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ADDITION OF FLUORINE TO TOLANES

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SUMMARY

The products obtained by the reaction of fluorine with various tolanes in freon 11 include 1,1,2,2-tetrafluoro-1,2-diarylethanes, cis- and trans-α,α'-difluorostilbenes, 1,2,2-trifluoro-1,2-diarylethanes, 1,2,2,2-tetrafluoro-1,1-diarylethanes, and 1,1-difluoro-2,2-diarylethenes. The 1,1,2,2-tetrafluoroethanes predominate at -78°C, while the α,α-difluorostilbenes predominate at 0°C. The relative rates of formation of the tetrafluorides and α,α-difluorostilbenes have been determined and show only a small substituent dependence.

INTRODUCTION

Bockemüller's work [1-3] in the early 1930's led to a useful application of fluorine in organic synthesis. He found that, by diluting fluorine with an inert gas and working at low temperatures, fluorinations could be conducted in a non-violent manner. He also found two pathways by which fluorine reacts with organic substrates. One was a substitution reaction and the other addition to sites of unsaturation.

In 1933, Miller, Calfee and Bigelow [4] published a paper confirming Bockemüller's findings on the controllability of the fluorination reaction. They also investigated the reaction of fluorine with toluene in carbon tetrachloride. One of their findings was that chlorine had been incorporated into the product. This for the first time led them to believe that a radical reaction had occurred.

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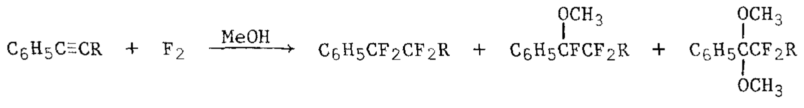
Miller subsequently published a series of papers on the reactions of perhaloolefins with fluorine in the liquid phase. The initial paper [5] described the fluorination of tetrachloroethylene in a freon 113 ($CF_2ClCFCl_2$) solution. The products from this reaction included the fluorine addition product (difluorotetrachloroethane) and a dimerization product (difluorooctachlorobutane). Similar addition and dimerization products were also obtained from the fluorination of $CFCl{=}CFCl$, $CF_3CCl{=}CF_2$, $CF_3CCl{=}CCl_2$, $(CF_2Cl)CF{=}CF(CF_2Cl)$ and $CF_3CF_2CF{=}CF_2$ [6]. Fluorination of $(CF_3)_2C{=}C(CF_3)_2$, however, gave no dimerization product. Perfluorobutadiene yielded simple addition products and high molecular weight solids formed by polymerization.

Attempts were made to establish the mechanism of the reaction of fluorine with olefins. The preceding work suggested that a radical mechanism was operative. Molecular fluorine was known not to be highly dissociated at room temperature ($K = 10^{-20}$) [7]; therefore, the initiation step was conceived to involve a reaction of molecular fluorine with the olefin to produce reactive radicals.

$$C{=}C \; + \; F_2 \longrightarrow F{-}C{-}C\cdot \; + \; F\cdot$$

This reaction was calculated to be exothermic by 1.2 kcal/mole, while the same reaction with chlorine was found to be endothermic by 22.5 kcal/mole [8]. The fluoroalkyl radical ($F{-}C{-}C\cdot$) could then react with F_2 to yield the addition product or it could combine with another fluoroalkyl radical to form the dimer. Of course, the fluorine atoms formed in the initial step could also react with olefin molecules to form new fluoroalkyl radicals.

The only reported investigation of the reactions of acetylenes with fluorine was by Merritt [9]. The reactions of phenyl-, diphenyl-, and methylphenylacetylene with fluorine were investigated. The reactions were conducted at -78°C in freon 11 or methanol solution. The fluorinations conducted in freon 11 solution resulted in the production of tetrafluoro compounds (I) with no difluoroolefins being observed. The reactions conducted in methanol solution again produced the tetrafluorides (I) as well as compounds incorporating a methoxy group (II) and (III).



$$C_6H_5C{\equiv}CR \; + \; F_2 \xrightarrow{MeOH} C_6H_5CF_2CF_2R \; + \; C_6H_5\overset{OCH_3}{\overset{|}{C}}FCF_2R \; + \; C_6H_5\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}CF_2R$$

$R = C_6H_5, CH_3, H$ (I) (II) (III)

An ionic reaction mechanism was proposed by Merritt.

The major objective of the present work was to study to reactions of diarylacetylenes with fluorine. We have found that the reactions of substituted tolanes with fluorine produce complex product mixtures, which we analyzed by GC/MS. The major reaction products include the tetrafluorides ($ArCF_2CF_2Ar$) and the cis and trans difluorides (ArCF=CFAr). The effects of changing the reaction conditions, such as varying the temperature or adding radical inhibitors, were studied. The relative rates of reaction of various substituted tolanes were determined by competition studies.

EXPERIMENTAL

All chemicals and solvents used in this study were of reagent grade quality unless otherwise noted.

Freon 11 ($CFCl_3$) and freon 12 (CF_2Cl_2) were obtained from Matheson. The freon 11, a very volatile liquid at room temperature (b.p. = 24°C), was obtained in three pound lots and was stored in metal cans. This solvent was found to contain a non-volatile residue after evaporation. Freon 11 was therefore purified by distillation. The freon 12 (b.p. = -30°C) was obtained in a lecture bottle and was used without further purification.

^1H and ^{19}F spectra were taken on a JEOL model JNH-MH-100, 100 MH_z nuclear magnetic resonance spectrometer. Mass spectra were taken on a Hitachi Perkin-Elmer RMU 7 mass spectrometer. GC/MS analyses were carried out at the State University of New York campus at Stony Brook, a Hewlett Packard model 5710 gas chromatograph in line with a Hewlett Packard model 5980 mass spectrometer being used. Infrared spectra were taken on a Perkin-Elmer model 735 B infrared spectrometer. Melting points were taken on a Thomas Hoover capillary melting point apparatus and were not corrected. Preparative GLC was effected on a Perkin-Elmer model F 21 preparative gas chromatograph. Analytical VPC was performed on either a Perkin-Elmer model 900 gas chromatograph equipped with a Perkin-Elmer Sigma One GC terminal, or a Hewlett Packard model 5830 A gas chromatograph equipped with a Hewlett Packard model 18850 A GC terminal. Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N.Y., 11377.

A 2% fluorine in nitrogen gas mixture was used in this study. This was obtained from Matheson and was assayed by iodometric titration [10]. The mixture was supplied in size 3F cylinders (6 inch diameter, 21 inch height), with an initial cylinder pressure of 500 psig. This corresponded to a gas volume of 8.16 cubic feet at one atmosphere. Mounted on the tank was a Matheson model B15F679 pressure regulator, which was specifically designed for use with fluorine. The fluorine-gas mixture was passed through an in-line sodium fluoride trap prior to use to remove any hydrogen fluoride that may have contaminated the mixture. After the fluorine exited from the NaF trap, it was passed through a needle valve that was used to control the flow rate. It next passed through a three-way stopcock that was connected to (1) the fluorine source, (2) a source of nitrogen used for purging the reaction vessel, and (3) the reaction vessel. After the fluorine-gas mixture had passed through the reaction vessel, any unreacted fluorine was scrubbed out by passing the gas through a soda lime trap. Flow rates were measured with a soap bubble flow meter or a Manostat model 36-541-03 flowmeter. These meters were in series following the soda lime trap. All valves, tubing, stopcocks, and connectors, through which fluorine passed, were made of stainless steel, polyethylene, monel, nickel, glass, or teflon.

Two basic types of reaction vessels were employed, depending upon the scale of the reaction. For large scale synthetic reactions, a two neck, round bottom flask equipped with a magnetic stirrer was employed. One neck consisted of a female 24/40 ground glass joint into which a glass gas inlet tube was inserted. A piece of polyethylene tubing carried the fluorine from the inlet tube to the bottom of the reaction flask. The second neck consisted of a female 12/18 ground glass joint into which the soda lime trap was placed. Small scale reactions were performed in a narrow cylindrical vessel in which the polyethylene tube terminated at the bottom of the vessel so that the gas bubbles, as they rose to the surface, would interact with the entire volume of solution. This design also made it a simple matter to immerse the reaction mixture in a dewar flask that contained a bath maintained at the desired temperature.

Preparation of substituted tolanes

Substituted tolanes were prepared by the method of Stephens and Castro [11]. Cuprous phenylacetylide was allowed to react with variously substituted phenyl iodides in refluxing pyridine. The pyridine was predried by stirring it with calcium hydride.

p-Phenoxytolane

To 5.0 g (17 mmols) of p-phenoxyiodobenzene [12, 13] were added 2.8 g (17 mmols) of cuprous phenylacetylide and 50 mL of dry pyridine. This mixture was refluxed with stirring for 24 h. After having been cooled, the reaction mixture was poured into cold water and extracted with ether. The ether solution was washed with water, 10% hydrochloric acid, sat. sodium bicarbonate solution, then water again. Evaporation of the ether solution, dried over anhydrous magnesium sulfate, gave a dark oil, which was subjected to column chromatography on silica gel, petroleum ether (b.p. = 30-60°) being used as eluent. The initial band yielded 2.2 g (44%) of p-phenoxyiodobenzene. The second band gave a white solid, which was recrystallized from hot methanol to yield 460 mg (1.7 mmols) of colorless plates; the yield of p-phenoxytolane was 23% based on unrecovered iodo compound; m.p. 77-78°C; NMR ($CDCl_3$) δ 7.2-7.9 (m); m/e 270 (base). Analysis: Found: C, 88.6; H, 5.2; O, 6.2. $C_{20}H_{14}O$ requires C, 88.9; H, 5.2; O, 5.9.

p-Methoxytolane

The yield of product obtained from 2.34 g (10 mmols) of p-iodoanisole and 1.64 g (10 mmols) of cuprous phenylacetylide based on unrecovered iodo compound, was 63%; m.p. 57-59°C (lit [11] 58-59°C); NMR ($CDCl_3$) δ 3.9 (s, 3), 6.8-7.0 (m, 4), 7.3-7.6 (m, 5); m/e 208 (base).

p-Methyltolane

Obtained in 28% yield, the m.p. of the compound was 70-71°C (lit [14] 71.5-72.5°C); NMR ($CDCl_3$) δ 2.4 (s, 3), 7.2-7.7 (m, 9); m/e 192 (base).

p-Fluorotolane

Obtained in 21% yield, the m.p. of the compound was 106-107°C (lit [15] 109-110°C); NMR ($CDCl_3$) δ 7.2-7.9 (m); m/e 196 (base).

m-Chlorotolane

Obtained in 25% yield, the m.p. of the compound was 29-30°C (lit [16] 30-31°C); NMR ($CDCl_3$) δ 7.5-7.9 (m); m/e 212, 214.

p-Trifluoromethyltolane

Obtained in 60% yield, the m.p. of the compound was 101-102°C (lit [15] 104-105°C); NMR ($CDCl_3$) δ 7.5-7.9 (m, 4), 8.0 (s, 5); m/e 246 (base).

p-Nitrotolane

Obtained in 56% yield, the m.p. of the compound was 120-121°C (lit [11] 119-120°C); NMR ($CDCl_3$) δ 7.6-7.8 (m, 5), 8.3 (dofd, 4, J=10); m/e 223 (base).

General procedure employed for the product distribution studies of the reactions of various tolanes with fluorine

Ten micromoles of the desired tolane was dissolved in 5 mL of freon 11. This solution was placed in a clean, dry fluorination flask that had been passivated with a 2% fluorine in nitrogen gas mixture and subsequently flushed with dry nitrogen. The solution was purged with dry nitrogen and was cooled to -78°C. A black cloth was wrapped around the reaction vessel to exlude light. Five mL of a 2% fluorine in nitrogen gas mixture was bubbled through the reaction mixture at a rate of 2 mL/min, after which the system was purged with nitrogen to remove any residual fluorine gas. The solution was allowed to warm to room temperature and the solvent was blown away with a stream of nitrogen. The residue was taken up in methylene chloride and a sample of this solution was taken for VPC analysis. A 6 foot, 0.125 inch, 10% SE-30 column was employed with a flow rate of 30mL/min. The column oven temperature used was dependent upon the tolane being studied. Three runs were made for each tolane. The results are given in Table I. (Details of the GC/MS determinations are available upon request).

General procedure employed for the competition reactions of various tolanes with fluorine

Ten micromoles each of the two substrates under study were accurately weighed (± 50 micrograms). This mixture was dissolved in 5 mL of freon 11 and subjected to reaction with fluorine in the same manner as described above. The type of column and temperatures employed in the analysis of products were dependent upon the compounds under study. Three runs were carried out for each pair. The results are summarized in Table II.

TABLE I

Product Distributions for the Reactions of Various Tolanes with Fluorine in Freon 11

Substituent[f]	$XC_6H_4CF_2CF_2C_6H_5$	$XC_6H_4CF{=}CFC_6H_5$	$XC_6H_4CHFCF_2C_6H_5$	Other[a,b]
H	36.27 ± 0.46	23.37 ± 1.07[c]	19.09 ± 1.57	21.27
p-C_6H_5O	45.81 ± 2.41	25.17 ± 2.11	9.33 ± 0.40	19.69
p-CH_3O	38.56 ± 0.05	24.11 ± 0.70	5.49 ± 0.14	31.84
p-CH_3	35.18 ± 0.03	25.71 ± 1.02[c]	23.24 ± 1.04	15.87
p-F	56.06 ± 1.31	25.35 ± 1.73	10.89 ± 0.90	7.70
m-Cl	36.33 ± 1.21	23.11 ± 1.51	---[d]	18.33
		23.23 ± 2.01	___	
p-CF_3	57.48 ± 1.46	18.68 ± 1.23	---[e]	23.84
p-NO_2	38.36 ± 2.63	30.34 ± 5.77	---[d]	31.30

[a] This category is composed of various unidentified compounds.

[b] These values were calculated by difference.

[c] Known to be the *cis* isomer by comparison with the authentic compound.

[d] This compound was not identified in the GC/MS studies.

[e] This value was unobtainable.

[f] The values are expressed in terms of percent product mixture.

Preparation of α,α'-difluorostilbenes

Ring substituted α,α'-difluorostilbenes were readily prepared by a two step synthesis starting from tetrafluoroethylene. In the first step, an aryllithium was allowed to react with an excess of tetrafluoroethylene to produce an α,β,β-trifluorostyrene according to the method of Dixon [17]. The styrene was allowed to react with a second aryllithium to give the desired α,α'-difluorostilbene as demonstrated by Talalaeva et al. [18].

TABLE II

Results from the Competition Reactions of Various Substrates with Fluorine

Competing Pair	$C_6H_5CF{=}CFC_6H_4X$	$C_6H_5CF_2CF_2C_6H_4X$
A. Tolanes		
p-C_6H_4O/H	2.82 ± 0.14	2.79 ± 0.03
p-C_6H_5O/p-CH_3O	1.07 ± 0.09	1.13 ± 0.12
p-C_6H_5O/p-CH_3	1.67 ± 0.18	1.62 ± 0.14
p-C_6H_5O/m-Cl	---	4.80 ± 0.20
m-Cl/H	0.402 ± 0.50	---
p-NO_2/H	0.209 ± 0.044	0.0794 ± 0.0026
p-C_6H_5O/p-F	5.04 ± 0.67	3.10 ± 0.16
p-C_6H_5O/p-CF_3	12.4 ± 1.60	3.40 ± 0.58
p-CH_3O/H[a]	2.64 ± 0.36	2.47 ± 0.29
p-CH_3/H[a]	1.69 ± 0.26	1.72 ± 0.16
m-Cl/H[a]	---	0.581 ± 0.056
p-F/H[a]	0.560 ± 0.100	0.900 ± 0.056
p-CF_3/H[a]	0.227 ± 0.023	0.820 ± 0.120

[a] Calculated from above experimental values.

p-Methyl-α,β,β-trifluorostyrene

A 15.2 g (152 mmols) quantity of tetrafluoroethylene was condensed in a graduated cold trap that was maintained at -130°C (n-pentane - liquid nitrogen slush). After the necessary volume was obtained, the tetrafluoroethylene was allowed to evaporate and was passed through a gas drying tube. It was then recollected in a 250 mL three neck flask that contained 150 mL of anhydrous diethyl ether maintained at -78°C. The reaction flask was equipped with a -130°C reflux condenser plus an addition funnel, and it was maintained under a nitrogen atmosphere. A previously prepared p-methylphenyllithium [19] solution containing ca. 46 mmols of the reagent was transferred by use of a syringe to the addition funnel which contained 100 mL of anhydrous ether. The aryllithium solution was slowly added to the reaction flask over a thirty minute period with vigorous stirring. After the addition was complete, the reaction mixture was allowed to stir at -78°C for 30 min. The reaction mixture was permitted to warm slowly to room temperature and 50 mL of 10% HCl was added with stirring. The layers were separated and the aqueous layer was extracted with ether, which was then washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* to give 6.3 g of a dark red liquid. This was distilled at 20 mm. During the distillation, iodine crystals formed in the condenser (*p*-methylphenyllithium having been prepared from *p*-iodotoluene and lithium metal). A 60-65°C fraction was collected, but it was badly contaminated with iodine. This material was dissolved in ether, and the resulting solution was washed three times with a 5% sodium bisulfite solution, then with water. The solution was dried over anhydrous magnesium sulfate and the ether was evaporated *in vacuo*; 1.57 g of a colorless liquid remained. The identity of this liquid as *p*-methyl-α,β,β-trifluorostyrene was confirmed by its successful use in the second step of the synthesis and by the presence of a C=C stretch at 1760 cm^{-1} in its IR spectrum (lit [20] 1767 cm^{-1}). The yield was 9 mmols or 19%. The material left in the still pot was dissolved in ether, washed with 5% sodium bisulfite solution, then with water. The ether solution was dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. An orange solid remained which was recrystallized four times from hot 95% ethanol; 251 mg of colorless leaf-like crystals were obtained, which proved to be trans-p,p'-dimethyl-α,α'-difluorostilbene. The m.p. was 108-109°C (lit [21] m.p. 108-109°C). The yield was 1 mmol or 4.3%.

p-Methyl-α,α'-difluorostilbene

A solution of 1.31 g (7.6 mmols) of *p*-methyl-α,β,β-trifluorostyrene in 100 mL of anhydrous ether was placed under a nitrogen atmosphere. The solution was cooled to -78°C and a previously prepared phenyllithium solution which contained *ca.* 8.5 mmols of the reagent was added over a 10 min period by use of a syringe, the mixture being stirred vigorously. The reaction mixture was stirred at -78°C for an additional 30 min. It was then allowed to warm to room temperature and 50 mL of 10% HCl was added. The layers were separated, and the aqueous layer was extracted with ether. The

TABLE III

^{1}H NMR Data for Various Stilbenes and α,α'-Difluorostilbenes

Compound	Proton Type	Chemical Shift[a]	Comments[c]
trans-$C_6H_5CH{=}CHC_6H_5$	Olefinic	7.1	Singlet
	Aromatic	7.2 to 7.7	Complex
cis-$C_6H_5CH{=}CHC_6H_5$	Olefinic	6.6	Singlet
	Aromatic	7.2	Singlet
trans-$C_6H_5CF{=}CFC_6H_5$	Aromatic	7.3 to 7.9	Complex
cis-$C_6H_5CF{=}CFC_6H_5$	Aromatic	7.3	Singlet
trans-p-$CH_3C_6H_4CF{=}CFC_6H_5$	Methyl	2.5	Singlet
	Aromatic	7.2 to 7.8	Complex
cis-p-$CH_3C_6H_4CF{=}CFC_6H_5$	Methyl	2.5	Singlet
	Aromatic	7.3	Singlet
	Aromatic	7.0 to 7.3	Complex
trans-(p-$CH_3C_6H_4CF{=})_2$	Methyl	2.5	Singlet
	Aromatic	7.3 and 7.7 J^b = 10	Doublet of Doublets
trans-p-$CF_3C_6H_4CF{=}CFC_6H_5$	Aromatic	7.2 to 7.7	Complex
trans-(p-$CF_3C_6H_4CF{=})_2$	Aromatic	7.2 and 7.8 J^b = 10	Doublet of Doublets

[a] Values are in ppm downfield from TMS.

[b] Values are in Hz.

[c] All integrations are in accord with the assigned structures.

ether portion was washed with water and dried over anhydrous magnesium sulfate. The ether was evaporated *in vacuo* to give a yellow liquid. This liquid was placed on a silica gel column, which was then eluted with petroleum ether (b.p. 30-60°C). The first band that was eluted gave 340 mg of a colorless liquid that proved to be a mixture of bromobenzene and *p*-methyl-α,β,β-trifluorostyrene. The second band gave a gummy white solid. This was recrystallized from 95% ethanol to give 585 mg of white needles.

TABLE IV

^{19}F NMR Data for Various α,α'-Difluorostilbenes

Compound	Chemical Shift[a]	Comments[c]
trans-$C_6H_5CF{=}CFC_6H_5$	152.0	
cis-$C_6H_5CF{=}CFC_6H_5$	128.6	
trans-*p*-$CH_3C_6H_4CF{=}CFC_6H_5$	151.4, 152.0	
cis-*p*-$CH_3C_6H_4CF{=}CFC_6H_5$	127.7, 130.0	Doublets J[b] = 13.2
trans-(*p*-$CH_3C_6H_4CF{=})_2$	152.2	
trans-*p*-$CF_3C_6H_4CF{=}CFC_6H_5$	63.6 147.9, 152.6	Trifluoromethyl Olefinic, Doublets, J[b] = 13.2
trans-(*p*-$CF_3C_6H_4CF{=})_2$	63.4 148.8	Trifluoromethyl Olefinic
cis-*p*-$CF_3C_6H_4CF{=}CFC_6H_4$	63.4, 63.6	Trifluoromethyl Ratio = 3 to 2
an Unknown Component	122.3, 130.6	Olefinic Ratio = 1 to 1

[a] Values are in ppm unfield from $CFCl_3$.

[b] Values are in Hz.

[c] All integrations are in accord with the assigned structures.

This proved to be trans-*p*-α,α'-difluorostilbene, m.p. 28-29°C. Analysis: Found: C, 78.4; H, 5.4; F, 16.8. $C_{15}H_{12}F_2$ requires C, 78.3; H, 5.2; F, 16.5. The yield was 2.5 mmols or 33%. The stereochemistry was assigned with the aid of the ^1H and ^{19}F NMR spectra (see Tables III and IV). The third band yielded 110 mg of a white solid which proved to be *cis*-*p*-methyl-α,α'-difluorostilbene, m.p. 45-46°C. Analysis: Found: C, 78.3; H, 5.2; F, 16.5. $C_{15}H_{12}F_2$ requires C, 78.3; H, 5.2; F, 16.5. The yield was 0.5 mmol or 6.6%. The stereochemistry was assigned with the aid of the ^1H and ^{19}F NMR spectra (see Tables III and IV).

α,β,β-Trifluorostyrene

A 15.2 g (152 mmols) quantity of tetrafluoroethylene was treated with phenyllithium in essentially the same manner as described above. The ether solution of the reaction mixture was evaporated *in vacuo* to give a yellow liquid. A fraction distilled at 45°C (20 mm) to give 607 mg of a clear liquid which proved to be α,β,β-trifluorostyrene (lit [17] b.p. 68°C at 75 mm). The infrared spectrum showed a C=C stretch at 1761 cm^{-1}. The yield was 4 mmols or 13%.

p-Trifluoromethyl-α,α'-difluorostilbene

A solution of 376 mg (2.5 mmols) of α,β,β-trifluorostyrene in 10 mL of anhydrous ether was placed under a nitrogen atmosphere. The solution was cooled to -78°C and a previously prepared *p*-trifluoromethylphenyllithium [22] solution which contained *ca.* 31 mmol of the reagent (prepared from *p*-iodobenzotrifluoride and *n*-butyllithium) was slowly added with stirring by use of a syringe. After addition was complete, the reaction mixture was allowed to warm to room temperature, and 10 mL of 10% HCl was then added. The layers were separated and the aqueous phase was extracted with ether. The ether portion was washed with water and then dried over anhydrous magnesium sulfate. The ether was evaporated *in vacuo* to give an orange solid. This was dissolved in the minimum amount of petroleum ether (b.p. 65-90°C). The resulting solution was placed on a silica gel column, which was eluted with petroleum ether. The initial band gave 266 mg of a colorless solid. This proved to be *trans*-*p*-trifluoromethyl-α,α'-difluorostilbene, m.p. 99-100°C. The yield was 0.94 mmols or 38%. The stereochemistry was assigned with the aid of the ^{19}F NMR spectrum (see Table IV). The second band gave 48 mg of a colorless liquid that consisted of two components, as shown by VPC analysis. One of the components was probably *cis*-*p*-trifluoromethyl-α,α'-difluorostilbene, as shown by the ^{19}F NMR (see Table IV). No attempt was made to purify further this material.

Preparation of cis-α,α'-difluorostilbene

Cis-α,α'-difluorostilbene was prepared by the photoisomerization of the *trans* isomer [23]. Specifically, 522 mg of *trans*-α,α'-difluorostilbene (PCR) was dissolved in 35 mL of n-pentane. This solution was placed in a quartz photolysis vessel equipped with a cooling water jacket. The stilbene solution was exposed to the light from a Hanovia medium pressure mercury vapor lamp for 30 min. The pentane was evaporated *in vacuo* to give a semi-solid residue. The isomers were separated by preparative GLC using a 3 meter, 0.250 inch, 10% DC-710 column at a temperature of 215°C and a carrier gas pressure of 1.2 atmospheres. A 150 mg quantity of the *cis* isomer and a 100 mg quantity of the *trans* isomer were isolated. The isomers were readily distinguished by their ^{19}F spectra (Table IV). The *cis* isomer was a liquid, whose mass spectrum was identical with that of the *trans* isomer.

1,1,2,2-Tetrafluoro-1,2-diphenylethane

A solution of 100 mg (0.46 mmol) of *trans*-α,α'-difluorostilbene in 10 mL of freon 11 was added to a clean dry fluorination vessel. The reaction mixture was purged with dry nitrogen and cooled to -78°C. A 2% fluorine in nitrogen gas mixture was then bubbled through the reaction mixture at a rate of 30 mL/min. The progress of the reaction was monitored by VPC, a 2 foot, 0.125 inch, 10% Carbowax 20M column at 170°C with a flow rate of 30mL/min being employed. After the reaction was complete the system was purged with nitrogen to remove any residual fluorine gas. The solution was allowed to warm to room temperature and 15 mL of methylene chloride was added. This solution was washed with saturated sodium bicarbonate solution, water, and was dried over anhydrous magnesium sulfate. The solvent was evaporated *in vacuo*, and the residue was recrystallized from hot 95% ethanol; 97 mg of white crystals were obtained; m.p. 118-119°C (lit [9] 119-120°C). The yield of 1,1,2,2-tetrafluoro-1,2-diphenylethane was 0.38 mmol or 83%.

1,1,2,2-Tetrafluoro-1-(*p*-methylphenyl)-2-phenylethane

A solution of 100 mg (0.43 mmol) of *trans*-*p*-methyl-α,α'-difluorostilbene in 50 mL of freon 11 was treated as described above. The solvent was evaporated *in vacuo* and the residual solution was placed on a silica gel column, which was eluted with petroleum ether (b.p. 30-60°C). One band which was eluted gave 46 mg of a white solid, m.p. 102-103°C. The yield of 1,1,2,2-tetrafluoro-1-(*p*-methylphenyl)-2-phenylethane was 0.17 mmol or 40%. Analysis: Found: C, 67.3; H, 4.5; F, 28.4. $C_{15}H_{12}F_4$ requires C, 67.2; H, 4.5; F, 28.4.

1,1,2,2-Tetrafluoro-1-(p-trifluoromethylphenyl)-2-phenylethane

A solution of 67 mg (0.24 mmol) of trans-p-trifluoromethyl-α,α'-difluorostilbene in 50 mL of freon 11 was treated as described previously. The solvent was evaporated in vacuo to give a viscous oil. This was dissolved in the minimum amount of methylene chloride and the resulting solution was placed on a silica gel column, which was eluted with petroleum ether (b.p. 30-60°C). One band which was eluted gave a white solid. This was sublimed at 48°C and 5 mm; 21 mg of a white solid was obtained, m.p. 48-50°C. The yield of 1,1,2,2-tetrafluoro-1-(p-trifluoromethylphenyl)-2-phenylethane was 0.065 mmol or 27%. Analysis: Found: C, 55.6; H, 2.9; F, 41.2. $C_{15}H_9F_7$ requires C, 55.9; H, 2.8; F, 41.3.

The reaction of trans-α,α'-difluorostilbene with ^{18}F labelled fluorine

Twelve mL of a 2 x 10^{-3} M solution of trans-α,α'-difluorostilbene in freon 11 was placed in a clean, dry, fluorination vessel that had been passivated by passing through a 0.1% fluorine in neon gas mixture followed by a neon flush. The solution was purged with neon and cooled to -78°C. The reaction vessel was covered with a black cloth to exclude light, and a 0.1% fluorine in neon gas mixture, containing ^{18}F-labelled fluorine was then bubbled through the solution. The ^{18}F-labelled fluorine was produced by bombarding a 0.1% fluorine in neon gas mixture with 13.6 MeV deuterons [24]. This was accomplished at the Brookhaven National Laboratory 60-inch cyclotron. After fluorine addition, the system was purged with neon to remove any residual fluorine gas. The reaction mixture was allowed to warm to room temperature and the freon 11 was removed in vacuo. The residue was taken up in methylene chloride and was analyzed on a 10 foot, 0.125 inch, 10% Carbowax 20M column at a temperature of 190°C with a flow rate of 50 mL/min. The eluted compounds were collected in activated charcoal traps and the amount of radioactivity in each trap was measured in a sodium iodide well counter. No activity was observed in the trap corresponding to the recovered starting material. All of the observed activity was located in the 1,1,2,2-tetrafluoro-1,2-diphenylethane. The final starting material to product ratio was ca. 1 to 1, as shown by the mass peaks on the VPC.

General procedure employed for the studies of the effects of oxygen on the reaction of tolane with fluorine

A solution of 10 micromoles of tolane in 5 mL of freon 11 was treated as described previously except that concomitant flows of fluorine and oxygen were utilized. Four mL of the cold reaction mixture was accurately measured in a volumetric flask, and, after having been warmed, the solvent was blown away with a stream of nitrogen. The residue was dissolved in precisely 50 micro liters of a standard 2 x 10^{-3} M solution of nitrobenzene in methylene chloride. The nitrobenzene acted as an internal standard for the VPC analysis. A sample of the resulting solution was then analyzed on a 50 foot, 0.02 inch, Carbowax 20M SCOT column at a temperature of 130°C and a carrier gas pressure of 15 psi. The results are given in Table V.

DISCUSSION

The reactions of substituted tolanes with F_2 in freon 11 yield complex product mixtures. The isolation of pure products from these mixtures proved to be impractical. Identification of the reaction products was accomplished by GC/MS analysis.

Low substrate concentrations (2 x 10^{-3} M) were used in order to minimize intermolecular reactions of the intermediates. A dilute fluorine gas mixture (2% F_2 in N_2) was also employed in order to effect more controlled reactions than would be possible using pure fluorine. Finally, only a relatively small amount of fluorine was added to the reaction mixture in order to minimize secondary reactions.

The products identified from these reactions included 1,1,2,2-tetrafluoro-1,2-diarylethanes, cis- and trans-α,α'-difluorostilbenes and 1,1,2-trifluoro-1,2-diarylethanes. Rearrangement products such as 1,1,1,2-tetrafluoro-2,2-diarylethanes and 1,1-difluoro-2,2-diarylethenes were also detected.

1,1,2,2-Tetrafluoro-1,2-diarylethanes were found in the reaction mixtures of all of the tolanes studied. The GC retention times and mass spectra of some authentic tetrafluorides (unsubstituted, p-methyl and p-trifluoromethyl) were obtained for comparison. The mass spectra of these compounds are very simple. Small parent ions are observed because these compounds readily fragment at the CF_2-CF_2 bond. The observed base ion is the fragment that gives the most stable radical cation. The base ions are $XC_6H_4CF_2\cdot^+$ or $C_6H_5CF_2\cdot^+$, depending on the electron donating ability of X.

TABLE V

Results from the Reactions of Tolane with Fluorine with Added Nitrogen or Oxygen

Run #	Gas Used	$\frac{C_6H_5CF_2CF_2C_6H_5}{C_6H_5NO_2}$	$\frac{\textit{cis}\text{-}C_6H_5CF{=}CFC_6H_5}{C_6H_5NO_2}$	$\frac{C_6H_5C{\equiv}CC_6H_5}{C_6H_5NO_2}$
1	N_2	8.40	2.33	163
2	N_2	7.35	2.67	168
Mean	N_2	7.87 ± 0.74	2.45 ± 0.31	166 ± 3
1	O_2	4.34	1.33	230
2	O_2	3.78	1.25	226
Mean	O_2	4.06 ± 0.40	1.90 ± 0.21	228 ± 3
	$\frac{N_2 \text{ Runs}}{O_2 \text{ Runs}}$	1.95 ± 0.22	1.90 ± 0.21	0.73 ± 0.2

α,α'-Difluorostilbenes were also found in all the tolane reaction mixtures. Authentic α,α'-difluorostilbenes (unsubstituted, *p*-methyl and *p*-trifluoromethyl) were synthesized for direct comparisons of the mass spectra and GC retention times. The mass spectra of these compounds display an intense parent ion. With the exception of the *p*-fluoro and *p*-methoxy compounds, all of these mass spectra display an ion at m/e equal to 165. This mass corresponds to a molecular formula of $C_{10}H_7F_2$. Since this ion is present in the mass spectrum of most of the α,α'-difluorostilbenes, the substituted ring must somehow undergo a fragmentation which removes the substituent and C_4H_3 (C_4H_4 when the stilbene is unsubstituted). The mass spectrum of *p*-fluoro-α,α'-difluorostilbene displays an ion at m/e equal to 183. This mass corresponds to a molecular formula of $C_{10}H_6F_3$ (165 - H + F). In this instance, the unsubstituted ring fragments in preference to the fluoro substituted one.

The GC/MS analyses of the tolane reaction mixture reveal a product that corresponds to the addition of three fluorine atoms and a hydrogen atom. This type of product is not seen in the m-chloro- and p-nitrotolane reaction mixtures. The mass spectra of these compounds are also very simple. Small parent ions are observed because these compounds readily fragment at the CHF--CF_2 bond. The base ions are those fragments that give the most stable radical cation ($ArCHF\cdot^+$ or $ArCF_2\cdot^+$). The hydrogen atom is incorporated alpha to the ring bearing an electron donating substituent and beta to a ring bearing an electron withdrawing substituent.

Two rearrangement products were detected in the product mixtures obtained by the reactions of certain tolanes with F_2. One rearrangement product (Ar_2CFCF_3) was observed in the reaction mixture of tolane with F_2 at 0°C. Analogous rearrangement products were produced in the reactions of p-phenoxy- and p-trifluoromethyltolanes with fluorine at -78°C. These rearrangement products have very simple mass spectra. Small parent ion peaks are formed, while the base ions are $Ar_2CF\cdot^+$, indicating that these compounds fragment at the CF--CF_3 bond.

Another rearrangement product was also observed in the GC/MS spectrum obtained from the reaction mixture of tolane with F_2 at 0°C. The mass spectrum of this product displays a strong parent ion corresponding to the addition of one molecule of fluorine (m/e = 216). The GC retention time, however, does not correspond to an α,α'-difluorostilbene, and the mass spectrum shows no ion at m/e equal to 165. The mass spectrum displays an ion whose mass (166) corresponds to $Ph_2C\cdot^+$. The evidence indicates that this compound is $Ph_2C{=}CF_2$.

A series of monosubstituted tolanes was allowed to react with fluorine at -78°C as described in the experimental section. The purpose of these fluorinations was to determine the effect of a change of substituent on the product distributions. The results are listed in Table I. The data show that varying the ring substituents had no consistent effect on the product distributions. For example, the amount of 1,1,2,2-tetrafluoro-1,2-diarylethanes varies randomly with change of ring substituent from 35% to 58% of the product mixture. The only consistency in the data for these compounds is that they are the major products of these fluorinations.

The data for the production of α,α'-difluorostilbenes are more consistent than those for the production of tetrafluorides. For most of the tolanes studied, the amounts of difluorides produced range between 23% to 25% of the product mixture. The two exceptions are from the fluorination of the *p*-trifluoromethyl- and *p*-nitrotolanes, with yields of 19% and 30%, respectively being obtained. The stereochemistry of all these difluorides produced is probably *cis*, with the exception of those obtained from *m*-chlorotolane, where both geometrically isomeric difluorides are observed. This assignment is made for the reason that authentic *cis*-*p*-methyl and *cis* unsubstituted difluorides take an approximately 40% longer time to be eluted from a column than do the tetrafluorides. The *trans* isomers are eluted much later and are difficult to separate from the starting tolanes. The difluorides obtained by the fluorination of the other tolanes take between a 32% to 44% longer time to be eluted than the tetrafluorides, so it is concluded that they are *cis*. No correlation is seen between the amounts of 1,1,2-trifluoro-1,2-diarylethanes produced and the various substituents on the starting tolanes. The same is true for the amounts of side products formed.

Tolane was allowed to react with fluorine at various temperatures. The percentage of 1,1,2,2-tetrafluoro-1,2-diphenylethane in the product mixture increases as the temperature is lowered. Conversely, the percentages of *cis*- and *trans*-α,α'-difluorostilbenes decrease with lower temperatures. A greater percentage of rearrangement products are formed at 0°C than at lower temperatures. The amounts of tetrafluoride and *cis* difluoride formed were compared at -78°C and -150°C. The amount of tetrafluoride formed at -150°C is about the same as that at -78°C, while the formation of *cis* difluoride decreases by a factor of 2.7 at the lower temperature.

The fact that such a large percentage of the product mixtures consist of 1,1,2,2-tetrafluoro-1,2-diarylethanes is intriguing. Small amounts of fluorine were used to avoid secondary reactions, and only a small percentage of the acetylene was consumed in each reaction. Another interesting observation is that the ratio of tetrafluoride to difluoride formed increases at lower temperatures. It was suggested by previous investigators of the reactions of fluorine with unsaturated hydrocarbons that the rate of fluorination of olefins is much greater than that of acetylenes [9]. However, if the rate of fluorination is vastly greater for an olefin than for an acetylene, then it would be expected that the tetrafluoride would also be the predominant product at higher reaction temperatures. This is not the case, so some other explanation in needed.

If it is assumed that the tolanes and α,α'-difluorostilbenes have approximately the same intrinsic susceptibility to attack by fluorine, then external effects may cause the product ratios to vary. A previous investigation has revealed that the reaction temperature affects the product distributions (addition vs. dimerization) obtained by the fluorinations of perhaloolefins (pure substrate or concentrated solutions being used) [25]. More dimerization occurs at lower temperatures. This increased dimerization is thought to be due to a relatively high concentration of fluoroalkyl radicals $(\mathrm{F}\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}\cdot)$ at the reaction site (near or at the gas-liquid interface) caused by slow diffusion rates of the fluoroalkyl radicals at low temperatures.

A similar situation may exist in the present study. After the addition of the first molecule of fluorine, the resulting α,α'-difluorostilbene would be at or near the gas-liquid interface. At higher temperatures the difluoride can more readily diffuse away from the interface to a region of lower fluorine concentration. On the other hand, at lower temperatures, the diffusion rate is slower, causing the difluoride to remain in a region of higher fluorine concentration, resulting in a greater conversion of difluoride to tetrafluoride.

The data obtained by the measurements of the amounts of tetrafluoride and *cis* difluoride formed at -78°C and -150°C are readily reconciled by this explanation. The total amount of products formed is, as expected, slightly less at the lower temperature. This is due to a reduction in the amount of the *cis* difluoride formed, while the amount of tetrafluoride formed remains constant. The rate of reaction of the acetylene is slower at the lower temperature. However, the resulting difluoride diffuses away from the gas-liquid interface slowly, thus allowing it to be converted to the tetrafluoride. The countering effects of less difluoride being generated and improved conditions for tetrafluoride formation balance out, leading to the formation of about the same amount of tetrafluoride at both temperatures. These effects result in formation of less difluoride at -150°C.

The presence of the 1,1,2-trifluoro-1,2-diarylethanes in the product mixtures is a surprising result. These products could not arise from the direct addition of HF, since the fluorine gas mixture was first passed through a sodium fluoride trap to insure that no HF was present. Also, no HF addition product is noted in the synthesis of 1,1,2,2-tetrafluoro-1,2-diarylethanes from *trans*-α,α'-difluorostilbenes. These products must arise by the abstraction of hydrogen from the aromatic rings, or, where possible, from the ring substituent. The glass walls of the reaction vessel may also be a source of hydrogen. Hydrogen abstractions are common in radical reactions. The question then arises as to when hydrogen incorporation occurs. As noted earlier, the incorporation does not occur by a reaction of the initially formed difluoride, so the hydrogen incorporation must occur with the acetylene, resulting in the formation of an HF addition product, which then undergoes further fluorination.

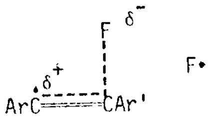
The relative rates of reaction of a series of monosubstituted tolanes with fluorines were determined by a competition method. A suitable pair of tolanes was allowed to compete for a small amount of fluorine, after which the amounts of products formed were measured. The additions of F_2 to unsaturated sites were the reactions of interest, so the formation of α,α'-difluorostilbenes and 1,1,2,2-tetrafluoro-1,2-diarylethanes were monitored. Table II gives the results of these competition reactions.

Two criteria were used to determine which pair of tolanes would be allowed to compete for a limited amount of fluorine. The most important one was the ease of separation of the various reaction products from each other and from the unreacted tolanes. The second was the employment of substrates of similar reactivities in order to permit the attainment of results of maximum accuracy. p-Phenoxytolane was found to be the most versatile acetylene for use in competition reactions with other tolanes. This was due to the comparatively low volatility of this compound, which allowed it and its reaction products to be separated readily by gas chromatography from the other tolane and the products of its reaction.

The data in Table II show that these reactions are assisted by the presence of electron donating substituents and hindered by the presence of electron withdrawing ones. This suggests the development of some degree of positive charge in the transition state for each reaction. However, the data also demonstrate that the reaction does not proceed by way of a fully cationic (vinyl cation or carbonium ion) unstable intermediate. To illustrate this, these data can be compared with those obtained from the brominations of substituted tolanes. The bromination of p-methoxytolane was found to be 4,000 times faster than that of tolane, while p-methyltolane underwent the reaction 40 times faster [26]. These bromination reactions were postulated to proceed by way of a cationic transition state. Our data show that the presence of p-methoxy and p-methyl substituents increase the rate of fluorination by a factor of but 2-3 and 1-2, respectively. It is obvious from these results that the fluorination reactions proceed by way of a transition state that has only a relatively small degree of charge separation associated with it.

The data in Table II have been correlated by use of the Hammett equation (σ substituent constants being used) for the production of both the tetrafluorides and the difluorides. The ρ values for tetrafluoride and difluoride production are -1.32 (correlation coef. = .982) and -1.09 (correl. coef. = .969), respectively. The use of σ^+ substituent constants [27] gave poorer correlations than the use of σ values. Neither of the ρ values are indicative of a reaction that has a large degree of positive charge in the transition state, such as in typical electrophilic addition reactions [28-33]. Instead, the ρ values are more in line with those obtained for radical reactions [34-41].

The evidence suggests that these fluorination reactions proceed by way of a radical type of transition state (or unstable intermediate), 4, which also has a small degree of charge separation.



4

The reaction of tolane with fluorine was carried out in the presence of oxygen. Control reactions were also carried out under the same conditions with nitrogen being used in place of oxygen. The results of these experiments are given in Table V. The data in Table V show that the reaction of tolane with fluorine is inhibited by the presence of oxygen. This is not surprising if one assumes that the reaction proceeds by a radical mechanism. Previous investigators have found that fluorine addition to perhaloolefins is inhibited by the presence of oxygen [42].

Finally, ^{18}F labelled 1,1,2,2-tetrafluoro-1,2-diphenylethane was prepared by allowing ^{18}F labelled F_2 to react with trans-α,α'-difluorostilbene. The ^{18}F-F_2 was prepared by the method of Wolf et al. [24] by bombarding a 0.1% mixture of F_2 in Ne with 13.6 MeV deuterons. The fluorination was stopped after approximately half of the starting olefin had been consumed, and the reaction mixture was analyzed by radio gas chromatography. All of the measured radioactivity was found to be in the tetrafluoride. None was found in the starting trans olefin nor in the time period of the gas chromatogram corresponding to the evolution of cis-α,α'-difluorostilbene. These observations indicate that the reaction is non reversible and that no olefin isomerization occurs during this reaction.

In summary, various mechanisms have been proposed for the additions of fluorine to olefins and acetylenes [4-6, 8, 9, 25, 43-53]. The information obtained from this study and various literature sources allows one to dismiss a number of these proposals for the tolane reactions.

Proposed mechanisms that involve a bridged or 4-centered transition state structure or unstable intermediate may be eliminated from further consideration inasmuch as either of these two types of unstable intermediates or transition states would necessarily yield stereospecific addition products. A bridged unstable intermediate, such as a halonium ion, would lead only to trans addition products, while only cis addition would result from a 4-centered transition state. The formation of cis- and trans-α,α'-difluorostilbene mixtures from the reactions of tolanes with F_2 show that these additions are not stereospecific.

The fluorinations of acetylenes do not proceed by way of cationic type transition state structures (vinyl cations). This conclusion is based mainly on the relative rate data obtained for the fluorinations of various tolanes.

The ρ values obtained from Hammett equation correlations using σ substituent constants have a smaller magnitude (-1.09 to -1.32) for these fluorinations than those usually associated with reactions having cationic intermediates. We will describe the reactions of tolanes and α,β-difluorostilbenes with fluorine in methanol solution in a subsequent publication. However, we can state here that the degrees of regioselectivity and stereospecificity in these reactions do not support a purely ionic mechanism, as proposed by Merritt [9].

The products obtained from the reactions of various substrates with fluorine are also in accord with a radical mechanism. Of special note are the 1,2-diaryl-1,2,2-trifluoroethanes obtained by the fluorination of tolanes. These products presumably arise by the abstraction of a hydrogen atom by a radical intermediate. The rearrangment products (Ar_2CFCF_3 and $Ar_2C{=}CF_2$) also obtained from the fluorination of tolanes, are in accord with a radical reaction (rearrangements involving migration of an aryl group are known to occur in radical reactions) [54]. Finally, the data obtained when oxygen is present in the tolane fluorinations can be reconciled by invoking a radical mechanism.

The above mentioned results lead us to believe that the transition state (or unstable intermediate) formed in each of these reactions consists of a fluorovinyl radical having a partial positive charge on carbon.

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