carried out on a Varian 3400 gas chromatograph (flame ionization detector, a 15000×0.53 mm capillary column, 1.5 mm DB-5, nitrogen as the carrier gas).

All operations were carried out under nitrogen. THF was purified by dispersed KOH (~50 g L^{-1}) and then distilled over $LiAlH_4$ in the presence of benzophenone in a nitrogen atmosphere. Butyllithium (a 1.6 *M* solution in hexane) and other reagents and solvents used in this study were commercial products.

1-Methyl-2,5-bis(methylthio)imidazole (6a). A solution of Bu^nLi (0.059 mol) in 37 mL of hexane was added to a solution of Bu^tOK (6.5 g, 0.058 mol) and Pr^i_2NH (6.5 g, 0.064 mol) in 70 mL of THF maintained at −50 °C. The mixture was cooled to −100 °C, and a solution of isothiocyanate **1** (3.8 g, 0.052 mol) in 20 mL of THF was added portionwise (over a period of ~1 min). Then the temperature of the reaction mixture was increased to −20 °C, 30 mL of DMSO was added, and the mixture was heated to 40 °C and stirred at this temperature for 15—20 min. After that, the mixture was cooled to −10 °C, and MeI (22 g, 0.153 mol) was added. The mixture was stirred for 15 min at 40 °C and diluted with 100 mL of water. The organic layer was thoroughly washed with water, the aqueous layer was extracted with pentane and with ether, and the combined extracts were dried with K_2CO_3. The solvents were evaporated under reduced pressure, and the residue was distilled *in vacuo* to give 3.1 g (71%) of imidazole **6a** of a 95.2% purity (GLC), b.p. 100—110 °C (0.8 Torr), n_D^{20} 1.5949. Found (%): C, 41.78; H, 6.07; N, 15.58; S, 37.01. $C_6H_{10}N_2S_2$. Calculated (%): C, 41.38; H, 5.75; N, 16.09; S, 36.78. IR, ν/cm^{-1}: 565, 635, 680, 700, 830, 935, 970, 1035, 1080, 1130, 1160, 1250, 1310, 1370, 1390, 1440, 1500, 1600, 2850, 2910, 2980, 3100. ^1H NMR, δ: 2.20 (s, 3 H, SMe); 2.57 (s, 3 H, SMe); 3.50 (s, 3 H, NMe); 7.05 (s, 1 H, CH=).

2,5-Bis(ethylthio)-1-methylimidazole (6b). A solution of Bu^nLi (0.120 mol) in 75 mL of hexane was added to a solution of Bu^tOK (12.57 g, 0.112 mol) and Pr^i_2NH (12.60 g, 0.125 mol) in 90 mL of THF maintained at −60 °C. The mixture was cooled to −100 °C, and a solution of isothiocyanate **1** (7.6 g, 0.104 mol) in 20 mL of THF was introduced with a syringe. The temperature of the reaction mixture was increased to −10 °C, and 55 mL of DMSO was added. Then the mixture was heated to 40 °C, stirred at 40—45 °C for 15 min, and cooled to 0 °C. After that, EtI (25 g, 0.158 mol) was added, and the reaction mixture was stirred at 40—45 °C for 15 min and diluted with 100 mL of water. The organic layer was washed with water, and the aqueous layer was extracted with ether and pentane. The combined extracts were dried with K_2CO_3, the solvents were evaporated, and the residue was distilled *in vacuo* to give 7.5 g (74.3%) of imidazole **6b** of a 96.6% purity (GLC), b.p. 155 °C (15 Torr), n_D^{20} 1.5645. Found (%): C, 47.86; H, 6.78; N, 13.79; S, 31.87. $C_8H_{14}N_2S_2$. Calculated (%): C, 47.52; H, 6.93; N, 13.86; S, 31.68. ^1H NMR, δ: 1.20 (t, 3 H, Me); 1.40 (t, 3 H, Me); 2.53 (q, 2 H, SCH_2); 3.17 (q, 2 H, SCH_2); 3.50 (s, 3 H, NMe); 7.07 (s, 1 H, CH=).

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Claisen aromatic amino rearrangement in the series of fluorinated anilines

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The effect of *meta*-substituents in the aromatic ring on the route of Claisen rearrangement of *N*-(pent-3-en-2-yl)-3-fluoro(or 3-trifluoromethyl, 3,4-difluoro)anilines induced by $ZnCl_2$ was investigated. The formation of two possible *ortho*-alkenylated reaction products was observed. The ratio of these isomers depends on the nature of the acid catalyst.

Key words: *N*-(pent-3-en-2-yl)-3-fluoroaniline, *N*-(pent-3-en-2-yl)-3,4-difluoroaniline, *N*-(pent-3-en-2-yl)-3-trifluoromethylaniline, Claisen amino rearrangement; 4-(pent-3-en-2-yl)-3-trifluoromethylaniline.

Substituents in the aromatic ring have a substantial effect on the Claisen rearrangement pathway.[1,2] It is known that, depending on the nature of the substituents in positions 2 and 5, *ortho—para* migrations of the allylic fragment can occur.[3,4] However, when a substituent is present in the *meta*-position, the two possible reaction sites become nonequivalent, and the migration of the alkenyl radical affords two *ortho*-isomers.[5] The ratio of

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Table 1. Reaction conditions, product yields, and product ratios for the rearrangement of *N*-(pent-3-en-2-yl)-3,4-difluoroaniline at 140 °C

Catalyst	Overall yield (%)	**9** : **10** : **11**
$BF_3 \cdot OEt_2$	71	6.5 : 1 : 2
CF_3COOH	75	10 : 6 : 1
$ZnCl_2$	64	9 : 1 : 4
HCl	69	5 : 1 : 2

these isomers depends on the nature of the *meta*-substituent.

In this work, we studied the effect of F atoms and a CF_3 group in the *meta*-position of the aromatic ring on the yield and the ratio of rearrangement products formed from *N*-(pent-3-en-2-yl)anilines.

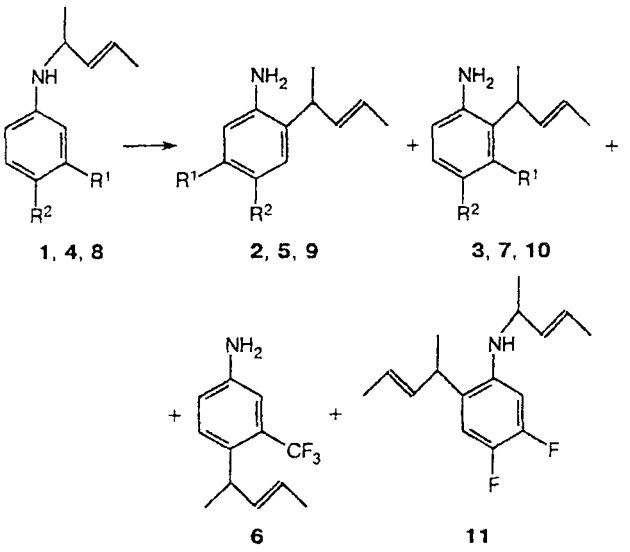
Keeping *N*-alkenylated 3-fluoroaniline **1** at 140 °C in the presence of $ZnCl_2$ leads to two *ortho*-isomers **2** and **3** in a ratio of 1 : 2. However, the rearrangement of 3-trifluoromethyl-substituted compound **4** yields only one *ortho*-product **5** and, in addition, *para*-alkenyl derivative **6**. The ratio of the products is again 1 : 2. Apparently, compound **6** results from the *ortho—para* Cope rearrangement of compound **7**.[3] This rearrangement occurs when a *m*-Me or *m*-OMe substituent[3,4] is present in the aromatic ring.

It should be noted that the rearrangement of *N*-(pent-3-en-2-yl)-3,4-difluoroaniline (**8**) occurs fairly easily, and its rate differs only slightly from the rate of this

Table 2. Yields, boiling points, and spectral characteristics of compounds **1—11** (with $ZnCl_2$ as the catalyst)

Compound	Yield (%)	B.p./°C (*p*/Torr)	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz)
1	78	93—94 (2)	780, 980, 1200, 1510, 1610, 2990, 3430	1.25 (d, CH_3, J = 6.3); 1.66 (d, CH_3, J = 5.4); 3.82 (m, CH_3); 3.82 (m, NH); 5.2—5.8 (m, HC=CH); 6.3 (m, 3 H, ArH); 7.0 (t, 1 H, ArH, J = 8.5)
2	26	—	780, 970, 1230, 1520, 1600, 2990, 3380, 3440	1.24 (d, CH_3, J = 7.04); 1.65 (d, CH_3, J = 4.22); 3.44 (m, CH); 3.44 (m, NH_2); 5.47 (m, CH=CH); 6.27—6.42 (dd, 2 H, ArH); 6.8—6.89 (dd, 1 H, ArH, J = 8.22)
3	59	100—103 (1)	980, 1230, 1510, 1600, 2990, 3380, 3440	1.33 (d, CH_3, J = 7.28); 1.67 (d, CH_3, J = 5.16); 3.5 (m, CH); 3.5 (s, NH_2); 5.2—5.6 (m, HC=CH); 6.2—6.5 (m, 2 H, ArH, J = 8); 6.86 (m, 1 H, ArH, J = 8)
4	75	105—107 (1)	760, 970, 1150, 1510, 1620, 2980, 3430	1.39 (d, CH_3, J = 7); 1.71 (d, CH_3, J = 4); 3.10 (m, CH); 3.39 (s, NH); 5.71—5.90 (m, HC=CH); 6.16—6.47 (m, 3 H, ArH); 7.01 (s, 1 H, ArH)
5	21	103—104 (2)	790, 980, 1360, 1520, 1610, 2980, 3390, 3460	1.32 (d, CH_3, J = 7); 1.67 (d, CH_3, J = 4); 3.34 (m, CH); 3.59 (s, NH); 5.60—5.88 (m, HC=CH); 6.20—6.61 (m, 2 H, ArH); 6.92 (s, 1 H, ArH)
6	45	97—99 (2)	760, 985, 1150, 1510, 1620, 2980, 3390, 3435	1.35 (d, CH_3, J = 7); 1.78 (d, CH_3, J = 4); 3.26 (m, CH); 3.47 (s, NH); 5.30—5.71 (m, HC=CH); 6.13—6.40 (m, 2 H, ArH); 6.96 (s, 1 H, ArH)
8*	81	97—99 (1)	850, 980, 1200, 1530, 1620, 2980, 3440	1.3 (d, CH_3, J = 6.5); 1.7 (d, CH_3, J = 6.5); 3.84 (m, CH); 3.6 (s, NH); 5.38—5.63 (dd, HC=CH); 6.24—6.38 (m, 2 H, ArH); 6.92 (ddd, 1 H, ArH, J = 8.95)
9*	41.1	98—100 (1)	980, 1240, 1520, 1610, 2990, 3390, 3460	1.3 (d, CH_3, J = 7.1); 1.7 (d, CH_3, J = 4.6); 3.33 (m, CH); 3.65 (m, NH_2); 5.45—5.5 (m, CH=CH); 6.45 (m, ArH, J = 7.3); 6.9 (dd, ArH, J = 8)
10	4.6	—	890, 980, 1200, 1525, 1620, 2980, 3390, 3470	1.23 (d, CH_3, J = 7); 1.67 (d, CH_3, J = 4); 3.37—3.58 (m, CH); 3.60 (s, NH_2); 5.44—5.66 (m, HC=CH); 6.33—6.52 (dd, ArH, J = 9); 6.77—6.98 (dd, ArH, J = 9)
11	18.3	—	890, 980, 1240,1495, 1610, 2980, 3440	1.3 (d, 4″-CH_3, J = 6.9); 1.4 (d, 4′-CH_3, J = 7.2); 1.68 (d, C(1″)CH_3, J = 4.6); 1.74 (d, C(1′)CH_3, J = 6.2); 3.3 (m, C(1″)H); 3.9 (m, C(1′)H); 5.45—5.5 (m, C(2″)H=C(3″)H); 5.55—5.8 (m, C(2′)H=C(3′)H); 3.8 (m, NH); 6.78—6.83 (dd, 2 H, ArH)

* ^{13}C NMR, δ: for compound **8**, 51.4 (C(1′)); 134.1 (C(2′)); 125.8 (C(3′)); 17.8 (C(4′)); 22.2 (C(1′)CH_3); 145.1 (C(1)); 102.2 (C(2)); 151.3 (C(3), J_{CF} = 243 Hz); 143.2 (C(4), J_{CF} = 245 Hz); 117.6 (C(5)); 108.9 (C(6)); for compound **9**, 36.6 (C(1′)); 134.1 (C(2′); 125.1 (C(3′)); 19.6 (C(1′)CH_3); 125.8 (C(1)); 141.0 (C(2)); 115.4 (C(3)); 143.5 (C(4), J_{CF} = 245 Hz); 149.5 (C(5), J_{CF} = 245 Hz); 104.5 (C(6)).



1—3: $R^1 = F$, $R^2 = H$
4, 5, 7: $R^1 = CF_3$, $R^2 = H$
8—10: $R^1 = R^2 = F$

reaction involving unsubstituted aniline. The ratio of products **9—11** varies as a function of the reaction conditions (Table 1). The results of the experiments show that the greatest proportion of compound **10** (~27%) in the product mixture is achieved when CF_3COOH is used as the catalyst; in other cases, the proportion of compound **10** does not exceed ~8%.

The formation of product **11** implies that the reaction does not occur by a concerted [3,3]-sigmatropic mechanism. Apparently, this reaction follows an intermolecular mechanism that includes the following elementary steps: catalytic cleavage of the N—C bond, electrophilic attack on the *ortho*-position of the aromatic ring by the pent-3-en-2-yl cation, and deprotonation of the σ-complex. Obviously, the electron densities in positions 2 and 6 of the ring differ insignificantly, and, therefore, the formation of two *ortho*-isomers is possible.

Experimental

IR spectra were recorded on a UR-20 instrument. ^1H and ^{13}C NMR spectra were measured on a Bruker AM 300 spectrometer (300 and 75 MHz). GLC analysis was carried out on a Chrom-5 chromatograph (flame ionization detector, SE-30 (5%) on Inerton-Super as the stationary phase, He (40 mL min^{-1}) as the carrier gas).

***N*-Alkenylation of fluorinated anilines (general procedure).** 4-Chloropent-2-ene[6] (80 mmol) was added to a solution containing an equimolar amount of a substituted aniline in triethylamine (20 mL), and the mixture was heated for 1—2 h at 80—90 °C. When the reaction was completed, 20—25 mL of water was added, and the product was extracted with ether (3×10 mL). The organic layer was separated, washed with water (3×10 mL), and dried with $CaCl_2$. After evaporation of the ether, the products **1**, **4**, and **8** were isolated by vacuum distillation.

Catalytic rearrangement of *N*-(pent-3-en-2-yl)arylamines 1, 4, and 8. *N*-(Pent-3-en-2-yl)arylamine (5 mmol) was refluxed in 10 mL of *o*-xylene in the presence of 0.5 mmol of a catalyst ($ZnCl_2$, CF_3COOH, HCl, $BF_3 \cdot OEt_2$) until the initial *N*-alkenylarylamine was entirely consumed (GLC monitoring). Then the reaction mixture was cooled, diluted with 10 mL of ether, washed with concentrated KOH (10 mL) and with water (3×10 mL), and dried with $CaCl_2$. The yields and physicochemical characteristics of the resulting compounds are listed in Table 2.

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