gave acetylferrocene [δ(CCl_4) 4.22 (5 H, s, cp), 4.50 (2 H, t) and 4.79 (2 H, t) (β- and α-protons of the substituted cp ring, respectively), and 2.41 (3 H, s, Me)] accompanied by a decreased quantity of FcCCl=CH_2.

(*f*) FcC≡CH *and* ArSCl (2:1). Ethynylferrocene (0.10 mmol) reacted with *p*-ClC_6H_4SCl (0.05 mmol) in anhydrous CH_2Cl_2 to yield a mixture containing unchanged ethynylferrocene, 1-chloro-1-ferrocenylethene, the substitution product FcC≡CSAr, and the adduct FcCCl=CHSAr, in the ratios 2:2:2:1, respectively. All the ArSCl reacted with the ferrocenyl compounds and was accounted for by the reaction products.

(*g*) FcC≡CH *and* ArSCl (1:2). FcC≡CH (0.05 mmol) and *p*-ClC_6H_4SCl (0.10 mmol) in anhydrous CH_2Cl_2 gave a mixture in which 50% of the starting ArSCl was accounted for by the reaction products (FcC≡CSAr and FcCCl=CHSAr, *ca.* 1:1) and the remaining 50% was recovered as the disulphide (ArSSAr). No ethynylferrocene remained unchanged.

(*h*) Blank experiments indicated that ArSCl is slowly converted into the disulphide ArSSAr. No reaction occurred when ethynylferrocene was treated with the disulphide.

(*i*) *In the presence of* Et_3N. FcC≡CH (0.01 mmol), *p*-ClC_6H_4SCl (0.1 mmol), and Et_3N (0.1 mmol) were mixed in anhydrous CH_2Cl_2 (2 ml). After 48 h FcC≡CSAr (95%) and FcCCl=CHSAr (4%) were recovered.

Reaction of Ethynylferrocene with 2,4-Dinitrobenzenesulphenyl Chloride.—FcC≡CH (1.4 mmol) and 2,4-dinitrobenzenesulphenyl chloride (1.4 mmol) were mixed in CH_2Cl_2 (15 ml) and the mixture was periodically examined by g.l.c. Species containing the 2,4-dinitrobenzene moiety are not detectable by this method. Nevertheless, the experiment indicated that ethynylferrocene reacted more slowly with 2,4-$(NO_2)_2C_6H_3SCl$ than with *p*-ClC_6H_4SCl, disappearing only after 14 h with the former reagent, whereas with the latter no ethynylferrocene was detected after 5 min (Figure). The relative amount of 1-chloro-1-ferrocenylethene diminished with time, to complete disappearance after 14 h. Acetylferrocene was present from the very beginning of the reaction (20 s) and was the only detectable species after 14 h.

Acetylferrocene (1.1 mmol, 78.5%) was isolated by column chromatography over silica gel. Another run, performed with dichloromethane distilled over P_2O_5, allowed us to isolate by column chromatography 1-chloro-1-ferrocenylethene (16%), acetylferrocene (47.6%), and two fractions with different but unattributed ^1H n.m.r. spectra (fast decomposition, with consequent broadening of the signals).

Any attempt to prepare 1-chloro-1-ferrocenyl-2-(2,4-dinitrophenylthio)ethene [FcCCl=$CHSC_6H_3(NO_2)_2$] independently from acetylferrocene (following the procedure of Kharasch[9] with acetophenone) failed. $FcCOCH_2SAr$ (58%) was obtained from the reaction of acetylferrocene and 2,4-dinitrobenzene-

sulphenyl chloride, but subsequent treatment with PCl_5 led only to decomposition.

Reaction of Ethynylferrocene with other Arenesulphenyl Chlorides.—(*a*) Equimolar amounts of ethynylferrocene and ArSCl were mixed in anhydrous CH_2Cl_2 and kept at room temperature. After the usual work-up and chromatography over a silica gel column, with CCl_4 and CH_2Cl_2 as eluants, the products were isolated and identified by ^1H n.m.r. and mass spectrometry.

(*b*) *In the presence of* Et_3N. Alkyne, ArSCl, and triethylamine in equimolar proportions were treated as in (*a*). The results are reported in the Table.

Characterization of Products.—FcC≡CSAr. Ar = C_6H_5: δ($CDCl_3$) 4.20 (5 H, s, cp), 4.54—4.58 and 4.78—4.83 (2 H each, complex, β- and α-protons of substituted cp ring, respectively), and 7.2—7.5 (5 H, complex, aromatic); Ar = *p*-$CH_3C_6H_4$: δ(CCl_4) 4.03 (7 H, s + br signal, unsubstituted cp and β-H of substituted cp, respectively), 4.30 (2 H, complex, α-H of substituted cp ring), 6.8—7.4 (complex, 4 H, aromatic), and 2.27 (3 H, s, CH_3), M^+ 332 (*M* 332.25); Ar = *p*-$CH_3OC_6H_4$: M^+ 350 (*M* 350.24); Ar = *p*-$NO_2C_6H_4$: δ($CDCl_3$) 4.25 (5 H, s, cp), 4.62 (2 H, t, *J* 2.0 Hz) and 4.86 (2 H, t, *J* 2.0 Hz) (β- and α-protons of substituted cp ring, respectively), and 7.48 (2 H, d, *J* 9.1 Hz) and 8.15 (2 H, d, *J* 9.1 Hz) (aromatic), M^+ 363 (*M* 363.21).

FcCCl=CHSAr. Ar = C_6H_5: δ($CDCl_3$) 4.17 (5 H, s, cp), 4.47 and 4.63 (2 H each, complex, β- and α-protons of substituted cp ring), 6.84 (1 H, s, vinylic), and 7.3—7.5 (5 H, complex, aromatic); Ar = *p*-$CH_3C_6H_4$: δ(CCl_4) 4.00 (5 H, s, cp), 4.10 and 4.53 (2 H each, t, β- and α-protons of substituted cp ring, respectively), 6.23 (1 H, s, vinylic), 6.8—7.2 (complex, 4 H, aromatic), and 2.22 (3 H, s, CH_3), M^+ 368/370 (*M* 368.70); Ar = *p*-$CH_3OC_6H_4$: δ($CDCl_3$) 4.22 (5 H, s, cp), 4.52 (2 H, t, *J* 2.0 Hz, β-H of cp), 4.78 (2 H, t, *J* 2.0 Hz, α-H of cp), 6.8—7.4 (complex, 5 H, aromatic and vinylic), and 3.95 (3 H, s, OCH_3), M^+ 386/388 (*M* 386.70); Ar = *p*-$NO_2C_6H_4$: δ($CDCl_3$) 4.25 (5 H, s, cp), 4.37 (2 H, t, *J* 2.0 Hz, β-H of substituted cp ring), 4.59 (2 H, t, *J* 2.0 Hz, α-H of the same ring), 6.55 (1 H, s, vinylic), and 7.62 (2 H, d, *J* 9.1 Hz) and 8.20 (2 H, d, *J* 9.1 Hz) (aromatic), M^+ 399/401 (*M* 399.67).

Kinetic Measurements.—The reaction was followed by the spectrophotometric method using a thermostatically controlled Cary 219 apparatus and silica cells with septa. The kinetic studies were performed under pseudo-first-order conditions either by keeping the substrate concentration at least 10 times as high as that of the sulphenyl chloride or *vice versa*. The solutions for the kinetic experiments were prepared immediately before use. Several runs were carried out under the conditions specified in the following (wavelengths in nm in parentheses).

In 1,1,2,2-*tetrachloroethane solution.* FcC≡CH 1.47×10^{-4} to 8.76×10^{-3}M; *p*-ClC_6H_4Cl 1.12×10^{-3} to 4.87×10^{-3}M (350, 360, 370, 376, 380, and 400); $k_2 = (2.4 \pm 0.2) \times 10^{-2}$ l mol^{-1} s^{-1}.

FcC≡CH 2.29×10^{-3} to 4.57×10^{-3}M; 2,4-$(NO_2)_2C_6H_3SCl$ 1.59×10^{-4} to 3.18×10^{-3}M (430, 440, and 470); $k_2 = (11.3 \pm 0.5) \times 10^{-2}$ l mol^{-1} s^{-1}.

In AcOH *solution.* FcC≡CH 2.86×10^{-4} to 2.67×10^{-3}M; *p*-ClC_6H_4SCl 3.90×10^{-4} to 6.03×10^{-3}M (350, 370, and 380); $k_2 = (6.2 \pm 0.8) \times 10^{-2}$ l mol^{-1} s^{-1}.

FcC≡CH 5.33×10^{-4} to 5.33×10^{-3}M; 2,4-$(NO_2)_2C_6H_3SCl$ 3.98×10^{-4} to 3.98×10^{-3}M (430, 440, and 470); $k_2 = (2.2 \pm 0.5) \times 10^{-2}$ l mol^{-1} s^{-1}.

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