1, J = 5 and 9 Hz); UV (EtOH) 236 nm (ε 1800), 295 (150); NaOH added 230 (7500), 320 (2400). Anal. $C_9H_{17}NO_3$: C, H, N. These data were in agreement with those of a sample prepared by the action of propyl nitrate on 2,2-dimethyl-3-heptanone in the presence of potassium *tert*-butoxide.[20]

Similarly, α-nitroimine **29** led to the same nitro ketone **31** in 75% yield.

Thermolysis of Nitrimine 4. VPC injection of **4** onto a 6-ft silicone rubber column at 100 °C (injection port temperature 250 °C) produced two major products which were collected. They were identified as 2-methyl-2-nitropropane (**32**) and valeronitrile (**33**) by comparison of their spectra with those of authentic samples.

Thermolysis of Camphor Nitrimine (1).[9,10] A solution of 1 g of **1** in 15 mL of xylene under argon was heated at reflux for 5 h. The solvent was evaporated and the remaining oil separated by distillation into two fractions. The lower boiling fraction [0.32 g, bp <40 °C (0.1 mm)] consisted of nitriles **35** and **36** in 20 and 14% yield, respectively. They were separated by preparative VPC and had spectra identical with those published.[10] The higher boiling fraction [0.48 g, bp >40 °C (0.1 mm)] contained two epimers of **34** (38%). Separation was achieved by chromatography on silica gel with hexane–ethyl acetate (4:1) as eluant. Epimer A: bp 65 °C (bath temperature) (0.1 mm); IR 2250, 1540, 1390, 1360 cm^{-1}; NMR δ 0.78 (s, 3), 1.23 (s, 3), 1.63 (s, 3), 1.5–3.2 (m, 7). Anal. $C_{10}H_{16}N_2O_2$: C, H, N. Epimer B: mp 74–75 °C (from ether); IR 2250, 1540, 1390, 1350 cm^{-1}; NMR δ 0.90 (s, 3), 0.93 (s, 3), 1.55 (s, 3), 1.5–3.2 (m, 7). Anal. $C_{10}H_{16}N_2O_2$: C, H, N.

Acknowledgment. We are indebted to Firmenich SA Geneva, Switzerland, for generous financial support.

Registry No. **1**, 31180-79-7; **4**, 71606-95-6; **5**, 71606-96-7; **6**, 71606-97-8; **7**, 71606-98-9; **8**, 71606-99-0; **9**, 71607-00-6; **10**, 29022-29-5; **11**, 1129-90-4; **12**, 1129-91-5; **13**, 2243-98-3; **14**, 56956-46-8; **15**, 60212-29-5; **16**, 65108-28-3; **17**, 31929-13-2; **18**, 71607-01-7; **19**, 20023-44-3; **20**, 71607-02-8; **21**, 62184-84-3; **24**, 71607-03-9; **25**, 71607-04-0; **26**, 71607-05-1; **27**, 71607-06-2; **28**, 71607-07-3; **29**, 71607-08-4; **30**, 35869-41-1; **31**, 71607-09-5; **32**, 594-70-7; **33**, 110-59-8; *cis*-**34**, 71607-10-8; *trans*-**34**, 71607-11-9; **35**, 15373-31-6; **36**, 15340-92-8; i, 71607-12-0; ii, 71607-13-1; 2,2-dimethyl-3-heptanone oxime, 71607-14-2; cyclododecanone oxime, 946-89-4; 2-undecanone oxime, 2158-28-3; 3,3-dimethyl-4-phenyl-2-butanone oxime, 71607-15-3; 1-(1-methylcyclohexene-4-yl)ethanone oxime, 71607-16-4; 1-cyclohexyl-2-methylpropanone oxime, 52247-05-9.

Fluorination with Xenon Difluoride. 21. Evidence for Free-Radical Intermediates in Trifluoroacetic Acid Catalyzed Fluorinations

Ana Gregorčič and Marko Zupan*

Department of Chemistry and "Jožef Stefan" Institute, University of Ljubljana, Ljubljana, Yugoslavia

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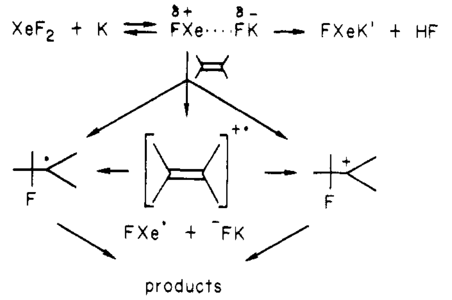
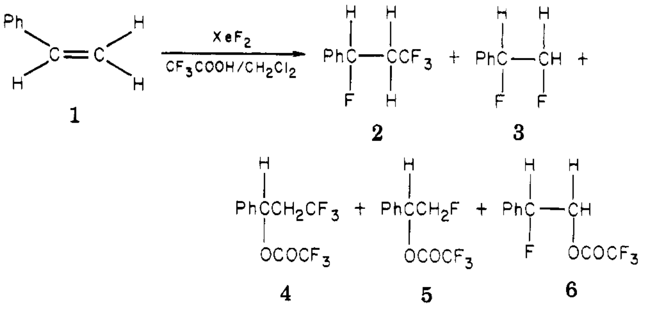
Trifluoroacetic acid catalyzed fluorination of styrene with xenon difluoride resulted in the formation of five products: 1-fluoro-1-phenyl-2-(trifluoromethyl)ethane (**2**), 1,2-difluoro-1-phenylethane (**3**), 1-(trifluoroacetoxy)-1-phenyl-2-(trifluoromethyl)ethane (**4**), 1-(trifluoroacetoxy)-1-phenyl-2-fluoroethane (**5**), and 1-fluoro-1-phenyl-2-(trifluoroacetoxy)ethane (**6**). The reaction with diphenylacetylene resulted in the formation of six products. The formation of fluoro radicals, trifluoromethyl radicals, and trifluoroacetoxy radicals, formed by decomposition of $FeXeOCOCF_3$, is suggested in order to explain the formation of products.

Scheme I



K = HF, HF/pyridine, BF_3, $BF_3 \cdot Et_2O$, C_6F_5SH, CF_3COOH, Br_2

Scheme II



It has been demonstrated that xenon difluoride is a mild fluorinating agent for fluorination of alkenes, acetylenes, and aromatic and hetereoaromatic molecules; this topic has been recently reviewed.[1] It is known that the mechanism of fluorine addition to olefins with xenon difluoride depends on the following factors: the structure of the olefin, the catalyst used, solvent polarity, and temperature. The formation of β-fluoro carbonium ions, free-radical intermediates, or ion radicals has been suggested to explain the formation of products (Scheme I). It has been demonstrated that the following substrates are convenient catalysts for fluorination of olefins with xenon difluoride: hydrogen fluoride,[2] hydrogen fluoride–pyridine,[3] boron trifluoride[4] (for less reactive organic molecules), boron trifluoride etherate,[5] pentafluorothiophenol[6] (for sensitive organic molecules), trifluoroacetic acid,[7] and bromine.[8] We have already demonstrated[9] that trifluoroacetic acid catalyzed fluorination of *cis*- and *trans*-1-phenylpropene resulted in the formation of vicinal difluorides and fluoride trifluoroacetates, and the formation of β-fluoro carbonium ions was suggested. We now report that small changes in the structure of the olefin, e.g., styrene, dramatically change the course of the reaction with xenon difluoride in

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(1) Filler, R. *Isr. J. Chem.* **1978**, *17*, 71.
(2) Zupan, M.; Pollak, A. *J. Chem. Soc., Chem. Commun.* **1973**, 845.
(3) Gregorčič, A.; Zupan, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 3192.
(4) Stavber, S.; Zupan, M. *J. Chem. Soc., Chem. Commun.*, **1978**, 969.
(5) Shackelford, S. A.; McGuire, R. R.; Pflug, J. L. *Tetrahedron Lett.* **1977**, 363.
(6) Zupan, M. unpublished observation.
(7) Zupan, M.; Pollak, A. *Tetrahedron Lett.* **1974**, 1015.
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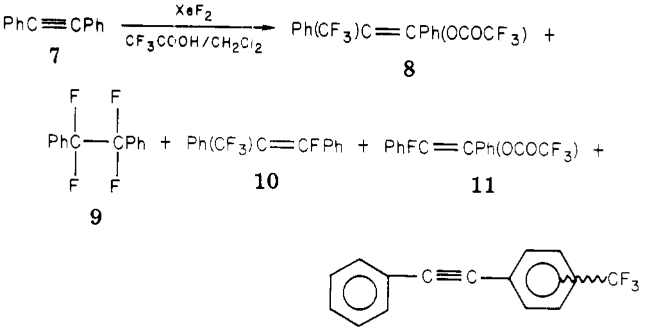
(9) Zupan, M.; Pollak, A. *Tetrahedron* **1977**, *33*, 1017.

0022-3263/79/1944-4120$01.00/0

Scheme III



12 (two isomers)

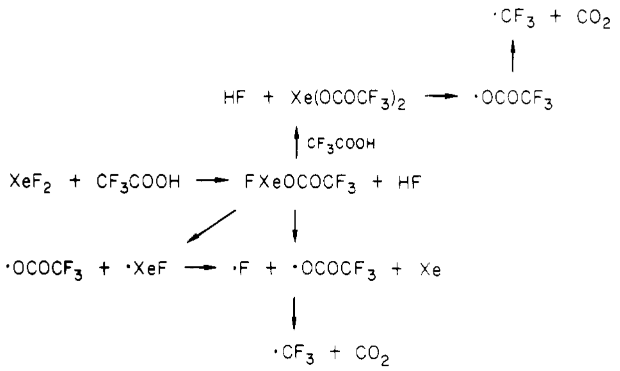
the presence of trifluoroacetic acid.

Results and Discussion

The CF_3COOH catalyzed reaction of styrene (1, Scheme II) with xenon difluoride in methylene chloride at room temperature resulted in the formation of a complex mixture, from which five products were isolated by preparative GLC (the numbering of the products is in the order of increasing GLC retention times). The first product (**2**) shows two signals in its ^{19}F NMR spectrum at 181.5 (m) and 66.75 ppm (dd), and its ^1H spectrum, besides the signal for aromatic protons, signals at 2.58 (m, 2 H) and 5.64 ppm (ddd, 1 H). On the basis of NMR, mass, and IR spectral data we established that 1-fluoro-1-phenyl-2-(trifluoromethyl)ethane (**2**) was formed. The spectroscopic data of the second product isolated are the same as those already published[10] and the formation of 1,2-difluoro-1-phenylethane (**3**) was established. The next product (**4**) shows signals in its ^{19}F spectrum at 66.75 (s) and 77.6 ppm (t), and in its ^1H spectrum a multiplet signal at 2.79 ppm (2 H) and a doublet of doublet singlet at 6.09 ppm (1 H). On the basis of the spectroscopic data, we established that 1-(trifluoroacetoxy)-1-phenyl-2-(trifluoromethyl)ethane (**4**) was formed. 1-(Trifluoroacetoxy)-1-phenyl-2-fluoroethane (**5**), the next product isolated, shows two signals in its ^{19}F NMR: a singlet signal at 77.25 ppm and a triplet of doublet signal at 226 ppm. The last product isolated, 1-fluoro-1-phenyl-2-(trifluoroacetoxy)ethane (**6**), also shows two signals in its ^{19}F NMR, at 78 (s) and 193.5 ppm (m). The ^{19}F NMR spectrum of the crude reaction mixture formed by fluorination of styrene shows all the signals corresponding to abovementioned products, which means that none of them has been formed during the GLC separation.

HF-catalyzed fluorination of diphenylacetylene resulted in the formation of tetrafluoro-1,2-diphenylethane,[11] while the trifluoroacetic acid catalyzed reaction resulted in the formation of a complex mixture, from which the following six products were isolated by preparative GLC and characterized on the basis of their spectroscopic data (numbering of the products is in the order of increasing GLC retention times): 1-(trifluoromethyl)-2-(trifluoroacetoxy)-1,2-diphenylethene (**8**), 1,1,2,2-tetrafluoro-1,2-diphenylethane (**9**), 1-fluoro-2-(trifluoromethyl)-1,2-diphenylethene (**10**), 1-fluoro-2-(trifluoroacetoxy)-1,2-diphenylethene (**11**), and two isomeric (trifluoromethyl)-phenylphenylacetylenes (**12**), Scheme III.

Scheme IV



It has been shown that xenon difluoride readily reacts with trifluoroacetic acid, giving xenon fluoride trifluoroacetate,[12] a reagent of electrophilic character. In the next step this electrophilic reagent can react with organic molecules (as has been already demonstrated[9]). However, xenon fluoride trifluoroacetate can decompose to XeF and trifluoroacetoxy radical and/or to a fluorine radical, a trifluoroacetoxy radical, and xenon, while the trifluoroacetoxy radical can further decompose to give a trifluoromethyl radical (Scheme IV). Xenon fluoride trifluoroacetate can also further react with trifluoroacetic acid, thus forming xenon bis(trifluoroacetate),[12] which after decomposition gives a trifluoroacetoxy radical, decomposing further to a trifluoromethyl radical. The formation of five products by the fluorination of styrene is presented in Scheme V. Styrene can react with xenon fluoride trifluoroacetate, thus forming the β-fluoro carbonium ion A, giving, after fluorine anion or trifluoroacetoxy anion attack, 1,2-difluoro-1-phenylethane (**3**) and 1-(trifluoroacetoxy)-1-phenyl-2-fluoroethane (**5**). The second possibility is homolytic Xe–F bond cleavage, resulting in the formation of fluoro-substituted radical intermediate B, which can be then further transformed to products **3** and **5**. The fluoro-substituted radical B can also be formed by attack of a fluorine radical or XeF formed by decomposition of xenon fluoride trifluoroacetate (Scheme IV). The formation of ion radicals, transforming further to β-fluoro carbonium ions A or fluoro-substituted radical B, is also taken into account. Styrene can also react with trifluoroacetoxy radical, thus forming radical intermediate C, giving, after further attack, product **6**. The trifluoromethyl radical can react with styrene, thus forming radical species D, which can be further transformed to products **2** and **4**.

Experimental Section

IR spectra were recorded using a Perkin-Elmer 257 spectrometer; ^1H and ^{19}F NMR spectra were recorded by a JEOL JNM-PS-100 from CCl_4 solution with Me_4Si or CCl_3F as internal reference. Mass spectra and high-resolution measurements were taken on a CEC 21-110 spectrometer. GLC was carried on a Varian Aerograph Model 1800 instrument. Styrene and diphenylacetylene were commercially available and purified before use. Trifluoroacetic acid was distilled before use. Methylene chloride was purified and stored over sieves.[13] Xenon difluoride was prepared by a photosynthetic method[14] and its purity was better than 99.5%.

Fluorination of Styrene. To a solution of 1 mmol of styrene in methylene chloride (2 mL) in a Kel-F vessel, 1 mL of a 1 M solution of trifluoroacetic acid in methylene chloride and 1 mmol of xenon difluoride was added with stirring at 25 °C. After a few seconds the colorless solution turned dark blue and xenon gas was evolved. After 1 h the reaction mixture was diluted with

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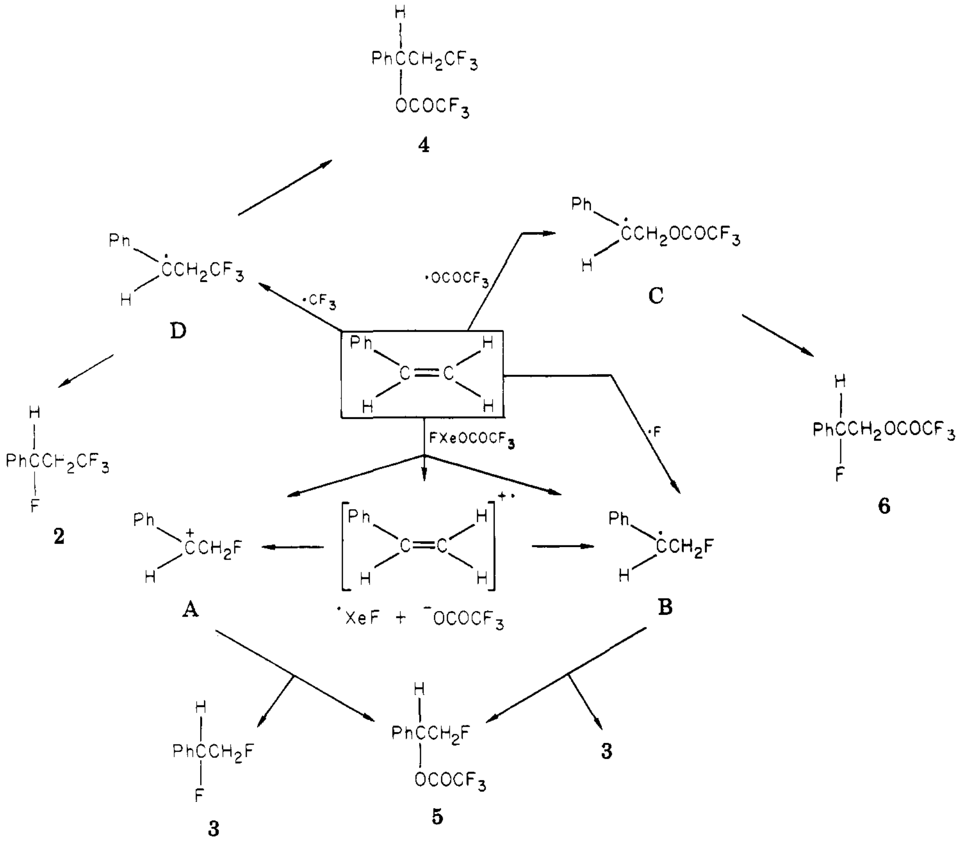
[11] Zupan, M.; Pollak, A. *J. Org. Chem.* **1974**, *39*, 2646.

[12] Eisenberg, M.; DesMarteau, D. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29. Musher, J. I. *J. Am. Chem. Soc.*, **1968**, *90*, 7371.

[13] Weissberger, A., Ed. "Techniques of Organic Chemistry"; Interscience: New York, 1955; Vol. VII.

[14] Williammson, S. M. *Inorg. Synth.* **1968**, *11*, 147.

Scheme V



methylene chloride, washed with 10 mL of $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The crude reaction mixture was analyzed by ^{19}F NMR spectroscopy and GLC (the experiment was repeated three times; the error in the determination of the composition was in the range of 2%). The composition of the reaction mixture was the following: 26% (**2**), 28% (**3**), 9% (**4**), 29% (**5**), 8% (**6**, relative yields). The crude reaction mixture was separated by preparative GLC (SE-30, T = 100 °C) and the following products were isolated.

1-Fluoro-1-phenyl-2-(trifluoromethyl)ethane (2): liquid product (13%); NMR δ_F 181.5 (m), δ_{CF_3} 66.75 (dd), δ_{CH_2} 2.58 (m), δ_{CH} 5.64 ppm (ddd), $^2J_{FH}$ = 46.5 Hz, $^3J_{FH}$ = 15 and 9 Hz, $^3J_{CF_3H}$ = 18 and 9 Hz, $^3J_{HH}$ = 9 and 3 Hz; mass spectrum, calcd for $C_9H_8F_4$ *m/e* 192.0562, found *m/e* 192.0561, *m/e* 192 (M^+, 38), 127 (14), 109 (100, PhCHF).

1,2-Difluoro-1-phenylethane (3): liquid product (15%); NMR δ_{F_1} 208.5 (dddd), δ_{F_2} 247.5 (tt), δ_{H_1} 5.66 (m), δ_{H_2} 4.6 ppm (m), $^2J_{F_2H}$ = 48 Hz, $^2J_{F_1H}$ = 50 Hz, $^3J_{FF}$ = 16 Hz, $^3J_{F_1H_2}$ = 30 and 22 Hz, $^3J_{F_2H_1}$ = 16 Hz, $^3J_{H_1H_2}$ = 7 and 4 Hz; mass spectrum, calcd for $C_8H_8F_2$ *m/e* 142.0603, found *m/e* 142.0592, *m/e* 142 (M^+, 33), 109 (100), 83 (7).

1-(Trifluoroacetoxy)-1-phenyl-2-(trifluoromethyl)ethane (4): liquid product (5%); NMR δ_{OCOCF_3} 66.75 (s), δ_{CF_3} 77.6 (t), δ_{CH} 6.09 (dd), δ_{CH_2} 2.79 ppm (m), $^3J_{CF_3H}$ = 9 Hz, $^3J_{HH}$ = 9 and 3 Hz; mass spectrum, calcd for $C_{11}H_8O_2F_6$ *m/e* 286.0428, found *m/e* 286.0429, *m/e* 286 (M^+, 27), 203 (13), 173 (38), 172 (100, $M^{+\cdot} - CF_3COO$), 109 (100), 105 (14), 104 (17), 103 (18), 77 (33), 51 (30).

1-(Trifluoroacetoxy)-1-phenyl-2-fluoroethane (5): liquid product (18%); NMR δ_{OCOCF_3} 77.25 (s), δ_F 226 ppm (td), δ_{H_1} 6 (ddd), δ_{H_2} 4.5 ppm (m), $^2J_{FH}$ = 48 Hz, $^3J_{FH}$ = 15 Hz, $^3J_{HH}$ = 6 and 3 Hz; mass spectrum, calcd for $C_{10}H_8O_2F_4$ *m/e* 236.0460, found *m/e* 236.0461, *m/e* 236 (M^+, 44), 203 ($M^+ - CH_2F$, 100), 175 (26), 127 (33), 123 (55), 105 (48), 103 (47), 77 (68), 51 (58).

1-Fluoro-1-phenyl-2-(trifluoroacetoxy)ethane (6): liquid product (4%); NMR δ_F 193.5 (m), δ_{OCOCF_3} 78 (s), δ_{H_1} 5.76 (ddd), δ_{H_2} 4.6 ppm (m), $^2J_{FH}$ = 48 Hz, $^3J_{HH}$ = 6 and 3 Hz; mass spectrum, calcd for $C_{10}H_8O_2F_4$ *m/e* 236.0460, found *m/e* 236.0460, *m/e* 236 (M^+, 8), 177 (10), 122 (69), 109 (PhCHF, 100), 77 (13), 69 (32).

Fluorination of Diphenylacetylene. The fluorination procedure and workup were the same as in the case of styrene. The crude reaction mixture was separated by preparative GLC (SE 30, T = 160 °C), and some products were again chromatographed on Carbowax 20M at T = 195 or 225 °C; the following products were isolated.

1-(Trifluoromethyl)-2-(trifluoroacetoxy)-1,2-diphenylethene (8): solid product (4%); mp 75–78 °C; NMR δ_{OCOCF_3} 77.5 (s), δ_{CF_3} 59 (s), δ_{Ph} 7.2 ppm (m); mass spectrum, calcd for $C_{17}H_{10}O_2F_6$ *m/e* 360.0584, found *m/e* 360.0594, *m/e* 360 (M^+, 100), 263 (25), 215 (15), 194 (34), 178 (24), 165 (45), 105 (86), 77 (58).

1,1,2,2-Tetrafluoro-1,2-diphenylethane (9): solid product (4%); mp 122–123 °C (lit.[11] mp 119.3–120.5 °C); NMR δ_F 120 ppm (br s); mass spectrum, calcd for $C_{14}H_{10}F_4$ *m/e* 254.0718, found *m/e* 254.0726, *m/e* 254 (M^+, 25), 127 (100), 77 (20).

1-Fluoro-2-(trifluoromethyl)-1,2-diphenylethene (10): oily product (7%); NMR δ_{CF_3} 58 (d), δ_F 80 (q), δ_{Ph} 7.5 ppm (m), $^4J_{CF_3F}$ = 12 Hz; mass spectrum, calcd for $C_{15}H_{10}F_4$ *m/e* 266.0718, found *m/e* 266.0721, *m/e* 266 (M^+, 100), 251 (15), 245 (13), 197 (41), 196 (40), 127 (12).

1-Fluoro-2-(trifluoroacetoxy)-1,2-diphenylethene (11): oily product (3%); NMR δ_{OCOCF_3} 76 (s), δ_F 115 (s), δ_{Ph} 7.3 ppm (m); mass spectrum, calcd for $C_{16}H_{10}O_2F_4$ *m/e* 310.0617, found *m/e* 310.0616, *m/e* 310 (M^+, 93), 213 (39), 185 (60), 127 (25), 105 (100), 77 (74), 53 (70).

(Trifluoromethyl)phenylphenylacetylene (12): first isomer, solid product (10%), mp 90 °C; NMR δ_{CF_3} 64 (d), δ_{Ph} 7.2 ppm (m); mass spectrum, calcd for $C_{15}H_9F_3$ *m/e* 246.0656, found *m/e* 246.0660, *m/e* 246 (M^+, 100), 245 (5), 226 (5), 176 (5), 98 (5); second isomer, oily product (11%); NMR δ_{CF_3} 64.5 (br s), δ_{Ph} 7.25 ppm (m); mass spectrum, calcd for $C_{15}H_9F_3$ *m/e* 246.0656, found *m/e* 246.0660, *m/e* 246 (M^+, 100), 245 (20), 226 (9), 196 (5), 176 (4), 169 (5), 98 (5).

Acknowledgment. We thank Professor J. Slivnik for the xenon difluoride. The financial assistance of the "Boris Kidrič" Foundation is acknowledged.

Registry No. 1, 100-42-5; 2, 71500-69-1; 3, 33315-79-6; 4, 71500-70-4; 5, 71500-71-5; 6, 71500-72-6; 7, 501-65-5; 8, 71500-73-7; 9, 425-32-1; 10, 384-90-7; 11, 71500-74-8; 12, 71500-75-9; trifluoroacetic acid, 76-05-1; xenon difluoride, 13709-36-9.