140. Acid-Catalyzed [3,3]-Sigmatropic Rearrangements of *N*-Propargylanilines

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Dedicated to *Albert Eschenmoser* on the occasion of his 65th birthday

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The acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-, *N*-(1′-methylprop-2′-ynyl)-, and *N*-(1′-arylprop-2′-ynyl)-2,6-, 2,4,6-, 2,3,5,6-, and 2,3,4,5,6-substituted anilines in mixtures of 1N aqueous H_2SO_4 and ROH such as EtOH, PrOH, BuOH *etc.*, or in $CDCl_3$ or CCl_4 in the presence of 4 to 9 mol-equiv. trifluoroacetic acid (TFA) has been investigated (*cf. Scheme 12–25* and *Tables 6* and *7*). The rearrangement of *N*-(3′-X-1′,1′-dimethylprop-2′-ynyl)-2,6- and 2,4,6-trimethylanilines (X = Cl, Br, I) in $CDCl_3$/TFA occurs already at 20° with $\tau_{1/2}$ of *ca.* 1 to 5 h to yield the corresponding 6-(1′-X-3′-methylbuta-1′,2′-dienyl)-2,6-dimethyl- or 2,4,6-trimethylcyclohexa-2,4-dien-1-iminium ions (*cf. Scheme 13* and *Footnotes 26* and *34*). When the 4 position is not substituted, a consecutive [3,3]-sigmatropic rearrangement takes place to yield 2,6-dimethyl-4-(3′-X-1′,1′-dimethylprop-2′-ynyl)anilines (*cf. Footnotes 26* and *34*). A comparable behavior is exhibited by *N*-(3′-chloro-1′-phenylprop-2′-ynyl)-2,6-dimethylaniline (**45**; *cf. Table 7*). The acid-catalyzed rearrangement of the anilines with a Cl substituent at C(3′) in 1N aqueous H_2SO_4/ROH at 85–95°, in addition, leads to the formation of 7-chlorotricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-ones as the result of an intramolecular *Diels-Alder* reaction of the primarily formed iminium ions followed by hydrolysis of the iminium function (or *vice versa; cf. Schemes 13, 23,* and *25* as well as *Table 7*). When there is no X substituent at C(1′) of the iminium-ion intermediate, a [1,2]-sigmatropic shift of the allenyl moiety at C(6) occurs in competition to the [3,3]-sigmatropic rearrangement to yield the corresponding 3-allenyl-substituted anilines (*cf. Schemes 12, 14–18,* and *20* as well as *Tables 6* and *7*). The rearrangement of (−)-(*S*)-*N*-(1′-phenylprop-2′-ynyl)-2,6-dimethylaniline ((−)-**38**; *cf. Table 7*) in a mixture of 1N H_2SO_4/PrOH at 86° leads to the formation of (−)-(*R*)-3-(3′-phenylpropa-1′,2′-dienyl)-2,6-dimethylaniline ((−)-**91**), (+)-(*E*)- and (−)-(*Z*)-6-benzylidene-1,5-dimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one ((+)-(*E*)- and (−)-(*Z*)-**92**, respectively), and (−)-(*S*)-2,6-dimethyl-4-(1′-phenylprop-2′-ynyl)aniline ((−)-**93**). Recovered starting material (10%) showed a loss of 18% of its original optical purity. On the other hand, (+)-(*E*)- and (−)-(*Z*)-**92** showed the same optical purity as (−)-**38**, as expected for intramolecular concerted processes. The CD of (+)-(*E*)- and (−)-(*Z*)-**92** clearly showed that their tricyclic skeletons possess enantiomorphic structures *(cf. Fig. 1)*. Similar results were obtained from the acid-catalyzed rearrangement of (−)-(*S*)-*N*-(3′-chloro-1′phenylprop-2′-ynyl)-2,6-dimethylaniline ((−)-**45**; *cf. Table 7*). The recovered starting material exhibited in this case a loss of 48% of its original optical purity, showing that the Cl substituent favors the heterolytic cleavage of the N–C(1′) bond in (−)-**45**. A still higher degree (78%) of loss of optical activity of the starting aniline was observed in the acid-catalyzed rearrangement of (−)-(*S*)-2,6-dimethyl-*N*-[1′-(*p*-tolyl)prop-2′-ynyl]aniline ((−)-**42**; *cf. Scheme 25*). *N*-[1′-(*p*-anisyl)prop-2-ynyl)-2,4,6-trimethylaniline (**43**; *cf. Scheme 25*) underwent no acid-catalyzed [3,3]-sigmatropic rearrangement at all. The acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)aniline (**25**; *cf. Scheme 10*) in 1N H_2SO_4/BuOH at 100° led to no product formation due to the sensitivity of the expected product **53** against the reaction conditions. On the other hand, the acid-catalyzed rearrangement of the corresponding 3′-Cl derivative at 130° in aqueous H_2SO_4 in ethylene glycol led to the formation of 1,2,3,4-tetrahydro-2,2-dimethylquinolin-4-on (**54**; *cf. Scheme 10*), the hydrolysis product of the expected 4-chloro-1,2-dihydro-2,2-dimethylquinoline (**56**). Similarly, the acid-catalyzed rearrangement of *N*-(3′-bromo-1′-methylprop-2′-ynyl)-2,6-diisopropylaniline (**37**; *cf. Scheme 21*) yielded, by loss of one i-Pr group, 1,2,3,4-tetrahydro-8-isopropyl-2-methylquinolin-4-one (**59**).

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[1]) Part of the Ph. D. thesis of *P. B.*, No. 890, University of Fribourg, 1985.

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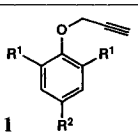
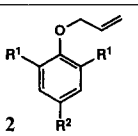
1. Introduction. – Several years ago,we reported on investigations on aromatic amino-*Claisen* rearrangements [1] and showed that the thermal rearrangement of *N*-allylanilines as well as that of the corresponding protonated *N*-allylanilinium ions, which leads in both cases to the 2-allylated anilines with an inverted allylic chain,respresent [3,3]-sigmatropic processes (*cf.* also [2]). However, in contrast to the anilines, their protonated forms rearrange much easier with acceleration factors ($(k_{H+}/k_A)_T$) of 10^5 to 10^7. This means that the acid-catalyzed rearrangement of *N*-allylanilines takes place already at temperatures of 50–160° and proceeds, in general, much cleaner than its uncatalyzed variant which requires temperatures of 200–330° and results in the formation of appreciable amounts of cleavage products. In the meantime, innumerable further examples of such charge-induced [3,3]-sigmatropic rearrangements (*cf.* [3]) in 3- and 2-azonia-*Cope* systems have been reported[3]). On the other hand, nearly nothing is known about acid-catalyzed amino-*Claisen* rearrangements of *N*-propargylanilines or other *N*-propargyleneammonium systems (*cf.* [5] [6] [10]).

A comparison of the thermal rearrangement of propargyl phenyl ethers and of the corresponding allyl phenyl ethers shows (*cf. Table 1*) that the conversion of the propargyl moiety into the allenyl moiety occurs as facile as the rearrangement of the allyl group in these aromatic systems. This seems also to be true for thermal amino-*Claisen* rearrangements of *N*-propargylamines according to the few known examples. For instance, 1- and 2-naphthyl-*N*-propargylamines [16] rearrange in the same temperature range of 240–260° as their *N*-allyl counterparts [17]. However, the primarily formed 1,2-dihydrobenzo[*h*]- and 1,2-dihydrobenzo[*f*]quinolines (as the result of the amino-*Claisen* rearrangement followed by [1,5]-sigmatropic H-shift and electrocyclization of the so created ω-vinyl iminoquinomethanes [16][4]) disproportionate under the reaction conditions to yield a

Table 1. *Kinetic Parameters for Thermal Rearrangements of Propargyl Phenyl and Allyl Phenyl Ethers at 170°* [a])

R^1	R^2	 1	 2
H	H	127.3/−69/94 [11][b])	131.0/−48/18 [12][c])
Me	Me	133.4/−33.5/6.2 [13]	126.5/−45/3.4 [14][d])
t-Bu	Me	132.1/−10/0.3 [13]	136.5/−12/1.0 [13]

[a]) Values in the following order: $\Delta H^{\#}$ [kJmol^{-1}]/$\Delta S^{\#}$ [JK^{-1}mol^{-1}]/$t_{½}$[h]; solvent: decane unless otherwise stated.

[b]) In 1,2-dichlorobenzene.

[c]) In carbitol.

[d]) Values of the corresponding 4-allylphenyl ether which are nearly identical with those for the ether carrying no substituent in the 4-position [15].

[3]) See especially the studies of *Katayama* (*e.g.* [4] and earlier literature cited therein) on the rearrangement of quaternary *N*-allylanilinium salts and the review of *Lutz* [5] on the catalysis of *Cope* and *Claisen* rearrangements. A further review has recently been published by *Przheval'skii* and *Grandberg* [6]. See also [7] [8] for additional reviews, and [9] [10] for older literature.

[4]) The amino-*Claisen* rearrangement of *N*-propargylarylamines, hence, follows the same reaction path as the *Claisen* rearrangement of their oxygen analogues (*cf.* [18] [19]).

mixture of the corresponding 1,2,3,4-tetrahydrobenzoquinolines and benzoquinolines. Rearrangement in $PhNO_2$ yields only the dehydrogenated compounds [16] [18]. On the other hand, the 'gem-dimethyl effect' (*cf.* [1] [11]) lowers the temperature for the *Claisen* rearrangement and, indeed, also *N*-(1,1-dimethylpropargyl)anilines are already transformed at temperatures of *ca.* 200° into the corresponding 1,2-dihydro-2,2-dimethylquinolines, however, in low yields [21] (*cf.* [22])[5]).

An inspection of the kinetic parameters in *Table 1* shows that alkyl substituents in both *ortho*-positions clearly favor the thermal *Claisen* rearrangement. This effect can mainly be attributed to an increase in the $\Delta S^{\neq}$ values ($\Delta S^{\neq}$ becomes more positive) which tends to be more pronounced in the propargyl cases. Therefore, we studied especially the H^+-catalyzed amino-*Claisen* rearrangement of *N*-propargylated 2,6-disubstituted anilines[6]).

2. Synthesis of Starting Materials. – 2.1. N-*(1',1'-Dialkylprop-2'-ynyl)anilines.* For the synthesis of these compounds, we followed, in principle, the procedure developed by *Hennion et al.* [23] which allows quite generally the alkylation of amines with 1,1-disubstituted propargyl halogenides in Et_2O/H_2O mixtures. In contrast to aliphatic amines, the alkylation of the weaker basic aromatic amines requires the presence of catalytic amounts of Cu(I) salts, Cu powder, and stoichiometric amounts of a stronger base such as Et_3N. So far, under these conditions the reaction of sterically hindered 2,6-disubstituted anilines with a 1,1-disubstituted propargyl halogenide has only been studied in one case. The reaction of 2,6-dimethylaniline with 1,1-dimethylprop-2-ynyl chloride gave 5% yield of *N*-(1',1'-dimethylprop-2-ynyl)-2,6-dimethylaniline [1] (**3**; *cf. Table 2*). Therefore, we tested other solvent systems and found that omission of H_2O raises the yield of **3** to 21%. A further improvement of the yield of the *N*-alkylated aniline was realized, when mesidine was reacted in dioxane instead of Et_2O or THF (*Table 2*). Also, the incorporation of basic properties in the solvent molecules gave quite good results as shown by the alkylations performed in *N*-ethylmorpholine (*Table 2*). Other solvent systems like hexane, benzene, MeCN, DMF, DMSO, HMPT, 2-nitropropane, butan-2-one, or acetone as well as protic solvents such as *t*-BuOH gave no better yields of *N*-propargylated anilines. On the contrary, the application of protic conditions enhanced the formation of *Schiff* bases (*Scheme 1*) which were observed in minor amounts also under the normal alkylation conditions as given in *Table 2*. However, the *Schiff* bases were isolated and characterized only in the four cases shown in *Scheme 1*. The formation of these by-products, which become the main products in the alkylation reactions in protic solvents, or when Cu(I) salts are omitted, is the result of a S_N2'-like reaction of the anilines with the propargyl chlorides followed by prototropic isomerization of the primarily formed *N*-allenylanilines (*Scheme 1*).

Anilines of low basicity ($pK_a < 0.8$ of the corresponding anilinium ions) such as 2-nitro-, 2-methyl-6-nitro-, 2,4,6-trichloro-, and 2,4,6-tribromoaniline could not be alky-

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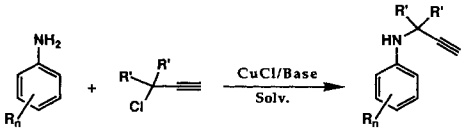
[5]) Cu(0)/Cu(I)-catalyzed rearrangements of *N*-(1,1-dimethylpropargyl)anilines seem to take place already at temperatures as low as 20° [23] [24] (*cf.* [25] as well as later).

[6]) Sterically conjested allyl(aryl)amines and ethers undergo acid-catalyzed *Claisen* rearrangements already at room temperatures (*cf.* [2] [26]). The differences in charge stabilization by solvation of the ground state and of the transition state seem to play a major role in these strongly 'charge-dependent' rearrangements (see also later).

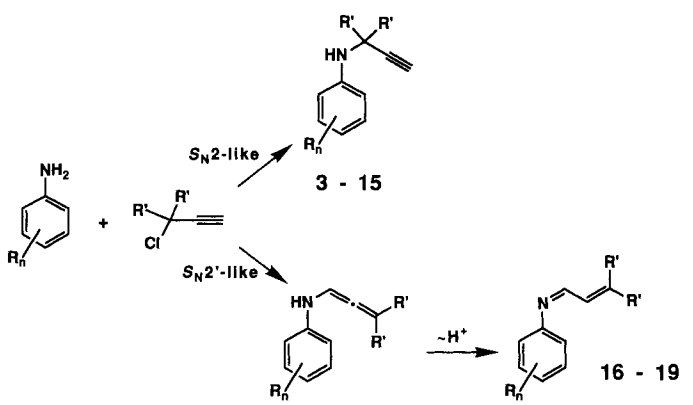
Table 2. *Preparation of* N-*(1′,1′-Dialkylprop-2′-ynyl)anilines*[a])



R_n	Base[b])	Solvent[c])	Temp. [°C]	Product	Yield [%]
A $R' = Me$					
2,6-Me_2	Et_3N	Et_2O	25	**3**	21
2,4,6-Me_3	Et_3N	Et_2O	5–10	**4**	25
2,4,6-Me_3	Et_3N	THF	5–10	**4**	25–30
2,4,6-Me_3	Et_3N	DX	5–10	**4**	60
2,6-Et_2	Et_3N	DX/H_2O	25	**5**	10[d])
2,6-(i-Pr)$_2$	NEM	NEM	5–10	**6**	38[d])
2,3,5,6-Me_4	Et_3N	DX	0–8	**7**	39
2,3,4,5,6-Me_5	Et_3N	DX	5–10	**8**	27
4-NH_2, 2,3,5,6-Me_4	NEM	DX	5–10	**9**	37[e])
2-I,4,6-Me_2	NEM	NEM	−10–0	**10**	38
2-Br,4,6-Me_2	Et_3N	DX	5–15	**11**	34
2,6-(EtO)$_2$	NEM	DX	−8–5	**12**	83
2,6-Cl_2	NEM	DX	0–20	**13**	2
2,6-Cl_2	PMP	DX	0–20	**13**	8
B $R'–R' = -(CH_2)_5-$					
2-MeO	NEM	DX	0–20	**14**	77
2,6-Me_2	Et_3N	DX	20	**15**	3[d])

[a]) For details, see *Exper. Part.*
[b]) NEM = *N*-ethylmorpholine; PMP = 1,2,2,6,6-pentamethylpiperidine.
[c]) DX = dioxane.
[d]) *Cf. Scheme 1* and text.
[e]) *N,N′*-Bis(1′,1′-dimethylprop-2′-ynyl)-2,3,5,6-tetramethyl-*p*-phenylenediamine (**9**).

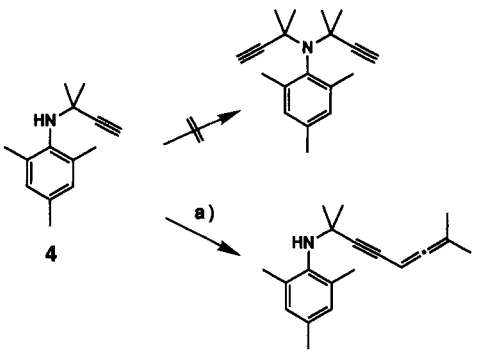
Scheme 1



R_n	R′	Compound (yield [%])	Remarks
2,4,6-Me_3	Me	**16** (12)	Alkylation in *t*-BuOH; see *Exper. Part.*
2,6-Et_2	Me	**17** (1.6)	See *Table 2.*
2,6-(i-Pr)$_2$	Me	**18** (7)	Alkylation without CuCl; see *Exper. Part.*
2,6-Me_2	$-(CH_2)_5-$	**19** (1)	See *Table 2.*

lated with 1,1-dimethylprop-2-ynyl chloride under the conditions given in *Table 2*. Similarly, sterically highly crowded anilines such as 2,4,6-triphenyl- and 2,4,6-tri(*tert*-butyl)aniline did not react with 1,1-dimethylprop-2-ynyl chloride under Cu(I) catalysis. Steric congestion also seems to be responsible for the fact that we never observed *N,N*-dialkylated products of the anilines mentioned in *Table 2*. When we tried to force the formation of such products by reacting *e.g.* 4 with 1,1-dimethylprop-2-ynyl chloride in dioxane in the presence of Et_3N and CuCl, we only observed the formation of the *C*-alkylation product **20** (*Scheme 2*).

Scheme 2

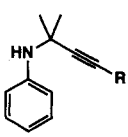


a) In dioxane with 1,1-dimethylprop-2-ynyl chloride; see *Table 2*.

On the other hand, **4** could be allylated with allyl bromide in the presence of collidine/K_2CO_3 to yield the 'mixed' aniline **21** (*Scheme 3*). The deprotonation of **4** in THF with 1 mol-equiv. of BuLi at $-60°$ and reaction with MeI led to a mixture of the *N*- and *C*-methylated anilines **22** and **23** (*Scheme 3*) which could easily be separated by chromatography. When TsCl was added instead of MeI, the *C*-chloro compound **24** was obtained in good yield (*Scheme 3*)[7]).

It has been reported that aliphatic amines can be alkylated with 3-chloro-3-methyl-1-phenylpent-1-yne in the presence of Cu(I)/Cu(0) [27]. We found that anilines, also those with unsubstituted *ortho*-positions, do not react with this highly substituted propargyl chloride under Cu(I)/Cu(0) catalysis. On the other hand, mesidine could be alkylated with 1,1-dimethylpenta-2,4-diynyl chloride under the usual conditions in low yield (*Scheme 4*). The low chemical stability of product **27** could be improved by silylation of the terminal acetylenic function with Me_3SiCl to yield compound **28.**

We were also interested to transform the acetylenic function *e.g.* in **4** into an allenyl group. The route for this transformation is shown in *Scheme 5* (*cf.* [28]). The reaction of **4** with $(i\text{-}Pr)_2NH/CH_2O$ in dioxane in the presence of CuBr, however, did not lead directly

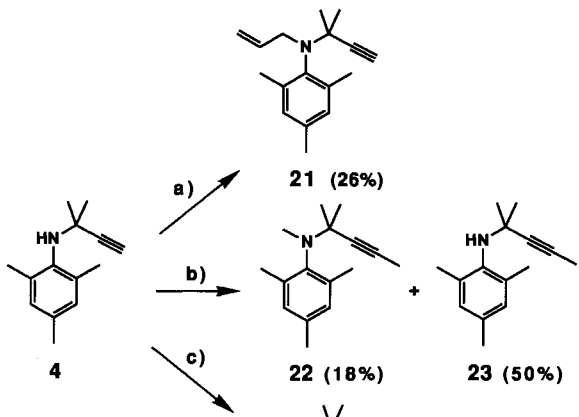


25 R = H

26 R = Cl

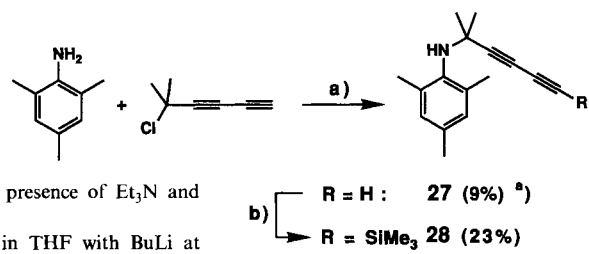
[7]) In the same manner, we obtained *N*-(3′-chloro-1′,1′-dimethylprop-2′-ynyl)aniline (**26**) from the corresponding aniline **25** [1].

Scheme 3



a) With allyl bromide in DMF in the presence of collidine/K_2CO_3 at 40–50°.
b) Deprotonation in THF with BuLi at –60° and addition of MeI.
c) Deprotonation in THF with BuLi at –60° and addition of TsCl.

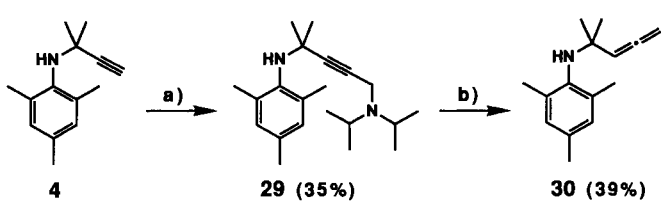
Scheme 4



a) In Et_2O in the presence of Et_3N and CuCl at 10–20°.
b) Deprotonation in THF with BuLi at –60° and addition of Me_3SiCl; –60 to10°.

a) Yields not optimized.

Scheme 5

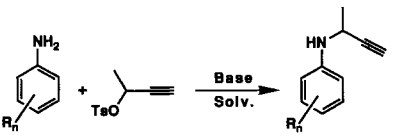


a) In dioxane with $(i\text{-}Pr)_2NH$ and 40% aq. CH_2O in presence of CuBr at reflux temperature.
b) Methylation with MeI in acetone at 20° followed by reductive elimination of $(i\text{-}Pr)_2NMe$ with $LiAlH_4$ in Et_2O at 20°.

to compound **30** as observed in other cases [28] (*cf.* [29])[8]). We isolated, as the main compound, the *Mannich* product **29**[9]). Methylation of **29** with MeI and reductive elimination of the ammonium function with $LiAlH_4$ in Et_2O yielded finally the expected product **30**.

2.2. N-*(1'-Methylprop-2'-ynyl)anilines*. The *N*-alkylation of the corresponding anilines could be performed with the tosylate of 1-methylprop-2-ynol in DMF in the presence of K_2CO_3 or $NaHCO_3$ in yields of *ca.* 30% (*Table 3*). In principle, the *N*-alkylation occurred also in dioxane in the presence of Et_3N and catalytic amounts of CuCl/Cu (*Table 3*). However, the yields of the *N*-alkylated anilines were generally lower. Neither 2,4,6-triphenylaniline nor 2,4,6-tri(*tert*-butyl)aniline could be *N*-alkylated with the tosylate of 1-methylprop-2-ynol under these conditions.

Table 3. *Preparation of* N-*(1'-Methylprop-2'-ynyl)anilines*[a])

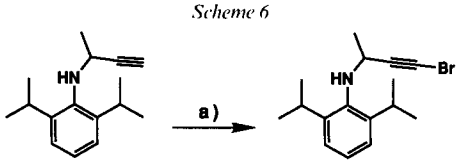


R_n	Base	Solvent	Temp. [°C]	Product	Yield [%]
2,6-Me_2	K_2CO_3	DMF	40–80	**32**	36
2,4,6-Me_3	K_2CO_3	DMF	70–75	**33**	26
2,6-(i-Pr)$_2$	Et_3N	DX[b])	20–30	**34**	28
2-Me-5,6-benzo	K_2CO_3	DMF	40–80	**35**	18
2,4-Me_2, 6-[(*E*)-styryl]	$NaHCO_3$	DMF	110	**36**	29

[a]) For details, see *Exper. Part* and *Table 2*.
[b]) In the presence of catalytic amounts of CuCl/Cu.

The *N*-propargylated aniline **34** was *C*-brominated with *N*-bromosuccinimide (NBS) after deprotonation with BuLi in THF/hexane (*Scheme 6*).

Scheme 6



34 **37 (26%)**

a) 1. BuLi/hexane, THF, –70°; 2. NBS.

2.3. N-*(1'-Arylprop-2'-ynyl)anilines*. To study the influence of aryl substituents at C(1') upon the cleavage of the N–C(1') bond in the course of the acid-catalyzed rearrangement of *N*-propargylated anilines, we synthetized the *N*-(1'-phenylprop-2'-ynyl)-anilines **38–41** (*Table 4*) by reaction of the corresponding anilines with 1-phenylprop-2-

[8]) It seems that the unprotected aniline function in **4** is responsible for the change of the reaction path (*cf.* [30]).

[9]) As a second product, the azetidine compund **31** was isolated in 5% yield. Presumably, **31** is formed *via* a cationic cyclization of the corresponding formiminium ion of **4** followed by hydride transfer to the generated vinyl cation.

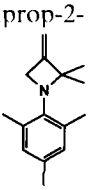


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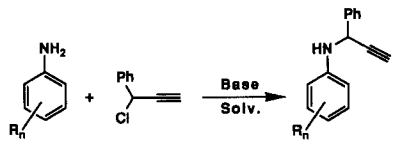
Table 4. *Preparation of* N-(*1′-Phenylprop-2′-ynyl*)*anilines*[a])



R_n	Base[b])	Solvent[c])	Temp. [°C]	Product	Yield [%]
2,6-Me_2	$NaHCO_3$	HMPT	70–80	**38**	31
2,6-Me_2	DMPM	DX	8–20	**38**	45[d])
2,4,6-Me_3	$NaHCO_3$	HMPT	20	**39**	33
2,4,6-Me_3	Et_3N	DX	5–20	**39**	18
2,3,5,6-Me_4	$NaHCO_3$	HMPX	70	**40**	36
2,6-Et_2	DMPM	DX	5–20	**41**	46[e])

[a]) For details, see *Exper. Part* and *Table 2.*

[b]) DMPM = (−)-(2*R*,3*S*)-3,4-dimethyl-2-phenylmorpholine, prepared from (−)-D-ephedrine according to [31].

[c]) The alkylation reactions in dioxane (DX) were performed in the presence of catalytic amounts of CuCl.

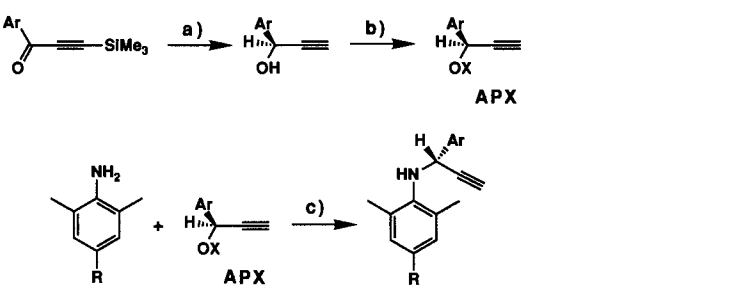
[d]) The purified material showed $[\alpha]_{589}^{20} = +1.05$ ($CHCl_3$); *i.e.* optical purity of *ca.* 0.9%.

[e]) The purified material showed $[\alpha]_{589}^{20} = -1.4$ ($CHCl_3$).

ynyl chloride in HMPT in the presence of $NaHCO_3$. The *N*-substituted anilines were also formed by reaction with 1-phenylprop-2-ynyl chloride in dioxane in the presence of CuCl and Et_3N or (−)-(2*R*,3*S*)-3,4-dimethyl-2-phenylmorpholine (DMPM; see [31]) as a base. The alkylation in the presence of DMPM was accompanied by an optical induction of *ca.* 1%.

For the synthesis of optically active *N*-(1′-arylprop-2′-ynyl)anilines of higher optical purity, we developed the pathway shown in *Scheme 7.* (−)-(*R*)-1-Arylprop-2-ynols (Ar=Ph and *p*-Tol) were obtained by asymmetric reduction of the corresponding 1-aryl-3-(trimethylsilyl)prop-2-ynones [32] with 9-borabicyclo[3.3.1]nonane (BBN) and (−)-α-pinene according to a procedure developed by *Midland et al.* [32], followed by

Scheme 7



(-) - 38 (22%) **Ar = Ph, R = H**

(-) - 39 (9%) **Ar = Ph, R = Me**

(-) - 42 (17%) **Ar = *p*-Tol, R = H**

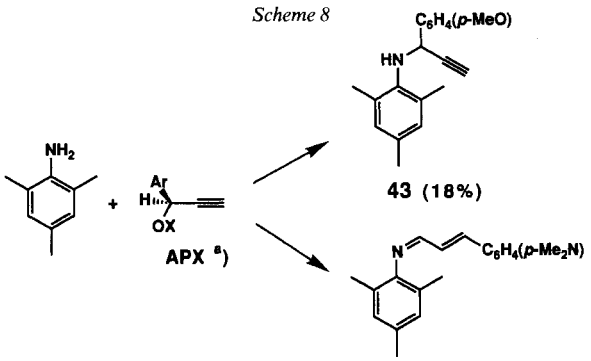
a) Reduction with BBN/(−)-α-pinene (o.p. 81%) in THF at 20° (*cf.* [32] and *Exper. Part*) followed by desilylation with NaOH in MeOH/H_2O.

b) Deprotonation in THF with BuLi in hexane at −60° and addition of MsCl and Et_3N (APX solution).

c) The corresponding aniline was added to the APX solution at −60°, alkylation at 10 to 20° (see *Exper. Part*).

desilylation. By this way, (−)-(*R*)-1-phenylprop-2-ynol was synthetized with $[\alpha]_{589}^{25} = -22.1$ ($CHCl_3$). Since the enantiomerically and optically pure alcohol shows $[\alpha]_{589}^{25} = 27.2$ ($CHCl_3$) [34], the (−)-(*R*)-antipode prepared according to *Scheme 7* possessed an optical purity (o.p.) of 81% in agreement with o.p. of the applied (−)-α-pinene (*cf.* [33]). The (−)-(*R*)-1-(*p*-tolyl)prop-2-ynol exhibited the same specific rotation as its Ph analogue. The *N*-alkylation of 2,6-dimethylaniline and 2,4,6-trimethylaniline was best performed with the mesylate (APX) of the optically active alcohols, prepared *in situ*, in THF in the presence of Et_3N. By this method, we obtained (−)-**38** with $[\alpha]_{589}^{25} = -57.5$ ($CHCl_3$) with an enantiomeric purity of 48%[10]). Similarly, the prepared (−)-**39** showed $[\alpha]_{589}^{25} = -50.3$, *i.e.* it must possess an optical purity comparable with that of (−)-**38**. This speaks for a loss of optical activity in the *N*-alkylation step of *ca.* 40%. Therefore, the reaction of the anilines with APX (*Scheme 7*) in THF seems to occur just at the borderline of a S_N2/S_N1 mechanism. This assumption is supported by the observation that the *N*-alkylation of 2,4,6-trimethylaniline with the tosylate of (−)-(*R*)-1-phenylprop-2-ynol yielded only (±)-**39**, and that the reaction of the mesylate of (−)-(*R*)-1-(*p*-tolyl)prop-2-ynol (o.p. *ca.* 81%) with 2,6-dimethylaniline led to the formation of (−)-**42** with $[\alpha]_{589}^{25} = -6.8$ ($CHCl_3$). This indicates a further substantial loss of optical activity in the alkylation step presumably due to the better charge stabilization at C(1) by the *p*-tolyl moiety as compared to the Ph group. To get more insight into the influence of *p*-substituents in the aryl moiety of APX (*Scheme 8*; Ar = *p*-NO_2Ph, *p*-MeOPh, and *p*-(Me_2N)Ph), we studied its reaction with 2,4,6-trimethylaniline in THF. The results are shown in *Scheme 8*. No product formation was observed with the *p*-NO_2 compound

Scheme 8



a) See *Scheme 7*; Ar = *p*-MeOPh and *p*-(Me_2N)Ph.

which was very labile in the presence of bases. The reaction with the *p*-MeO mesylate led to the formation of the expected *N*-alkylated product **43** in 18% yield. However, APX with the strongly electron-donating Me_2N group was too reactive, and only product **44**, presumably formed *via* the corresponding allenyl derivative (*cf. Scheme 1*), could be isolated in pure form in low yield. The latter case shows that, in a S_N1-type reaction, the APX molecule is attacked at C(3) by the sterically congested aniline.

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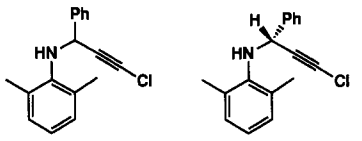
[10]) The 400-MHz ^{1}H-NMR spectrum of (−)-**38** in $CDCl_3$ in the presence of an excess of (+)-1-(9-anthryl)-2,2,2-trifluoromethanol ((+)-TAE) showed two *s* at 2.218 and 2.213 ppm in a ratio of 1:2.86 for Me–C(2) and Me–C(6).

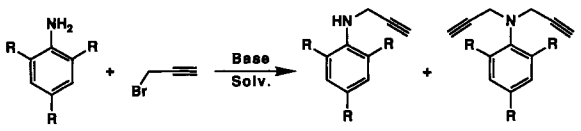


(±) - 45 (–) - 45

To study the influence of a Cl substituent at C(3) of the *N*-(1′-arylprop-2′-ynyl)anilines upon the acid-catalyzed rearrangement of these anilines, we synthetized the Cl derivative (±)-**45** and (–)-**45** of (±)-**38** and (–)-**38**, respectively, by reaction of the deprotonated anilines with MsCl (*cf. Scheme 3*). We assign the (*S*)-configuration to the anilines with (–)-rotation in $CHCl_3$ at 589 nm according to their preparation starting with the (–)-(*R*)-1-arylprop-2-ynols[11]).

2.4. N-*(Prop-2′-ynyl)anilines.* The alkylation of 2,4,6-trimethyl-, 2,4,6-triphenyl-, and 2,4,6-tri(*tert*-butyl)aniline with prop-2-ynyl bromide was performed in DMF or HMPT in the presence of K_2CO_3 and $NaHCO_3$, respectively (see *Table 5*). Whereas 2,4,6-

Table 5. *Preparation of* N-*(Prop-2′-ynyl)- and* N,N-*Di(prop-2′-ynyl)anilines*[a])



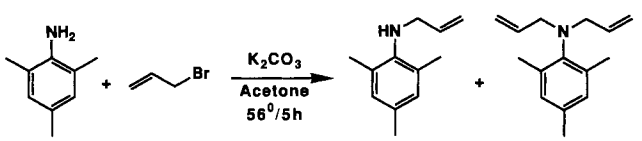
NPA NNPA

R	Base	Solvent	Temp. [°C]	NPA (yield [%])	NNPA (yield [%])
Me	K_2CO_3	DMF	75	**46** (14)	**47** (43)
Ph	$NaHCO_3$	HMPT	80	**48** (12)	**49** (48)
t-Bu	$K_2CO_3/NaHCO_3$	HMPT	90	**50** (3)	–[b])

[a]) For details, see *Exper. Part* and *Table 2.*
[b]) The formation of the NNPA product was not observed.

triphenylaniline could be alkylated in the same way as 2,4,6-trimethylaniline, yielding the *N,N*-disubstituted anilines as the main product, 2,4,6-tri(*tert*-butyl)aniline formed only the *N*-monosubstituted aniline **50** in low yield. The allylation of 2,4,6-trimethylaniline could easily be realized with allyl bromide in acetone in the presence of K_2CO_3 (*Scheme 9*). The *N,N*-diallylated compound was again the main product.

Scheme 9



51 (32%) **52** (61%)

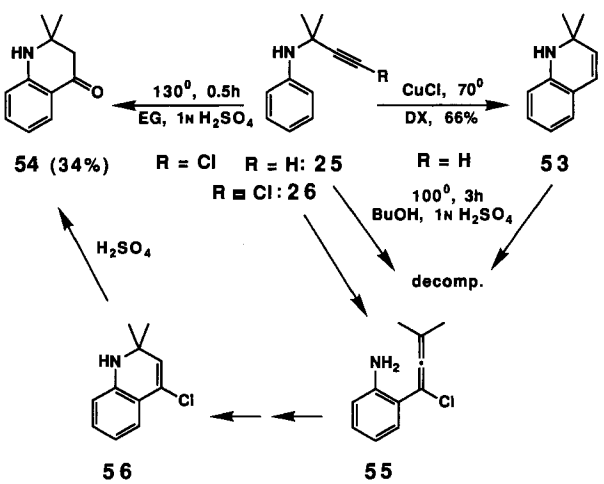
[11]) The (–)-enantiomer of *N*-(1′-phenylethyl)aniline possesses (*R*)-configuration [35]. However, *Hart* and *Eleuterio* [36] have found that 1-phenylethyl phenyl ether and its 2,6-dimethyl as well as its 2,4,6-trimethyl derivative show despite the same configuration at C(1′) opposite signs of rotation at 589 nm.

3. Rearrangements. – In general, the rearrangements of the *N*-propargylated anilines were performed under N_2 in the presence of *ca.* 1 equiv. of 0.1 to 1N aqueous H_2SO_4 in a miscible organic solvent at the boiling point of the mixture. The temperature range of 75 to 100° was attained with an admixture of the C_1–C_4 primary alcohols. For the temperature range of 100 to 120°, ethylene glycol (EG) was added as solvent. Rearrangements of unreactive anilines were carried out in sealed glass bombes at 130 to 250°. Analytical rearrangements of the anilines were studied in CCl_4 or $CDCl_3$ in the presence of 2–9 equiv. of CF_3COOH (TFA) at 20 to 30° directly in normal NMR tubes (diameter 5 mm)[12]).

3.1. N-*(1',1'-Dialkylprop-2'-ynyl)anilines with Unsubstituted* ortho-*Positions.* It is well established that this type of anilines can be rearranged in the presence of CuCl already at temperatures below 100° into the corresponding 2,2-dialkyl-1,2-dihydroquinolines in high yields (see [1] [23] [24] as well as [5] and literature cited therein). The non-catalyzed rearrangement requires, as mentioned, temperatures of *ca.* 200° [21].

The attempted acid-catalyzed rearrangement of the prototype **25** of these anilines at 100° led only to complete decomposition (*Scheme 10*)[13]). To prove the product stability under the reaction conditions, we synthetized the expected product **53** by the CuCl-catalyzed rearrangement of **25** [24]. Indeed, also **53** was completely decomposed at 100° in $BuOH/H_2SO_4$[14]). Further evidence for the fact that the acid-catalyzed rearrangement of **25** may occur, but that the lability of the formed product **53** under the reaction conditions is responsible for the observed decomposition, comes from the result of the acid-catalyzed rearrangement of the *C*-chloro derivative **26** of **25**. This compounds needs 120 to 130° for its acid-catalyzed rearrangement and yields the dihydroquinolone **54**. We interprete the

Scheme 10[a])



[a]) EG = ethylene glycol.

[12]) We observed that, under these conditions, a noticeable rearrangement within 10 min indicated a transformation within minutes in the aqueous system at 80°. On the other hand, no observable change of the corresponding aniline in the presence of TFA in CCl_4 or $CDCl_3$ within 24 h signified that the reaction in the aqueous system needed temperatures above 100° and reaction times of several hours.

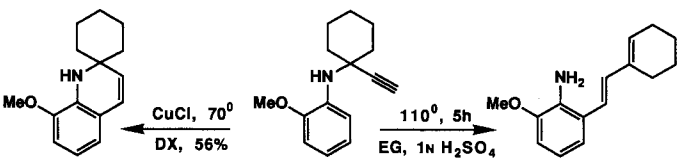
[13]) At lower temperatures, no reaction at all could be observed.

[14]) Decomposition of **53** was also observed in $CDCl_3$/TFA at 20°.

formation of **54** as the result of a hydrolysis of the rearrangement product **56** formed in usual way *via* the corresponding (1′-chloroallenyl)aniline **55** (see *Introduction* and later)[15]).

As a further example, we studied the acid-catalyzed rearrangement of the *N*-(ethynylcyclohexyl)aniline **14** which resulted in the formation of aniline **57** with a conjugated (*E*)-configurated buta-1,3-dienyl[16]) sub-structure in the side chain. It seems that in this case the primarily formed 2-allenyl-6-methoxyaniline is isomerized (at least in part) under the acidic conditions to form the buta-1,3-dienyl side chain. The rearrangement of **14** in the presence of CuCl yielded the expected spiro[cyclohexane-1,2′-1′,2′-dihydroquinoline] **58**. This compound, again, was not stable under the conditions of the acid-catalyzed rearrangement of **14**[17]). This observation excluded the possibility that **58** is the precursor of **57**.

Scheme 11



58 **14** **57** (19%)

These few experiments already show that acid catalysis is not a good alternative to the CuCl catalysis in the rearrangement of *N*-(1′,1′-dialkylprop-2′-ynyl)anilines with at least one unsubstituted *ortho*-position. On the other hand, the acid-catalyzed rearrangement of the (3-chloropropargyl)anilines (*e.g.* **26**) to yield the corresponding dihydroquinolones (*e.g.* **54**) may be a quite general method for the synthesis of this type of compounds, especially in view of the results of *Ariamala* and *Balasubramanian* (see *Footnote 15*).

3.2. N-*(1′,1′-Dialkylprop-2′-ynyl)anilines with Substituted* ortho-*Positions.* In view of the earlier results obtained in the catalyzed *Claisen* rearrangement of comparable allyl phenyl ethers (with BCl_3; see [38]) and propargyl phenyl ethers (with $AgBF_4$; see [25]), we studied the acid-catalyzed rearrangement of this class of anilines in more detail. The main feature of this mode of rearrangements is the formation of *m*-allyl- or *m*-allenyl-substituted phenols. Similarly, *Katayama et al.* [4] observed the formation of *m*-allylated anilines in the charge-induced rearrangement of *N*-allyl-*N,N*-dialkylanilinium ions with substituted *ortho*- and *para*-positions.

The acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-2,4,6-trimethylaniline (**4**) in a mixture of 0.1N aqueous H_2SO_4 and MeOH at 75–80° led after 2 h to a single product which was isolated in 41% yields. Its spectroscopic data established that it was the mesidine **59** carrying the 3-methylbuta-1,2-dienyl group at C(3) (*Scheme 12*). When the acid-catalyzed rearrangement of **4** was performed at 140°, the formation of a 12:1 mixture of (*E*)- and (*Z*)-**60** was isolated in 22% yield. It has been shown that thermal [1,5s]-sigmatropic H-shifts occur in allenylmesitylenes already at temperatures of *ca.* 160°

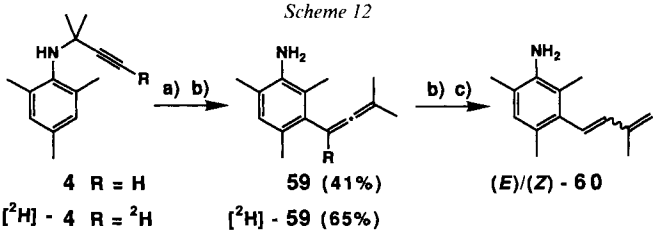
[15]) Recently *Ariamala* and *Balasubramanian* [37] have shown that the thermal rearrangement of 3-haloprop-2-ynyl phenyl ethers in refluxing EG leads to the formation of the corresponding chroman-4-one in high yields.

[16]) On the basis of J(H–C(1′),H–C(2′)) = 15.9 Hz.

[17]) Rapid decomposition of **58** occurred also in $CDCl_3$/TFA at 20°.

[39]. In the case of the desamino compound of **59**, the [1,5s]-H shifts are followed by corresponding [1,7a]-H shifts to yield (*Z*)-(3′-methylbuta-1′,3′-dienyl)mesitylene as the sole product, as a result of the cyclic transition state of the final [1,7a]-H shift [39]. Similarly, when **59** was heated in boiling 3-methylnonane for 1.8 h, only (*Z*)-**60** was formed. This selective transformation is a further chemical support for the structure of **59**, and it also shows that (*E*)/(*Z*)-**60** is presumably formed *via* an acid-catalyzed isomerization of **59**[18]). To demonstrate that, under the acidic conditions of the rearrangement, no proton exchange takes place in the propargyl moiety, we rearranged [^{2}H]-**4**[19]) under slightly improved acidic conditions as compared with the acid-catalyzed rearrangement of **4**. The sole product isolated in 65% yield was [^{2}H]-**59** carrying the ^{2}H-label exclusively at C(1′) (*Scheme 12*).

Scheme 12



a) **4**→**59**: MeOH/0.1N H_2SO_4, 75–80°, 3 h; [^{2}H]-**4**→[^{2}H]-**59**: DMF/*t*-BuOH/1N H_2SO_4, 95°, 0.5 h.
b) **4**→(*E*)/(*Z*)-**60**: MeOH/0.1N H_2SO_4, 140°, 3 h (glass bomb).
c) **59**→(*Z*)-**60**: 168° (boiling 3-methylnonane), 1.8 h.

The acid-catalyzed rearrangement of **4** in ROH/0.1 to 1N H_2SO_4 could not be performed at temperatures < 70°. Also, no rearrangement of **4** occurred on acidic silica gel or aluminium oxide (*cf.* [2]). Attempted rearrangements of **4** in the presence of CuCl (also with addition of anilinium hydrochloride) (*cf.* [23] [24]) also failed. Cleavage to mesidine was partly observed. Similarly, the attempted rearrangements of **4** in the presence of $AgBF_4$ (*cf.* [25]) or BCl_3 (*cf.* [38]) were unsuccessful. Thus, it seems that preparative rearrangements of the *N*-propargylated anilines with substituted *ortho*-positions can best be performed only with protic acids. For rearrangements on an analytical scale TFA (2–9 equiv.[20])) in $CDCl_3$ or CCl_4 turned out to be very effective (see below).

When *N*-(3′-chloro-1′,1′-dimethylprop-2′-ynyl)-2,4,6-trimethylaniline (**24**) was treated with 9 equiv. of TFA in $CDCl_3$ at 20°, a complete rearrangement of **24** took place to yield the iminium ion **61** which was identified by its ^{1}H- and ^{13}C-NMR spectrum (*Scheme 13;* see *Fig. 3* and *4* in *Chapt. 4*). Additional heating at 90° for 0.75 h led to a number of products of unknown structure (*cf.* [40] [41]). On the other hand, when **24** was rearranged with aqueous H_2SO_4 at 100°, the formation of a sole new product, namely the

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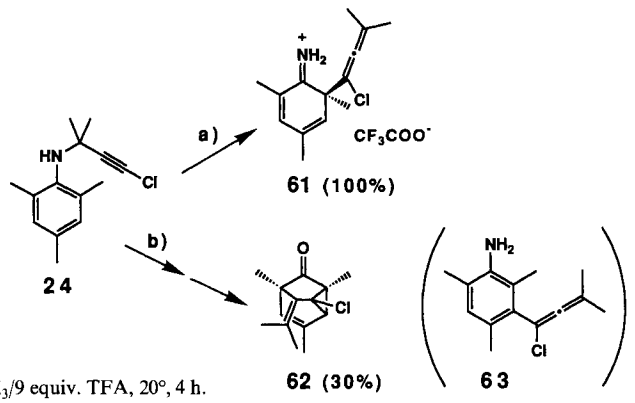
[18]) When **59** was heated at 180° for 3 h without a solvent, a 1:1 mixture of (*E*)- and (*Z*)-**60** resulted.

[19]) Prepared from **4** by ^{1}H/^{2}H-exchange with basic [$^2H_2$]O in dioxane (see Exper. Part).

[20]) The ^{1}H-NMR spectrum of **4** in $CDCl_3$ shows significant low-field shifts for all H-atoms after addition of up to 2 equiv. of TFA. Further addition of TFA results in no further significant change in the position of the ^{1}H signals. The *C*-chloro derivative **24** of **4** shows in the ^{13}C-NMR spectrum in $CDCl_3$ changes in the chemical shift of the ^{13}C-atoms after addition of up to 4 equiv. of TFA. Further addition of TFA induces no further change of the position of the ^{13}C signals. We conclude from these observation that 2–4 equiv. of TFA is sufficient for complete protonation of the *N*-propargylanilines in $CDCl_3$ (or CCl_4).

Scheme 13

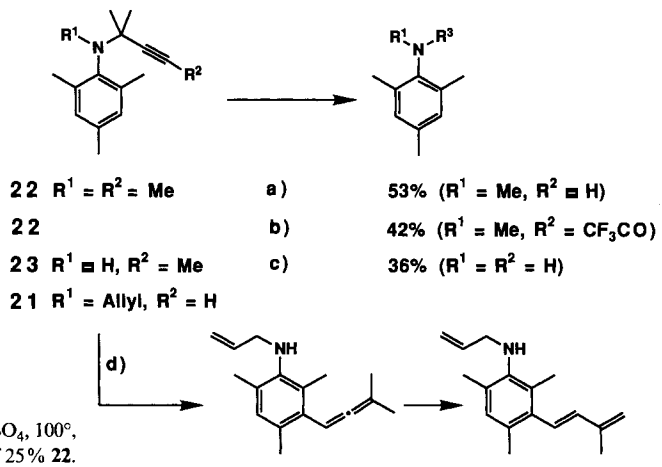


a) **24**→**61**: $CDCl_3$/9 equiv. TFA, 20°, 4 h.
b) **24**→**62**: i-BuOH/1N H_2SO_4,100°, 0.75 h.

tricyclic ketone **62** (*cf.* [41] [42]) was observed. It was isolated in a yield of 30% (*Scheme 13*). The formation of a 3-allenylated product, namely **63**, comparable with **59** (see *Scheme 12*) was not observed. These results indicate that iminium ions of type **61** may undergo in aqueous systems at 100° hydrolysis to the corresponding 6-allenylated cyclohexa-2,4-dienones which, then, yield the tricyclic ketones of type **62** by an intramolecular *Diels-Alder* reaction (see [41] [42][21]).

Less successful were the attempted acid-catalyzed rearrangements of *N*-(1′,1′-dimethylbut-2′-ynyl)-2,4,6-trimethyl- and *N*-(1′,1′-dimethylbut-2′-ynyl)-*N*,2,4,6-tetra-

Scheme 14



a) **22**: DMF/1N H_2SO_4, 100°, 1.5 h; recovery of 25% **22**.
b) **22**: TFAA in CH_2Cl_2, 42°, 2 h.
c) **23**: DMF/1N H_2SO_4, 100°, 1 h.
d) **21**: CH_2Cl_2/1 equiv. TFA, 42°, 3.5 h; 72% of **21** were unchanged.

[21]) Indeed, we cannot exclude the reverse reaction sequence, *i.e.* intramolecular *Diels-Alder* reaction of the iminium ions followed by hydrolysis of the formed tricyclic iminium ions.

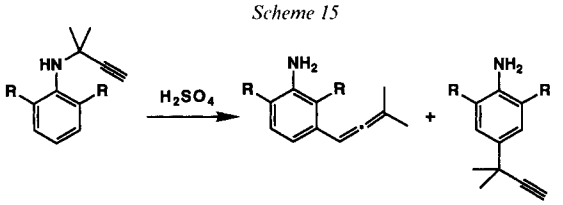
methylaniline (**23** and **22**, respectively). In the presence of aqueous H_2SO_4 at 100°, only dealkylation to the parent anilines were observed (*Scheme 14*). Also with TFA in $CDCl_3$ at 60°, only cleavage to the parent anilines occurred. When **22** was treated with trifluoroacetic anhydride (TFAA; *cf.* [43]) in boiling CH_2Cl_2 again cleavage took place to yield *N*-methyl-*N*-(trifluoroacetyl)mesidine (42%). These results show that an alkyl substituent in the 3-position of the propargyl moiety completely prevents the acid-catalyzed rearrangement of the corresponding anilines. It seems that electronic effects (σ-donor effect of the 3-alkyl substituent) are responsible for this fact, since the acid-catalyzed rearrangement of corresponding anilines with a 3-halogen substituent (*e.g.* **24**; see also below) occurs readily at temperatures of 20–100°.

That a further substituent at the N-atom does not effect the acid-catalyzed rearrangement is shown by the *N*-allyl derivative **21** of **4** which yielded in CH_2Cl_2 with 1 equiv. TFA the rearrangement product **64** within 3.5 h at 42° (*Scheme 14*)[22]).

We were not able to rearrange the *N*-(1′,1′-dimethylpentadi-2′,4′-ynyl)anilines **27** and **28** (*cf. Scheme 4*) neither in aqueous H_2SO_4 nor in $CDCl_3$/TFA. Prolonged reaction times and temperature of up to 105° led only to a destruction of the starting materials. Also the *N*-(1′,1′-dimethylbuta-2′,3′-dienyl)aniline **30** (*Scheme 5*) was destroyed under these reaction conditions.

The acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-2,6-dimethylaniline (**3**) in PrOH/0.05N H_2SO_4 at 90° led to the formation of the corresponding 3-allenylated aniline **66** which was isolated in 17% yield (*Scheme 15*)[23]). The low yield of

Scheme 15



3 R = Me	a)	**66** (17%)	– [a])
5 R = Et	b)	**67** (21%)	**68** (5%) [b])
12 R = EtO	c)	–	**69** (23%)
13 R = Cl	d)	–	–

a) PrOH/0.05N H_2SO_4, 90°, 1.5 h.
b) MeOH/1N H_2SO_4, 85°, 4 h.
c) EG/1N H_2SO_4, 125°, 0.8 h.
d) EG/1N H_2SO_4, 110°, 10 min; only decomposition.

[a]) Not observed.
[b]) Yield of purified material (analytical yield > 14%).

66 is due to its lability under the conditions of rearrangement. A *para*-rearrangement product was not detected. However, we found the comparable product **68** after the acid-catalyzed rearrangement of the corresponding 2,6-diethylaniline derivative **5** which also yielded the 3-allenylated aniline **67**.

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[22]) In the presence of an excess of TFA in $CDCl_3$ or CCl_4 at 20°, the starting aniline **21** was transformed, within 24 h, *via* **64** into the isomerized aniline (*E*)-**65** (*Scheme 14*).

[23]) *N*-(1′,1′-Dimethylprop-2′-enyl)-2,6-dimethylaniline undergoes the acid-catalyzed rearrangement into 4-(1′,1′-dimethylprop-2′-enyl)-2,6-dimethylaniline in benzene/H_2SO_4 already at 20° [2].

Interestingly, the 2,6-diethoxyaniline **12** could be rearranged at 125° in a mixture of EG and 1N H_2SO_4 to yield only the corresponding *para*-substituted product **69**. The 3-allenylated aniline was not observed in this case. The attempted acid-catalyzed rearrangement of the 2,6-dichloroaniline **13** led only to the destruction of the aniline[24]).

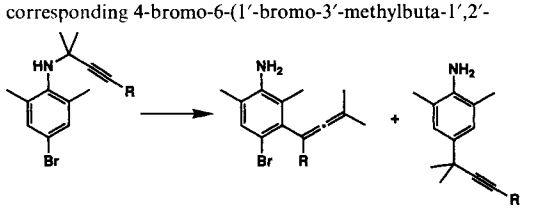
To investigate the influence of a Br and I substituent in the *ortho*-position of the anilines upon the acid-catalyzed rearrangement, the anilines **10** and **11** were heated at 86° or 94° in aqueous H_2SO_4 (*Scheme 16*). The rearrangement of the iodoaniline **10** was accompanied by an appreciable production of I_2, and the two allenyl-substituted anilines **70** and **71** were isolated only in low yield. We assume that the acid-catalyzed deiodation takes place already in the starting material **10**, and that the possibly formed 1,2-dihydro-2,2,6,8-tetramethylquinoline is destroyed under the acidic conditions (see *Chapt. 3.1*). The formation of **71** may be the result of a competing rearrangement of the deiodated aniline *via* the *ortho*-position occupied by the Me group. The formation of the allenyl-substituted aniline **72** from **11** shows that, in this case, the rearrangement of the dimethylpropynyl moiety has occurred mainly *via* the *ortho*-position occupied with the Me group[25])[26]).

Finally, we were interested in the acid-catalyzed rearrangement of the *N*-(1,1-dimethylprop-2-ynyl) derivative of pentamethyl- and 2,3,5,6-tetramethylaniline, since the first one has all termini for rearrangements occupied by Me groups and the latter one has, at least, both *meta*-positions substituted by Me groups[27]).

[24]) The thermal rearrangement of propargyl 2,6-dihalophenyl ethers at 230° in decane leads to a complex mixture of products due to the migration of halogen atoms [43].

[25]) There is evidence that the BCl_3-catalyzed rearrangement of allyl phenyl ethers with two different substituents at the *ortho*-positions as well as the rearrangement of the corresponding '*ortho*-dienones' include [3,3]-, [1,2]-, and to some extent [3,4]-sigmatropic rearrangements [38]. [3,4]-Sigmatropic rearrangements with propargyl moieties have been observed in the TFAA-catalyzed dienone-phenol rearrangement of 6-propargylated cyclohexa-2,4-dienones [44] as well as in the acid-catalyzed dienol-benzene rearrangement of the corresponding cyclohexa-2,4-dienols [45]. If [3,4]-sigmatropic rearrangements would play a role in the acid-catalyzed rearrangement of **10**, or especially **11**, the formation of *meta*-substituted anilines with a 1,1-dimethylprop-2-ynyl group should be observed. Isolated anilines **70**–**72** possess a allenyl group in the *meta*-position. Thus, they must be formed *via* the reaction sequence [3,3]- and [1,2]-sigmatropic rearrangement.

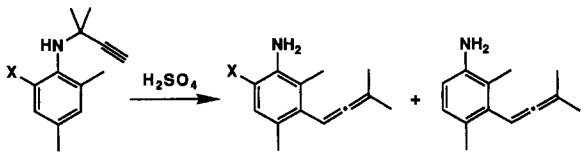
[26]) In preliminary experiments, we studied the acid-catalyzed rearrangement of 4-bromo-*N*-(1′,1′-dimethylprop-2′-ynyl)-2,6-dimethylaniline (**a**), structurally isomeric with **11**, and of its *N*-(3′-bromo-1′,1′-dimethylprop-2-ynyl) derivative **b** (synthetized from **a** according to *Scheme 6*). The formation of **c** and **d** from **a** shows that a Br substituent in the aniline part does not deactivate the aromatic system for the [3,3]-sigmatropic rearrangement in the anilinium ion, and that a Br-substituted C-atom in a corresponding 6-allenylated cyclohexa-2,4-dien-1-iminium ion can be the terminus in a [3,3]-sigmatropic rearrangement. This observation is further supported by the rearrangement of **b** in $CDCl_3$/TFA at 20°. The corresponding 4-bromo-6-(1′-bromo-3′-methylbuta-1′,2′-dienyl)-2,6-dimethylcyclohexa-2,4-dien-1-iminium ion is the intermediate that can be detected (by ^1H- and ^{13}C-NMR spectroscopy) after short reaction times. Prolonged reaction times lead to the formation of **e** as the sole final product. It is evident that allenyl moieties with a halogen substituent at C(1) (*cf. Scheme 13*) do not undergo [1,2]-sigmatropic rearrangements in the corresponding iminium ions.



a R = H BuOH/1N H_2SO_4, 100° **c** (37%) **d** (10%)
b R = Br $CDCl_3$/TFA, 20° – **e** (>50%)

[27]) The *p*-phenylenediamine derivative **9** (*cf. Table 2*) which may also be considered within this class of highly substituted *N*-propargylated anilines gave, on treatment with 1N H_2SO_4 at 80°, mainly decomposition and a mixture (*ca.* 15%) of several products which were not further investigated (ν(C=O) and ν(OH, phenol) vibrations were present in the IR spectrum of the mixture).

Scheme 16

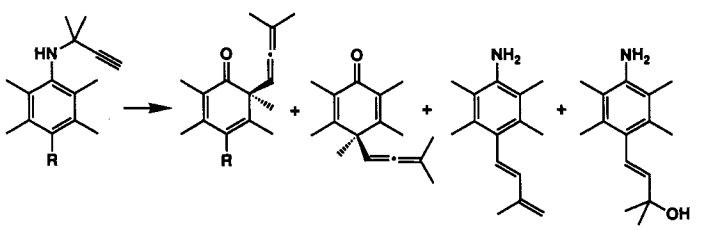


10 X = I	a)	**70** (3%)	**71** (3%)
11 X = Br	b)	**72** (30%)	–

a) PrOH/EG/1N H_2SO_4, 86°, 1.4 h; 9% of **10** recovered.
b) i-BuOH/EG/1N H_2SO_4, 94°, 1 h.

The acid-catalyzed rearrangement of the pentamethylaniline **8** led to the formation of a neutral product contaminated (10:1) by a second product of similar spectroscopic properties. The spectroscopic data showed that the main product was the *para*-dienone **74** accompanied presumably by the corresponding *ortho*-dienone **73** (*Scheme 17*). It is of interest to note that the *para*-dienone bears the 3-methylbuta-1,2-dienyl moiety. This structural feature indicates that **74** must be formed from **73** or its corresponding iminium structure *via* two consecutive [1,2]-sigmatropic rearrangements. The structures of the products from the acid-catalyzed rearrangement of **7** are in full agreement with these observations (*Scheme 17*). Despite the fact that the aniline **7** has an unsubstituted

Scheme 17



8 R = Me	a)	**73** [a])	**74** (15%)	-	-
7 R = H	b)	**75** (11%)	-	**76** (5%)	**77** (10%)

a) EtOH/1N H_2SO_4, 84°, 2 h.
b) EtOH/1N H_2SO_4, 85°, 1 h.

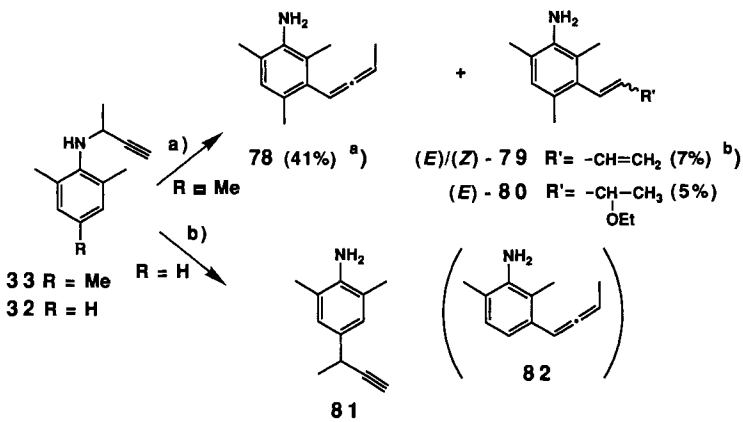
[a]) The dienone **74** contained 9% of second dienone which is presumable **73**.

para-position, the *ortho*-dienone **75** is stable enough to be isolable. It shows no great tendency to rearrange under the reaction conditions to a corresponding *para*-dienone which would rapidly be enolized to yield *para*-substituted phenols. This type of compounds was not detected in the reaction mixture of **7** (see also *Chapt. 3.3*). On the contrary, the produced *para*-substituted compounds **76** and **77** are isomerized anilines that can structurally be traced back to 2,3,5,6-tetramethyl-4-(3′-methylbuta-1′,2′-dienyl)-

aniline and the corresponding iminium ion as its precursor. From these observation, we can conclude that the iminium ion resulting from the [3,3]-sigmatropic rearrangement in the anilinium ion of **7** undergoes two competing reaction, *i.e.* hydrolysis to the *ortho*-dienone **75** and two consecutive [1,2]-sigmatropic shifts of the allenyl moiety to yield a corresponding 4-allenylcyclohexa-2,5-dien-1-iminium ion which rapidly tautomerizes to the aniline structure from which **76** and **77** can be derived by acid-catalyzed side-chain isomerization (see the preceding examples) followed by acid-catalyzed hydratization of the terminal C=C bond.

3.3. N-*(1'-Methylprop-2'-ynyl)anilines with Substituted* ortho-*Positions*. This type of anilines remained completely unchanged over days when treated with TFA in aprotic solvents such as $CDCl_3$ or CCl_4 at 30°. Also, no reaction was observed, when they were kept in ROH/1N H_2SO_4 at temperatures up to 100° for 2 h. Heating aniline **33** for 2 h at 134° in EtOH/1N H_2SO_4 in a glass bomb led to 74% of conversion, yielding the products shown in *Scheme 18*. The main component was the expected 3-(buta-1',2'-dienyl)-2,4,6-

Scheme 18



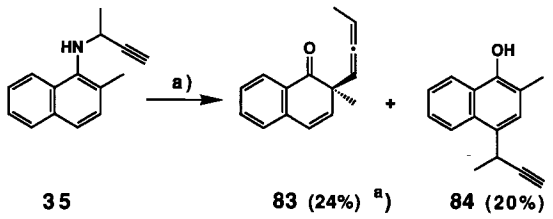
a) EtOH/1N H_2SO_4, 134°, 2 h; recovery of 26% of **33**.
b) EtOH/1N H_2SO_4, 140°, 2.5 h.

[a]) Yields calculated for rearranged **33**.
[b]) Isolated as a 1:1 mixture with **78**.

trimethylaniline (**78**) that was in part already isomerized to (*E*)/(*Z*)-**79** which, in turn, had added EtOH under the acidic conditions. The acid-catalyzed rearrangement of the *N*-propargylated aniline **32** led in a yield of 23% to a high-boiling material which might be a dimer or oligomer of the expected 3-(buta-1,2-dienyl)aniline **82**. The 4-propargylated aniline **81** was isolated in only 2% yield. In general, the behavior of **32** under acid catalysis is comparable with those of the *N*-(1',1'-dimethylprop-2'-ynyl)anilines **3** and **5** (see *Scheme 15*).

It is well known that the thermal *Claisen* and amino-*Claisen* rearrangement in naphthalene systems require lower temperatures due to smaller $\Delta H^{\neq}$ and similar $\Delta S^{\neq}$ values as compared to benzene systems (*cf. e.g.* [1] [46]). Nevertheless, the acid-catalyzed rear-

Scheme 19



35 **83** (24%) [a]) **84** (20%)

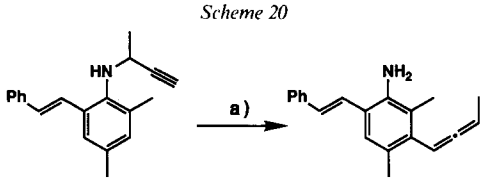
a) PrOH/1N H_2SO_4, 135°, 3 h (glass bomb).

[a]) Mixture (3:4) of the two possible diastereoisomers.

rangement of the 1-naphthylamine derivative **35** in PrOH/1N H_2SO_4 required conditions similar to those for the rearrangement of **32** and **33** (*Scheme 19*). The structure of the two products **83** and **84** shows that the deamination took place after the first [3,3]-sigmatropic rearrangement. The [1,2]-sigmatropic shift in **83** or in its iminium precursor is hindered by the benzoannelation (*cf.* [38]).

The 'out-of-ring'-*Claisen* rearrangement is a well-established phenomenon of the thermal behavior of 2- and 4-vinyl-substituted allyl dimethylphenyl ether (*cf.* [46] [47]). Therefore, we were interested in the acid-catalyzed rearrangement of the aminostilbene derivative **36** (*Scheme 20*). The only product that could be isolated beside the starting material was the buta-1,2-dienyl derivative **85**. Thus, the (2*E*)-styryl-substituted C-atom of **36** seems not to be a terminus for the [3,3]-sigmatropic rearrangement in the anilinium ion of **36**[28]).

Scheme 20



36 **85** (7%) [a])

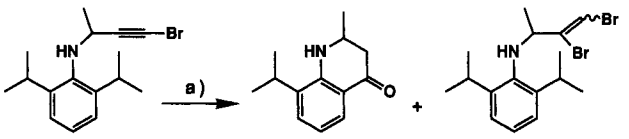
a) EG/1N H_2SO_4, 130°, 2 h; 41% of **36** were recovered.

[a]) Based on rearranged **36**.

As the last example, we studied the acid-catalyzed rearrangement of *N*-(3′-bromo-1′-methylprop-2′-ynyl)-2,6-diisopropylaniline (**37**) that occured in EG/1N H_2SO_4 at 115–125° within 50 min (*Scheme 21*). It opened a new aspect of this type of rearrangement, since the structure of the main product **86** clearly showed that, in the course of the rearrangement, one i-Pr group had been eliminated. A similar loss of a *t*-Bu group (as

[28]) We suppose that the 3-(buta-1,2-dienyl) isomer of **85** would cyclize to yield strongly fluorescing naphthalene derivatives (*cf.* [48]).

Scheme 21

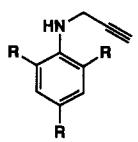


37 **86 (59%)** **87 (16%) [a])**

a) EG/1N H_2SO_4, 115–125°, 0.8 h; some **37** (*ca.* 10%) could be determined.

[a]) Configuration not determined.

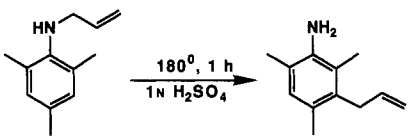
isobutene) in a *retro*-ene reaction was observed in thermal rearrangement of the ethers **1** and **2** ($R^1 = t$-Bu, R^2 = Me, *cf. Table 1*) [13]. So, we postulate that the iminium ions arising from the [3,3]-sigmatropic rearrangement in the anilinium ions of **37** lose propene in a *retro*-ene reaction to yield the corresponding 2-(1′-bromobuta-1′,2′-dienyl)-6-isopropylaniline, which undergoes ring closure and hydrolysis as shown in *Scheme 10* for **55** (*cf.* also [37]). The formation of compound **87** may best be explained as the result of a attack of Br-atoms upon the starting material (*cf.* [37]).



46 R = Me
48 R = Ph
50 R = *t*-Bu

None of the *N*-(prop-2′-ynyl)anilines **46**, **48**, and **50** showed any change when heated in 1N H_2SO_4 in glass bombs at temperatures $\leq$ 180°. Temperatures of 190–240° led within 1 to 3 h to a nearly complete destruction of the reactants. Aniline **48** showed after heating in 1N H_2SO_4 at 230° (20 min) and at 248° for additional 20 min 90% decomposition and the formation of 4% of 2,4,6-triphenylaniline. On the other hand, *N*-allyl-2,4,6-trimethylaniline (**51**) was rearranged within 1 h to yield the expected 3-allyl-2,4,6-

Scheme 22

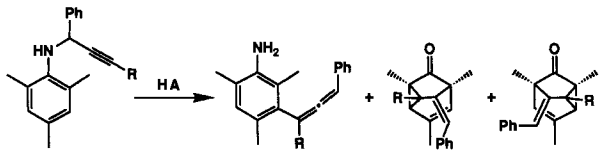


51 **88 (32%)**

trimethylaniline (**88**) when heated in 1N H_2SO_4 at 180° (*Scheme 22*). These conditions are comparable with those for the acid-catalyzed rearrangement of *N*-allyl-2,6-dimethylaniline (2N H_2SO_4, 155°, 2 h) which leads to the exclusive formation of 4-allyl-2,6-dimethylaniline [2].

3.4. N-*(1′-Arylprop-2′-ynyl)anilines with Substituted* ortho-*Positions.* This type of anilines turned out to be the most reactive in the acid-catalyzed rearrangements. For example, aniline **39** underwent rearrangement already in part during the ^{1}H-NMR measurement, when it was dissolved in CCl_4/2.7 equiv. TFA at 20°. The reaction was completed after 7 h at 20° and yielded 2,4,6-trimethyl-3-(3′-phenylpropa-1′,2′-dienyl)aniline

Table 6. *Acid-Catalyzed Rearrangements of 2,4,6-Trimethyl-N-(1′-phenylprop-2′-ynyl)anilines* (**39**)



39 **89** (*E*)-**90** (*Z*)-**90**

Compound	R	HA/Solvent	Temp. [°C]	Time [h]	Yield [%]		
					89	(*E*)-**90**	(*Z*)-**90**
39	H	TFA/CCl_4	20	7	40	–	–
39	H	1N H_2SO_4/BuOH[a])	92	1.2	38	11[b])	8[b])
(–)-**39**[c])	H	1N H_2SO_4/PrOH	85	1.3	38[d])	8[e])	8[e])
[^{2}H]-**39**[f])	^{2}H	1N H_2SO_4/i-BuOH	92	1.0	50	12[b])	10[b])

[a]) 7% of the starting material were recovered.
[b]) The mixture (*E*)/(*Z*)-**90** was not separated.
[c]) $[\alpha]_{589}^{20} = -50.3$ ($CDCl_3$); o.p. 48% (see *Exper. Part*).
[d]) The allene showed $[\alpha]_{589}^{20} = -280$ ($CHCl_3$).
[e]) The (*E*)/(*Z*)-mixture showed $[\alpha]_{589}^{20} = +89.4$ ($CHCl_3$); it was composed of (+)-(*E*)- and (–)-(*Z*)-**90** (see text).
[f]) Prepared by ^{1}H/^{2}H exchange of **39** with [^{2}H]$_2$O/NaO^{2}H in DX.

(**89**) as the sole product (*Table 6.*). The acid-catalyzed rearrangement of **39** in a mixture of BuOH/1N H_2SO_4 at 92° yielded, beside the allene **89**, the (*E*)/(*Z*)-mixture of the tricyclic ketones **90**. The mixture was not separated.

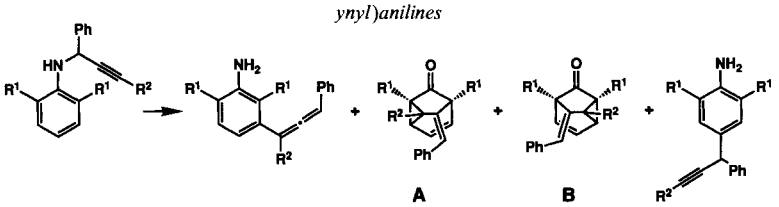
Nevertheless, the diastereoisomeric ketones could be unequivocally characterized in the mixture by their ^{1}H- and ^{13}C-NMR spectra (see *Chapt. 4.3*). The analogous rearrangement of (–)-**39** led to the formation of (–)-**89** and the (*E*)/(*Z*)-mixture of ketone **90** which showed a global positive sign of rotation at 589 nm (see *Table 6*). We assume that the mixture consisted of (+)-(*E*)-**90** and (–)-(*Z*)-**90** according to the experiments with (–)-**38** (see below). The acid-catalyzed rearrangement of [^{2}H]-**39** yielded [^{2}H]-**89** and the (*E*)/(*Z*)-[^{2}H]-**90** with a well-defined position of the ^{2}H-label in both products, in agreement with a [3,3]-sigmatropic process followed by an intramolecular, possibly acid-catalyzed *Diels-Alder* reaction[29]) or by an acid-catalyzed [1,2]-sigmatropic shift of the allenyl side chain[30]).

The results of the acid-catalyzed rearrangement of *N*-(1′-phenylprop-2′-ynyl)- and *N*-(3′-chloro-1′-phenylprop-2′-ynyl)anilines with an unsubstituted *para*-position are shown in *Table 7* and in *Scheme 23*. It can be seen that the 2,6-dialkylaniline derivatives **38**, **41**, and **45** behave similarly to the corresponding 2,4,6-trimethylanilines (*Table 6* and *Scheme 13*) except the fact that now the corresponding *para*-alkylated anilines are also formed. The exclusive formation of products (*cf.* **93**, **96**, and **98**) with the prop-2-ynyl side

[29]) In a control experiment, we reacted 2,4,6-trimethylphenol with 1-phenylprop-2-ynyl chloride in the presence of K_2CO_3 in boiling acetone. After 48 h, a 1:1.3 mixture (*E*)/(*Z*)-**90** was isolated in a yield of 1%. This experiment indicates that the intramolecular *Diels-Alder* reaction, at least on the ketone stage, occurs already at *ca.* 56° without acid catalysis.

[30]) The allene (–)-**89** from the rearrangement of (–)-(*S*)-**39** (see *Table 6*) should posses the (*R*)-configuration on the basis of *Lowe*'s rule for optically active 1,3-diarylallenes [49] (*cf.* [50]). This assignment is in agreement with a suprafacial [3,3]-sigmatropic rearrangement occurring with inversion of configuration with respect to the transposition of the propargyl into the allenyl moiety (*cf.* the correlation of centers of chirality with axes of chirality *via* the *Claisen* rearrangement (*cf.* [51] and literature cited therein)).

Table 7. *Acid-Catalyzed Rearrangements of 2,6-Dialkyl-*N*-(1′-phenylprop-2′-ynyl)- and* N*-(3′-Chloro-1′-phenylprop-2′-ynyl)anilines*

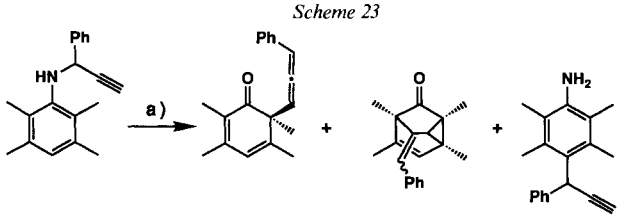


A B

Compound	R^1	R^2	HA/Solvent	Temp. [°C]	Time [h]	3-Allenyl Compound (yield [%])	Ketone A (yield [%])	Ketone B (yield [%])	4-Alkyne (yield [%])
38	Me	H	1N H_2SO_4/EtOH[a])	78	3	**91** (21)[b])	(*E*)-**92** (9.5)	(*Z*)-**92** (9.5)	**93** (25)
(−)-**38**[c])	Me	H	1N H_2SO_4/PrOH[d])	86	0.83	(−)-**91** (2)[e])	(+)-(*E*)-**92**[f]) (4.4)	(−)-(*Z*)-**92**[f]) (3.6)	(−)-**93**[g]) (8)
41	Et	H	1N H_2SO_4/EtOH	78	1.2	**94** (11)	(*E*)-**95**[h]) (*ca.* 4)	(*Z*)-**95**[h]) (*ca.* 4)	**96** (32)
45	Me	Cl	1N H_2SO_4/i-BuOH[i])	100	4	–[j])	(*Z*)-**97**[k]) (22)	(*E*)-**97**[k]) (22)	**98** (4)
(−)-**45**[l])	Me	Cl	1N H_2SO_4/i-BuOH[m])	90	1.2	–[j])	(+)-(*Z*)-**97**[n]) (22)	(+)-(*E*)-**97**[n]) (26)	–[o])

[a]) 20% of the starting material were recovered.
[b]) Obtained as the mixture with **93**. Distillation (180°/high vacuum) destroyed **91** and yielded pure **93**.
[c]) (*S*)-Configuration; $[\alpha]_{589}^{20} = -55.2$ ($CHCl_3$; e.e. = 48%; see *Exper.Part.*)
[d]) 10% of the starting material with $[\alpha]_{589}^{20} = -45.2$ ($CHCl_3$; *i.e.* o.p. 39%) were recovered.
[e]) Yield of (−)-**91** after rigorous purification by flash chromatography; $[\alpha]_{589}^{20} = -420$ ($CHCl_3$); presumably (*R*)-configurated (see *Footnote 30*).
[f]) The pure diastereoisomers were obtained by prep. HPLC. Their CD spectra are shown in *Fig. 1*. Determination of e.e. with (−)-1-(9-anthryl)-2,2,2-trifluoroethanol ((−)-TAE) gave for both forms 46%.
[g]) The purified material gave $[\alpha]_{589}^{20} = -13.1$ ($CHCl_3$) of unknown o.p. It should possess (*S*)-configuration (see text).
[h]) Only the *ca.* 1:1 mixture (8%) of the diastereoisomers was investigated.
[i]) 25% of the starting material were recovered.
[j]) The corresponding allene was not detected in the reaction mixture.
[k]) The diastereoisomers were separated by chromatography on silica gel.
[l]) $[\alpha]_{589}^{20} = -16.8$ ($CHCl_3$; o.p. 48% according to that of (−)-**38**; see *Exper. Part*).
[m]) 17% of the starting material with $[\alpha]_{589}^{20} = -8.7$ ($CHCl_3$; *i.e.* o.p. *ca.* 25%).
[n]) (+)-(*Z*)-**97** showed $[\alpha]_{589}^{20} = +134.8$ ($CHCl_3$; e.e. (measured in the presence of (−)-TAE) *ca.* 49%). (+)-(*E*)-**97** showed $[\alpha]_{589}^{20} = +5.3$ ($CHCl_3$; e.e. (measured in the presence of (−)-TAE) *ca.* 49%). For the ORD curves of both forms, see *Fig. 2*.
[o]) Not isolated.

Scheme 23



40 **99** (6%)[a]) (*E*)/(*Z*)-**100** (20%)[b]) **101** (23%)

a) 1 mol-equiv. (+)-campher-10-sulfonic acid in EtCOMe/H_2O at 74° for 1 h; 1.4% of racemic starting material was observed.

[a]) Mixture (*ca.* 1:1) of the diastereoisomers; the mixture showed no optical rotation.
[b]) (*E*)- and (*Z*)-**100** (1:1 mixture) were not separated; the mixture showed no optical rotation.

chain indicates that these compounds are formed by two consecutive [3,3]-sigmatropic rearrangements. This view is supported by the fact that the acid-catalyzed rearrangement of (−)-**38** leads to the formation of (−)-**93** which should possess the (*S*)-configuration according to the double inversion process of the rearranging propynyl moiety (*cf. Footnote 30*). That the first sigmatropic process is clearly intramolecular and leads, according to the topicity of the aniline part, to the formation of diastereoisomeric 6-allenyl-substituted 2,6-dialkylcyclohexa-2,4-dien-1-iminium ions is shown by the formation of the (*E*)- and (*Z*)-configurated tricyclic ketones as a result of the following intramolecular *Diels-Alder* reaction. This reaction sequence occurs without loss of stereochemical information as is shown by the same e.e. values of starting materials and (*E*)- and (*Z*)-configurated tricyclic ketones. Moreover, the CD spectra of (*E*)- and (*Z*)-**92** as well as the ORD curves of (*Z*)- and (*E*)-**97**[31]) (*cf. Fig. 1* and *2*) clearly exhibit mirror-image behavior which demonstrates that the tricyclic skeletons of the (*E*)- and (*Z*)-isomers are enantiomorphic. On the basis of the inversion of configuration in the first [3,3]-sigmatropic step (*cf. Footnote 30* and *Table 7*) and the consecutive intramolecular [4s+2s] cycloaddition reaction, (*E*)-**92** and (*Z*)-**92** must possess the (1*S*,2*S*,5*R*,7*S*)- and the (1*R*,2*R*,5*S*,7*R*)-configuration, respectively, and correspondingly, (*Z*)-**97** and (*E*)-**97** the (1*R*,2*R*,5*R*,7*R*)- and

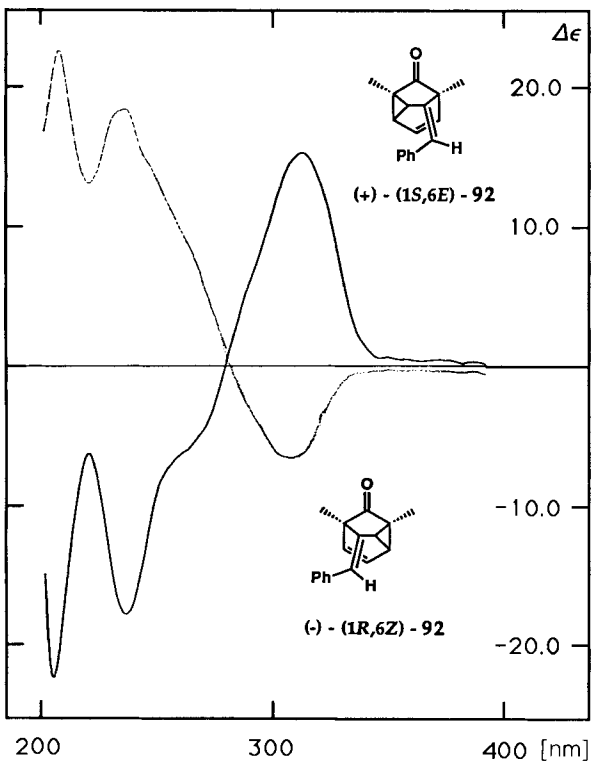


Fig. 1. *CD Spectra* (dioxane) *of chemically pure (+)-(E)- and (−)-(Z)-***92** *from the acid-catalyzed rearrangement of (−)-***38**

[31]) Compounds (*E*)-**92** and (*Z*)-**97** as well as (*Z*)-**92** and (*E*)-**97** have the same configuration at the exocyclic C=C bond. The stereochemical designator changes according to the priorities of the subsituents (*i.e.* Cl > H).

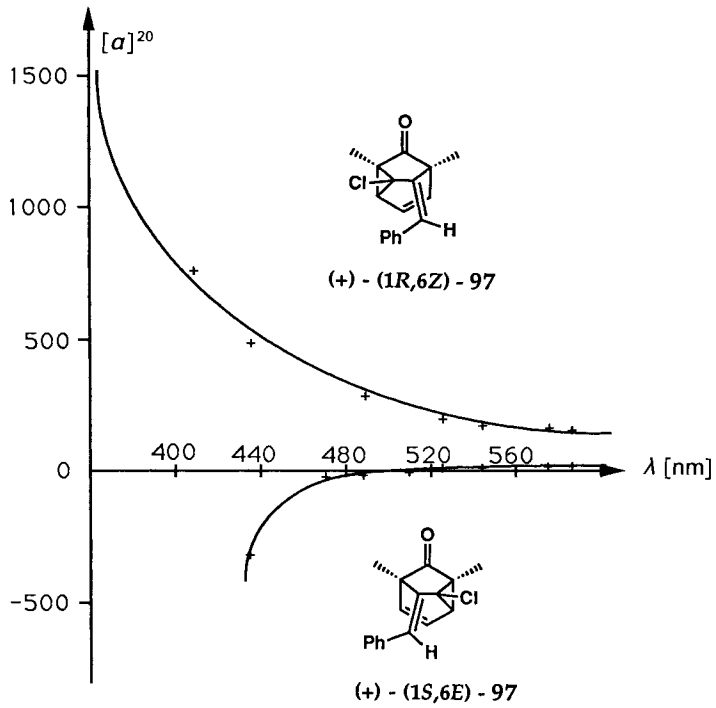
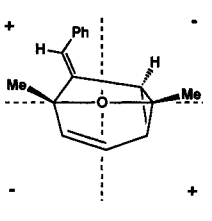


Fig. 2. *ORD Plain curves above 360 nm* ($CHCl_3$) *of chemically pure (+)-(Z)- and (+)-(E)-***97** *from the acid-catalyzed rearrangement of (−)-***45**

(1*S*,2*S*,5*S*,7*S*)-configuration, respectively. The observed CE's are in accordance with assignment of the absolute configurations for the (*E*)- and (*Z*)-isomers[32]).

The acid-catalyzed rearrangement of **45** yielded no *meta*-substituted allene derivative. This shows again (*cf. Scheme 13* and *Footnote 26*) that a 1′-halogen substituent in allenyl moiety of the cyclohexa-2,4-dien-1-iminium intermediate hinders strongly the sigmatropic [1,2]-shift of the allenyl group. Also, the [3,3]-sigmatropic rearrangement to yield the *para*-propynylated products seems to be retarded in favor of the intramolecular *Diels-Alder* reaction leading to the tricyclic ketones with a 1′-Cl substituent in the allenyl side chain (*cf.* the yields of **93** and **96** in comparison to that of **98**; *Table 7*).

[32]) The CE's observed above 300 nm can be attributed to n→π* transitions of the C=O group enhanced by homoconjugation with the C(6)=C(9) bond. The position and magnitude of the CE is clearly dependent on the relative location of the Ph group at C(9). Compounds (+)-(*E*)-**92** and (+)-(*Z*)-**97** with the same absolute configuration and the same relative location of the Ph group show the maximum at 312.4 ($\Delta\varepsilon$ = +15.4) and 313.8 nm ($\Delta\varepsilon$ = +28.1), respectively. Compound (−)-(*Z*)-**92** which exhibits strong steric interactions between Me–C(5) and Ph–C(9), turning Ph–C(9) out of conjugation with the C(6)=C(9) bond (*cf. Chapt. 4.3*), shows the maximum at 307.0 nm ($\Delta\varepsilon$ = −6.6). The sign of the CE's are in accordance with the extended octant rule for β,γ-unsaturated ketones and a *transoid*-orientation of the C(6)=C(9) bond with respect to the C=O group (see [52] and literature cited therein). A more detailed chiral sphere analysis (see [53] and examples discussed therein) of the whole tricyclic skeleton confirms these assignments, since mainly (+)-contributions, for example for (+)-(*E*)-**92**, are expected from the dominating parts of the molecule in the upper-left and lower-right octants.

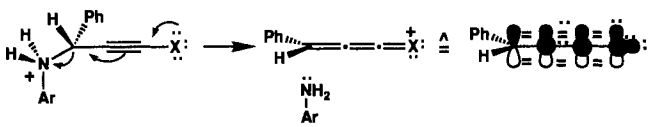


(+) - (*E*) - 92

The acid-catalyzed rearrangement of 2,3,5,6-tetramethyl-*N*-(1′-phenylprop-2′-ynyl)-aniline (**40**) in the presence of (+)-campher-10-sulfonic acid led, in addition to the product types already discussed (*Tables 6* and *7*), to the formation of the corresponding 6-allenyl-substituted cyclohexadienone **99** as a mixture of the expected diastereoisomers (*Scheme 23*). All compounds showed no optical induction. It is of interest to note that the acid-catalyzed rearrangement of the corresponding *N*-(1′,1′-dimethylprop-2′-ynyl)-aniline **7** (*cf. Scheme 17*) did not lead to the formation of a tricyclic ketone, and that the observed *para*-substituted products are derived from the corresponding allenylated aniline. These observations indicate that the 3-methylbuta-1,2-dienyl moiety in the intermediate cyclohexadieniminium ions tends to undergo preferably [1,2]-sigmatropic shifts, whereas the corresponding 3-phenylprop-1,2-dienyl substituent favors the intramolecular *Diels-Alder* reaction leading to the tricyclic ketones in competition to the [3,3]-sigmatropic rearrangement yielding the *para*-propynylated anilines[33]).

The results of the acid-catalyzed rearrangements of (−)-**38** and its 3′-Cl derivative (−)-**45** reveal another interesting aspect of this type of charge-induced reactions. The optical activity of the starting materials recovered after 90% ((−)-**38**) and 83% ((−)-**45**) conversion indicate a loss of 19% and 48%, respectively, of the original optical activity. This finding indicates that the [3,3]-sigmatropic process in the corresponding anilinium ions takes place at the borderline of a heterolytic cleavage of the N–C(1′) bond and, thus, a certain degree of freedom of the formed prop-2′-enyl cation so that an exchange of its enantiotopic sites can occur. The 3′-Cl substituent clearly favors the cleavage process, since it stabilizes the prop-2′-ynyl cation by its π-donor ability (*Scheme 24*). The heterolysis of the N–C(1′) bond should be further accentuated by donor substituents in the Ph moiety at C(1′). This is, indeed, the case as is shown by the acid-catalyzed rearrangement of *p*-tolyl- and *p*-anisyl-substituted compounds (−)-**42** and **43**, respectively.

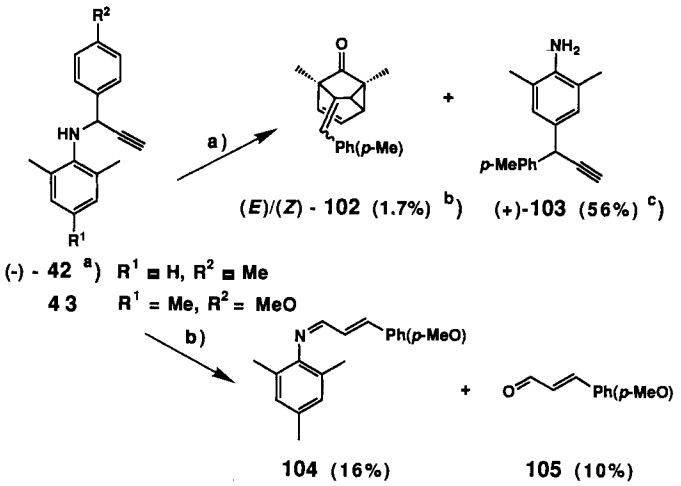
Scheme 24



Heating (−)-**42** in a mixture of PrOH/EG in the presence of 1N H_2SO_4 at 95° for 20 min led to a 90% conversion of the starting material (*Scheme 25*). The recovered starting material showed a loss of 78% of its original optical activity. Also the main product, the *para*-substituted aniline **103**, showed only a very small $[\alpha]_{589}^{25}$ value. The tricyclic ketones (*E*)- and (*Z*)-**102** were isolated in a small yield only. The corresponding 3-allenylated aniline was not observed. The effect of a 1′-anisyl group upon the behavior of **43** under acid catalysis was still more pronounced, since no product of a [3,3]-sigmatropic rearrangement at all could be identified. The observed products (**104**, **105**, and 2,4,6-trimethylaniline) are typical for a process starting with the heterolysis of the N–C(1′) bond to yield a complex of the corresponding aniline and prop-2′-ynyl ion (*cf. Scheme 24*). Imine **104** arises then from the primary allenyl-recombination product by

[33]) The acid-catalyzed rearrangement of **40** in 1N H_2SO_4/EG at 120° led to the formation of 37% of **101** and only of 4% of (*E*)/(*Z*)-**100**, *i.e.* higher temperatures seem to favor the [3,3]-sigmatropic rearrangement.

Schema 25



a) 1N H_2SO_4/PrOH/EG, 95°, 0.33 h. 10% of the starting material was recovered showing $[\alpha]_{589}^{25} = -1.5$ ($CHCl_3$); *i.e.* a loss of about 78% of the optical activity.

b) 1N H_2SO_4/EtOH/PrOH, 85–90°, 0.5 h. No starting material was present. However, 9% of 2,4,6-trimethylaniline were isolated beside of **104** and **105**.

a) $[\alpha]_{589}^{25} = -6.8$ ($CHCl_3$); o.p. (estimated on the basis of that of (−)-**38**) ≤ 6%.

b) Obtained as a 1:1.7 mixture of the (*E*)- and (*Z*)-form; $[\alpha]_{589}^{25}$ not measured.

c) $[\alpha]_{589}^{25} = +0.5$ ($CHCl_3$); o.p. unknown.

isomerization (*cf. Scheme 1*), and **105** is the hydrolysis product of **104**. These results show again that charge-induced [3,3]-sigmatropic rearrangements of 3-hetereo-*Cope* systems will effectively by competed by cleavage processes, when charge stabilization becomes better in the allylic (or propargylic) part of the system than in the transition state of the [3,3]-transposition. The built-up of the latter will strongly be influenced by intrinsic steric and electronic factors as well as solvation effects (*cf.* [1] [2] [5] [38])[34]).

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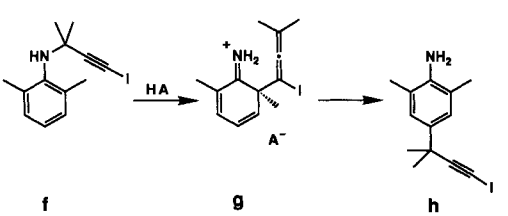
[34]) In preliminary experiments, we studied the acid-catalyzed rearrangement of *N*-(3′-iodo-1′,1′-dimethylprop-2′-ynyl)-2,6-dimethylaniline (**f**) which is easily obtained from **3** by deprotonation with BuLi in THF at –60° and reaction with I_2. In the presence of 1N H_2SO_4 in BuOH at 100°, 4-(3′-iodo-1′,1′-dimethylprop-2′-ynyl)-2,6-dimethylaniline (**h**) is obtained as the sole product. Reaction of **f** in the presence of 9 equiv. of TFA in $CDCl_3$, CD_3CN, $(CD_3)_2CO$, and CD_3OD at 25° yields the iminium ion **g** as intermediate and then **h**. The half-life times ($\tau_{1/4}$, 25°) of protonated **f** under these conditions are *ca.* 1 h ($CDCl_3$; **g** is the main product which slowly forms **h**), 14 h (CD_3CN; **g** is detectable, however, mainly **h** is formed), 30 h ($(CD_3)_2CO$; see CD_3CN), and 40 h (CD_3OH; see CD_3CN). These measurements clearly indicate that the rate of rearrangement of protonated **f** depends on the polarity of the solvent (*cf. e.g.* the E_T values of the protio forms of the applied solvents), *i.e.* the better it can solvate the starting anilinium ion the lower is the rate of rearrangement. Therefore, one driving force for the charge-induced [3,3]-sigmatropic rearrangement seems to be the better charge stabilization in the transition state as compared to the ground state.



4. Structural Assignments of the Main Rearrangement Products. – 4.1. *Cyclohexadiene-iminium and -dienone Structures.* As reported in the preceding *Chapt.* the TFA-catalyzed reaction of the 2,6-disubstituted and 2,4,6-trisubstituted *N*-(1′,1′-dimethylprop-2′-ynyl)- and *N*-(1′-phenylprop-2′-ynyl)anilines in solvents such as CCl_4 and $CDCl_3$ allows the direct observation of the primary products resulting from the [3,3]-sigmatropic rearrangement, *i.e.* the corresponding 6-allenylated cyclohexa-2,4-dien-1-iminium ions, by NMR spectroscopy. As an example, *Fig. 3* shows the ^{1}H-NMR spectrum obtained from *N*-(3′-chloro-1′,1′-dimethylprop-2′-ynyl)-2,4,6-trimethylaniline (**24**) in $CDCl_3$/9 equiv. TFA after 4 h at 20°. The symmetrical starting material **24** has completely been transformed into a new unsymmetrical structure with five distinguishable Me groups, two olefinic H, and two broad low-field signals attributable to 2 H of an iminium group (*cf.* [54] [55]). The observed ^{1}H-NMR spectrum is in full accord with the structure of 6-(1′-chloro-3′-methylbuta-1′,2′-dienyl)-2,4,6-trimethylcyclohexa-2,4-diene-1-iminium ion (**61**) formed from **24** by a [3,3]-sigmatropic process. The low-field position of the signals corresponding to H–C(3) and H–C(5) is typical for comparable *ortho*-dienones (*cf.* [38] [44] [45] [56–58]), however, clearly accentuated by the charge of the N-atom. The presence of an allene system is indicated by the signals at 1.935 and 1.929 ppm for two diastereotopic olefinic Me groups due to the center of chirality created at C(6). Decoupling experiments allow to assign the signals at 2.21 and 2.09 ppm to CH_3–C(4) and CH_3–C(2), respectively (*cf. Fig. 3*).

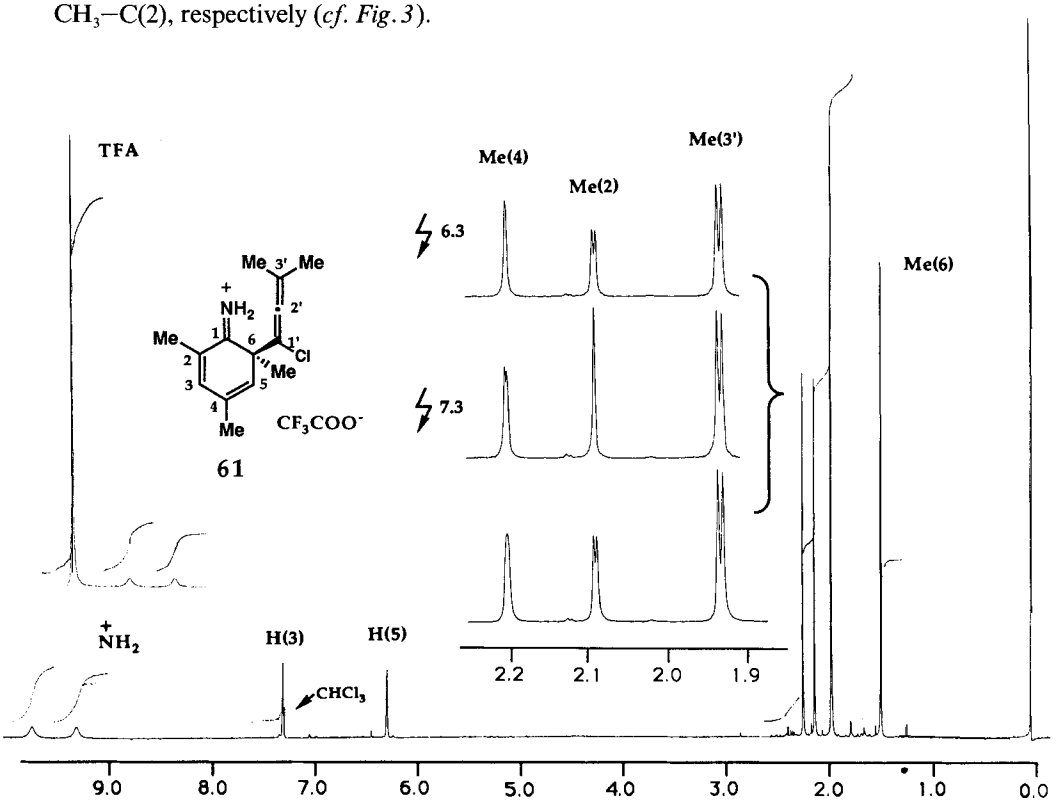


Fig. 3. *^{1}H-NMR Spectrum* [ppm] *of the iminium ion* **61** *formed from* **24** *at 20° in $CDCl_3$/9 equiv. TFA*

Further confirmation for the structure of **61** can be deduced from its ^{13}C-NMR spectrum (*Fig. 4*). The resonance positions of the ring C-atoms and the Me substituents are in full accord with those of comparable '*ortho*-dienones' (*cf.* [58]). The allene structure of the side chain at C(6) is supported by the signal at 197 ppm which can be attributed to C(2′) (calc. 193 ppm; with increments from [59]). The signal of C(2′) appears in the undecoupled ^{13}C-spectrum as a *septet* with $^3J = 2.7$ Hz, indicating the neighborhood of two Me groups. In accord with this assignment is the signal for C(3′) at 114 ppm (calc. 107 ppm; *cf.* [59]) which also appears as a *septet* with $^2J = 6.7$ Hz in the undecoupled spectrum. The signals of the Me groups at C(3′) appear at 21.11 and 20.49 ppm as two *quartets* of *quartets* with $^1J = 129.5$ to 129.8 and $^3J = 4.1$ to 4.2 Hz, thus indicating again their position at an axis of prochirality linked to a center of chirality. Next to the signals for 2 Me–C(3′) lies the signal for Me–C(4) at 20.28 ppm. It appears in the undecoupled spectrum as a *quartet* of two *doublets* with $^1J = 128.3$, and $^3J = 5.4$ and 3.3 Hz. The Me group at C(6) (*quartet* with $^1J = 137$ Hz at 26.75 ppm) is strongly deshielded, as also observed in comparable '*ortho*-dienones' [58]. The signal for Me–C(2) appears as a *quartet* of *doublets* ($^1J = 129.5$ and $^3J = 5.4$ Hz) at highest field (15.5 ppm) due to proximity effects which are also observed in *ortho*-substituted anilines [60] and in cyclohexadienones [58].

The ^{1}H- and/or ^{13}C-NMR data *(cf. Exper. Part)* of the dienones **74**, **75** (*Scheme 17*), **83** (*Scheme 19*), and **99** (*Scheme 23*), obtained from acid-catalyzed rearrangements of the corresponding anilines in aqueous systems, are in full agreement with the proposed structures (*cf.* [25] [38] [44] [45] [56–58]).

4.2. *3-Allenyl- and 4-Alkynylaniline Structures.* The 3-allenylated anilines obtained from the acid-catalyzed rearrangements of the *N*-propargylated anilines with substituents in 2,6- and 2,4,6-positions showed in the IR spectrum the characteristic ν_{as} (C=C=C) vibration in the range of 1930 to 1940 cm^{-1} for the 1,3-diarylallene structures and of 1960 to 1965 cm^{-1} for the alkyl(aryl)allene structures. The deuterated allenes showed, in comparison with their protio structures, a low-frequency shift of this vibration by 5–10 cm^{-1}.

The ^{1}H- and ^{13}C-NMR data (*cf. Tables 8* and *9, Exper. Part*) of the 3-allenylated anilines clearly showed that the allenyl side chain occupies a *meta*-position. For example, 3-(3′-methylbuta-1′,2′-dienyl)-2,6-dimethylaniline (**66**; *cf. Scheme 15*) showed in the ^{1}H-NMR spectrum (CCl_4) signals of two aromatic H at 6.71 and 6.52 ppm with an *ortho*-coupling constant of 8 Hz. The allene structure can be deduced from a characteristic *septet* with $^5J = 3.0$ Hz at 6.05 ppm for H–C(1′) and a *doublet* with $^5J = 3.0$ Hz at 1.78 for Me–C(3′) (*cf.* [61]). Other allene structures showed the characteristic coupling patterns with ^3J (Me–C(3′), H–C(3′)) = 7, ^4J (H–C(1′), H–C(3′)) = 6–7, and ^5J (H–C(1′), Me–C(3′)) = 3–3.5 Hz (*cf.* [61]). In the ^{13}C-NMR spectra, the signal for C(2′) appeared at 202 to 207 ppm (calc. 201 to 211 ppm; with increments from [59]). The signals of the lateral C-atoms appeared at 88 to 99 pm. The exact positions for the signals of C(1′) and C(3′) were taken from undecoupled ^{13}C spectra and corresponding spectra of the allenes deuterated at C(1′).

The 4-alkynylanilines were characterized by their strong ν(≡C–H) vibration at 3290 cm^{-1} and the corresponding very weak ν(C≡C) vibration at about 2120 cm^{-1} (2210 cm^{-1} for ν(C≡C–Cl)) in the IR spectrum. A band at 640 cm^{-1} of medium intensity can be attributed to δ(C≡C–H) vibration. Structure and position of the alkynyl group in

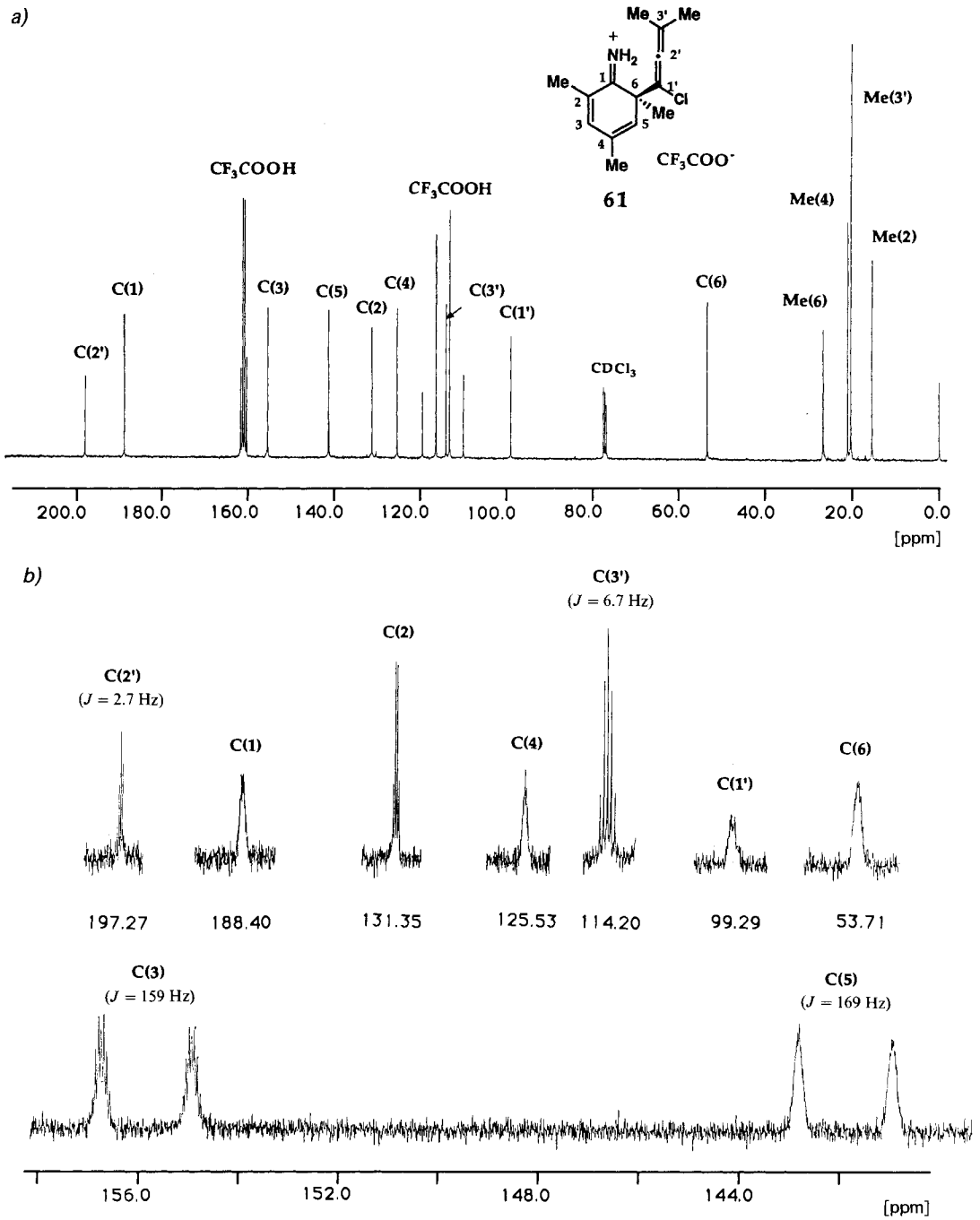
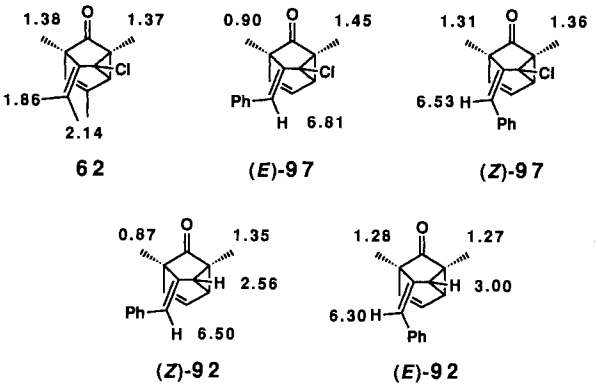


Fig. 4. *^{13}C-NMR Spectra* ($CDCl_3$/9 equiv. TFA; *cf. Fig. 3*) *of* **61**. [a]) ^{1}H-decoupled survey spectrum; [b]) selected ^{1}H-coupled ^{13}C-signals.

anilines can clearly be decuced from the ^{1}H-NMR spectra (*cf. Table 10, Exper. Part*). H–C(3′) appeared as a *singlet* at *ca.* 2.10 ppm in the case of 2 Me–C(1′) and as a *doublet* with ^4J(H–C(1′), H–C(3′)) = 2–3 Hz at 2.06 ppm (Me–C(1′)), and at *ca.* 2.25 ppm in the case of Ph–C(1′).

4.3. *Tricyclo[3.2.1.0^{2,7}]oct-3-en-8-one Structures.* These structures were identified by a strong ν(C=O) vibration at about 1740 cm^{-1} (*cf.* [13] [42]; overtone at 3460 to 3470 cm^{-1}) which is characteristic for strained five-membered cyclic ketones. The exocyclic double bond at C(6) is indicated by a ν(C=C) vibration at 1650 to 1660 cm^{-1} of weak-to-medium intensity. The main structural informations stem from the corresponding ^{1}H- and ^{13}C-NMR data (*cf. Tables 12* and *13, Exper. Part,* as well as [13] [42]). The (*E*)- and (*Z*)-configuration of the 6-benzylidene-substituted compounds can unequivocally be derived from their ^{1}H-NMR spectra in CCl_4. *Scheme 26* represents some typical structures with chemical shifts which are important for the assignment of the configuration. As can

Scheme 26[a])



[a]) ^{1}H-NMR Chemical shifts in ppm (CCl_4).

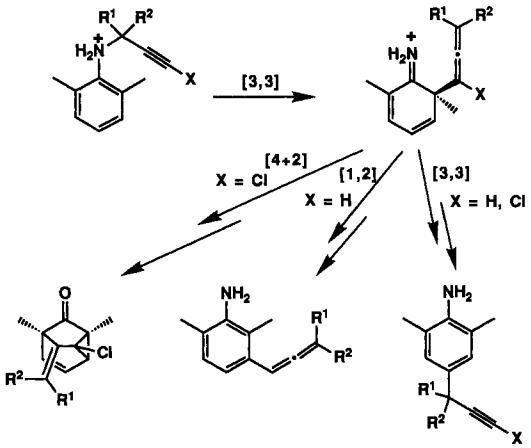
be seen, the relative position of the Ph group at C(9) exerts a remarkable influence upon the chemical shift of Me–C(5). A strong high-field shift is observed for one diastereoisomer, regardless of the substituent at C(7) (Cl or H). On the other hand, in the case of **92**, the chemical shift of H–C(7) is also strongly dependent on the relative position of the Ph group at C(9). The diastereoisomer that exhibits similar chemical shifts for Me–C(1) and Me–C(5) shows a significant low-field shift for H–C(7) as compared with the chemical shifts in the other isomer. Models of both isomers clearly show that, in (*E*)-**97** and (*Z*)-**92**, the Ph group at C(9) comes very close to the Me group at C(5). The steric interactions can only be reduced, when the Ph group is twisted by *ca.* 90° with respects to the π plane of the C(9)=C(6) bond, thus placing the Me group at C(5) above the π plane of the Ph ring, *i.e.* in the strongly shielding region of the Ph ring. The proximity of Ph–C(9) and Me–C(5) is also documented by a NOE experiment: irradiation of Me–C(5) in (*E*)-**97** yields an enhancement of 2.8% for the *ortho*-, of 2.6% for the *meta*-, and of 1.7% for the *para*-H-atoms of the Ph ring at C(9). The diastereosiomer (*Z*)-**97**, when irradiated at 1.31 ppm (Me–C(5)), shows a NOE of 4.6% for H–C(9) and of 1.9% for H–C(4). Further support for the structural and configurational assignments of (*Z*)- and (*E*)-**92** can be

derived from the chemical shift of H–C(7) which appears as a *doublet* (^3J(H–C(2), H–C(7) = 7 Hz) in both isomers. The significant shift difference for H–C(7) and especially the low-field position in (*E*)-**92** is linked to the proximity of the Ph ring at C(9). Models show again that, in this diastereoisomer, the conjugated styrene-type system (C(6)–C(9)–Ph) should sterically not be perturbed. That means for this isomer that H–C(7) is perfectly oriented within the π plane of the Ph ring at C(9), *i.e.* in the aromatic deshielding region.

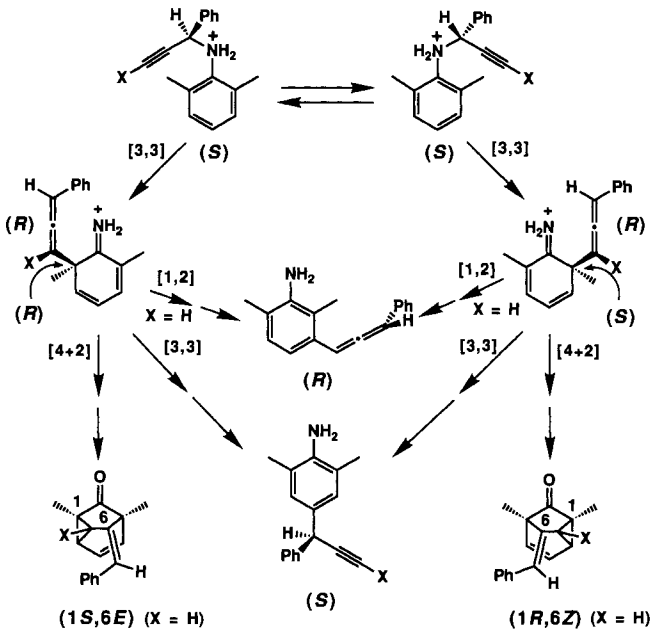
The ^{1}H- and ^{13}C-NMR data of the tricyclic ketones of this work, supplemented with data from earlier work [13] [42], are summarized in *Tables 12* and *13* (*Exper. Part*). The data allow a coherent assignment of all H- and C-atom positions of these tricyclic structures.

5. Concluding Remarks. – The main features of the acid-catalyzed rearrangement of the *N*-propargylanilines are illustrated in *Schemes 27* and *28*. The first step represents a charge-induced [3,3]-sigmatropic rearrangement of the corresponding anilinium ions. It is clearly favored by the degree of substitution at C(1′) as has been observed for the corresponding *N*-allylanilines [1] [2]. A halogen substituent at C(3′) also seems to favor the charge-induced [3,3]-sigmatropic process, since the intermediate iminium ions can directly be observed by ^{1}H- and ^{13}C-NMR spectroscopy. A Ph substituent at C(1′) seems to exert a similar accelerating effect as two Me groups. However, electron-donating groups at C(1′) will also favor the formation of the corresponding propynyl cations arising form a heterolytic cleavage of the N–C(1′) bond in the anilinium ions. This cleavage process, which is further favored by at least a Cl substituent at C(3′) (*cf. Scheme 24*), leads, under the conditions of rearrangement, to partial racemization of the optically active anilinium ions (R^1 = Ph, R^2 = X = H: 18%; R^1 = Ph, R^2 = H, X = Cl: 48%; R^1 = *p*-Tol, R^2 = X = H: 78%), as long as a tight ion pair is formed. In the case where the ion pair is loose and, thus, solvent-separated according to strong charge stabilization (R^1 = *p*-anisyl, R^2 = X = H), rearrangement to the corresponding *N*-allenyl-substituted aniline takes place, further yielding the corresponding *Schiff* base (*cf. Scheme 25*). The charge-induced [3,3]-sigmatropic process is completely suppressed by this mode of competing reactivity.

Scheme 27

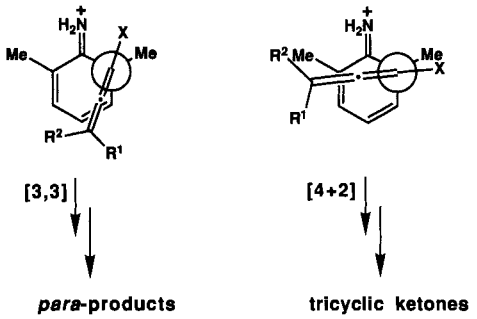


Scheme 28



The further fate of the formed iminium ions is dependent on the nature of X (X = H or halogen) and the degree of substitution at the cyclohexadiene ring as well as at C(3′) of the allenyl group. A halogen substituent at C(1′) completely suppresses the [1,2]-sigmatropic shift of the allenyl group to yield the corresponding 3-allenylanilines. Thus, the charge-induced [3,3]-sigmatropic rearrangement to yield the corresponding 4-(prop-2′-ynyl)anilines can take place. However, this process is competed by the intramolecular [4+2] cycloaddition, a reaction which may also be regarded in this special case as a 6e-homoelectrocyclic ring closure. We assume that this reaction occurs in the iminium ion, and hydrolysis takes place after the cycloaddition. A Cl substituent at C(1′) clearly favors the intramolecular cycloaddition to yield the 7-Cl-substituted tricyclic ketones (*cf. Table 7*). Our preliminary experiments show that an I substituent at C(1′) seems to favor the [3,3]-sigmatropic process at least at 20° (*cf. Footnote 34*). This effect may be due to the different bulkiness of the two halogen substituents at an sp^2-hybridized C-atom. The optimal conformations for attaining the transition state of the [3,3]-sigmatropic process and of the intramolecular [4+2] cycloaddition should be slightly different according to *Dreiding* model (*cf. Scheme 29*). The [3,3]-sigmatropic process should start from the 'staggered' conformation shown in *Scheme 29*, whereas the cycloaddition needs as starting point a conformation with a nearly eclipsed orientation of X–C(1′) and Me–C(6) (*cf. Scheme 29*). Therefore, an increasing steric demand of the X substituent at C(1′) should favor the [3,3]-sigmatropic process. In the case where $R^1 \neq R^2$ (*e.g.* H and Ph, or *p*-Tol), (*E*)- and (*Z*)-configurated tricyclic ketones are formed (*cf. Tables 6* and *7* as well as *Schemes 23* and *25*). Two factors may influence the ratio in which the two diastereoisomers are formed. These factors are *i*) the ratio in which the two diastereoisomeric primary

Scheme 29

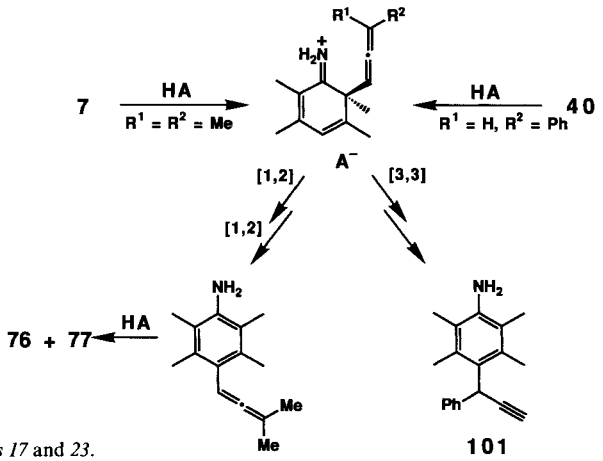


iminium ions are formed in the [3,3]-sigmatropic rearrangement of the starting anilinium ions (*cf. Scheme 28*) and *ii*) the possibly different reactivity ratio with respect to the discussed [3,3]-sigmatropic process and the intramolecular [4+2] cycloaddition in the two diastereoisomeric primary iminium ions. However, in all studied rearrangements, we observed a nearly 1:1 ratio of the (*E*)- and (*Z*)-forms of the tricyclic ketones. This observation is best explained by assuming that the two diastereoisomeric primary iminium structures are already formed in a kinetic ratio of *ca.* 1:1, and that there is no kinetic differentation for the further reactions in these iminium structures. It seems that the aryl substituent at C(1′) in the allenyl side chain is too far away from the Me group at C(2) to exert any steric differentiation in its (*R*)- or (*S*)-position at C(3′) (*cf. Scheme 29*; R^2 = aryl, R^1 = H or R^2 = H, R^1 = aryl for X = H and *vice versa* for X = Cl). This view is supported by the fact that the 2,3,5,6-tetramethyl-6-(3′-phenylpropa-1′,2′-dienyl)-cyclohexa-2,4-dienone (**99**), obtained from the acid-catalyzed rearrangement of the corresponding aniline **40** (*cf. Scheme 23*), represents a *ca.* 1:1 mixture of the two diastereoisomers. Similarly, the acid-catalyzed rearrangement of 2-methyl-*N*-(1′-methylprop-2′-ynyl)-1-naphthaleneamine (**35**) leads to a 3:4 mixture of the two diastereoisomeric *ortho*-dienones (*cf. Scheme 19*).

The charge-induced [3,3]-sigmatropic rearrangement in the primarily formed iminium ions seems to be influenced by the degree of substitution at C(3′) of the allenyl side chain, at least when there are additional Me substituents at the cyclohexadiene ring at C(3) and C(5). The results of the acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-2,3,5,6-tetramethylaniline and 2,3,5,6-tetramethyl-*N*-(1′-phenylprop-2′-ynyl)aniline (**7** and **40**, respectively; *cf. Schemes 17* and *23*) show that the iminium structure resulting from **7** (R^1 = R^2 = Me; *cf. Scheme 30*) undergoes preferentially two consecutive [1,2]-sigmatropic shifts of the allenyl group, whereas the iminium structure arising from **40** (R^1 = H, R^2 = Ph; *cf. Scheme 30*) undergoes rearrangement by the [3,3]-sigmatropic process. This different behavior of the two iminium salts may be due to the greater steric effects in the transition state of the [3,3]-sigmatropic rearrangement in the case of R^1 = R^2 = Me.

The [1,2]-sigmatropic shift of the allenyl moiety in the primary iminium ions seems to be suppressed, when an alkoxy substituent is located at C(6) of the cyclohexadiene ring, since the acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-2,6-diethoxyaniline (**12**) yielded only the 4-(1′,1′-dimethylprop-2′-ynyl)aniline **69** as the result of a [3,3]-sigmatropic rearrangement (*cf. Scheme 15*).

Scheme 30[a])



[a]) *Cf.* also *Schemes 17* and *23*.

The described acid-catalyzed pericyclic processes are strictly intramolecular and concerted. This assertion can be made on the basis of the results of the acid-catalyzed rearrangement of the optically active *N*-(1′-phenylprop-2′-ynyl)anilines (*cf. Tables 6* and *7*, and *Scheme 28*). Starting with (−)-(*S*)-**38** (*cf. Scheme 28*), the isolated 3-allenylaniline **91** possesses, according to its (−)-rotation, (*R*)-configuration in agreement with a suprafacial [3,3]-transposition of the prop-2′-ynyl moiety followed by a suprafacial [1,2]-shift. That the intermediate diastereoisomeric iminium ions are formed without loss of optical activity can be seen from the enantiomeric purity of the formed (*E*)- and (*Z*)-configurated tricyclic ketones which is the same as that of the starting aniline within the range of experimental error (±5%). The enantiomeric purity of the diastereoisomers also shows that the intramolecular *Diels-Alder* reaction is a really concerted process. Otherwise, an (*E*/*Z*)-isomerization in an intermediate vinyl-allyl diradical (created by an advanced bond formation between C(3) and C(2′)) would lead to racemization in the tricyclic ketones, since the two clearly defined diastereoisomeric reaction pathways have to yield, as a consequence of concertedness, (*E*)- and (*Z*)-configurated tricyclic ketones with an enantiomorphic arrangement of their skeletons (*cf. Scheme 28*). An (*E*/*Z*)-isomerization on the way to the tricyclic products would, therefore, lead to a certain extent of racemization identical with the extent of (*E*/*Z*)-isomerization.

If we compare the acid-catalyzed rearrangement of *N*-(1′,1′-dimethylprop-2′-ynyl)-2,6-dimethyl- and 2,6-dimethyl-*N*-(1′-methylprop-2′-ynyl)aniline (**3** and **32**, respectively; *cf. Schemes 15* and *18*) with that of the corresponding *N*-allyl-substituted anilines [2], we recognize that the allyl moieties are only involved in [3,3]-sigmatropic rearrangement. [1,2]-Sigmatropic shifts of allyl moieties are only observed, when the 2- and 4-positions of the cyclohexadiene-ring system are occupied by alkyl substituents (*cf. Scheme 22* as well as [4]). This observation is quite general (*cf.* [3] [25] [38] [44] [45] [62]).

In conclusion, we can state that the acid-catalyzed rearrangements of *N*-propargylanilines represent further examples of a charge-induced [3,3]-sigmatropic process. The formed iminium ions behave differently compared to those formed in the [3,3]-sigma-

tropic rearrangement of corresponding *N*-allylanilines, due to the different electronic nature and reactivity of an allenyl as compared to an allyl group.

We thank Dr. *M. Cosandey*, Dr. *T. Jenny*, Dr. *W. Bernhard*, Dipl.-Chem. *G. Holze*, and *F. Nydegger*, Institut de chimie organique de l'Université de Fribourg, and Dr. *W. Arnold* and Dr. *K. Noack*, Physical department of the Central Research Units of *F. Hoffmann-La Roche AG*, Basle, for NMR, mass, and CD spectra as well as for HPLC and elemental analyses. We gratefully acknowledge partial support of this work, which had mainly been performed in 1981–1985 at the Institut de chimie organique de l'Université de Fribourg, by the *Swiss National Science Foundation*. *H.-J. H.* thanks especially Prof. Dr. *A. Gossauer* for his support of this work with infrastructure of the institute in Fribourg.

Experimental Part

General. Et_2O, THF, and dioxane (DX) were dried by heating under N_2 in the presence of Na and benzophenone, until the blue color of the ketyl radicals was persistent. Chlorinated solvents were dried over P_2O_5. The glass ware was heated to 130–140° and cooled in a dry N_2 stream before use. M.p. on a *Büchi* apparatus (model *SMP-20*). The values are not corrected. TLC on silica gel plates (*60-F-254* plates, *Merck*). The spots in aniline mixtures were developed with *Ehrlich*'s reagent [63] (1 g of 4-(dimethylamino)benzaldehyde dissolved in a mixture of 95 ml of EtOH and 5 ml of 20% aq. HCl): primary anilines turned yellow at 20°, secondary only after heating at *ca.* 100°, and tertiary never turned yellow, however, sometimes weakly colored. Sterically congested primary anilines such as 2,4,6-tri(*tert*-butyl)aniline turned yellow only very slowly at 20–25°. 1,2-Dihydroquinolines became blue (after oxidation in the air). Other unsaturated compounds were developed with a basic soln. of $KMnO_4$. Prep. TLC also on silica gel (*GF DC Woelm*; 30 g spread over plates of the dimension 20 × 20 cm). Column chromatography (CC) under 'flash' conditions [64] with a pressure of N_2 (2 bar) and solvent mixtures of increasing polarity. Evaporation of solvents on a rotatory evaporator at 0–40° and 15 Torr. Bulb-to-bulb distillations in a *Büchi* apparatus (model *GKR-50*). Distillations in high vacuum at 0.01 Torr. Cap. GC on a *Carlo Erba* instrument (model *Fractovap 4160 HRGC*) on a glass capillary column (25 m; diameter 0.4 mm) coated with *SE 54*; carrier gas H_2. Normally, the GC were run with a standard temp. programme: 1 min at 140° and then with 30°/min up to 250°. Electronic integration of the signals with a *Supergrator 2 (Columbia Scientific Industries)*. Optical rotations on a *Perkin-Elmer* instrument (model *241 MC*); specific rotations as $[\alpha]_\lambda$ (*T* in °C; λ in nm; *c* in g/100 ml of $CHCl_3$). UV spectra on a *Perkin-Elmer* instrument (model *320*); λ_{max} and λ_{min} in nm (log ε). IR spectra (film; KBr) on a *Perkin-Elmer* instrument (model *599*); band positions are given in cm^{-1}. ^{1}H-NMR spectra on *Bruker* instruments (models *WP 80CW* and *AM 360 FT*); ^{13}C-NMR spectra on a *Varian* instrument at 25.2 MHz (model *XL 100*) and a *Bruker* instrument at 90.5 MHz (model *AM 360 FT*); solvents and mol-equiv. of trifluoroacetic acid (TFA) in brackets; chemical shifts in ppm with respect to TMS (= 0) as internal standard; coupling constants *J* in Hz. MS on a *Du Pont* instrument (model *21-491*) and a *VG Manchester* instrument (model *70-70E*) at 70eV; ions in *m/z* (rel. %).

1. Syntheses of the Starting Anilines. – All *N*-alkylated anilines showed, after chromatography and distillation or crystallization, the expected spectroscopic properties and correct elemental-analysis data (for details see the thesis of *P.B., cf. Footnote 1*).

1.1. N-*(1',1'-Dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**3**; *Table 2*): 12.1 g (0.1 mol) of 2,6-dimethylaniline, 25 ml of Et_3N, 100 mg of CuCl (*Merck* or freshly prepared according to [65]), 100 mg of Cu powder, and 11.5 g (0.11 mol) of 3-chloro-3-methylbut-1-yne [66] [67] in 10 ml Et_2O; 3 h at 25°: 4.0 g of **3** (21%); 80°/high vacuum. TLC ($CHCl_3$): R_f 0.62. GC: 97%.

1.2. N-*(3'-Iodo-1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**f**; *Footnote 34*). Compound **3** (3.5 g, 19 mmol) in 50 ml of THF at −50° was treated with 15 ml of 1.6N BuLi in hexane. After 10 min, 4.96 g (20 mmol) of I_2 in 50 ml of THF were added at −40°. After 10 min at −20°, sat. NaCl soln. was added. CC (hexane/CH_2Cl_2 5:1 to 3:1) yielded 1.96 g of **f** (33%). M.p. 50–51° (hexane). TLC(CH_2Cl_2): R_f 0.52.

1.3. N-*(1',1'-Dimethylprop-2'-ynyl)-2,4,6-trimethylaniline* (**4**; *Table 2*) *and 2,4,6-Trimethyl-*N-*(3'-methylbut-2'-enylidene)aniline* (**16**; *Scheme 1*). 1.3.1. *Alkylation in DX:* 13.5 g (0.1 mol) of 2,4,6-trimethylaniline, 15 g (0.15 mol) of Et_3N, 30 ml of DX, 100 mg of CuCl, 100 mg of Cu powder, and 14.5 g (0.14 mol) of 3-chloro-3-methylbut-1-yne in 30 ml of DX; 35 min at 5–10°: 12 g of **4** (60%); 100–110°/high vacuum. TLC($CHCl_3$): R_f 0.6. GC: 99%. Similar runs in the presence of Et_2O or THF instead of DX gave **4** in 25–30% yield.

Alkylation of 2,4,6-trimethylaniline with 1,1-dimethylprop-2-ynyl acetate in DX in presence of CuCl/Cu and Et_3N at 20° during 33 h gave **4** in a yield of 36%.

1.3.2. *Formation of* **16**. 3-Chloro-3-methylbut-1-yne (13.5 g, 0.13 mol) in 11 ml of *t*-BuOH at 25° was added to a cooled soln. of 13.5 g (0.1 mol) of 2,4,6-trimethylaniline in 15 g (0.15 mol) of Et_3N in the presence of 0.5 g of CuCl and 0.5 g of Cu powder. Workup after 2 h gave 11 g of a mixture consisting of 40% of starting aniline, 14% of **4**, and 45% of **16** (GC). CC yielded 1.7 g (8%) of **4** and 2.4 g (12%) of **16** as a yellow oil. GC: 99%. IR: 2980*m*, 2920*s*, 2860*m*, 1650*s*, 1610*s*, 1480*s*, 1445*m*, 1380*m*, 1220*s*, 1140*m*, 1050*w*, 860*m*. ^{1}H-NMR(CCl_4): 7.98 (*d*, $J = 9.3$, H–C(1′)); 6.68 (*s*, H–C(3,5)); 6.17 (*d sept.*, $J = 9.3, 1.5$, H–C(2′)); 2.20 (*s*, CH_3–C(4)); 2.00 (*s*, CH_3–C(2,6)); 1.94 (*d*, $J = 1.5$, $2CH_3$–C(3′)). MS: 202 (62, $[M+1]^+$), 201 (100, M^+), 200 (28), 186 (80), 171 (47), 158 (43), 146 (79), 135 (58), 134 (37), 120 (41), 91 (34).

The alkylation of 2,4,6-trimethylaniline with 1,1-dimethylprop-2-yn-1-ol in 1N aq. H_2SO_4 at reflux temp. during 8 h yielded, after workup, 29% of **16**.

1.3.3. N-*(1′,1′-Dimethyl[3′-^{2}H]prop-2′-ynyl)-2,4,6-trimethylaniline* ([^{2}H]-**4**). Compound **4** (2.01 g, 10 mmol) was dissolved in 2 ml of DX, and 3 ml of [$^2H_2$]O and 100 mg of NaH (50% NaH dispersed in oil) were added. The mixture was stirred during 17 h at 20°. Workup yielded 1.6 g of [^{2}H]-**4**. GC: 98%. ^{1}H-NMR (CCl_4): 90% ^{2}H at C(3′).

1.4. N-*(3′-Chloro-1′,1′-dimethylprop-2′-ynyl)-2,4,6 trimethylaniline* (**24**; *Scheme 3*). To a soln. of 1.08 g (5.37 mmol) of **4** in 20 ml of THF at $-80°$ were added, within 5 min, 4 ml of 1.6N BuLi in hexane. After 10 min at $-80°$, a soln. of 1.23 g (6.47 mmol) of TsCl in 10 ml of THF was injected. The yellow mixture turned turbid at $-30°$. Workup after 1 h at 20° and distillation (150°/high vacuum) yielded 0.93 g (73%) of **24** as an oil that could not be crystallized from hexane at $-30°$. TLC ($CHCl_3$): R_f 0.6. GC: 97%. IR: No band at 3305 (≡C–H); 2210*w* (–C≡C–).

1.5. N-*(1′,1′-Dimethylbut-2′-ynyl)-2,4,6-trimethylaniline* (**23**) *and* N-*(1′,1′-dimethylbut-2′-ynyl)*-N,*2,4,6-tetramethylaniline* (**22**; *Scheme 3*). As described above, 6.23 g (31 mmol) of **4** were deprotonated with 1.6N BuLi in hexane at $-80°$. To this soln. was injected a soln. of 4.7 g (33 mmol) of MeI in 10 ml of THF. The yellow color disappeared at $-20°$. Workup after 30 min at 20° and distillation (130–150°/high vakuum) yielded a mixture **22**/**23** which was separated by CC with hexane/CH_2Cl_2 10:1 to 2:1. After distillation (110°/high vacuum), 1.28 g (18%) of **22** were obtained as the less polar compound which crystallized in the refrigerator. M.p. 25°. TLC (CCl_4): R_f 0.50. GC: 99%. The fractions with the more polar compound yielded, after distillation (110°/high vacuum), 3.38 g (50%) of **23**. TLC ($CHCl_3$): R_f 0.50. GC: 97%.

1.6. N-*(1′,1′-Dimethylprop-2′-ynyl)-2,4,6-trimethyl*-N-*(prop-2″-enyl)aniline* (**21**; *Scheme 3*). Compound **4** (2.5 g, 12.4 mmol), 6.7 g (55 mmol) of allyl bromide, 5.0 g (36 mmol) of K_2CO_3, and 1.5 g (12 mmol) of collidine were stirred in 20 ml of DMF at 40–50° during 38 h. GC indicated the formation of 35% of a new product. Workup and distillation (100°/high vacuum) yielded 0.8 g (26%) of **21** as a colorless oil. TLC (CCl_4): R_f 0.6. GC: 99%.

1.7. *2,4,6-Trimethyl*-N-*(1′,1′,6′-trimethylhepta-4′,5′-dien-2′-ynyl)aniline* (**20**; *Scheme 2*). Compound **4** (1.8 g, 8.95 mmol), 0.12 g (0.9 mmol) of 2,4,6-trimethylaniline, 0.2 g of CuCl, and 5 ml of Et_3N were dissolved in 20 ml of DX at 20°. A soln. of 5.0 g (49 mmol) of 3-chloro-3-methylbut-1-yne in 10 ml of DX was added within 1 h at 20°. After additional 5 h at 25° and addition of H_2O, the products were isolated by CC (hexane/CH_2Cl_2 10:1 to 1:1). The first fractions comprised an unknown compound (160–170°/high vacuum) that contained no nitrogen. Later fractions yielded, after distillation (140°/high vacuum), 0.25 g (6%) of **20** as an oil. TLC ($CHCl_3$): R_f 0.62 (R_f identical with that of **4**). IR: 3340*w* (NH), 2980*s*, 2920*s*, 2860*m*, 1955*vw* (>C=C=C<), 1610*w*, 1580*w*, 1450*s*, 1375/1360*m* (>$C(CH_3)_2$), 1220*s*, 1175*m*, 1160*s*, 850*m*. ^{1}H-NMR (CCl_4/CCl_4+TFA): 6.70/6.94 (*s*, H–C(3), H–C(5)); 5.04/5.04 (*sept.*, $J = 2.9$, H–C(4′)); 2.85/– (*s*, NH); 2.29/2.47 (*s*, CH_3–C(2), H–C(6)); 2.19/2.31 (*s*, CH_3–C(4)); 1.71/1.71 (*d*, $J = 2.9$, $2CH_3$–C(6′)); 1.43/1.88 (*s*, $2CH_3$–C(1′)).

1.8. N-*(1′,1′-Dimethylprop-2′-ynyl)-2,6-diethylaniline* (**5**; *Table 2*). To a mixture of 22 g (0.15 mol) of 2,6-diethylaniline, 50 ml of DX, 10 ml of H_2O, 25 g of Et_3N, and 300 mg of CuCl was added dropwise a soln. of 17 g (0.17 mol) of 3-chloro-3-methylbut-1-yne in 20 ml of DX. The mixture was kept below 25° for 31 h. CC and distillation (100°/high vacuum) yielded 3.37 g (10%) of **5**. TLC ($CHCl_3$): R_f 0.73. GC: 96%.

Continuation of CC (hexane/Et_2O 10:1 to 5:1) and distillation (100°/high vacuum) yielded 0.5 g (1.6%) of *2,6-diethyl*-N-*(3′-methylbut-2′-enylidene)aniline* (**17**; *Scheme 1*) as a yellow oil. TLC ($CHCl_3$): R_f 0.34. GC: 92%. IR: 3070*w*, 2980*s*, 2940*s*, 2890*m*, 1655*s*, 1615*s*, 1595*m*, 1455*s*, 1445*s*, 1380*m*, 1215*s*, 855*m*, 770*s*. ^{1}H-NMR (CCl_4): 8.00 (*d*, $J = 9.4$, H–C(1′)); 6.88 (*s*, H–C(3,4,5)); 6.19 (*dsept.*, $J = 9.4$, H–C(2′)), 2.39 (*d*, $J = 7.4$, CH_3CH_2); 1.93 (br. *s*, $2CH_3$–C(3′)); 1.09 (*t*, $J = 7.4$, CH_3CH_2). MS: 216 (57 $[M+1]^+$), 215 (100, M^+), 214 (27), 200 (70), 186 (30), 160 (95), 144 (27), 132 (35).

1.9. N-*(1′,1′-Dimethylprop-2′-ynyl)-2,6-diisopropylaniline* (**6**; *Table 2*). 2,6-Diisopropylaniline (8.85 g, 50 mmol) was dissolved in 25 ml of *N*-ethylmorpholine (NEM) and reacted with 5.5 g (65 mmol) of 3-chloro-3-methylbut-1-yne under N_2 at 5–10° in the presence of 200 mg of CuCl. After a further h at 10°, the mixture was kept at r.t. overnight and then worked up. CC (hexane/CH_2Cl_2 10:1 to 5:1) and distillation (150°/high vacuum)

yielded 4.62 g (38%) of colorless **6** which crystallized in the refrigerator. M.p. 35–36°. TLC ($CHCl_3$): R_f 0.90. GC: 97%.

The reaction of 3.54 g (20 mmol) of 2,6-diisopropylaniline and 3.0 g (26 mmol) of *t*-BuOK in 10 ml of DX with 2.04 g (20 mmol) of 3-chloro-3-methylbut-1-yne in 10 ml of DX at 20° and later at 40° during 2 h yielded after workup and distillation, 2.0 g of starting aniline (110°/high vacuum) and then 0.35 g (7%) of *2,6-diisopropyl-*N-*(3'-methylbut-2'-enylidene)aniline* (**18**; *Scheme 1*) as yellow oil (120°/high vacuum). TLC ($CHCl_3$): R_f 0.45. GC: 86%. IR: 3060*w*, 2960*s*, 2920*s*, 2860*m*, 1645*s*, 1610*s*, 1585*m*, 1455*m*, 1435*m*, 1375*m*, 1360*m*, 1205*m*, 855*s*, 760*s*. ^{1}H-NMR (CCl_4): 7.96 (*d*, $J = 9$, H–C(1')); 6.95 (*m*, H–C(3,4,5)); 6.22 (*dsept.*, $J = 9$, 1, H–C(2')); 2.88 (*sept.*, $J = 7$, $(CH_3)_2CH$); 1.98 (br. *s*, 2 CH_3–C(3')); 1,14 (*d*, $J = 7$, $(CH_3)_2CH$). MS: 244 (2, $[M+1]^+$), 234 (28, M^+), 228 (26), 186 (199), 177 (50), 162 (100).

1.10 N-*(1',1'-Dimethylprop-2'-ynyl)-2,3,5,6-tetramethylaniline* (**7**; *Table 2*). 1.10.1. *2,3,5,6-Tetramethylaniline*. It was prepared according to [68] from 1,2,4,5-tetramethyl-3-nitrobenzene or from 1-bromo-2,3,5,6-tetramethyl-4-nitrobenzene. M.p. 73° (hexane; 72° [68]).

1.10.2. *Alkylation of 2,3,5,6-Tetramethylaniline*. The aniline (1.1 g, 7.3 mmol) was dissolved in 10 ml of Et_3N, and 40 ml of DX and 200 mg of CuCl as well as 100 mg of Cu powder were added. 3-Chloro-3-methylbut-1-yne (4.0 g, 39 mmol) in 20 ml DX was added at 0–8°. The products were isolated after 2 h at 5–10° and an additional h at 35°. CC and distillation (120°/high vacuum): 0.62 g (39%) of colorless **7**. TLC ($CHCl_3$): R_f 0.55. GC: 96%.

1.11. N-*(1',1'-Dimethylprop-2'-ynyl)-2,3,4,5,6-pentamethylaniline* (**8**; *Table 2*). Pentamethylaniline (5.0 g, 30 mmol; prepared from pentamethylbenzene according to [68]; m.p. 152° ([68]: 152–153°)) and 100 mg CuCl were dissolved in 5.0 g (49 mmol) of Et_3N and 30 ml of DX at 5–10°. A soln. of 5.0 g (49 mmol) of 3-chloro-3-methylbut-1-yne in 10 ml of DX was added within 10 min. As soon as the exothermic reaction had ceased, the ice-bath was removed. After 30 min at 25°, the mixture was extracted with CH_2Cl_2. CC and distillation (140°/high vacuum) yielded 1.9 g (27%) of colorless **8** which crystallized in the refrigerator. M.p. 27°. TLC ($CHCl_3$): R_f 0.60. GC: 98%.

1.12. N,N'-*Bis(1',1'-dimethylprop-2'-ynyl)-2,3,5,6-tetramethylbenzene-1,4-diamine* (**9**; *Table 2*). To the dark soln. of 8.2 g (50 mmol) of 2,3,5,6-tetramethylphenylenediamine (*diaminodurene*; *Fluka*), 300 mg of CuCl, and 100 mg of Cu powder in 20 g NEM at 5–10° were added 11.0 g (0.11 mol) of 3-chloro-3-methylbut-1-yne in 20 ml of DX within 45 min. After standing overnight at 25°, the product was isolated by CC (hexane/CH_2Cl_2 10:1 to 3:1) and purified by crystallization from hexane: 5.46 g (37%) of **9**. M.p. 73°. TLC ($CHCl_3$): R_f 0.45. GC: 97%.

1.13. N-*(1',1'-Dimethylprop-2'-ynyl)-2-iodo-4,6-dimethylaniline* (**10**; *Table 2*). To a mixture of 9.9 g (400 mmol) of 2-iodo-4,6-dimethylaniline (prepared from 2,4-dimethylaniline by iodation with I_2; m.p. 67° (EtOH; [69]: 65°)), 200 mg of CuCl, and 15 g NEM were added, under N_2, 5.0 g (49 mmol) of 3-chloro-3-methylbut-1-yne within 30 min at – 10 to 0°. After removal of the ice-bath, the mixture was stirred during 4 h at 25°. Workup, including CC (hexane/CH_2Cl_2 10:1 to 5:1) and distillation (200°/high vacuum), yielded 4.87 g (38%) of **10** as a colorless oil. TLC ($CHCl_3$): R_f 0.85. GC: 99%.

1.14. *2-Bromo-*N-*(1',1'-dimethylprop-2'-ynyl)-4,6-dimethylaniline* (**11**; *Table 2*). To 12.0 g (60 mmol) of 2-bromo-4,6-dimethylaniline (prepared from 2,4-dimethylaniline by direct bromination according to [70]; m.p. 43–44° ([70]: 46–47°)) and 200 mg of CuCl, stirred in 10.1 g (0.1 mol) of Et_3N and 10 ml of DX, were added 10.2 g (0.1 mol) of 3-chloro-3-methylbut-1-yne in 10 ml DX of within 15 min at 5–15°. After additional stirring at 25° during 45 min, 500 ml of dil. NH_3 were added. Workup, including CC and distillation (130°/high vacuum), yielded 5.46 g (34%) of **11** as a colorless oil. TLC ($CHCl_3$): R_f 0.5. GC: 99%.

1.15. *4-Bromo-*N-*(1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**a**; *Footnote 26*). 4-Bromo-2,6-dimethylaniline (10.0 g, 50 mmol) and 100 mg of CuCl (prepared by heating $CuCl_2$ in glycerol at the b.p. during 24 h, washing with EtOH, and drying in high vacuum) were stirred in 25 g of NEM at 0–5°, and 6.0 g (60 mmol) of 3-chloro-3-methylbut-1-yne in 10 ml of THF added within 30 min. After 30 min at 10°, H_2O was added. CC (hexane/CH_2Cl_2 4:1) and distillation (180–190°/high vacuum) yielded 6.25 g (46%) of **a** as a colorless oil. TLC (CH_2Cl_2): R_f 0.63.

1.16. *4-Bromo-*N-*(3'-bromo-1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**b**; *Footnote 26*). Compound **a** (2.04 g, 7.6 mmol; see above) was dissolved in 30 ml of THF, cooled to – 60 to – 70°, and 4 ml 1.6N BuLi (hexane) were added within 5 min. Then, 1.4 g (8 mmol) of NBS, suspended in 30 ml of THF, were added, and the mixture was warmed up to r.t. within 30 min and stirred overnight. The product was isolated and purified by CC (hexane/CH_2Cl_2 4:1 to 3:1). Compound **b** was obtained as a colorless oil (25%). TLC (CH_2Cl_2): R_f 0.69.

1.17. N-*(1',1'-Dimethylprop-2'-ynyl)-2,6-diethoxyaniline* (**12**; *Table 2*). To a well-stirred mixture of 4.73 g (26 mmol) of 2,6-diethoxyaniline (prepared according to [71] [72] from resorcine; m.p. 57° (pentane)); 100 mg of CuCl, 15 ml of NEM, and 15 ml of DX were added, under N_2, 3.0 g (29 mmol) 3-chloro-3-methylbut-1-yne in 5 ml of DX at – 8 to + 5°. DX (20 ml) was added, and the mixture stirred overnight at 25°. Distillation (150°/high vacuum)

and crystallization from hexane yielded 5.4 g (83%) of **12** in colorless crystals. M.p. 95°. TLC ($CHCl_3$): R_f 0.3–0.35. GC: 99%.

1.18. *2,6-Dichloro-*N*-(1',1'-dimethylprop-2'-ynyl)aniline* (**13**; *Table 2*). A soln. of 5.0 g (49 mmol) of 3-chloro-3-methylbut-1-yne in 15 ml of DX was added to a mixture of 6.4 g (40 mmol) of 2,6-dichloroaniline, 100 mg of CuCl, 5 ml of 1,2,2,6,6-pentamethylpiperidine (PMP), and 30 ml of DX at 5°. No exothermic reaction was observed. After 12 h stirring at 20°, aq. NaOH and Et_3N were added, and after an additional h the mixture was extracted with Et_2O. Distillation and CC (hexane/CH_2Cl_2 10:1 to 6:1) yielded, after foreruns of the starting aniline, 0.74 g (8%) of **13** as a colorless oil (120°/high vacuum). TLC ($CHCl_3$): R_f 0.85. GC: 98%. A similar run with NEM instead of PMP gave **13** in a yield of only 2%.

1.19. *N-(1'-Ethynylcyclohexyl)-2,6-dimethylaniline* (**15**; *Table 2*). To a mixture of 6.05 g of 2,6-dimethylaniline, 100 mg of CuCl, 6.0 g (59 mmol) of Et_3N, and 40 ml of DX were added, under N_2 at 20° within 20 min, 7.0 g (50 mmol) of 1-chloro-1-ethynylcyclohexane [67] in 10 ml of DX. Usual workup after 2 h at 25° yielded 0.36 g (3%) of **15** as a colorless oil. TLC ($CHCl_3$): R_f 0.65. GC: 99%.

Continuation of CC with hexane/Et_2O 5:1 and distillation (150°/high vacuum) yielded 0.1 g (1%) of *N-(2'-cyclohexylidenethylidene)-2,6-dimethylaniline* (**19**; *Scheme 1*) as a yellow oil. GC: 91%. IR: 3030*w*, 2940*s*, 2870*s*, 1650*s*, 1615*s*, 1600*s*, 1475*s*, 1450*s*, 1210*s*, 1180*m*, 1160*m*, 1095*m*, 770*s*. ^{1}H-NMR (CCl_4): 8.04 (*d*, J = 9.4, H–C(1')); 7.0–6.9 (*m*, H–C(3,4,5)); 6.13 (*d*, J = 9.4, H–C(2')); 2.28 (*m*, 2 H–C(4',8')); 2.04 (*s*, CH_3–C(2,6)); 1.61 (br. *s*, 2 H–C(5',6',7')).

1.20. *N-(1'-Ethynylcyclohexyl)-2-methoxyaniline* (**14**; *Table 2*). To a mixture of 7.15 g (50 mmol) of 2-methoxyaniline, 100 mg of CuCl, 8.0 g (69 mmol) of NEM, 5.2 g (50 mmol) of styrene, and 20 ml of DX at 5° was added a soln. of 8.1 g (57 mmol) of 1-chloro-1-ethynylcyclohexane in 10 ml of DX within 15 min. The exothermic reaction suddenly started. The temp. was kept below 25° by intensive stirring and cooling. The red mixture was kept overnight at 20°; then H_2O was added. Workup by distillation (200°/high vacuum), CC (hexane/Et_2O 10:1 to 1:1), and crystallization from hexane at – 30° yielded 8.9 g (77%) of **14** in colorless crystals. M.p. 59–60°. TLC ($CHCl_3$): R_f 0.65. GC: > 99%.

1.21. *N-(1',1'-Dimethylpenta-2',4'-diynyl)-2,4,6-trimethylaniline* (**27**; *Scheme 4*). To a mixture of 8.24 g (61 mmol) of 2,4,6-trimethylaniline, 200 mg of CuCl, 18.0 g (0.18 mol) of Et_3N, and 30 ml of Et_2O were added, at 10°, 8.45 g (67 mmol) of 5-chloro-5-methylhexa-1,3-diyne (prepared according to [73]) in 10 ml of Et_2O within 15 min. The ice-bath was removed and the reaction started according to a change in the color (pale yellow→brownish red). After 15 h at 20°, aq. NaOH was added. Usual workup, distillation (130°/high vacuum), and crystallization from hexane at – 30° yielded 1.25 g (9%) of colorless crystals of **27**. M.p. 38–39°. TLC ($CHCl_3$): R_f 0.70. GC: 96%.

1.22. *N-[1',1'-Dimethyl-5'-(trimethylsilyl)penta-2',4'-diynyl)]-2,4,6-trimethylaniline* (**28**; *Scheme 4*). The above mentioned aniline (1.0 g, 4,44 mmol) was deprotonated in THF (20 ml) at – 80° with 1.6N BuLi in hexane (4.96 mmol), and 0.50 g (4.62 mmol) of Me_3SiCl, dissolved in THF, were injected. The temp. raised to – 60°. After an additional h at 10°, dil. aq. AcOH was added. Workup, including CC (hexane/CH_2Cl_2 9:1 to 8:1) and distillation (70°/high vacuum), yielded 0.31 g (23%) of **28** as a colorless oil. TLC ($CHCl_3$): R_f 0.76. GC: 99%.

1.23. *N-(1',1'-Dimethylbuta-2',3'-dienyl)-2,4,6-trimethylaniline* (**30**; *Scheme 5*). 1.23.1. *N-[4'-(Diisopropylamino)-1',1'-dimethylbut-2'-ynyl]-2,4,6-trimethylaniline* (**29**; *Scheme 5*). According to a general procedure (*cf.* [28]), a mixture of 4.0 g (20 mmol) of **4**, 0.96 g of CuBr, 2.5 g (25 mmol) of (i-Pr)$_2$NH, and 2.5 g 40% aq. CH_2O in 20 ml of DX was heated at reflux during 4 h, whereby the color of the mixture turned from greenish to dark red to violet. Workup and CC (hexane/CH_2Cl_2 10:1 and then hexane/Et_2O 10:1 to 4:1) followed by distillation yielded as the first compound 0.24 g (5%) of *2,2-dimethyl-3-methylidene-1-(2',4',6'-trimethylphenyl)azetidine* (**31**; *Footnote 9*) (150°/high vacuum). TLC ($CHCl_3$): R_f 0.77 (the spot turned violet after development with *Ehrlich*'s reagent and heating). GC: 98%. IR 3060*w*, 2960*s*, 2920*s*, 2850*m*, 2800*s*, 1605*w*, 1475*s*, 1440*s*, 1370/1350*m* ($(CH_3)_2C\prec$), 1330*s*, 1270*s*, 1190*m*, 1165*m*, 1010*m*, 850*m*, 715*s*. ^{1}H-NMR (CCl_4/CCl_4+TFA): 6.74/6.96 (*s*, H–C(3',5')); 5.77/5.92 (*s*/*m*, H_2C=C(3)); 4.04/4.90 (*s*/br. *s*, 2 H–C(4)); 2.21/2.47, 2.28 (2*s*, CH_3–C(2',4',6')); 1.14/1.53 (*s*, 2 CH_3–C(2)). MS: 215 (2, M^+), 201 (16), 200 (100), 185 (9), 184 (5).

The second compound, 2.2 g (35%), represented **29** as a colorless oil. TLC ($CHCl_3$): R_f 0.1.

1.23.2. *Methylation and Reductive Elimination.* Compound **29** (2.2 g, 7 mmol) and 5.0 g (35 mmol) of MeI were stirred in 30 ml of acetone during 14 h at 20°. The solvent was removed (RE) and the residue suspended in 70 ml of Et_2O. $LiAlH_4$ (4.0 g) was added and the mixture stirred during 20 h at 20°. Cautious hydrolysis of the mixture and workup, including CC (hexane/CH_2Cl_2 6:1) and distillation (160–170°/high vacuum), yielded 0.59 g (39%) of **30** as a colorless oil. TLC ($CHCl_3$): R_f 0.53. IR: 3380–3340*w* (NH), 2980*s*, 2920*s*, 2860*m*, 2730*w*, 1955*s* (allene), 1610*w*, 1480*s*, 1460*s*, 1380/1360 ($(CH_3)_2C\prec$), 1300*w*, 1225*s*, 1155*s*, 870*m*, 850*s*, 840*s*. ^{1}H-NMR (CCl_4): 6.69 (*s*, H–C(3,5)); 5.24 (*t*, J = 6.5, H–C(2')); 4.65 (*d*, J = 6.5, 2 H–C(4')); 2.22 (*s*, CH_3–C(2,6)); 2.18 (*s*, CH_3–C(4)); 1.25 (*s*, 2 CH_3–C(1')). Compound **30** readily decomposed, when TFA was added to its soln. in CCl_4. ^{13}C-NMR ($CDCl_3$):

205.5 (*s*, C(3')); 140.4 (*s*, C(1)); 134.5 (*s*, C(2,6)); 132.6 (*s*, C(4)); 129,1 (*d*, C(3,5)); 100.6 (*d*, C(2')); 76.9 (*t*, C(4')); 55.9 (*s*, C(1')); 29.4 (*q*, CH_3–C(1')); 20.6 (*q*, CH_3–C(4)); 20.1 (*q*, CH_3–C(2,6). MS: 216 ($[M+1]^+$), 215 (21, M^+), 200 (17), 176 (27), 135 (100), 120 (18).

1.24. *2,4,6-Trimethyl-*N*-(1'-methylprop-2'-ynyl)aniline* (**33**; *Table 3*). A mixture of 17.0 g (0.13 mol) of 1-methylprop-2-ynyl *p*-toluenesulfonate (prepared according to [74]), and 18.0 g (0.13 mol) of K_2CO_3 in 70 ml of DMF was heated at 70–75° during 8 h. Workup, distillation (100–120°/high vacuum), and CC (hexane/CH_2Cl_2 5:1 to hexane/Et_2O 5:1) yielded 7.1 g (26%) of **33** as a colorless oil (95°/high vacuum). TLC ($CHCl_3$): R_f 0.56. GC: 99%.

1.25. *2,6-Dimethyl-*N*-(1'-methylprop-2'-ynyl)aniline* (**32**; *Table 3*). To a mixture of 18.3 g (0.15 mol) of 2,6-dimethylaniline and 20 g (0.16 mol) of K_2CO_3 in 70 g of DMF (dried over molecular sieves 4 Å) were added 46.0 g (0.2 mol) of 1-methylprop-2-ynyl *p*-toluenesulfonate at 20° within 14 h. After heating at 40° during 24 h and additional 8 h at 80°, the product was isolated by distillation (130–230°/high vacuum), CC (hexane/CH_2Cl_2 8:1 to 1:1), and crystallization from hexane at – 30° to yield 9.5 g (36%) of **32** as colorless crystals. M.p. 35–36°. TLC ($CHCl_3$): R_f 0.53. GC: 98%.

1.26. *2,6-Diisopropyl-*N*-(1'-methylprop-2'-ynyl)aniline* (**34**; *Table 3*). To a mixture of 17.7 g (0.1 mol) of 2,6-diisopropylaniline (*Fluka*; purity 95%), 15.1 g (0.15 mol) of Et_3N, 0.2 g of Cu powder, 0.2 g of CuCl, and 10 ml of DX were added, under N_2, 23 g (0.1 mol) of 1-methylprop-2-ynyl *p*-toluenesulfonate in 40 ml of DX at 20–30°. After 20 h stirring, an additional amount of 6.0 g (27 mmol) of *p*-toluenesulfonate and 5 g of Et_3N were added. Workup was performed after 54 h. Distillation (140–200°/high vacuum) and CC (hexane/CH_2Cl_2 8:1 to 4:1) yielded 6.5 g (28%) of **34** as a colorless oil (140°/high vacuum). TLC ($CHCl_3$): R_f 0.62. GC: 93%.

1.27. *N-(3'-Bromo-1'-methylprop-2'-ynyl)-2,6-diisopropylaniline* (**37**; *Scheme 6*). Aniline **34** (5.97 g, 26 mmol) was deprotonated in a soln. of 70 ml of THF at –70° with 30 ml of 1.6N BuLi in hexane. After 10 min, 7.0 g (40 mmol) of NBS were added, and the suspension was slowly warmed up to 20° within 30 min. After additional 30 min at 20°, sat. NaCl soln. was added. Distillation at 200°/high vacuum and CC (hexane/CH_2Cl_2 5:1) yielded, after a second distillation (200°/high vacuum), 2.10 g (26%) of **37** as a colorless oil which solidified upon standing at r.t. M.p. 45–47°. TLC ($CHCl_3$): R_f 0.67. GC: 97%.

1.28. *2-Methyl-*N*-(1'-methylprop-2'-ynyl)-1-naphthaleneamine* (**35**; *Table 3*). A mixture of 5.0 g (32 mmol) of 2-methyl-1-naphthaleneamine (prepared according to [75]), 13.8 g (0.1 mol) of K_2CO_3, and 14.5 g (64 mmol) of 1-methylprop-2-ynyl *p*-toluenesulfonate was heated in 50 ml of DMF during 4 h at 40° and then 16 h at 80°. Usual workup yielded, after distillation (160°/high vacuum) and crystallization from hexane at – 30°, 1.2 g (18%) of **35**. M.p. 43°. TLC ($CHCl_3$): R_f 0.37. GC: > 99%.

1.29. *2,4-Dimethyl-*N*-(1'-methylprop-2'-ynyl)-6-[(*E*)-2''-phenylethenyl]aniline* (**36**; *Table 3*). 1.29.1. *(*E*)- and (*Z*)-2-Amino-3,5-dimethylstilbene*. In analogy to [75], 6.2 g (26.6 mmol) of 2-iodo-4,6-dimethylaniline (*cf. 1.13*), 6.0 g (57 mmol) of styrene, 5.0 g (49 mmol) of Et_3N, and 0.1 g of $Pd(Ac)_2$ were heated under Ar at 80–83° during 2.75 h, until all of the aniline had been consumed. The brownish mixture was extracted with Et_2O to yield a yellow oil. Crystallization from hexane yielded 3.56 g (60%) of the (*E*)-stilbene. M.p. 73–74°. TLC ($CHCl_3$): R_f 0.40; the spot showed fluorescence and turned orange after treatment with *Ehrlich's* reagent. GC: > 99%. IR (CCl_4): 3460/3380 (NH_2), 3010*s*, 2900*s*, 2850*m*, 1615–1580*s*, 1470*s*, 1440*s*, 1290*m*, 1260*s*, 1240*s*, 955*s* (conj. (*E*)-CH=CH), 685*s*, 555*m*, 515*m*. ^{1}H-NMR (CCl_4/CCl_4+TFA): 7.5–6.8/7.4–7.2 (*m*, 7 arom. H); 7.06, 6.78/7.06, 7.02 (*AB*, J = 15.6, CH=CH); 3.45/- (*s*, NH_2); 2.20, 2.11/2.38 (2*s*/s, CH_3–C(3,5)). MS: 224 (22, $[M+1]^+$), 223 (100, M^+), 222 (49), 207 (19), 146 (71), 131 (13), 97 (12). Anal. calc. for $C_{16}H_{17}N$ (223.32): C 86.05, H 7.67, N. 6.27; found: C 86.11, H 7.78, N 6.13.

Evaporation (RE) of the mother liquor of the crystallization of the (*E*)-stilbene and CC (hexane/CH_2Cl_2 10:1 to 1:1) followed by distillation (190°/high vacuum) yielded 0.16 g (2.7%) of the (*Z*)-stilbene as an oil. TLC ($CHCl_3$): R_f 0.55. GC: 97%. IR: 3440/3360*m* (NH_2), 3000*m*, 2900*m*, 2840*m*, 1610*s*, 1595*s*, 1470*s*, 1435*s*, 1265*m*, 1235*m*, 900*m*, 860*m*, 775*s*, 705*s*, 610*m*, 550*m*. ^{1}H-NMR (CCl_4/CCl_4+TFA): 7.24, 7.21/7.25 (2*s*/s, 5 arom. H); 6.68, 6.72/7.14, 7.06 (2*s*, H–C(4,6)); 5.69, 5.23/6.00, 5.36 (*AB*, J = 10.6, CH=CH); 3.2/- (*s*, NH_2); 2.19, 2.06/2.38 (2*s*/*s*, CH_3–C(3,5)). MS: 224 (11, $[M+1]^+$), 223 (69, M^+), 222 (100), 209 (8), 208 (45), 207 (11), 206 (9), 112 (7), 97 (9).

1.29.2. *Alkylation of (*E*)-2-Amino-3,5-dimethylstilbene*. A mixture of 3.6 g (16 mmol) of the (*E*)-stilbene, 6.5 g (29 mmol) of 1-methylprop-2-ynyl *p*-toluenesulfonate, and 10 g of $NaHCO_3$ was heated in 15 ml of DMF during 2 h at 110°. The evolution of CO_2 was registered. Additional 6.0 g of the *p*-toluenesulfonate were added and heating continued for 1 h. Workup, CC (hexane/CH_2Cl_2 10:1 to 6:1), and crystallization from hexane at – 30° yielded 1.31 g (29%) of **36** as colorless crystals. M.p. 91–92°. TLC ($CHCl_3$): R_f 0.64; strongly fluorescent.

1.30. rac-*2,6-Dimethyl-*N*-(1'-phenyl-2'-propynyl)aniline* ((±)-**38**; *Table 4*). 1.30.1. *3-Chloro-3-phenylprop-1-yne*. The corresponding alcohol (54 g, 0.41 mol) was dissolved in 150 ml of Et_2O, and 62 g (0.52 mol) of $SOCl_2$ were added at – 40° within 10 min. Warming up to 36° caused a vivid evolution of gas during 30 min. $NaHCO_3$ (35 g,

0.41 mol) and $MgSO_4$ (5 g) were added at 10°. After the evolution of CO_2 had ceased, an additional amount of 40 g of $MgSO_4$ was added and the mixture stirred during 30 min. The salts were removed by filtration, Et_2O was evaporated (RE) and the residue distilled at 115°/high vacuum to yield 46.5 g (75%) of colorless chloride, free of the corresponding allene. GC: 98%.

1.30.2. *Alkylation of 2,6-Dimethylaniline.* A mixture of 6.0 g (50 mmol) of the aniline, 5.0 g (59 mmol) of $NaHCO_3$, and 6.0 g (40 mmol) of 3-chloro-3-phenylprop-1-yne was heated in 10 ml of HMPT at 70–80° during 48 h. Workup, distillation (150–200°/high vacuum), CC (hexane/CH_2Cl 5:1), and again distillation (150–160°/high vacuum) yielded, after crystallization from hexane, 2.96 g (31%) of (±)-**38** as colorless crystals. M.p. 53–45°. TLC ($CHCl_3$): R_f 0.65. GC: 98%.

1.31. *(−)-(S)-2,6-Dimethyl-*N*-(1-phenylprop-2'-ynyl)aniline* ((−)-**38**; *Scheme 7*). 1.31.1. *(−)-(*R*)-1-Phenylprop-2-yn-1-ol.* In analogy to a general procedure described in [32], 12.2 g (0.1 mol) of 9-borabicyclo[3.3.1]nonane (BBN) and 14.0 g (0.1 mol) of (−)-α-pinene (*Fluka;* $[\alpha]_{546} = -50 \pm 2$, *i.e.* o.p. 81%) were heated in 100 ml of THF during 45 min at reflux. At 10°, 10.1 g (50 mmol) of 1-phenyl-3-(trimethylsilyl)prop-2-ynone (prepared according to [33]) were injected, and the clear soln. was stirred during 50 h at 20°. The addition of 5.0 g (0.11 mol) of acetaldehyde induced an exothermic reaction. After 15 min, the solvent was evaporated (RE) and the residue dissolved in Et_2O. 2-Aminoethanol (6.1 g, 0.1 mol) was added at 0°. The soln. was filtered after 15 min and Et_2O removed (RE). The residue was distilled (100–120°/high vacuum) and the orange distillate separated by CC (hexane/CH_2Cl_2 10:1 to 3:1, then hexane/Et_2O 5:1). The less polar component (1.0 g, 7%) represented trimethylsilyl 1-phenyl-3-(trimethylsilyl)prop-2-ynyl ether which was distilled at 150°/high vacuum. TLC ($CHCl_3$): R_f 0.83. GC: 98%.

The more polar component (150°/high vacuum) represented (−)-(*R*)-1-phenyl-3-(trimethylsilyl)prop-2-ynol (5.0 g; 49%). TLC (CH_2Cl_2): R_f 0.5. GC: 99%. $[\alpha]^{20}$ (1.46) = −17.7 (589); −18.8 (579); −22.2 (546); −40.3 (365); −150.2 (313).

Desilylation was performed in MeOH/2N NaOH at 20° during 20 min. Distillation (130°/high vacuum) yielded (−)-(*R*)-1-phenylprop-2-ynol (47% over both steps). TLC (CH_2Cl_2): R_f 0.44. GC: 97%. $[\alpha]^{20/25}$ (2.186) = −21.9/−21.5 (589); −23.1/−22.6 (579); −27.0/−26.5 (546); −49.7/−48.2 (435); −90.8/−89.6 (365); −178,8/−176.1 (313). ($[\alpha]^{25} = -27.2°$ (589) for o.p. = 100% [34]; i.e. o.p. = 81% for the synthesized, chemically pure alcohol).

1.31.2. *Alkylation of 2,6-Dimethylaniline.* The (−)-alcohol (2.52 g; 19 mmol) was deprotonated in THF (30 ml) at −90° with 1.6N BuLi in hexane (12.5 ml) and 2.3 g (20 mmol) of freshly distilled MsCl and 1.0 g of Et_3N in 5 ml of THF were injected. After 30 min at −50°, 3.0 g (24.7 mmol) of freshly distilled 2,6-dimethylaniline were added, and the mixture was slowly warmed up to r.t. (1.5 h). GC showed the presence of 36% of (−)-**38** and 48% of the starting aniline. The amount of (−)-**38** was not changed very much after additional 3 h reaction at r.t. Workup followed by CC (hexane/CH_2Cl_2 10:1 to 6:1) and distillation (200°/high vacuum) yielded 1.0 g (22%) of (−)-**38** as colorless oil. GC: 96%. $[\alpha]^{20}$ (1.71) = −55.2 (589), −58.2 (579), −67.5 (546), 126.9 (436), −231.2 (365). Crystallization from pentane at −30° led to 99.6% of pure (−)-**38**. M.p. 35–45°. $[\alpha]^{20}$ (2.31) = −57.5 (589), −60.1 (579), −69.9 (546), −131.0 (436), −163.6 (404). ^{1}H-NMR (400 MHz, $CDCl_3$) of 2.8 mg of (−)-**38** in the presence of 37 mg (+)-1-(9-anthryl)-2,2,2-trifluoroethanol ((+)-TAE) showed for CH_3–C(2,6) two *s* in a ratio of 63:180, *i.e.* e.e. = 48%.

The pentane mother liquor yielded after distillation (200°/high vacuum) 0.12 g of (−)-**38** as a colorless oil that did not crystallize, even at −30°. GC: 99%. $[\alpha]^{20}$ (2.40) = −65.7 (589).

1.31.3. *Alkylation of 2,6-Dimethylaniline in the Presence of (−)-(2*R*,3*S*)-3,4-Dimethyl-2-phenylmorpholine* (DMPM; *Table 4*). To a mixture of 3.6 g (30 mmol) of 2,6-dimethylaniline, 100 mg of CuCl, 100 mg of Cu powder, 8.4 g (43 mmol) of DMPM (prepared from (−)-D-ephedrine according to [31]), and 10 ml of DX at 0° was added a soln. of 4.45 g (29.6 mmol) of 3-chloro-3-phenylprop-1-yne in 10 ml of DX within 30 min. The temp. raised to 8° despite cooling and intense stirring. After 40 h at r.t., workup as described (see *1.30.2*) yielded 3.1 g (45%) of (+)-**38**. $[\alpha]^{25}_{589}$ (1.43) = +1.05 (*i.e.* o.p. *ca.* 0.9%). Crystallization from hexane led to (+)-**38** with $[\alpha]^{25}_{589} = +0.7$. The mother liquor showed $[\alpha]^{25}_{589} = -2.8$. Two further crystallizations of (−)-**38** from hexane yielded from the mother liquors finally 40 mg of (−)-**38** with $[\alpha]^{20}_{589}$ (0.8) = −7.3 (*i.e.* o.p. *ca.* 6.3%).

1.32. rac-N-*(3'-Chloro-1'-phenylprop-2'-ynyl)-2,6-dimethylaniline* ((±)-**45**). Aniline **38** (1.9 g; 8 mmol) in THF (20 ml) was deprotonated with 1.6N BuLi in hexane (5.5 ml) at −80°. NaH (0.2 g in 50% dispersion in oil) and MsCl (1.7 g; 8.9 mmol) were added to the yellow soln. at −80°. The mixture was warmed up to 0° within 1 h. Already at −40°, the mixture turned brownish and became inhomogeneous. Workup, CC (hexane/CH_2Cl_2 10:1 to 1:1), and crystallization from hexane at −30° yielded 1.15 g (53%) of (±)-**45** in colorless crystals. M.p. 48°. TLC ($CHCl_3$): R_f 0.8. GC: > 97%; not stable on heating.

1.33. *(−)-(S)-N-(3'-Chloro-1'-phenylprop-2'-ynyl)-2,6-dimethylaniline* ((−)-**45**). The optically active aniline (−)-**38** (0.604 g, 2.57 mmol), in 30 ml of THF, was deprotonated with 1.6N BuLi in hexane (2.0 ml) at −90°. After 5 min, TsCl (0.56 g; 2.9 mmol) in 5 ml of THF was added (NaH was omitted what turned out to be a mistake). During the period of warming up, the mixture suddenly turned from yellow to dark. Workup as described (see *1.32*) yielded 200 mg of contaminated product and then 0.117 g (17%) of (−)-**45**. M.p. 50–52°. TLC ($CHCl_3$): R_f 0.77. GC: > 95%. $[\alpha]^{20}$ (1.186) = −16.8 (589), −17.7 (579), −21.0 (546), −39.6 (435), −46.3 (404), −101.7 (365).

1.34. rac-*2,4,6-Trimethyl-N-(1'-phenylprop-2'-ynyl)aniline* ((±)-**39**; *Table 4*). 7.0 g (51 mmol) 2,4,6-Trimethylaniline (7.0 g, 51 mmol) was alkylated in HMPT at 20° during 60 h *(cf. 1.30.2)*; 4.4 g of the starting aniline were recovered by distillation (140–250°/high vacuum). Crystallization from pentane at −30° yielded 4.3 g (33%) of (±)-**39** as colorless crystals. M.p. 41–42°. TLC ($CHCl_3$): R_f 0.65.

The alkylation of 2,4,6-trimethylaniline (7.0 g) in DX in the presence of CuCl at 5–20° gave **39** in a yield of only 18% (2.4 g).

1.34.1. rac-*2,4,6-Trimethyl-N-(1'-phenyl[3'-^{2}H]prop-2'-ynyl)aniline* ((±)-[^{2}H]-**39**). Aniline **39** (1.32 g, 5.31 mmol) was dissolved in 5 ml of DX and stirred with 10 ml of $[^2H]_2O$ (in which 0.2 g (8 mmol) Na had been dissolved) at 20° during 7 h. Removal of DX and $[^2H]_2O$ (RE), and distillation (210°/high vacuum) yielded 1.25 g (93%) of (±)-[^{2}H]-**39**. IR showed a ^{2}H content of 92% at C(3'); ν(≡C−D) at 2590. MS: 251 (27, $[M+1]^+$), 250 (39), 249 (10).

1.35. *(−)-(S)-2,4,6-Trimethyl-N-(1'-phenylprop-2'-ynyl)aniline* ((−)-**39**; *Scheme 7*). (−)-(*R*)-1-Phenylprop-2-ynol (1.28 g, 9.7 mmol; $[\alpha]_{589}^{20} = -21.9$; see *1.31.1*) was transformed into the methanesulfonate (see *1.31.2*) in the presence of 1.0 g of LiBr. 2,4,6-Trimethylaniline (1.35 g, 10 mmol) was added to the soln. at −60°. After slowly warming up to r.t. GC indicated the presence of only 14% of (−)-**39**. Workup, CC and distillation (200°/high vacuum) yielded 0.21 g (9%) of crude (−)-**39**. TLC ($CHCl_3$): R_f 0.65. GC: 77%. $[\alpha]^{20}$ (1.61) = −38.8 (589), −40.7 (579), −47.2 (546), −84.7 (435). The chemically pure (−)-**39** should show $[\alpha]_{589}^{20} = -50.4$, *i.e.* the optical purity of chemically pure (−)-**39** must be similar to that of (−)-**38** (see *1.31.2*).

1.36. *2,3,5,6-Tetramethyl-N-(1'-phenylprop-2'-ynyl)aniline* (**40**; *Table 4*). A mixture of 10.0 g (67 mmol) of 2,3,5,6-tetramethylaniline (see *1.10.1*), 7.0 g (83 mmol) of $NaHCO_3$, 17.0 g (86 mmol) of 3-chloro-3-phenylprop-2-yne in 50 ml of HMPT was kept during 20 h at 70°. The usual workup yielded, after distillation (220°/high vacuum) and crystallization from hexane, 6.48 g (36%) of **40** as colorless crystals. M.p. 110°. TLC ($CHCl_3$): R_f 0.90. GC: 99%.

1.37. *2,6-Diethyl-N-(1'-phenylprop-2'-ynyl)aniline* (**41**; *Table 4*). To a mixture of 7.5 g (50 mmol) of freshly distilled 2,6-diethylaniline, 0.4 g of CuCl, 13.0 (75 mmol) of DMPM in 50 ml of DX under N_2 at 5° was added a soln. of 7.0 g (50 mmol) of 3-chloro-3-phenylprop-1-yne in 30 ml of DX within 25 min. The mixture was stirred during 15 h at 20°. Workup followed by distillation (150–230°/high vacuum), CC (hexane/CCl_4 5:1, then hexane/CH_2Cl_2 10:1), and again distillation (170°/high vacuum) yielded 6.04 g (46%) of **40** as a colorless oil. $[\alpha]^{20}$ (2.1) = −1.4 (589), −2.8 (435). TLC ($CHCl_3$): R_f 0.91. GC: 96%.

1.38. *(−)-(S)-2,6-Dimethyl-[1'-(4''-methylphenyl)prop-2'-ynyl]aniline* ((−)-**42**; *Scheme 7*). 1,38.1. *(−)-(R)-1-(4''-methylphenyl)prop-2-ynol.* The asymmetric reduction of 1-(4''-methylphenyl)-3-(trimethylsilyl)prop-2-ynone (10.8 g, 50 mmol; prepared according to [33]) was performed as described under *1.31.1*. The crude alcohol, obtained after treatment with 2-aminoethanol, was desilylated at r.t. in 50 ml of MeOH and 20 ml of 1N NaOH within 15 min. CC (hexane/Et_2O 4:1 to 1:1) gave no fractions of the pure (−)-alcohol. Careful fractionation (150°/high vacuum) finally yielded 2.4 g (28%) of the (−)-alcohol. GC: 88%. TLC (CH_2Cl_2): R_f 0.20. $[\alpha]^{20}$ (1.316) = −21.9 (589), −23.1 (579), −26.6 (546), −50.4 (436), −91.9 (365) for the chemically pure compound; *i.e.* the o.p. is comparable to those of (−)-(*R*)-1-phenylprop-2-yn-1-ol (see *1.31.1*).

1.38.2. *Alkylation of 2,6-Dimethylaniline.* The (−)-alcohol (2.3 g, 15.7 mmol) and Et_3N (5.05 g; 50 mmol) were dissolved in THF (40 ml). MsCl (2.5 g; 21.8 mmol) was added at −60°. After 15 min at −20° and additional 15 min. at −40°, a soln. of 2,6-dimethylaniline (2.6 g; 21.5 mmol) in THF (10 ml) was injected. The temp. raised to −20°. After 23 h at 10°, the reaction was quenched with sat. NaCl soln. CC and crystallization from hexane at −30° yielded 0.69 g (17%) of (−)-**42** as colorless crystals. M.p. 67–68°. TLC ($CHCl_3$): R_f 0.79. GC: 96%. $[\alpha]^{20}$ (1.47) = −6.8 (589), −7.5 (579), −9.1 (546), −17.6 (436).

1.39. *N-(1'-(4''-Methoxyphenyl)prop-2'-ynyl)-2,4,6-trimethylaniline* (**43**; *Scheme 8*). 1.39.1. *1-(4'-Methoxyphenyl)prop-2-ynol.* A sat. soln. of acetylene in THF (150 ml) was deprotonated at −60° with 1.6N BuLi in hexane (70 ml). After 10 min, a soln. of 13.6 g (0.1 mol) of *p*-anisaldehyde in 10 ml of THF was injected and the cooling bath removed. After 5 h, 15% NaCl soln. was added. Distillation (170°/high vacuum) and crystallization from toluene at −30° yielded 11 g (68%) of the colorless alcohol which turned yellow within a day. GC: 98%.

1.39.2. *Alkylation of 2,4,6-Trimethylaniline.* The alcohol (2.4 g, 14.8 mmol) and 2.0 g (20 mmol) of Et_3N were dissolved in a mixture of 30 ml of THF and 10 ml of HMPT, and 1.84 g (16 mmol) of MsCl were added at −40°. After 10 min at −20°, 2.16 g (16 mmol) 2,4,6-trimethylaniline were injected, and the reaction mixture was kept for 3 h at −40°. Workup, distillation (200–250°/high vacuum), CC (hexane/CH_2Cl_2 5:1), and two crystallizations from hexane yielded 0.75 g (18%) of **43** in colorless crystals. M.p. 73–74°. TLC ($CHCl_3$): R_f 0.57. GC led to decomposition.

Continuation of CC (hexane/Et_2O 10:1 to 2:1) and crystallization from CH_2Cl_2 yielded 0.13 g (4%) of *N*-(2,4,6-trimethylphenyl)methanesulfonamide in colorless crystals. M.p. 154°. GC: 99%. IR (CH_2Cl_2): 3350 (NH). ^{1}H-NMR ($CDCl_3$): 3.02 (*s*, CH_3SO_2); 5.99 (*s*, NH). MS: 214 (9, $M+1]^+$), 213 (64, M^+), 135 (45), 134 (100).

1.40. N-{*3'-[4"-(Dimethylamino)phenyl]prop-2'-enylidene*}*-2,4,6-trimethylaniline* (**44**; *Scheme 8*). 1.40.1. 1-[4'-(Dimethylamino)phenyl]prop-2-ynol. The alcohol was prepared in analogy to *1.39.1* from acetylene and 4-(dimethylamino)benzaldehyde in yield of 85%. Distillation (180°/high vacuum) gave the alcohol showing some violet discoloration. TLC (CH_2Cl_2): R_f 0.10. TLC (Et_2O): R_f 0.95. GC: 98%. Since the alcohol was sensitive to light and was readily transformed in soln. in the presence of air in a red dye, further purification by crystallization (*cf.* [77]: m.p. 72°) was omitted.

1.40.2. *Alkylation of 2,4,6-Trimethylaniline.* To a mixture of the alcohol (4.0 g, 22.8 mmol) and Et_3N (3.5 g, 34.6 mmol) in CH_2Cl_2 (40 ml) was added, at −30°, freshly distilled MsCl (2.89 g; 25.2 mmol). After 25 min at −40°, 2,4,6-trimethylaniline (3.37 g; 25.2 mmol) was injected to yield a darkly red soln. Workup and distillation (250°/high vacuum) yielded a brownish red oil as a mixture of compounds. Several crystallization from toluene yielded at last, as one of the compounds, **44** (0.34 g; 4%) in orange-red crystals. M.p. 99°. TLC ($CHCl_3$): R_f 0.25. GC: 96%. IR (CCl_4): 2900*m*, 1590*s* (br.), 1515*s*, (br.), 1470*s*, 1435*m*, 1350*s*, 1240*m*, 1210*m*, 1180*m*, 1135*s* (br.), 975*w* ((*E*)-CH=CH), 945m. MS: 292 (37, M^+), 291 (100), 213 (6), 175 (26), 134 (55).

1.41. *2,4,6-Trimethyl-*N*-(prop-2'-ynyl)- and* N,N*-Bis(prop-2'-ynyl)-2,4,6-trimethylaniline* (**46** and **47**, resp.). 2,4,6-Trimethylaniline (6.76 g, 50 mmol), 21.0 g (0.15 mol) of K_2CO_3, and 14.0 g (0.1 mol) of prop-2-ynyl bromide were heated in 50 ml of DMF at 75° during 5 h. Workup followed by CC (hexane/CH_2Cl_2 10:1 to 1:1) and distillation (140°/high vacuum) yielded 4.6 g (43%) of **47** as the less polar compound. TLC (CCl_4): R_f 0.54. GC: 98%.

The more polar compound (100°/high vacuum) represented **46** (1.2 g; 14%) which crystallized in the refrigerator. M.p. 52°. TLC ($CHCl_3$): R_f 0.30. GC: > 99%.

1.42. *2,4,6-Triphenyl-*N*-(prop-2'-ynyl)- and* N,N*-Bis(prop-2'-ynyl)-2,4,6-triphenylaniline* (**48** and **49** resp.). 2,4,6-Triphenylaniline (2,6 g, 8 mmol); prepared according to [78], 5.0 g (60 mmol) of $NaHCO_3$, and 5.0 g (42 mmol) of prop-2-ynyl bromide were heated in 20 ml of HMPT at 80° during 48 h. Workup and CC (hexane/CCl_4 10:1, then hexane/CH_2Cl_2 5:1) followed by two crystallizations from hexane/benzene 10:1 yielded 1.55 g (48%) of **49** as the less polar compound. M.p. 176°. TLC (CCl_4): R_f 0.48.

The more polar compound represented **48** (0.36 g; 12%) which could not be crystallized, even at −30°. TLC (CCl_4): R_f 0.10–0.15.

1.43. *2,4,6-Tri(*tert*-Butyl)-*N*-(prop-2'-ynyl)aniline* (**50**). 2,4,6-Tri(*tert*-butyl)aniline (2.0 g, 7.6 mmol); prepared according to [79]), 5.0 g (60 mmol) of $NaHCO_3$, 2.0 g of K_2CO_3, and 4.0 g (33.6 mmol) of prop-2-ynyl bromide were heated in 20 ml of HMPT at 90° during 24 h. GC showed the presence of 18% of **50**. A second portion prop-2-ynyl bromide (5.0 g, 42 mmol) was added and heating continued at 90° during 62 h. Workup, distillation, and several crystallizations yielded at least 60 mg (2.6%) of **50**. M.p. 76–77°. TLC ($CHCl_3$): R_f 0.89. GC: 98%.

1.44. *2,4,6-Trimethyl-*N*-(prop-2'-enyl) and* N,N*-Di(prop-2'-enyl)aniline* (**51** and **52**, resp.; *Scheme 9*). 2,4,6-Trimethylaniline (6.76 g, 50 mmol), 21.0 g of K_2CO_3, and 13.5 g (0.11 mol) of allyl bromide were heated in 50 ml of acetone at reflux during 11 h. Usual workup yielded 6.6 g (61%) of **52** as the less polar compound (110°/high vacuum). TLC (CCl_4): R_f 0.72. GC: 99%.

The more polar compound in CC represented **51** (2.8 g; 32%). TLC (CCl_4): R_f 0.1. GC: 99%.

2. Acid-Catalyzed Rearrangements of the Anilines. – See the general remarks in *Chapt. 3 (Theor. Part)*. Only the characteristic spectroscopic data of the products will be given (for details, see the thesis of *P.B.* cited under *Footnote 1*).

2.1. *Rearrangement of* **3** (*Scheme 15*). Compound **3** (0.506 g, 2.7 mmol) was heated in a mixture of 40 ml of 0.05N H_2SO_4 and 5 ml of PrOH at 90° for 15 h. Dil. NaOH was added and the mixture extracted with Et_2O. Distillation (120–200°/high vacuum), CC (hexane/Et_2O 10:1 to 5:1), and again distillation (120°/high vacuum) yielded 0.09 g (17%), of *2,6-dimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**66**). TLC (CH_2Cl_2): R_f 0.5. GC: 94% (isomerization!). IR: 3480*w*/3400*m* (NH_2), 1960*w* (allene). ^{1}H-NMR: see *Table 8*. MS: 188 (31, $[M+1]^+$), 187 (100, M^+), 172 (90).

2.2. *Rearrangement of* **f** (*Footnote 34*). 2.2.1. *With H_2SO_4:* 0.683 g (2.5 mmol) of **f** were heated in a mixture of 12 ml of 2N H_2SO_4 and 10 ml of BuOH at 85° for 20 min. (TLC ($CDCl_3$) indicated only **h**). CC yielded 0.364 g (53%) of *4-(3'-iodo-1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**h**). ^{1}H-NMR ($CDCl_3$/$CDCl_3$ + 10–11 equiv. of TFA): 7.06/7.33 (*s*, H–C(3,5)); 3.50/– (br. *s*, NH_2); 2.19/2.41 (*s*, CH_3–C(2,6)); 1,55/1,55 (*s*, 2 CH_3–C(1')). ^{13}C-NMR ($CDCl_3$/$CDCl_3$+10–11 TFA): 141.2/148.8 (*s*, C(1)); 135.5/123.1 (*s*, C(4)); 121.4/131.1 (*s*, C(2,6)); 125.2/127.3 (*d*, C(3,5)); 101.7/99.8 (*s*, C(2')); 37.1/38.1 (*s*, C(1')); 31.7/31.2 (*q*, 2 CH_3–C(1')); 17.8/17.0 (*q*, CH_3–C(2,6)); –5.0/–3.1 (*s*, C(3')).

2.2.2. *With TFA in $CDCl_3$, CD_3CN, CD_3COCD_3, and CD_3OD. Ca.* 0.1 g of **h** was dissolved at 0° in the respective solvent (0.5 ml), and 9 equiv. of TFA were added. No change occurred at 0° within 1 h.

In $CDCl_3$. Rearrangement took place at 25°; after 1 h, *ca.* 50% of **f** had been transformed into *6-(1'-iodo-3'-methylbuta-1',2'-dienyl)-2,6-dimethylcyclohexa-2,4-dien-1-iminium trifluoroacetate* (**g**). After 10 h, mainly **h** was detectable by ^{1}H- and ^{13}C-NMR. ^{1}H-NMR ($CDCl_3$/9 equiv. TFA) of **f**: 7.2–7.4 (*m*, H–C(3,4,5)); 2.51 (*s*, CH_3–C(2,6)); 1.90 (*s*, 2 CH_3–C(1')); of **g**: 7.45 (*m*, H–C(3)), 6.55–6.7 (*m*, H–C(4,5)); 2.22 (*s*, CH_3–C(2')); 1.88 (*s*, 2 CH_3–C(3')); 1.49 (*s*, CH_3–C(6)); of **h**: see *2.2.1.* ^{13}C-NMR ($CDCl_3$/9 equiv. of TFA) of **f**: 133.1 (*d*, C(4)); 130.6 (*d*, C(3,5)); 128.6 (*s*, C(2,6)); 128.6 (covd. C(1)); 89.9 (*s*, C(2')); 65.6 (*s*, C(1')); 28.2 (*q*, 2 CH_3–C(1')); 18.7 (*q*, CH_3–C(2,6)); 11.6 (*s*, C(3')); of **g**: 207? (C(2')); 189.0 (C(1)); 150.4 (C(3)); 148.1 (C(5)); 131.2 (C(2)); 122.3 (C(4)); 108.5 (C(3')); 55.6 (C(6)); 50.0 (C(1')); 27.3 (CH_3–C(6)); 19.9, 19.4 (2 CH_3–C(3')); 15.3 (CH_3–C(2)); of **h**: see *2.2.1.*

In CD_3CN. Slow rearrangement at 25°; **g** and **h** side by side detectable; after 14 h, *ca.* 50% of **f** had been transformed into **g** and **h**. ^{1}H-NMR (CD_3CN/9 equiv. of TFA) of **f**: 7.25–7.3 (*m*, H–C(3,4,5)); 2,48 (*s*, CH_3–C(2,6)); 1.81 (*s*, 2 CH_3–C(1')); of **g**: 7.40 (*m*, H–C(3)); 6.57 (*m*, C(4,5)); 2,13 (*s*, CH_3–C(2)); 1.88, 1.84 (2*s*, 2 CH_3–C(3')); 1.44 (*s*, CH_3–C(6)); of **h**: 7.32 (*s*, H–C(3,5)); 2.37 (*s*, CH_3–C(2,6)); 1.53 (*s*, 2 CH_3–C(1')). ^{13}C-NMR (CD_3CN + 9 equiv. of TFA) of **f**: 135.0 (*d*, C(3,5)); 131.6 (*d*, C(4)); 131.6 (*s*, C(1)); 91.2 (*s*, *m* (C(2')); 66.5 (*s*, C(1')); 28.9 (*q*, 2 CH_3–C(1')); 19.9 (*q*, CH_3–C(2,6)), 15.1 (*s*, (C(3')); of **g**: C(2') not detectable; 189.8 (C(1)); 151.0 (C(3)); 148.3 (C(5)); 126.8 (C(2)); 123.3 (C(4)); 108.8 (C(3')); 56.1 (C(6)); 27.6 (CH_3–C(6)); 20? (2 CH_3–C(3')); 15.0 (CH_3–C(2)); of **h**: 149.0 (*s*, C(1)); 133.1 (*d*, C(3,5)); 128.0 (*s*, C(2,6)); 127.0 (*s*, C(4)); 101.0 (*s*, C(2')); 38.8 (*s*, C(1')); 31.7 (*q*, 2 CH_3–C(1')); 18.2 (*q*, CH_3–C(2,6)); –0.2 (*s*, C(3')).

In CD_3COCD_3. Slow rearrangement at 25°; **g** not clearly detectable; **h** sole product after 30 h, when 50% of **f** had been transformed. ^{1}H-NMR (CD_3COCD_3/9 equiv. of TFA) of **f**: 7.3–7.4 (*m*, H–C(3,4,5)); 2.62 (*s*, CH_3–C(2,6)); 1.99 (*s*, 2 CH_3–C(1')); of **h**: 7.48 (*s*, H–C(3,5)); 2.30 (*s*, CH_3–C(2,6)); 1.61 (*s*, 2 CH_3–C(1')).

In CD_3OD. Very slow rearrangement at 25°; **h** sole product after 40 h, when 50% of **f** had been transformed. Formation of CF_3COOCD_3 was observed. ^{1}H-NMR (CD_3OD + 9 equiv. of TFA) of **f**: Signals at 7.2–7.3; 2.57; 1.86; of **h**: Signals at 7.35; 2.47; 1.57.

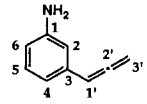
2.3. *Rearrangement of* **4** (*Scheme 12*). 2.3.1. *With H_2SO_4 at 140°:* 40 mg (0.2 mmol) of **4** were heated in a sealed glass bomb in a mixture of 2 ml of 0.1N H_2SO_4, 10 ml of MeOH, and 10 ml of H_2O during 3 h. Workup and distillation (150°/high vacuum) yielded 9 mg (22%) of a colorless 12:1 mixture of *(E)*- and *(Z)-2,4,6-trimethyl-3-(3'-methylbuta-1',3'-dienyl)aniline* ((*E*)- and (*Z*)-**60**, resp.). TLC (CH_2Cl_2): R_f 0.55. GC: 89%. IR: 3470*w*/3390*w* (NH_2), 1630*s*, (C=C), 975*m* ((*E*)-CH=CH). ^{1}H-NMR (CCl_4): 6.60 (*s*, H–C(5)); 6.48, 6.10 (2*d*, J = 17, H–C(1',2') of (*E*)-**60**); 6.20 (*s*, H–C(1',2') of (*Z*)-**60**); 4.92 (*s*, 2 H–C(4')); 3.12 (*s*, NH_2); 2.16 (*s*, CH_3–C(2,4,6)); 1.95 (*d*, J = 1, CH_3–C(3')); in the presence of TFA in CCl_4, CH_3–C(2,4,6) gave 3*s* at 2.33, 2.30, and 2.25; 2 H–C(4') gave also 2*s* at 5.08 and 5.02.

2.3.2. *With H_2SO_4 at 75–80°:* 1.03 g (5.12 mmol) of **4** were heated in a mixture of 45 ml of 0.1N H_2SO_4, 20 ml of MeOH, and 100 ml of H_2O during 2 h. Workup and distillation (130°/high vacuum) gave 0.68 g of crude material which upon prep. TLC (CH_2Cl_2) and distillation (130°/high vacuum) yielded 0.42 g (41%) of colourless *2,4,6-trimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**59**). It crystallized in the refrigerator. M.p. 25–26°. TLC (CH_2Cl_2): R_f 0.42. GC: 95%. IR: 3470*w*/3390*m* (NH_2), 1965*w* (allene). ^{1}H-NMR: see *Table 8*. MS: 202 (38, $[M + 1]^+$), 201 (91, M^+), 187 (38), 186 (94), 172 (47), 171 (100), 159 (17). Anal. calc. for $C_{14}H_{19}N$ (201.31): C 83.52, H 9.51, N 6.96; found: C 83.43, H 9.57, N 6.84.

Thermal isomerization of **59** (29 mg, 0.14 mmol) in 3-methylnonane (2 ml; b.p. 168°) at reflux for 100 min and distillation (130°/high vacuum) yielded pure (*Z*)-**60** (27%). IR (CCl_4): 3480*w*/3400*w* (NH_2), 1620 (C=C), 715 ((*Z*)-CH=CH). ^{1}H-NMR (CCl_4): 6.62 (*s*, H–C(5)); 6.21 (*s*, H–C(1',2')); 4.80 (br. *s*, 2 H–C(4')); 3.30 (br. *s*, NH_2); 2.12, 2.07 (2*s*, CH_3–C(2,4,6,3')).

2.3.3. *Rearrangement of [^{2}H]-***4** (*Scheme 12*): 1.2 g (5.94 mmol) [^{2}H]-**4** were heated in a mixture of 5 ml of 1N H_2SO_4, 5 ml of DMF, 5 ml of *t*-BuOH, and 50 ml of H_2O at 95° for 30 min. Workup and distillation (90–150°/high vacuum) gave 1.07 g of a reddish mixture which was purified by CC (hexane/CH_2Cl_2 5:1 to 1:1) and again distillation (120°/high vacuum); 0.79 g (65%) of *2,4,6-trimethyl-3-(3'-methyl[1'-^{2}H]buta-1',2'-dienyl)aniline*

Table 8. *^{1}H-NMR Data of* 3-(*Propa-1′,2′-dienyl*)*anilines* [a])[b])



Nr. (*Sect.*)	Position of Me Substituents; others	H–C(4)	H–C(5)	H–C(1′)	H–C(3′)	Me–C(2), Me–C(4), Me–C(6)	Others at C(2), C(4), C(6)	Me–C(3′)
66 (*2.1*)	2,6,3′,3′	6.52 (*d*, *J* = 8)	6.71 (*d*, *J* = 8)	6.05 (*sept.*, *J* = 3)	–	2.10	–	1.78 (*d*, *J* = 3)
59 (*2.3.2*)	2,4,6,3′,3′	–	6.58 (*s*)	5.93 (*sept.*, *J* = 3)	–	2.11; 2.05; 2.00	–	1.68 (*d*, *J* = 3)
[^{2}H]-**59** (2.3.3)	2,4,6,3′,3′; [1′-^{2}H]	–	6.61 (*s*)	–	–	2.17; 2.12; 2.08	–	1.74 (*s*)
64 (*2.5*)	2,4,6,3′,3′; *N*-Allyl	–	6.69 (*s*)	cvd.	–	2.20/2.24	–	1.75 (*d*, *J* = 3)
67 (*2.8*)	3′,3′; 2,6-Et$_2$	6.57 (*d*, *J* = 7.8)	6.74 (*d*, *J* = 7.8)	6.05 (*sept.*, *J* = 3)	–	–	2.60/2.43(*q*) 1.20/1.12(*t*)	1.79 (*d*, *J* = 3)
70 (*2.13*)	2,4,3′,3′; 6-I	–	7.27 (*s*)	5.90 (*sept.*, *J* = 3.1)	–	2.19; 2.17	–	1.74 (*d*, *J* = 3.1)
71 (*2.13*)	2,4,3′,3′	–	6.68 (*d*, *J* = 8)	5.95 (*sept.*, *J* = 3.1)	–	2.18; 2.08	6.30 (*d*, *J* = 8)	1.74 (*d*, *J* = 3.1)
72 (*2.14*)	2,4,3′,3′; 6-Br	–	7.04 (*s*)	5.89 (*sept.*, *J* = 3.1)	–	2.17	–	1.74 (*d.*, *J* = 3.1)
c[c]) (*2.15*)	2,6,3′,3′; 4-Br	–	7.15 (*s*)	6.17 (*sept.*, *J* = 3)	–	2.11; 2.21	–	1.76 (*d*, *J* = 3)
78 (*2.24*)	2,4,6,3′	–	6.62 (*s*)	6.06 (*qd*, *J* = 7, 3.5)	5.11 (*qd*, *J* = 7, 3.5)	2.17; 2.12; 2.08	–	1.72 (*dd*, *J* = 7, 3.5)
85[c]) (*2.28*)	2,4,3′; 6-[(*E*)-Styryl]	–	7.12 (*s*)	6.16 (*dq*, *J* = 6.8, 3.4)	5.24 (*qd*, *J* = 6.9, 3.5)	2.22; 2.30	7.16; 6.95[d]) (*AB*; *J* = 16)	1.73 (*dd*, *J* = 6.9, 3.4)
91 (*2.31*)	2,6; 3′-Ph[e])	6.7–7.5	6.7–7.5	cvd.	6.38 (*d*, *J* = 6)	2.07; 2.14	–	–
89 (2.34)	2,4,6; 3′-Ph	–	6.64 (*s*)	6.60 (*d*, *J* = 6.8)	6.21 (*d*, *J* = 6.8)	2.27; 2.14; 2.06	–	–
[^{2}H]-**89** (*2.34.2*)	2,4,6; [1′-^{2}H],3′-Ph	–	6.60s	–	6.20(*s*)	2.23; 2.14; 2.06	–	–
94 (*2.37*)	2,6-Et$_2$,3′-Ph	6.73(*s*)	6.73s	6.72 (*d*, *J* ≈ 7)	6.4 (*d*, *J* ≈ 7)	–	2.7–2.0(*m*) 1.35–0.8(*m*)	–

[a]) Unless otherwise stated spectra in CCl_4.

[b]) NH_2 as br. *s* in the range of 2.8 to 3.8.

[c]) In $CDCl_3$.

[d]) H–C(1) and H–C(2) of the (*E*)-styryl moiety; Ph: 7.49 (*d*, *J* = 7.4, H–C(2), H–C(6)); 7.34 (*t*, *J* = 7.4; H–C(3), H–C(5)); 7.23 (*t*, *J* = 7.4, H–C(4)).

[e]) Ph: *ca.* 7.2 (*m*, 5 arom. H).

([^{2}H]-**59**) were obtained. TLC ($CHCl_3$): R_f 0.55. GC: 97%. IR: 3480*w*/3390*w* (NH_2), 2210*w* (C–D), 1960 (allene). ^{1}H-NMR (CCl_4; *cf. Table 8*): no signal at 5.93 (H–C(1')); *s* instead of *d* at 1.74 (2 CH_3–C(3')). ^{13}C-NMR ($CDCl_3$; *cf. Table 9*): 88.2 (*t*, C(1')). MS (14, $[M+1]^+$), 202 (93, $M^{+\cdot}$), 201 (10), 188 (12), 187 (100), 186 (26), 173 (10), 172 (96), 159 (40). Anal. calc. for $C_{14}H_{18}{}^2HN$ (202.31): C 83.12, H/^{2}H 9.96, N 6.92; found: C 83.13, H 9.96, N 6.75.

2.4. *Rearrangement of* **24** (*Scheme 13*). 2.4.1. *With TFA in $CDCl_3$:* 80 mg of **24** were dissolved in 0.5 ml of $CDCl_3$, and 9 equiv. of TFA were added at –30°. Warming up to 20° started the rearrangement into *6-(1'-chloro-3'-methylbuta-1',2'-dienyl)-2,4,6-trimethylcyclohexa-2,4-dien-1-iminium trifluoroacetate* (**61**) which was completed after 4 h according to ^{1}H- and ^{13}C-NMR (*cf. Fig. 3* and *4*). ^{1}H-NMR: 9.71, 9.28 (2 br. *s*, $=NH_2$); 7.30 (br. *s*, H–C(3)); 6.29 (*s*, H–C(5)); 2.21 (*s*, CH_3–C(4)); 2.09 (*d*, J = 1.4, CH_3–C(2)); 1.94, 1.93 (2*s*, 2 CH_3–C(3')); 1.45 (*s*, CH_3–C(6)). ^{13}C-NMR: 197.3 (*sept.* J = 2.7, C(2'')); 188.4 (*s*, C(1)); 155.4 (*dm*, J = 159.5, 5.1, C(3)); 141.3 (*dm*, J = 169, C(5)); 131.3 (*q*, J = 6.5, C(2')); 125.5 (*s*, C(4)); 114.2 (*sept.*, J = 6.7, C(3')); 99.3 (*s*, C(1')); 53.7 (*s*, C(6)); 26.7 (*q*, J = 134.4, CH_3–C(6)); 21.1, 20.5 (2*qq*, J = 129.5, 4.2, resp. 129.8, 4.1, 2 CH_3–C(3')); 20.3 (*qm*, J = 128.2, CH_3–C(4)); 15.5 (*qd*, J = 129.5, 5.4, CH_3–C(2)).

2.4.2. *With H_2SO_4 in i-BuOH:* 0.58 g (2.45 mmol) of **24** were heated in a mixture of 2.4 ml of 1N H_2SO_4 and 3 ml of i-BuOH at 100° for 45 min. GC indicated 94% of a new product. Workup and distillation (170°/high vacuum) gave a colorless oil which was further purified by CC (hexane/CH_2Cl_2 3:1). Crystallization from hexane at –30° yielded 0.15 g (30%) of *7-chloro-6-isopropylidene-1,3,5-trimethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* (**62**) as heavy, colorless crystals. M.p. 105–106°. TLC ($CHCl_3$): R_f 0.50. GC: 98%. IR (CCl_4): 2900*s*, 1730*s* (strained C=O), 1530*w*, 1435*s*, 1375*m*, 1320*m*, 1285*s*, 1245*m*, 610*w*. ^{1}H-NOE ($CDCl_3$): 1.86 (CH_3–C(9))→1.38 (1.7%; CH_3–C(5)). 5.26 (H–C(4)), 2.15 (H–C(2) or 1.81 (CH_3–C(9)) induced no NOE. ^{1}H- and ^{13}C-NMR: see *Tables 12* and *13*, resp. MS: 238/236 (3/7, $M^{+\cdot}$), 223/221 (4/11), 210(208 (25/75), 193 (18), 173 (100), 158 (54). Anal. calc. for $C_{16}H_{17}ClO$ (236.74): C 71.03, H 7.24; found: C 70.91, H 7.42.

2.5. *Rearrangement of* **21** (*Scheme 14*). Compound **21** (0.21 g 0.87 mmol) was dissolved in 5 ml of CH_2Cl_2 and 100 mg (0.87 mmol) of TFA added. The mixture was heated at reflux for 3.5 h. GC indicated the presence of a new compound (18%) beside **21** (72%). Distillation (130°/high vacuum) yielded 0.13 g (62%) of starting aniline and at 140–150°/high vacuum 30 mg (14%) of *2,4,6-trimethyl-3-(3'-methylbuta-1',2'-dienyl)-*N*-(prop-2''-enyl)aniline* (**64**). TLC ($CHCl_3$): R_f 0.73. GC: 95%. IR (CCl_4): 3380*w* (NH), 1955 (allene), 1640*w* (C=C), 995*m*/920*s* ($CH=CH_2$). ^{1}H-NMR: see *Table 8*.

2.6. *Attempted Rearrangement of* **22** (*Scheme 14*). Compound **22** (0.2 g, 0.87 mmol) was stirred in 1 ml of TFAA at 20° during 24 h. No conversion was observed. Therefore, the mixture was heated at reflux for 2 h. Distillation (130°/high vacuum) yielded 90 mg (42%) of *N*,2,4,6-tetramethyl-*N*-(trifluoroacetyl)-2,4,6-trimethylaniline. GC 96%. Crystallization from hexane at –30° yielded colorless crystals. M.p. 65°.

2.7. *Attempted Rearrangement of* **23** (*Scheme 14*). Compound **23** (0.33 g, 1.54 mmol), heated in a mixture of DMF (4 ml) and 1N H_2SO_4 (1.4 ml) at 100° during 1 h, yielded only 0.12 g (36%) of 2,4,6-trimethylaniline.

2.8. *Rearrangement of* **5** (*Scheme 15*). Compound **5** (1.075 g, 5 mmol) was heated in a mixture of 4 ml of 1N H_2SO_4, 5 ml of MeOH, and 35 ml of H_2O at 85° during 4 h. Workup yielded a mixture (GC) of 11% of **5**, 15% of *4-(1',1'-dimethylprop-2'-ynyl)-2,6-diethylaniline* (**68**), and 63% of *2,6-diethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**67**). Prep. TLC ($CHCl_3$) yielded, as the most apolar component, 18 mg of **5** (TLC ($CHCl_3$): R_f 0.85). The component of medium polarity represented **67**. Distillation (105°/high vacuum) yielded 0.24 g (21%) which crystallized in the refrigerator at –15°. IR: 3480*w*/3400*w* (NH_2), 1950 (allene). ^{1}H-NMR: see *Table 8*. MS: 216 (32, $[M+1]^+$), 215 (100, $M^{+\cdot}$), 201 (11), 200 (64), 186 (13), 185 (9), 172 (29), 171 (16), 170 (9).

The most polar compound represented **68** which was purified a second time by prep. TLC. Distillation (100°/high vacuum) yielded 40 mg (5%) of **68** which contained *ca.* 10% of **67** (GC). ^{1}H-NMR: see *Table 10*. MS: 216 (9, $[M+1]^+$), 215 (45, $M^{+\cdot}$), 200 (100).

2.9. *Rearrangement of* **6**. The rearrangement of **6** (0.95 g; 3.9 mmol) with camphor-10-sulfonic acid (1,3 g; 5.2 mmol) in i-PrOH (16 g) at 81° during 1 h led to the formation of a mixture of 4 unknown products (74%) which could neither be separated nor analyzed. Similar results were obtained with 1N H_2SO_4 in i-BuOH (90°/30 min). Again, the mixture of the unknown products (76%) was obtained.

2.10. *Rearrangement of* **7** (*Scheme 17*). Compound **7** (0.56 g, 2.6 mmol) was heated in a mixture of 2.8 g of 1N H_2SO_4, 4 ml of EtOH, and 20 ml of H_2O at 85° for 1 h. Workup and CC (hexane/CH_2Cl_2 10:1 to acetone) yielded 17 mg (3%) of **7** and, as second apolar component, after distillation (120°/high vacuum) 58 mg (11%)

Table 9. *^{13}C-NMR Data of 3-(Propa-1′,2′-dienyl)anilines* [a])

Nr. (*Sect.*)	Position of Me Substituents; others	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	C(1′)	C (2′)	C (3′)	Me-C(2)	Me-C(4)	Me-C(6)	Me-C(3′)
[^{2}H]-**59** (*2.3.3*)	2,4,6,3′,3′; [1-^{2}H]	140.6	119.9	131.3	125.7	129.3	120.0	88.2	203.8	94.5	14.2	20.3	17.5	20.4
70 (*2.13*)	2,4,3′,3′; 6-I	142.9	121.0	134.5	128.1	137.1	83.0	88.1	204.3	95.2	15.5	20.2	–	20.2
72 (*2.14*)	2,4,3′,3′; 6-Br	140.3	121.8	133.3	127.3	130.8	107.8	88.1	204.2	95.2	15.2	20.4	–	20.2
c (*2.15*)	2,6,3′,3′; 4-Br	142.4	121.9	132.0	112.0	131.2	121.5	90.5	204.4	95.7	15.0	–	17.3	20.1
85 (*2.28*)	2,4,3′; 6-[(*E*)-Styryl]	140.3	121.2	132.8	126.6	130.6	122.3	90.0	206.9	85.9	14.5	20.7	–	13.9
89 (*2.34*)	2,4,6; 3′-Ph	140.5	120.2	134.1	126.0	129.5	120.7	94.3	207.1	94.8	14.45	20.6	17.5	–

[a]) *Cf. Table 8;* spectra in $CDCl_3$.

of *2,3,5,6-tetramethyl-6-(3'-methylbuta-1',2'-dienyl)cyclohexa-2,4-dien-1-one* (**75**). TLC ($CHCl_3$): R_f 0.41. IR: 2980*m*, 2930*m*, 2860*m*, 1965*m* (allene), 1655*m* (C=C), 1640*s* (dienone), 1585*m*, 1445*m*, 1375*m*, 1360*m*, 1310*m*, 1020*w*. ^{1}H-NMR (CCl_4): 5.76 (*s*, H–C(4)); 4.69 (sept. J = 2.9, H–C(1')); 1.95, 1.83, 1.78 (3*s*, CH_3–C(2,3,5); 1.72, 1.66 (2*d*, J = 2.9, 2 CH_3–C(3')); 1.21 (*s*, CH_3–C(6)); irr. at 4.69→1.72 and 1.66 (2*s*). MS: 216 (10, M^+), 202 (14), 201 (100), 188 (23), 186 (21), 173 (45), 158 (24).

The fractions of the more polar components yielded after distillation (130–140°/high vacuum) 20 mg (5%) of *(E)-2,3,5,6-tetramethyl-4-(3'-methylbuta-1',3'-dienyl)aniline* (**76**). TLC ($CHCl_3$): R_f 0.37. GC: 96%. IR: 3480*w*/3400*w* (NH_2), 1620*s* (C=C), 970*s* ((*E*)-CH=CH). ^{1}H-NMR (CCl_4): 6.51, 6.00 (*AB*, J = 16.3, H–C(1,'2')); 4.89 (br. *s*, 2 H–C(4')); 3.32 (*s*, NH_2), 2.15, 2.04 (2*s*, 1:1, CH_3–C(2,3,5,6)); 2.00 (*d*, J = 1, CH_3–C(3')). MS: 216 (18, $[M + 1]^+$), 215 (43, M^+), 201 (14), 200 (81), 186 (17), 185 (100).

The most polar component yielded, after distillation (170°/high vacuum) and crystallization from hexane, 55 mg (10%) of colorless crystals representing *(E)-4-(3'-hydroxy-3'-methylbut-1'-enyl)-2,3,5,6-tetramethylaniline* (**77**). M.p. 94°. TLC ($CHCl_3$): R_f 0.08. IR (CH_2Cl_2): 3590*m* (OH), 3470*w*/3400*w* (NH_2), 1625*s* (C=C), 975*s* ((*E*)-CH=CH). ^{1}H-NMR ($CCl_4/CDCl_3$): 6.49 (*d*, J = 16.3, H–C(1')); 5.54 (*d*, J = 16.3, H–C(2')); 2.75 (br. *s*, OH and NH_2); 2.15, 2.07 (2*s*, 1:1, CH_3–C(2,3,5,6)); 1.40 (*s*, 2 CH_3–C(3')). ^{1}H-NMR ($CDCl_3$ + TFA): signals of **76**. MS: 233 (38, M^+), 218 (47), 215 (20), 200 (74), 185 (100).

2.11. *Rearrangement of* **8** (*Scheme 17*). Compound **8** (0.321 g, 1.4 mmol) heated in a mixture of 1.6 g of 1N H_2SO_4, 6 ml of EtOH, and 6 ml of H_2O at 80° during 2 h, yielded, after prep. TLC (CH_2Cl_2) and distillation (140°/high vacuum), 50 mg (15%) of a colorless 10:1 mixture of *2,3,4,5,6-pentamethyl-4-(3'-methylbuta-1',2'-dienyl)cyclohexa-2,5-dien-1-one* (**74**) as main component and presumably its *ortho*-dienone isomer **73** as by-product. TLC ($CHCl_3$): R_f 0.26. IR: 1965*w* (allene), 1655*m* (dienone), 1625*s* (C=C). ^{1}H-NMR (CCl_4): 4.53 (sept. J = 2.7, H–C(1')); 1.88, 1.83 (2*s*, 1:1, CH_3–C(2,3,5,6)); 1.78 (*d*, J = 2.7, 2 CH_3–C(3')); 1.17 (*s*, CH_3–C(4)); irrad. at 4.53→1.78 (s). ^{13}C-NMR ($CDCl_3$): 202.5 (*s*, C(2')); 1.85 (*s*, C(1)); 155.6 (*s*, C(3,5)); 130.4 (*s*, C(2,6)); 99.3 (*s*, C(3')); 93.7 (*d*, C(1')); 47.7 (*s*, C(4)); 21.6 (*q*, CH_3–C(4)); 20.6 (*q*, 2 CH_3–C(3')); 17.0 (*q*, CH_3–C(3,5)); 11.7 (*q*, CH_3–C(2,6)). MS: 230 (5, M^+), 229 (22), 215 (6), 214 (10), 176 (100), 163 (28), 147 (21).

2.12. *Rearrangement of* **9**. 2.12.1. *With H_2SO_4*. Heated in a mixture of 1N H_2SO_4 (12 ml) and butan-2-one (30 ml) at 80°, **9** (1.30 g; 4.4 mmol) was consumed within 90 min: 68 mg (5%) **9** were recovered beside 0.21 g of a mixture of products which could not be identified. IR indicated the presence of phenol and cyclohexadienone derivatives.

2.12.2. *With $KHSO_4$*. The diamine (1.0 g, 3.4 mmol) was heated in a mixture of $KHSO_4$ (0.92 g; 6.7 mmol) and DMF (35 ml) at 95° for 30 min: 65 mg (6.5%) **9** were recovered. A mixture of polar compounds (104 mg) could not be identified.

2.13. *Rearrangement of* **10** (*Scheme 16*). Compound **10** (2.35 g, 7.5 mmol) was heated in a mixture of 5 ml of 1N H_2SO_4, 6 ml of PrOH, and 5 ml of EG under Ar at 86° for 85 min. The violet-to-black colored mixture was extracted with Et_2O after addition of a buffer soln. (pH 7). CC (hexane/CH_2Cl_2 5:1 to 3:1) yielded 0.22 g (9%) of **10** and, then from the more polar fractions, after 2 crystallizations from hexane, 70 mg (3%) of *6-iodo-2,4-dimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**70**). M.p. 76–77°. TLC ($CHCl_3$): R_f 0.45. IR (CCl_4): 3460*w*/3370*w* (NH_2), 1955*w* (allene). ^{1}H-NMR: see *Table 8*. ^{13}C-NMR: see *Table 9*. MS: 313 (43, M^+), 298 (32), 270 (26), 171 (100). Anal. calc. for $C_{13}H_{16}IN$ (313.18): C 49.85, H 5.15, N 4.47; found: C 49.81, H 4.96, N 4.18.

Continuation of CC (hexane/CH_2Cl_2 2:1) and distillation (160°/high vacuum) yielded 45 mg (3%) of *2,4-dimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**71**). TLC ($CHCl_3$): R_f 0.33. GC: 92%. IR: 3440*m*/3350*m*/3220*w* (NH_2), 1950*w* (allene). ^{1}H-NMR: see *Table 8*. MS: 188 (16, $[M + 1]^+$), 187 (100, M^+), 171 (63), 157 (62), 144 (24).

2.14. *Rearrangement of* **11** (*Scheme 16*). The aniline (3.1 g, 11.6 mmol) was heated in a mixture of 9 g of 1N H_2SO_4, 7 ml of i-BuOH, and 5 ml of EG at 94° for 1 h. The deep-red mixture was extracted with CH_2Cl_2 after addition of sat. $NaHCO_3$ soln. Two crystallizations from hexane at −20° yielded 0.93 g of colourless crystals of *6-bromo-2,4-dimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**72**). M.p. 69°. TLC ($CHCl_3$): R_f 0.68. GC: 97%. IR (CCl_4): 3460*m*/3380*m* (NH_2). 1950*w* (allene). ^{1}H-NMR: see *Table 8*. ^{13}C-NMR: see *Table 9*. MS: 267/268 (68/67, M^+), 252/250 (27/26), 224/222 (18/18), 185 (5), 171 (100). Anal. calc. for $C_{13}H_{16}BrN$ (266.18): C 58.66, H 6.06, N 5.26; found: C 58.58, H 5.97, N 5.27.

2.15. *Rearrangement of* **a** (*Footnote 26*). Compound **a** (0.59 g, 2.2 mmol) was heated in a mixture of 1 ml of 1N H_2SO_4, 2 ml of EG, 2 ml of diglyme, 2 ml of BuOH, and 1 ml of H_2O at 100–110° for 1 h (*ca.* 50% conversion after 30 min). The dark-brown mixture was extracted with Et_2O, after addition of dil. NaOH. CC (hexane/CH_2Cl_2 3:1 to 2:1) yielded 0.12 g (20%) of starting aniline (TLC ($CHCl_3$): R_f 0.67). Continuation of CC (hexane/CH_2Cl_2 1:1 to CH_2Cl_2) yielded 12 mg (*ca.* 2%) of a non-basic compound, probably 3-bromo-6-isopropylidene-1,5-dimethyltricy-

clo[3.2.1.$0^{2,7}$]oct-3-en-8-one, and then 0.22 g (37%) of *4-bromo-2,6-dimethyl-3-(3'-methylbuta-1',2'-dienyl)aniline* (**c**). TLC ($CHCl_3$): R_f 0.52. ^{1}H-NMR: see *Table 8*. ^{13}C-NMR: see *Table 9*. Continuation of CC (hexane/Et_2O 10:1 to 3:1) yielded 42 mg (10%) of *4-(1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**d**). TLC ($CHCl_3$): R_f 0.34. ^{1}H-NMR: see *Table 10*. ^{13}C-NMR: see *Table 11*.

2.16. *Rearrangement of* **b** (*Footnote 26*). *Ca.* 0.1 g of **b** was dissolved at 0° in 0.5 ml of $CDCl_3$, and 9 equiv. TFA were added. Rearrangement took place at 25° to yield 4-bromo-6-(1'-bromo-3'-methylbuta-1',2'-dienyl)-2,6-dimethylcyclohexa-2,4-dien-1-iminium trifluoroacetate with $\tau_{1/2}$ 5 h. ^{1}H-NMR: 8.4 (br. *s*, $=NH_2$); 7.31 (*s*, H–C(3)); 6.69 (*s*, H–C(5)); 2.24 (*s*, CH_3–C(2)); 1.94 (*s*, 2 CH_3–C(3')); 1.52 (*s*, CH_3–C(6)). ^{13}C-NMR: 198.2 (*s*, C(2')); 186.6 (*s*, C(1)); 151.5 (*d*, C(3)); 143.7 (*d*, C(5)); 127.9 (*s*, C(2)); 114.2 (*s*, C(4)); 113.5 (*s*, C(3')); 83.7 (*s*, C(1')); 56.5 (*s*, C(6)); 30.9 (*q*, CH_3–C(6)); 20.5, 19.8 (2*q* CH_3–C(3')); 15.5 (*q*, CH_3–C(2)). After 20 h the spectra of the iminium ions were changed into those of protonated *4-(3'-bromo-1',1'-dimethylprop-2'-ynyl)-2,6-dimethylaniline* (**e**). ^{1}H-NMR: 8.50 (br. *s*, NH_3^+), 7.28 (*s*, H–C(3,5)); 2.39 (*s*, CH_3–C(2,6)); 1.57 (*s*, 2 CH_3–C(4)). ^{13}C-NMR: 148.1 (*s*, C(1)); 131.2 (*s*, C(2,6)); 1.27.0 (*d*, C(3,5)); 125.0 (*s*, C(4)); 85.6 (*s*, C(2')); 41.4 (*s*, C(3')); 36.9 (*s*, C(1')); 31.0 (*q*, 2 CH_3–C(1')); 17.1 (*q*, CH_3–C(2,6)). ^{13}C-NMR: see *Table 11*.

2.17. *Rearrangement of* **12** (*Scheme 15*). Compound **12** (0.81 g, 3.26 mmol) **12**, heated in a mixture of 2 g of 1N H_2SO_4 and 8 g of EG at 125° for 50 min (no reaction at 95°), yielded, after distillation (180°/high vacuum) and crystallization from pentane 0.184 g (23%) of colorless crystals of *4-(1',1'-dimethylprop-2'-ynyl)-2,6-diethoxyaniline* (**69**). M.p. 50°. TLC ($CHCl_3$): R_f 0.3. GC: 99%. IR (CCl_4): 3470*w*/3380*w* (NH_2), 3300*m* (≡C–H), 2100*vw* (C≡C). ^{1}H-NMR: see *Table 10*. ^{13}C-NMR: see *Table 11*. MS: 248 (12, $[M+1]^+$), 247 (68, $M^{+\cdot}$), 233 (20), 232 (100), 218 (12), 204 (12). Anal. calc. for $C_{15}H_{21}NO_2$ (247.34): C 72.84, H 8.56, N 5.66; found: C 72.84, H 8.60, N 5.72.

2.18. *Attempted Rearrangement of* **13** (*Scheme 15*). Compound **13** (0.23 g, 1 mmol) was heated in a mixture of 1.1 ml of 1N H_2SO_4 and 3 ml of i-BuOH at 85° for 30 min. No reaction occurred. EG (3 ml) and H_2O (1 ml) were added and i-BuOH distilled of (R.V.) until 110° were attained. After 10 min, neither **13** nor a new product could be detected (TLC, GC).

2.19. *Attempted Rearrangement of* **15**. The aniline was destroyed, when dissolved in CCl_4 and treated with 4 equiv. of TFA at 20° (20°; 3 h).

2.20. *Rearrangement of* **14** (*Scheme 11*). 2.20.1. *In the Presence of CuCl.* Compound **14** (0.73 g, 3.2 mmol) and 400 mg (4 mmol) of CuCl were heated under N_2 in 10 ml of DX at 70° during 8 h. CC (hexane/CH_2Cl_2 5:1 to 3:1) and distillation (200°/high vacuum) yielded 0.41 g (56%) of colorless *8'-methoxyspiro[cyclohexane-1,2'-1',2'-dihydroquinoline]* (**58**). TLC ($CHCl_3$): R_f 0.8; deep blue spot after 3 h. GC: 94%. IR: 3400 (NH), 1630 (C=C). ^{1}H-NMR (CCl_4): 6.5–6.3 (*m*, H–C(5,6,7)); 6,18 (*d*, J = 9.7, H–C(4)); 5.42 (*d*, J = 9.7, H–C(3)); 4.3 (*s*, NH); 3.79 (*s*, CH_3O–C(8)); 1.57 (br. *s*, cyclohexyl). MS: 229 (46, M^+), 200 (7), 186 (100), 173 (21), 158 (11). Anal. calc. for $C_{15}H_{19}NO$ (229.32): C 78.56, H 8.35, N 6.11; found: C 78.58, H 8.39, N 6.14.

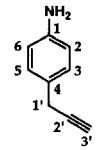
The 1,2-dihydroquinoline was destroyed when heated at 85° for 3 h (1N H_2SO_4 in EtOH) or 110° for 2 h.

2.20.2. *With H_2SO_4.* Compound **14** (0.63 g, 2.7 mmol) was heated in a mixture of 3 ml of 1N H_2SO_4 and 3 ml of PrOH at 85° for 16 h. Only 3% of a new product could be detected. Exchange of PrOH by EG and heating at 110° for 5 h led to a relative amount of 80% of the new product. Prep. TLC (hexane/CH_2Cl_2 2:1) yielded 0.12 g (19%) of colorless *(E)-2-[2'-(cyclohex-1''-enyl)ethenyl]-6-methoxyaniline* (**57**) which crystallized in the refrigerator. M.p. 84–85°. TLC ($CHCl_3$): R_f 0.39; fluorescent. GC: 94%. IR (CCl_4): 3460*w*/3380*w* (NH_2), 1610*m* (C=C), 955 (*E*)-CH–CH). ^{1}H-NMR ($CDCl_3$): 6.954 (*dd*, J = 6.6, 1.5, H–C(5)); 6.7–6.5 (*m*, H–C(3,4)); 6.657, 6.468 (*AB*, J = 15.9, H–C(1',2')); 5.86 (*t*, H–C(2'')); 3.95 (br. *s*, NH_2); 3.82 (*s*, CH_3O–C(6)); 2.28–2.26, 2.17–2.16 (2*m*, 2 H–C(3'', 6'')); 1.74–1.70, 1.65–1.61 (2*m*, 2 H–C(4'',5'')). ^{1}H-NMR (CCl_4/TFA): 7.39 (*t*, J = 7.8, H–C(4)); 7.18, 6.89 (2*d*, J = 8, H–C(3,5)); 6.74, 6.34 (*AB*, J = 16, H–C(1',2')); 6.00 (br. *s*, H–C(2'')); 3.93 (*s*, CH_3O–C(6)). MS: 230 (17, $[M+1]^+$), 229 (100, M^+), 228 (31), 214 (44), 200 (64), 186 (24), 170 (20). Anal. calc. for $C_{15}H_{19}N$ (229.32): C 78.56, H 8.35, N 6.11; found: C 78.86, H 8.66, N 5.89.

2.21. *Attempted Rearrangement of* **27**. Compound **27** (0.112 g, 0.5 mmol) was heated in a mixture of 0.5 ml of 1N H_2SO_4, 1 ml of PrOH, and 5 ml of H_2O at 85°. The soln. became orange red and then brown red. GC and TLC showed that **27** had disappeared. Only traces of 2,4,6-trimethylaniline could be detected after 7 h.

2.22. *Attempted Rearrangement of* **28**. Compound **28** (0.23 g, 0.77 mmol) **28** was heated in a mixture of 0.8 ml of 1N H_2SO_4, 2 ml of i-BuOH, and 3 ml of EG under N_2 at 105°. After 1 h, **28** was completely decomposed. Neither 2,4,6-trimethylaniline nor any other product could be detected (TLC, GC).

Table 10. *^{1}H-HMR Data of 4-(Prop-2′-ynyl)anilines* [a])[b])



Nr. (*Sect.*)	Position of Me Substituents; others	H–C(3,5)	H–C(1′)	H–C(3′)	Me–C(1′)	Me–C(2), Me–C(6)	Others
d[c]) (*2.15*)	2,6,1′,1′	7.11 (*s*)	–	2.30 (*s*)	1.56 (*s*)	2.19 (*s*)	–
68 (*2.8*)	1′,1′; 2,6-Et_2	6.97 (*s*)	–	2.12 (*s*)	1.52 (*s*)	–	2.50 (*q*, J = 7.5); 1.24 (*t*, J = 7.5)
69 (*2.17*)	1′,1′; 2,6-$(OEt)_2$	6.57 (*s*)	–	2.14 (*s*)	1.52 (*s*)	–	4.04 (*q*, J = 7); 1.42 (*t*, J = 7)
81 (*2.25*)	2,6,1′	6.79 (*s*)	3.52 (*dq*, J = 7, 3)	2.06 (*d*, J = 3)	1.41 (*d*, J = 7)	2.12 (*s*)	–
93 (*2.30*)	2,6; 1′-Ph	6.77 (*s*)	4.73 (*d*, J = 2.6)	2.26 (*d*, J = 2.6)	–	2.07 (*s*)	7.2–7.0 (*m*)
101 (*2.36*)	2,3,5,6; 1′-Ph	–	5.47 (*d*, J = 2.5)	2.22 (*d*, J = 2.5)	–	2.10 (*s*)	2.02 (*s*); 7.4–7.0
96 (*2.37*)	2,6-Et_2,1′-Ph	6.79 (*s*)	4.77 (*d*, J = 2.4)	2.25 (*d*, J = 2.4)	–	–	2.40 (*q*, J = 7); 1.18 (*t*, J = 7)
103 (*2.38*)	2,6; 1′-(*p*-Tol)	6.75 (*s*)	4.38 (*d*, J = 2.3)	2.24 (*d*, J = 2.3)	–	2.06 (*s*)	7.14 (*d*, J = 8); 6.96 (*d*, J = 8); 2.27 (*s*)

[a]) Unless otherwise stated spectra in CCl_4.
[b]) All compounds showed NH_2 as br. *s* in the range of 3.25 to 3.55.
[c]) $CDCl_3$.

Table 11. *^{13}C-NMR Data of 4-(Prop-2′-ynyl)anilines* [a])

Nr. (*Sect.*)	Position of Me Substituents; others	C(1)	C(2),C(6)	C(3),C(5)	C(4)	C(1′)	C(2′)	C(3′)	Me–C(1′)	Me–C(2), Me–C(6)	Others
d (*2.15*)	2,6,1′,1′	141.2	135.7	125.3	121.5	34.8	91.9	69.0	31.7	17.8	–
69 (*2.17*)	1′,1; 2,6-$(OEt)_2$	135.2	146.2	102.9	124.3	35.6	91.5	69.2	31.8	–	64.2; 15.1 (2,6-$(OEt)_2$)
98 (*2.32*)	2,6; 1′-Ph,3′-Cl	141.6	121.9	127.5	130.4	42.5	70.7	61.6	–	17.7	–
101 (*2.36*)	2,3,5,6: 1′-Ph	141.7	118.7	127.8	132.8	39.9	84.7	71.3	–	13.8	17.5 (3,5–Me_2)
103 (*2.38*)	2,6; 1′-(*p*-Tol)	141.5	121.8	127.5	130.6	41.7	85.6	72.8	–	17.7	21.0 (Me–C(4″))
h (*2.2.1*)	2,6,1′,1′; 3′-I	141.2	121.4	125.2	135.6	37.1	101.7	–5.0	31.7	17.8	–
e[b]) (*2.16*)	2,6,1′,1′; 3′-Br	148.1	131.2	127.0	125.0	36.9	85.6	41.4	31.0	17.1	–

[a]) *Cf. Table 10*; spectra in $CDCl_3$.
[b]) In $CDCl_3$/4 equiv. TFA.

and 3 ml of EG under N_2 at 105°. After 1 h, **28** was completely decomposed. Neither 2,4,6-trimethylaniline nor any other product could be detected (TLC, GC).

2.23. *Rearrangement of* N-*(3'-Chloro-1',1'-dimethylprop-2'-ynyl)aniline* (**26**; *Scheme 10*). The aniline (0.65 g, 3.35 mmol), prepared from **25** [1] as described under *1.4* for **24** (TLC($CHCl_3$): R_f 0.45), when heated in a mixture of 3 ml of 1N H_2SO_4 and 8 ml of i-BuOH at 95°, showed no reaction after 30 min. i-BuOH was exchanged by 10 ml of EG and the mixture heated at 130° for 30 min. The dark-red mixture was extracted with CH_2Cl_2 after addition of dil. NaOH. CC (hexane/CH_2Cl_2 3:1 to 1:1, then hexane/Et_2O 10:1) and distillation (210°/high vacuum), followed by crystallization (2 times) from tetrachloroethylene yielded slighthly yellow colored crystals (0.203 g; 34%) of *1,2,3,4-tetrahydro-2,2-dimethylquinolin-4-one* (**54**). M.p. 85°. IR (CCl_4): 3390*w* (NH), 1670*s* (>C=O). ^{1}H-NMR ($CDCl_3$): 7.77 (*dd*, J = 7.9, 1.6, H–C(5)); 7.24 (*ddd*, J = 8.3, 7.1, 1.6, H–C(7)); 6.64 (*ddd*, J = 7.9, 7.2, 0.9, H–C(6)); 6.62 (*ddd*, J = 8.3, 0.9, 0.5, H–C(8)); 4.57 (*s* NH); 2.56 (*s*, 2 H–C(3)); 1.29 (*s*, 2 CH_3–C(2)). ^{13}C-NMR ($CDCl_3$): 194.1 (*s*, C(4)); 150.2 (*s*, C(4a)); 135.3 (*d*, C(7)); 127.0 (*d*, C(5)); 117.8 (*s*, C(8a)); 117.1 (*d*, C(6)); 115.9 (*d*, C(8)); 53.4 (*s*, C(2)); 50.6 (*t*, C(3)); 27.5 (*q*, CH_3–C(2)). MS: 176 (77, $[M+1]^+$), 175 (100, M^+), 161 (100), 160 (100), 132 (15), 130 (16). Anal. calc. for $C_{11}H_{13}NO$ (175.23): C 75.39, H 7.48, N 7.99; found: C 75.37, H 7.60, N 7.93.

2.24. *Rearrangement of* **33** (*Scheme 18*). Compound **33** (0.303 g, 1.62 mmol) was heated in a mixture of 1.8 g of 1N H_2SO_4 and 6 g of EtOH in a glass bomb at 134° for 3 h. Workup and distillation (110–150°/high vacuum) yielded 79 mg (26%) of starting aniline and then 180 mg of an oil that was further purified by prep. TLC (CH_2Cl_2) to yield after distillation (120°/high vacuum) 93 mg (31%) of *3-(buta-1',2'-dienyl)-2,4,6-trimethylaniline* (**78**). TLC (CH_2Cl_2): R_f 0.25. IR: 3460*w*/3380*w* (NH_2), 1950*m* (allene). ^{1}H-NMR: see *Table 8*. The extraction of the more polar zone of the TLC (0.4–0.5) yielded 32 mg of a 1:1 mixture of **78** and of *(E)/(Z)-3-(buta-1',3'-dienyl)-2,4,6-trimethylaniline* ((*E*)/(*Z*)-**79**) (according to ^{1}H-NMR)). The polar zone (TLC: R_f 0.05) yielded 18 mg of a mixture of which the main component was *(E)-3-(3'-ethoxybut-1'-enyl)-2,4,6-trimethylaniline* ((*E*)-**80**). IR (CCl_4): 3480/3400 (NH_2); 1620 (C=C); 975 ((*E*)-CH=CH). ^{1}H-NMR (CCl_4): 6.62 (*s*, H–C(5)); 6.45 (*d*, J = 16, H–C(1')). 6.38 (*dd*, J = 16, 7, H–C(2')); 3.90 (*quint.*, J = 7, H–C(3')); 3.47 (*m*, CH_3CH_2O–C(3')); 3.24 (*s*, NH_2); 2.10 (*s*, CH_3–C(2,4,6)); 1.30 (*d*, J = 7, CH_3–C(3')); 1.10 (*t*, CH_3CH_2O–C(3')).

2.25. *Rearrangement of* **32** (*Scheme 18*). Compound **32** (0.346 g, 2 mmol) was heated in a mixture of 2 g of 1N H_2SO_4 and 1 ml of EtOH in a sealed glass bomb at 140° for 2.5 h. Extraction with CH_2Cl_2, after addition of dil. NaOH, and distillation (up to 240°/high vacuum) yielded only 28 mg of a colorless distillate. Prep. TLC (CH_2Cl_2) and distillation (100°/high vacuum) gave 8 mg (2%) of *2,6-dimethyl-4-(1'-methylprop-2'-ynyl)aniline* (**81**). TLC (CH_2Cl_2): R_f 0.35. GC: 92% + 8% 2,6-dimethylaniline. IR (CCl_4): 3480*w*/3400*w* (NH_2), 3310*m* (≡C–H), 2120 *vw* (–C≡C–). ^{1}H-NMR: see *Table 8*.

Continuation of the first high-vacuum distillation above 240° yielded 80 mg (23%) of a colorless glassy solid which possibly represented dimerization products of *3-(buta-1',2'-dienyl)-2,6-dimethylaniline* (**82**).

2.26. *Rearrangement of* **37** (*Scheme 21*). Compound **37** (0.924 g (3 mmol) was heated in a mixture of 4 ml of 1N H_2SO_4 and 10 ml of EG under Ar at 115–125°. After 50 min, the color of the mixture had turned from colorless to deep red. GC indicated two new products and *ca.* 9% of starting aniline. Workup and CC (hexane/CH_2Cl_2 7:1 to 4:1) followed by distillation (180°/high vacuum) yielded 0.176 g (16%) of N-*(2',3'-dibromo-1'-methylprop-2'-enyl)-2,6-diisopropylaniline* (**87**) of unknown configuration. TLC ($CHCl_3$): R_f 0.72. GC: 99%. IR: 3375*w* (NH), 3057*m*. ^{1}H-NMR ($CDCl_3$): 7.07 (*s*, H–C(3,4,5)); 6.49 (*s*, H–C(3')); 3.64 (*d*, J = 7, H–C(1')); 3.34 (br. *s*, NH); 3.21 (*sept.*, J = 6.8, $(CH_3)_2CH$); 1.43 (*d*, J = 7, CH_3–C(1')); 1.22, 1.20 (2*d*, J = 6.8, $(CH_3)_2CH$). MS: 391/389/387 (3:5:3, M^+), 376/374/372 (1:2:1), 268/266 (6:7), 176 (100).

Continuation of CC (hexane/Et_2O 1:1 to Et_2O) yielded, after distillation (150°/high vacuum), 0.36 g (59%) of crystalline *1,2,3,4-tetrahydro-8-isopropyl-2-methylquinolin-4-one* (**86**). M.p. 81–82°. TLC ($CHCl_3$): R_f 0.20. GC: 98%. IR: 3378*m* (NH), 1664*s* (CO). ^{1}H-NMR ($CDCl_3$): 7.74 (*dd*, J = 7.9, 1.4, H–C(5)); 7.26 (*dd*, J = 7.3, 1.5, H–C(7)); 6.70 (*t*, J = 7.7, H–C(6)); 4.54 (*s*, NH), 3.74 (*m*, H–C(2)); 2.86 (*sept.*, J = 6.8, $(CH_3)_2CH$–C(8)); 2.61 (*dm*, J = 16, H–C(3)); 2.44 (*dd*, J = 16, 12.7, H–C(3)); 1.36 (*d*, J = 6.7, CH_3–C(2)); 1.25, 1.23 (2*q*, J = 6.8, $(CH_3)_2CH$–C(8)). ^{13}C-NMR ($CDCl_3$): 194.3 (*s*, C(4)); 148.6 (*s*, C(4a)); 132.9 (*s*, C(8)); 130.7, 125.0; 117.3 (3*d*, C(5,6,7)); 118.9 (*s*, C(8a)); 48.8 (*d*, C(2)); 45.4 (*t*, C(3); 27.0 (*d*, $(CH_3)_2CH$–C(8)); 22.2, 22.1 (2*q*, $(CH_3)_2CH$–C(8)); 21.3 (*q*, CH_3–C(2)).

2.27. *Rearrangement of* **35** (*Scheme 19*). The amine (0.41 g, 1.96 mmol), heated in a mixture of 1N H_2SO_4 (2.4 g), i-PrOH (2 ml), and H_2O (7 ml) in a glass bomb at 135° for 3 h, yielded, after prep. TLC (hexane/CH_2Cl_2 1:2), 102 mg (24%) of *2-(buta-1',2'-dienyl)-1,2-dihydro-2-methylnaphthalen-1-one* (**83**) as a mixture of diastereoisomers (4:3). TLC ($CHCl_3$): R_f 0.63. GC: > 99%. IR: 1960*w* (allene), 1675*s* (C=O), 1645*m* (C=C). ^{1}H-NMR (CCl_4): 7.96 (*dd*, J = 7.4, 1.6, H–C(8)); 7.5–7.0 (*m*, H–C(5,6,7)); 6.46 (*d*, J = 9.8, H–C(4)); 6.07, 6.05 (2*d*, J = 9.8, H–C(3) in

both diastereoisomers); 5.3–5.0 (*m*, H–C(1′,3′)); 1.68, 1.56 (2*dd*, *J* = 6, 4.3, CH_3–C(3′) in both diastereoisomers); ($CDCl_3$): 8.02 (*ddd*, *J* = 7.8, 1.3, 0.6, H–C(8)); 7.55 (*td*, *J* = 7.6, 1.3, H–C(6)); 7.34 (*td*, *J* = 7.6, 1.3, H–C(7)); 7.21 (*dd*, *J* = 7.6, 1.3, H–C(5)); 6.54 (*d*, *J* = 9.7, H–C(4)); 6.14, 6.11 (2*d*, *J* = 9.7, H–C(3)); 5.3–5.2 (*m*, H–C(1′,3′)); 1.67, 1.56 (2*dd*, *J* = 7.0, 3.2, and *J* = 6.3, 3.8, CH_3–C(3′)). ^{13}C-NMR ($CDCl_3$): 203.8/203.7 (*s*, C(2′)); 201.0 (*s*, C(1)); 138.65 (*d*)/138.6 (*d*); 138.1 (*s*); 134.1 (*d*); 127.8 (*d*); 127.3 (*d*); 127.2 (*d*); 127.1 (*d*); 123.3 (*d*)/123.2 (*d*); 94.71/94.46 (*d*, C(1′)); 89.56/89.42 (*d*, C(3′)); 49.03/48.93 (*s*, C(2)); 24.88/24.48 (*q*, CH_3–C(2)); 14.31/14.13 (*q*, CH_3–C(3′)).

From the zone of the more polar compounds, TLC yielded a mixture of 150 mg (36%) of **83** (18%), **35** (16%), and *2-methyl-4-(1′-methylprop-2-ynyl)naphth-1-ol* (**84**; 54%). IR (CCl_4): 3610*m* (OH, free), 3480*w* (OH, bound), 3310*s* (≡C–H), 2210*vw* (–C≡C–). ^{1}H-NMR (CCl_4): 8.2–6.9 (*m*, 5 arom. H); 4.28 (*qd*, *J* = 7, 2, H–C(1′)); 2.27 (*s*, CH_3–C(2)); 2.14 (*d*, *J* = 2, H–C(3′)); 1.54 (*d*, *J* = 7, CH_3–C(1′)).

2.28. *Rearrangement of* **36** (*Scheme 20*). Compound **36** (1.1 g, 4 mmol) was heated in a mixture of 1N H_2SO_4 (2 g) and EG (5 ml) at 130° for 2 h. Workup and CC (hexane/CH_2Cl_2 3:1 to 2:1) firstly yielded 0.45 g (41%) of starting **36**. The following fractions yielded after 2 crystallizations from hexane at –30°, 43 mg (4%) of *3-(Buta-1′,2′-dienyl)-2,4-dimethyl-6-[(*E*)-2″-phenylethenyl]aniline* (**85**). M.p. 53°. TLC ($CHCl_3$): R_f 0.5; strongly fluorescent. IR (CCl_4): 3640*w*/3380*w* (NH_2), 1940*w* (allene), 995*s* (*E*)-CH=CH, conj.). ^{1}H-NMR: see *Table 8*. ^{13}C-NMR: see *Table 9*.

2.29. *Rearrangement of* **51** (*Scheme 22*). Compound **51** (0.37 g, 2.1 mmol) was heated in 30 ml of 0.1N H_2SO_4 in a sealed glass bomb at 180°. Workup followed by distillation (150°/high vacuum), prep. TLC (CH_2Cl_2), and again distillation (120°/high vacuum) yielded 0.12 g (32%) of *2,4,6-trimethyl-3-(prop-2′-enyl)aniline* (**88**) which crystallized in the refrigerator. M.p. 31°. TLC ($CHCl_3$): R_f 0.35. GC: 96%. IR: 3460*w*/3380*w* (NH_2), 1620*s* (C=C), 995*m*/915*m* (–CH=CH_2). ^{1}H-NMR (CCl_4/CCl_4 + TFA): 6.61/6.99 (*s*, H–C(5)); 5.83/5.80 (*ddt*, *J* = 16, 10, 5, H–C(2′)); 4.93/5.01 (*dq*, *J* = 10, 1.7, (*E*) H–C(3′)); 4.73/4.73 (*dq*, *J* = 16, 1.7, (*Z*) H–C(3′)); 3.30/3.40 (*dt*, *J* = 5, 1.7, 2 H–C(1′)); 3.23/– (*s*, NH_2); 2.12; 2.07; 2.01/2.35; 2.30; 2.27 (3*s*, CH_3–C(2,4,6)). MS: 176 (21, $[M+1]^+$), 175 (100, M^+), 174 (14), 150 (35), 145 (14), 144 (10), 134 (9).

2.30. *Rearrangement of* **38** (*Table 7*). Compound **38** (1.17 g, 5 mmol) was heated in a mixture of 5 ml of 1N H_2SO_4 and 20 ml of EtOH at 78° for 3 h. Usual workup yielded in the order of increasing polarity (CC with hexane/CH_2Cl_2 10:1 to 5:1) 0.234 g (20%) of starting **38**, 0.225 g (19%) of colorless *(E)*- and *(Z)-6-benzylidene-1,5-dimethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)- and (*Z*)-**92**) as a 1:1 mixture, 0.252 g (21%) of *2,6-dimethyl-3-(3′-phenylpropa-1′,2′-dienyl)aniline* (**91**) which was destroyed during distillation (180°/high vacuum), and 0.292 g (25%) of *2,6-dimethyl-4-(1′-phenylprop-2′-ynyl)aniline* (**93**).

*(E)- and (Z)-***92**: 1 mg of both diastereoisomers was obtained in pure form by HPLC. TLC ($CHCl_3$): R_f 0.65. GC: 99%. IR (1:1 mixture): 3470*vw* (overtone of (C=O), 3080*w*, 3050*m*, 3020*m*, 2970*m*, 2930*m*, 2960*w*, 1745*s* (C=O), 1660*m* (C=C), 1610*w*, 1600*w*, 1490*m*, 1450*m*, 1380*w*m 1280*w*, 920*m*, 855*w*, 720*m*, 695*s* (Ph), 655*m*. ^{1}H-NMR: see *Table 12*. ^{13}C-NMR: see *Table 13*. MS (1:1 mixture): 236 (15, M^+), 222 (4), 221 (16), 208 (100), 193 (69), 192 (23), 178 (57), 165 (25), 152 (9), 131 (14), 129 (7), 115 (27), 91 (16), 89 (15), 77 (15). Anal. calc. for $C_{17}H_{16}O$ (236.32): C 86.40, H 6.82; found: C 86.11, H 6.77.

Allene **91**: TLC ($CHCl_3$): R_f 0.44.

Alkyne **93**: It is sensitive in soln. in air and turns rapidly red. TLC ($CHCl_3$): R_f 0.37. GC: 96%. IR (CCl_4): 3480*w*/3400*w* (NH_2), 3310*s* (≡C–H), 2120*vw* (–C≡C–), 695*s* (Ph). ^{1}H-NMR: see *Table 10*. MS: 236 (19, $[M+1]^+$), 235 (100, M^+), 234 (20), 221 (15), 220 (86), 204 (13), 158 (37). Anal. calc. for $C_{17}H_{17}N$ (235.33): C 86.76, H 7.28, N 5.95; found: C 86.82, H 7.30, N 5.94.

2.31. *Rearrangement of (–)-(S)-***38**. Compound (–)-**38** (0.66 g, 2.8 mmol; $[\alpha]_{589}^{20} = -57.5$ ($CHCl_3$)) was heated in a mixture of 2 ml of 1N H_2SO_4 and 5 ml of PrOH under N_2 at 86° during 50 min. Workup and CC yielded 69 mg (10%) of (–)-**38**, 53 mg (8%) of (+)-(*E*)- and (–)-(*Z*)-**92** as a 1:1.25 mixture, 13.5 mg (2%) of (–)-**91**, and 55 mg (8%) of (–)-**93**.

*Recovered (–)-***38**: GC: 94.4%. $[\alpha]^{20}$ (1.38) = –45.2 (589), –47.4 (579), –55.1 (546), –104.0 (436), –188.2 (365); *i.e.* o.p. = 83% of that of the starting material.

*(+)-(E)/(–)-(Z)-***92** *Mixture:* GC: 99.7%. $[\alpha]^{20}$ (1.06) = 110.6 (589), +115.9 (579), +137.6 (546), +294.6 (436), +400.0 (404). ^{1}H-NMR ($CDCl_3$; 0–1.5 ppm): 1.349 (*s*, CH_3–C(1) in (*Z*)-**92**); 1.281, 1.274 (2*s*, CH_3–C(1,5) in (*E*)-**92**); 0.866 (*s*, CH_3–C(5) in (*Z*)-**92**); ratio of the *s* 1:1.25. ^{1}H-NMR of (*E*)/(*Z*)-**92** (30 mg) in the presence of (–)-TAE (37 mg) in $CDCl_3$ (= 0–1.5 ppm): 1.259/1.250 (2*s*, ratio 3.96:1.42; *i.e.* e.e. = 47%; CH_3–C(1) in (*Z*)-**92**); 1.207/1.198 (2*s*, ratio 2.34:0.86; *i.e.* ee = 46%; CH_3–C(1) in (*E*)-**92**); 1.172/1.169 (2*s*, ratio 1.01:2.88, *i.e.* e.e. = 48%; CH_3–C(5) in (*E*)-**92**); 0.817/0.813 (2*s*, ratio 1.16:3.13; *i.e.* e.e. = 45%; CH_3–C(5) in (*Z*)-**92**). HPLC yielded 180 μg and 330 μg of pure (+)-(*E*)- and (–)-(*Z*)-**92**, resp. CD (1.39 mmol/l DX; 25°) of (–)-(*Z*)-**92** (*cf. Fig. 1*; λ (nm)/$\Delta\varepsilon/\theta$): 400/–0.27/–0.90; 365/–0.20/–0.65; 362/–0.31/–1.03; 345/–0.35/–1.17; 307 (neg. max.)/

−6.59/−21.76; 234.9 (pos. max.)/+18.62/+61.46; 220.4 (pos. min.)/+13.23/+43.66; 207.4 (pos. max.)/+22.84/+75.38; 201.0/+17.02/+56.17. CD (1.55 mmol)/l DX; 25°) of (+)-(*E*)-**92** (*cf. Fig. 1*): 400/+0.51/+1.68; 392.2/+0.15/+0.48; 381.9/+0.18/+0.60; 246.9/0.58/+1.92; 312.4 (pos. max.)/+15.44/+50.95; 262 (*sh*)-/−6.15/−20.28; 237.0 (neg. max.)/−17.99/−59.35; 220.6 (neg. min.)/−6.27/−20.68; 205.5 (neg. max.)/−22.56/−74.65; 202.0/−15.03/−49.60.

Allene (−)-**91**: $[\alpha]^{20}$ (0.27) = −420.3 (589), −442.6 (579), −525.9 (546), −1124 (436). IR (CCl_4): 3470*w*/3390*w* (NH_2), 1930*m* (allene). ^{1}H-NMR (CCl_4): 7.5–6.7 (*m* with *s* at 7.20, 7 arom. H, H−C(1′)); 6.38 (*d*, *J* = 6, H−C(3′)); 3.37 (br. *s*, NH_2); 2.14; 2.07 (2*s*, CH_3−C(2,6)).

Alkyne (−)-**93**: GC: 96%. $[\alpha]^{20}$ (0.8) = −13.1 (589), −13.7 (579), −16.5 (546), −31.2 (436), −37.1 (404).

2.32. *Rearrangement of (±)*-**45** (*Table 7*). Compound (±)-**45** (0.93 g, 3.45 mmol) was heated in a mixture of 3 ml of 1N H_2SO_4 and 5 g of i-BuOH at 100° during 4 h. Workup and CC (hexane/CH_2Cl_2 6.1 to 3:1) yielded 0.235 g (25%) of starting (±)-**45**, 0.218 g (22%) of *(E)-6-benzylidene-7-chloro-1,5-dimethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)-**97**), and then 0.212 g (22%) of (*Z*)-**97**. Continuation of CC (hexane/Et_2O 10:1 to 4:1) yielded, after distillation (240°/high vacuum), 46 mg (4%) of *4-(3′-chloro-1′-phenylprop-2′-ynyl)-2,6-dimethylaniline* (**98**).

(*E*)-**97**: TLC ($CHCl_3$): R_f 0.77. GC: 99%. Distillation at 110°/0.01 Torr. IR: 3040*m*, 3020*m*, 2960*m*, 2920*m*, 2860*w*, 1735*s* (br.) (strained C=O), 1655*m* (C=C), 1605*w*, 1595*w*, 1485*m*, 1440*s*, 1375*m*, 1270*s*, 1205*w*, 1065*w*, 1045*m*, 920*m*, 860*m*, 825*m*, 790*s*, 745*s*, 725*m*, 695*s* (Ph), 670*s*, 630*w*. ^{1}H-NMR: see *Table 12*. ^{13}C-NMR: see *Table 13*. ^{1}H-NOE ($CDCl_3$): irr. 0.9 (*s*, CH_3−C(5))→2.8% (H−C(4)); 2.6% (*o*-H in Ph−C(9)), 1.7% (*m*- and *p*-H in Ph−C(9)); irr. 1.45 (CH_3−C(1))→1.5% (H−C(2)); irr. 6.81 (H−C(9))→3.9% (*o*−H in Ph−C(9)).

(*Z*)-**97**: TLC ($CHCl_3$): R_f 0.71. GC: 95%. Distillation at 110°/0.01 Torr. IR: 3040*m*, 3020*w*, 2960*m*, 2860*w*, 1730*s* (strained C=O), 1655*m* (C=C), 1610*w*, 1595*w*, 1485*w*, 1440*m*, 1375*m*, 1280*s*, 1205*w*, 1135*w*, 1065*w*, 1045*w*, 925*m*, 875*w*, 850*w*, 820*m*, 770*m*, 740*s*, 725*m*, 690*s* (Ph), 660*m*, 625*w*. ^{1}H-NMR: see *Table 12*. ^{13}C-NMR: see *Table 13*. ^{1}H-NOE ($CDCl_3$): irr. 1.36 (*s*, CH_3−C(1))→1.6% (H−C(2)); irr. 1.31 (*s*, CH_3−C(5))→4.6% (H−C(9)), 1.9% (H−C(4)).

Alkyne **98**: TLC ($CHCl_3$): R_f 0.4. GC: 88%. IR (CCl_4): 3460*w*/3390*w* (NH_2), 2220v*w* (−C≡C−), 690*s* (Ph). ^{1}H-NMR (CCl_4): 7.19 (*s*, 5 arom. H); 6.73 (*s*, H−C(3,5)); 4.73 (*s*, H−C(1′)); 3.30 (br. *s*, NH_2); 2.07 (*s*, CH_3−C(2,6)). ^{13}C-NMR ($CDCl_3$): 141.6 (*s*, C(1,1″)); 130.3 (*s*, C(4)); 128.4 (*d*, C(3″,5″)); 127.6 (*d*, C(2″,6″)); 127.5 (*d*, C(3,5)); 126.7 (*d*, C(4″)); 121.9 (*s*, C(2,6)); 70.7 (*s*, C(2′)); 61.6 (*s*, C(3′)); 42.5 (*d*, C(1′)); 17.7 (*q*, CH_3−C(2,6)).

2.33. *Rearrangement of (−)-(S)*-**45**. Compound (−)-**45** (100 mg, 0.37 mmol; $[\alpha]_{589}^{20}$ = −16.8 ($CHCl_3$)) was heated in a mixture of 0.5 ml of 1N H_2SO_4, 6 ml of i-BuOH, and 6 ml of H_2O at 90° during 70 min (GC indicated 90% of products and 4% of (−)-**45**). Workup and CC yielded after distillation (240°/high vacuum) 17 mg of (−)-**45**, 22 mg (22%) of (+)-(*E*)-**97**, and 26 mg (26%) of (+)-(*Z*)-**97**.

Recovered (−)-**45**: GC: 99%. $[\alpha]^{20}$ (1.7) = −8.7 (589), −9.4 (579), −11.2 (546); *i.e.* o.p. = 51% of that of (−)-**45**.

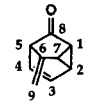
(+)-(*E*)-**97**: GC: 98% + 2% of (−)-**45**. $[\alpha]^{20}$ (0.38) = +15.3 (589), +5.3 (579), +1.8 (546), +1.3 (525), −1.6 (510), −6.6 (490), −15.8 (470), −310.5 (436). UV (EtOH): λ_{max} 236 (8770), 250 (7590), λ_{min} 225 (8520), sh at 300–330. UV ($CHCl_3$): λ_{max} 302 (730), λ_{min} 286 (520).

(+)-(*Z*)-**97**: GC: > 99%. $[\alpha]^{20}$ (2.5) = +134.8 (589), +143.2 (579), +176.0 (546), +204.2 (525), +269.7 (490), +466.0 (436), +756 (410); $[\alpha]^{20}$ (0.5) = +147.2 (589), +156.0 (579), +191.4 (546), +514.0 (436), +1843 (365). UV (EtOH): λ_{max} 233 (7220), 250 (6930); λ_{min} 226 (6130). UV ($CHCl_3$): λ_{max} 302 (790), λ_{min} 292 (760). CD (7.8 mmol/l DX; 25°): 400/−0.26/0.86; 372/0.21/0.03; 351/+0.21/0.03; 313.8 (pos. max.)/8.50/28.05; 279.3/−0.08/−0.26; 260.3 (neg. max.)/−3.18/−10.49; 254.7 (neg. min.)/−3.03/−9.99; 238.9 (neg. max.)/−5.98/−19.72; 223.5 (neg. min.)/−0.89/−2.95; 210.1 (neg. max.)/−7.65/−25.25; 206.0/−4.79/−15.80. ^{1}H-NMR of (+)-(*Z*)-**97** (20 mg) in the presence of (−)-TAE (34 mg) in $CDCl_3$ (0–1.5 ppm): 1.292/1.283 (2*s*, ratio 2.76:8.14; *i.e.* e.e. = −49%; CH_3−C(1)); 1.254/1.241 (2*d*, ratio 2.55: 7.73; *i.e.* e.e. = 50%). MS: 272/270 (3/10, $M^{+\cdot}$); 244 (12), 243 (8), 242 (39), 207 (71), 206 (31), 193 (21), 192 (100), 191 (27), 176 (47).

2.34. *Rearrangement of (±)*-**39** (*Table 6*).

2.34.1. *With TFA*: 0.96 g (3.85 mmol) of (±)-**39** were dissolved in 10 ml of CCl_4 and 0.44 g (3.81 mmol) of TFA added. No reaction occurred at 20° during 2.5 h. Therefore, a further amount of 1.17 g (10 mmol) of TFA was added. Nearly all (±)-**39** was consumed after 7 h at 20°. Workup and CC (hexane/CH_2Cl_2 3:1) yielded 39 mg (4%) of **39** and then (with hexane/EtO_2 10:1 to 5:1) 0.39 g (40%) of *2,4,6-trimethyl-3-(3′-phenylpropa-1′,2′-dienyl)aniline* (**89**). The attempt to distil the aniline (220°/high vacuum) led to nearly complete dimerization. TLC (**89**; $CHCl_3$): R_f 0.41. Soln. of **89** in air rapidly turned red. IR: 3460*w*/3380*w* (NH_2), 3060*w*, 3030*w*, 3010*w*, 2970*m*, 2920, 2860*m*, 1940*m*

Table 12. *^{1}H-NMR Data of Tricyclo[3.2.1.0^{2,7}]oct-3-en-8-ones* [a])



Nr. (*Sect.*)	Position of Me Substituents; others	H–C(2)	H–C(3)	H–C(4)	H–C(7)	H–C(9)	Me–C(1)	Me–C(3)	Me–C(5)	Others
62 (*2.5.2.*)	1,3,5,9,9; 7-Cl	2.14 (*d*, J = 3)	–	5.26 (*sext.*-like, $J \approx 1.5$)	–	–	1.37(*s*)	1.81 (*d*, J = 1.7)	1.38(*s*)	2.14 (*s*, 9*Z*) 1.86 (*s*, 9*E*)
(*E*)-**90** (*2.34.2*)	1,3,5; (9*E*)-Ph	2.23 (*dd*, J = 7, 3.7)	–	5.22 (*qd*, J = 3.5, 1.7)	2.99 (*d*, J = 7)	6.25 (*s*)	1.26(*s*)	1.86 (*d*, J = 1.7)	1.22(*s*)	7.25–7.1 (*m*, Ph)
(*Z*)-**90** (2.34.2)	1,3,5; (9*Z*)-Ph	2.13 (*dd*, J = 7, 3.7)	–	5.27 (*qd*, J = 3,5,1.7)	2.51 (*d*, J = 7)	6.46 (*s*)	1.33 (*s*)	1.87 (*d*, J = 1.7)	0.82 (*s*)	7.25–7.1 (*m*, Ph)
(*E*)-[^{2}H]-**90** (*2.34.3*)	1,3,5; [7-^{2}H], (9*E*)-Ph	2.16 (*m*, J = 7, < 1.5)	–	5.20 (br.*s*)	–	6.17 (*s*)	1.25 (*s*)	1.86 (*s*)	1.17 (*s*)	7.2–7.1 (*m*, Ph)
(*Z*)-[^{2}H]-**90** (*2.34.3*)	1,3,5; [7-^{2}H], (9*Z*)-Ph	2.01 (*dd*, J = 7, < 1.5)	–	5.20 (br.*s*)	–	6.38 (*s*)	1.31 (*s*)	1.88 (*s*)	0.75 (*s*)	7.2–7.1 (*m*, Ph)
(*E*)-**92** (*2.30*)	1,5; (9*E*)-Ph	2.47 (*ddd*, J = 7, 4.8, 3.3)	6.04 (*dd*, J = 7.7, 4.8)	5.59 (*dd*, J = 7.7, 3.3)	3.00 (*d*, J = 7)	6.30 (*s*)	1.28 (*s*)	–	1.27 (*s*)	7.35–7.2 (*m*, Ph)
(*Z*)-**90** (*2.30*)	1,5; (9*Z*)-Ph	2.38 (*ddd*, J = 7, 4.8, 3.3)	6.00 (*dd*, J = 7.5, 4.8)	5.65 (*dd*, J = 7.5, 3.3)	2.56 (*d*, J = 7)	6.50 (*s*)	1.35 (*s*)	–	0.87 (*s*)	7.25–7.15 (*m*, Ph)
(*Z*)-**97** (*2.32*)	1,5; 7-Cl, (9*Z*)-Ph	2.49 (*dd*, J = 5.0, 3.1)	6.10 (*dd*, J = 7.5, 5.0)	5.62 (*dd*, J = 7.5, 3.2)	–	6.53 (*s*)	1.36 (*s*)	–	1.31 (*s*)	7.27 (br. *s*, Ph)
(*E*)-**97** (*2.32*)	1,5; 7-Cl, (9*E*)-Ph	2.57 (*dd*, J = 4.7, 3.1)	6.03 (*dd*, J = 7.5, 5.0)	5.68 (*dd*, J = 7.5, 3.0)	–	6.81 (*s*)	1.45 (*s*)	–	0.90 (*s*)	7.3–7.15 (*m*, Ph)
(*E*)-**100**[b]) (*2.36*)	1,2,4,5; (9*E*)-Ph	–	~ 5.45 (*q*, J = 2)	–	2.47 (*s*)	6.13 (*s*)	1.19 (*s*)	–	1.19 (*s*)	1.68 (*d*, J = 2, Me–C(4)) 1.38 (*s*, C(2))
(*Z*)-**100**[b]) (*2.36*)	1,2,4,5; (9*Z*)-Ph	–	~ 5.45 (*q*, J = 2)	–	2.03 (*s*)	6.32 (*s*)	1.25 (*s*)	–	0.73 (*s*)	1.68 (*d*, J = 2, Me–C(4)) 1.41 (*s*, Me–C(2))

Table 12 (cont.)

Nr. (*Sect.*)	Position of Me Substituents; others	H–C(2)	H–C(3)	H–C(4)	H–C(7)	H–C(9)	Me–C(1)	Me–C(3)	Me–C(5)	Others
(*E*)-**95**[c]) (*2.37*)	1,5-Et_2, (9*E*)-Ph	2.5–2.0 (*m*)	6.1–5.5 (*m*)		2.85 (*d*, *J* = 7.5)	6.21 (*s*)	–	–	–	1.9–1.3 (*m*, Et-C(2,6)) 1.04 (*t*); 0.93 (*t*, Et-C(2,6))
(*Z*)-**95**[c]) (*2.37*)	1,5-Et_2, (9*Z*)-Ph	2.5–2.0 (*m*)	6.1–5.5 (*m*)		2.48 (*d*, *J* = 7.5)	6.43 (*s*)	–	–	–	1.9–1.3 (*m*, Et-C(2,6)); 0.95 (*m*); 0.31 (*t*, Et-C (2,6))
(*E*)-**102**[d]) (*2.38*)	1,5; (9*E*)-(*p*-Tol)	2.5–2.35(*m*)	6.0–5.8 (*m*)	5.53 (*dd*, *J* = 7.5, 3.3)	2.88 (*d*, *J* = 7)	6.17 (*s*)	1.25 (*s*)	–	1.21 (*s*)	2.32 (*s*, Me–C(4′))
(*Z*)-**102**[d]) (*2.38*)	1,5; (9*Z*)-(*p*-Tol)	2.5–2.35(*m*)	6.0–5.8 (*m*)	5.63 (*dd*, *J* = 7.5, 3.3)	2.44 (*d*, *J* = 7)	6.36 (*s*)	1.31 (*s*)	–	0.81 (*s*)	2.32 (*s*, Me–C(4′))
[42]	1,5,7	2.04 (*dd*)	5.91 (*dd*)	5.41 (*dd*)	–	4.72 (*s*); 4.67 (*s*)	1.21 (*s*)	–	1.14 (*s*)	1.44 (*s*, Me–C(7))
[42]	1,5; (9*E*)	2.4–2.2 (*m*)	5.86 (*dd*)	5.43 (*dd*)	2.59 (*d*)	5.19 (*q*)	1.26 (*s*)	–	1.08 (*s*)	1.73 (*s*, Me–C(9))
[42]	1,5; (9*Z*)	2.2–2.05 (*m*)	5.84 (*dd*)	5.47 (*dd*)	2.4–2.2 (*m*)	5.20 (*q*)	1.25 (*s*)	–	1.34 (*s*)	1.74 (*d*, Me–C(9))
[42]	1,3,5	2.05 (*dd*)	–	5.11 (*m*)	2.41 (*d*)	4.73 (*s*) 4.64 (*s*)	1.27 (*s*)	1.83 (*d*)	1.07 (*s*)	–
[13]	3; 1,5-$(i\text{-Pr})_2$	2.08 (*dd*)	–	5.5–5.4 (*m*)	2.48 (*d*)	4.90 (*s*) 4.76 (*s*)	–	1.83 (*d*)	–	2.1–1.9 (*m*) 1.3–0.9 (*m*) } (i-Pr)
[13]	3; 1,5-$(t\text{-Bu})_2$	2.04 (*dd*)	–	5.6–5.4 (*m*)	2.38 (*d*)	5.04 (*s*) 4.94 (*s*)	–	1.85 (*d*)	–	1.17 (*s*, *t*-Bu)

[a]) Spectra in CCl_4.
[b]) Ph at 7.3–6.9
[c]) Ph at 7.24 and 7.15 in (*E*)- and (*Z*)-form.
[d]) *p*-Tol at 7.10 and 6.95 in (*E*)- and (*Z*)-form.

Table 13. *^{13}C-NMR Data of Tricyclo[3.2.1.0^{2,7}]oct-3-en-8-ones* [a])

Nr. (*Sect.*)	Position of Me Substituents; others	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	C (7)	C (8)	C (9)	Me–C(1)	Me–C(3)	Me–C(5)	Others
62 (*2.5.2*)	1,3,5,9,9; 7-Cl	35.4 (*s*)	49.6 (*d*, *J* = 168)	134.0 (*s*, *J* = 7)	128.1 (*d*, *J* = 169; 6)	53.0 (*s*)	128.9 (*s*)	58.3 (*s*)	211.0 (*s*)	126.0 (*s*, *J* = 5)	9.7 (*q*, *J* = 129; 4.5)	19.8 (*q*, *J* = 127; 4.6; 2.8)	17.6 (q, *J* = 128; 4.3)	23.5 (*q*, *J* = 126, 5, (9*E*)-Me); 23.3 (*q*, *J* = 127; 4.8 (9*Z*)-Me))
(*Z*)-**90** (*2.34.2*)	1,3,5; (9*Z*)-Ph[b])	30.2 (*s*)	40.8 (*d*, *J* = 165; 5)	134.4 (*s*)	125.7 (*d*, *J* = 169; 6)	50.8 (*s*)	141.9 (*s*)	39.3 (*d*, *J* = 175 ;4)	213.7 (*s*)	119.3 (*d*, *J* = 154; 2)	12.1 (*q*, *J* = 127; 8)	20.0 (*q*, *J* = 128;3.1)	14.7 (*q*, *J* = 128; 4.2)	–
(*E*)-**90** (*2.34.2*)	1,3,5; (9*E*)-Ph	31.4 (*s*)	41.5 (*d*, *J* = 165; 2)	134.5 (*s*)	125.3 (*d*, *J* = 169; 6)	51.0 (*s*)	141.7 (*s*)	35.7 (*d*, *J* = 177; 8)	212.8 (*s*)	116.0 (*d*, *J* = 155; 0)	12.1 (*q*, *J* = 127; 7)	19.9 (*q*, *J* = 127; 3.1)	12.9 (*q*, *J* = 127; 4.2)	–
(*Z*)-[^{2}H]-**90** (*2.34.3*)	1,3,5; [7-^{2}H], (9*Z*)-Ph	30.0 (*s*)	40.6 (*d*)	134.3 (*s*)	125.5 (*d*)	50.7 (*s*)	141.6 (*s*)	38.8 (*t*)	212.9 (*s*)	119.1 (*d*)	12.1 (*q*)	19.9 (*q*)	14.7 (*q*)	–
(*E*)-[^{2}H]-**90** (*2.34.3*)	1,3,5; [7-^{2}H], (9*E*)-Ph	31.2 (*s*)	41.3 (*d*)	134.3 (*s*)	125.1 (*d*)	50.9 (*s*)	141.5 (*s*)	35.3 (*t*)	212.5 (*s*)	115.8 (*d*)	12.1 (*q*)	19.8 (*q*)	12.8 (*q*)	–
(*Z*)-**92** (*2.30*)	1,5; (9*Z*)-Ph	29.8 (*s*)	39.2 (*d*)	125.1 (*d*)	132.8 (*d*)	52.3 (*s*)	141.2 (*s*)	37.2 (*d*)	212.8 (*s*)	120.1 (*d*)	11.9 (*q*)	–	14.6 (*q*)	–
(*E*)-**92** (*2.30*)	1,5; (9*E*)-Ph	31.0 (*s*)	37.8 (*d*)	125.0 (*d*)	132.5 (*d*)	52.6 (*s*)	141.0 (*s*)	35.7 (*d*)	212.5 (*s*)	116.7 (*d*)	12.0 (*q*)	–	12.8 (*q*)	–
(*E*)-**97** (*2.32*)	1,5; 7-Cl, (9*E*)-Ph	34.9 (*s*)	45.0 (*d*)	124.8 (*d*)	133.8 (*d*)	53.4 (*s*)	139.3 (*s*)	59.7 (*s*)	209.3 (*s*)	120.7 (*d*)	9.4 (*q*)	–	14.7 (*q*)	–
(*Z*)-**97** (*2.32*)	1,5; 7-Cl, (9*Z*)-Ph	36.6 (*s*)	46.6 (*d*)	124.9 (*d*)	133.9 (*d*)	54.2 (*s*)	138.1 (*s*)	56.9 (*s*)	209.2 (*s*)	119.3 (*d*)	9.3 (*q*)	–	13.1 (*q*)	–
(*Z*)-**102** (*2.38*)	1,5; (9*Z*)-(*p*-Tol)	30.0 (*s*)	39.2 (*d*)	125.0 (*d*)	132.9 (*d*)	52.3 (*s*)	140.7 (*s*)	37.2 (*d*)	212.6 (*s*)	120.1 (*d*)	12.0 (*q*)	–	14.7 (*q*)	21.2 (*q*, Me–C(4′))
(*E*)-**102** (*2.38*)	1,5; (9*E*)-(*p*-Tol)	31.0 (*s*)	37.8 (*d*)	125.0 (*d*)	132.5 (*d*)	52.6 (*s*)	140.1 (*s*)	35.8 (*d*)	212.3 (*s*)	116.5 (*d*)	12.1 (*q*)	–	12.8 (*q*)	21.2 (*q*, Me–C(4′))
[13]	1,3,5	30.8	40.7	134.1	124.8	50.5	148.1	37.9	212.3	99.5	11.9	19.8	12.3	–
[13]	1,3; 5-(*t*-Bu)	30.9	39.9	134.6	120.8	59.2	145.5	39.6	211.6	103.5	12.2	20.9	–	31.9 (*t*-Bu–C(5))

[a]) *Cf. Table 12;* spectra in $CDCl_3$; multiplicities for ^1J; in some cases ^NJ.

[b]) Typical ranges for C(1′) to C(6′) of Ph are: 135.6–137.3 (C(1′)); 128.3–129.5 (C(2′), C(6′)); 127.6–128.4 (C(3′), C(5)), 126.4–127.1 (C(4′)).

(allene), 1620*s*, 1595*m*, 1490*m*, 1475*s*, 1450*m*, 1305*w*, 1260*w*, 875*m*, 785*m*, 690*s* (Ph). ^{1}H-NMR: see *Table 8*. ^{13}C-NMR: see *Table 9*.

2.34.2. *With H_2SO_4:* 1.24 g (5 mmol) of **39** were heated in a mixture of 7 g of 1N H_2SO_4 and 30 ml of BuOH at 92° for 70 min. Workup and CC (hexane/CH_2Cl_2 9:1 to 3.1) yielded at first 93 mg (7%) of **39**, then 0.233 g (18.8%) of a colorless 1.4:1 mixture of *(E)-* and *(Z)-6-benzylidene-1,3,5-trimethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)- and (*Z*)-**90**, resp.), and finally 0.47 g (38%) of **89**.

*Mixture of (E)- and (Z)-***90**: TLC ($CHCl_3$): R_f 0.73. GC: 99%. IR (CCl_4): 3470v*w* (overtone, strained C=O), 1740*s* (br.; strained C=O), 1660*s*, (C=C), 695*s* (Ph). ^{1}H-NMR: see *Table 12*. ^{13}C-NMR: see *Table 13*. MS: 250 (11, M^+), 235 (16), 223 (21), 222 (100), 221 (22), 207 (45), 192 (45), 178 (15), 165 (23).

2.34.3. *Rearrangement of (±)-[^{2}H]-***39** (*Table 6*). Compound (±)-[^{2}H]-**39** (1.25 g, 5 mmol) was heated in a mixture of 9 g of 1N H_2SO_4 in 25 of ml i-BuOH at 90° for 1 h. The yellow oil (1.22 g), resulting from workup, was separated by CC (hexane/CH_2Cl_2 4:1) to yield 0.283 g (22.6%) of a 1.2:1 mixture (*E*)/(*Z*)-[^{2}H]-**90** (GC 99.7%) and then 0.63 g (50%) of [^{2}H]-**89**.

(*E*)/(*Z*)-[^{2}H]-**90**: IR (CCl_4): 3470v*w* (overtone, strained C=O), 1740*s* (strained C=O), 1665*m* (C=C), 695*s* (Ph). ^{1}H-NMR (CCl_4; *cf. Table 12*): No signal at 2.99 and 2.51 (H–C(7) in (*E*)- and (*Z*)-**90**, resp.), 2.16–2.01 (*m*, $J(2,4) = 3.5$, $J(2.7) < 1.5$; H–C(2) in (*E*)- and (*Z*)-**90**). ^{13}C-NMR ($CDCl_3$; *cf. Table 13*): 38.8, 35.3 (2*t*, $^1J(C,^2H) = 27.7$, C(7) in (*Z*)- and (*E*)-**90**, resp.). The following ^{1}H/^{2}H isotopic shifts (10^{-3} ppm) in ^{13}C-NMR were observed:

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	(C9)
(*E*)-**90**	76	111	11	8	0	59	350	40
(*Z*)-**90**	98	115	11	10	0	24	1400	48

MS: 251 (11, M^+), 236 (16), 224 (19), 223 (100), 222 (25), 208 (42), 192 (43), 179 (13), 166 (18).

[^{2}H]-**89**: TLC ($CHCl_3$): 0.45. IR: 3460*w*/3380*w* (NH_2), 2210v*w* (C–^{2}H), 1930*m* (allene), 1620*s*, 1480*s*, 1465*s*, 750*s*, 695*s* (Ph). ^{1}H-NMR (CCl_4/CCl_4 + TFA): 7.20/7.24 (*s*, 5 arom. H); 6.60/6.99 (*s*, H–C(5)); no signal at 6.56 (H–C(1')); 6.20/6.37 (*s*, H–C(3')); 3.25/– (br. *s*, NH_2); 2.23; 2.14; 2.06/2.386; 2.385; 2.355 (3*s*, CH_3–C(2,4,6)). ^{13}C-NMR ($CDCl_3$): Identical with that of **89** except for C(1') at 94.3 (*t* instead of *d*).

2.35. *Rearrangement of (–)-(S)-***39**. Compound (–)-**39** (0.20 g, 0.8 mmol; $[\alpha]_{589}^{20} = -50.4$ ($CHCl_3$) for the chemically pure compound) was heated in a mixture of 1 ml) of 1N H_2SO_4 and 5 ml of PrOH at 85° during 78 min. Workup and CC (hexane/Et_2O 20:1 to 5:1) yielded 33 mg (16%) of a 1:1 mixture of (+)-(*E*)/(*Z*)-**90** and then 76 mg (38%) of (–)-**89**.

(+)-(*E*)/(*Z*)-**90**: GC: 100%. $[\alpha]^{20}$ (0.66) = +89.4 (589), +93.2 (579), +110.6 (546), +246.0 (436), +615.1 (365). Estimated for (+)-(*E*)-**90** $\alpha]_{589} = +224°$ and for (–)-(*Z*)-**90** $[\alpha]_{589} = -34°$.

*Allene (–)-***89**: GC: 91%. $[\alpha]^{20}$ (1.52) = –255.5 (589), –268.3 (579), –317.5 (546), –656.5 (436); estimated for chemically pure (–)-**89**: $[\alpha]_{589} = -280°$.

2.36. *Rearrangement of* **40** (*Scheme 23*). Compound **40** (1.68 g, 6.38 mmol) was heated in a mixture of 1.77 g (7 mmol) of (+)-camphor-10-sulfonic-acid hydrate, 30 ml of ethyl methyl ketone, and 1 ml of H_2O at 74° during 60 min. GC indicated only 2% of **40**. Workup and CC (hexane/CH_2Cl_2 10:1 to 5:1) yielded 23 mg (1.4%) of **45** and then 0.336 g (20%) of a colorless 1:1 mixture of *(E)-* and *(Z)-6-benzylidene-1,2,4,5-tetramethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)- and (*Z*)-**100**, resp.) Continuation of CC (hexane/CH_2Cl_2 3:1) yielded 0.109 g (6%) of *2,3,5,6-tetramethyl-6-(3'-phenylpropa-1',2'-dienyl)cyclohexa-2,4-dien-1-one* (**99**) as a 1:1 mixture of both diastereoisomers. Finally, CC (hexane/Et_2O 10:1 to 5.1) yielded after distillation (200–250°/high vacuum) 0.832 g (49%) of a yellow oil. Two crystallizations from CCl_4 yielded 0.40 g (23%) of colorless crystals of *2,3,5,6-tetramethyl-4-(1'-phenylprop-2'-ynyl)aniline* (**101**).

(*E*)/(*Z*)-**100**: TLC ($CHCl_3$): R_f 0.63, weakly fluorescent. GC: 99%. IR (CCl_4): 1740*s* (strained C=O), 1660*m* (C=C), 700*s* (Ph). ^{1}H-NMR: see *Table 12*.

Allene **99**: TLC ($CHCl_3$): 0.57. IR (CCl_4): 3030*w*, 2970*m*, 2860*m*, 1950*w* (allene), 1660*s* (C=C), 1645*s* (dienone), 1585*m*, 1490*w*, 1445*w* (br.), 1375*m*, 1310*m*, 690*w*. ^{1}H-NMR (CCl_4): 7.5–7.0 (*m*, 5 arom. H); 6.19 (*d*, $J = 6.4$, H–C(3')); 5.81 (br. *s*, H–C(4)); 5.32 (*d*, $J = 6.4$, H–C(1')); 2.15; 1.98; 1.86; 1.81 (4*s*, CH_3–C(2,3,5) in both diastereoisomers); 1.32, 1.25 (2*s*, CH_3–C(6) in both diastereoisomers).

Alkyne **101**: M.p. 122–123°. TLC ($CHCl_3$): R_f 0.42. GC: 99%. IR (CCl_4): 3480*w*/3410*w* (NH_2), 3310*s*, (≡C–H), 2110v*w* (–C≡C–), 695*s*, (Ph). ^{1}H-NMR (CCl_4/CCl_4+TFA): 7.4–7.0/7.20 (*m*, 5 arom. H); 5.47/5.65 (*d*, $J = 2.5$, H–C(1')); 3.32/- (br. *s*, NH_2); 2.22/2.23 (*d*, $J = 2.5$, H–C(3')); 2.10, 2.02/2.30, 2.23 (2*s*, CH_3–C(2,6), CH_3–C(3,5)). ^{13}C-NMR: see *Table 11*. MS: 263 (26, M^+), 248 (14), 215 (36), 186 (26), 177 (22), 146 (65), 115 (100). Anal. calc. for $C_{19}H_{21}N$ (263.38): C 86.64, H 8.04, N 5.31; found: C 86.79, H 7.80, N 5.44.

2.37. *Rearrangement of* **41** (*Table 7*). Compound **41** (1.326 g, 5.04 mmol) was heated under Ar in a mixture of 5 ml of 1N H_2SO_4 and 9 ml of EtOH at 78° during 72 min. Workup of the reddishly colored mixture yielded 1.2 g of a mixture of products which was separated by CC (hexane/CH_2Cl_2 3:1 to 1:1) to yield, after distillation (200°/high vacuum), 0.106 g (8%) of a mixture of *(E)*- and *(Z)-6-benzylidene-1,5-diethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)- and (*Z*)-**95**, resp.) with a slight preponderance of the (*E*)-isomer. Continuation of CC yielded 82 mg (6%) of *2,6-diethyl-3-(3'-phenylpropa-1',2'-dienyl)aniline* (**94**), and then a mixture of **94** and *2,6-diethyl-4-(1'-phenylprop-2'-ynyl)aniline* (**96**). Several distillations (230°/high vacuum) destroyed the allene (65 mg; 5%) and yielded 0.43 g (32%) of **96** as a colorless oil that on standing in air turned yellow within 24 h.

(*E*)/(*Z*)-**95**: TLC ($CHCl_3$): R_f 0.63. GC: 99%. IR (CCl_4): 3450*vw* (overtone, strained C=O), 1735*s* (br., strained C=O), 1655*m* (C=C), 690*m* (Ph). ^{1}H-NMR: see *Table 12*.

Allene **94**: TLC ($CHCl_3$): R_f 0.54. IR (CCl_4): 3470*w*/3395*w* (NH_2), 1930*w* (allene), 685*s* (Ph). ^{1}H-NMR: see *Table 8*.

Alkyne **96**: TLC ($CHCl_3$): R_f 0.47. GC: 97%. IR: 3480*w*/3380*w* (NH_2), 3280*m* (≡C–H), 2100*vw* (C≡C). ^{1}H-NMR (CCl_4/CCl_4 + TFA): 7.19/7.29 (br. *s*, 5 arom. H); 6.79/7.25 (*s*, H–C(3,5)); 4,77/4.97 (*d*, *J* = 2.4, H–C(1')); 3.32/- (*s*, NH_2); 2.40/2.71, 1.18/1.26 (*q* and *t*, *J* = 7, CH_3CH_2–C(2,6)); 2.25/2.45 (*d*, *J* = 2.4, H–C(3')).

2.38. *Rearrangement of (–)-(S)-***42** (*Scheme 25*). Compound (–)-**42** (0.60 g 2.4 mmol; $[\alpha]_{589}^{20} = -6.8$ ($CHCl_3$)) was heated in a mixture of 1.7 g of 1N H_2SO_4, 5 g of EG, and 10 ml of PrOH at 95° during 20 min. Workup and CC (hexane/CH_2Cl_2 3:1) yielded, after distillation (245°/high vacuum), 62 mg (10%) of (–)-**42** and then 10.2 mg (1.7%) of a 1:1.7 mixture of *(E)*- and *(Z)-6-[(4'-methylphenyl)methylidene]-1,5-dimethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-one* ((*E*)- and (*Z*)-**102**, resp.). Continuation of CC (hexane/CH_2Cl_2 2:1 to 1:1) yielded 0.337 g (56%) *2,6-dimethyl-4-[1'-(4''-methylphenyl)prop-2'-ynyl]aniline* (**103**). Further purification of this chemically unstable compound by CC and distillation yielded 41 mg of (+)-**103** as a colorless oil which rapidly turned yellow again.

*Recovered (–)-***42**: GC: 89%. $[\alpha]^{20}$ (0.8) = –1.5 (589), –2.3 (579), –3.1 (546), –4.1 (436); *i.e.* o.p. 25% of that of the starting aniline.

(*E*)/(*Z*)-**102**: TLC ($CHCl_3$): R_f 0.63. GC: 99.6%. $[\alpha]^{20}$ not determined. IR (CCl_4): 1735*m* (strained C=O), 1650*w* (C=C), 1535*m*, 1240*s*, 1210*m*, 1095*w*, 975*m*, 855*s*. ^{1}H-NMR: see *Table 12*. ^{13}C-NMR: see *Table 13*.

*Alkyne (+)-***103**: TLC ($CHCl_3$): R_f 0.52. GC: 99%. $[\alpha]_{589}^{20}$ (0.82) = +0.5. IR: 3450*w*/3380*m* (NH_2), 3280*s* (≡C–H). ^{1}H-NMR (CCl_4): 7.14, 6.96 (2*d*, *J* = 8, 4 arom. H in *p*-tolyl); 6.75 (*s*, H–C(3,5)); 4.38 (*d*, *J* = 2.3, H–C(1')); 3.27 (br. *s*, NH_2); 2.27 (*s*, CH_3 in *p*-tolyl); 2.24 (*d*, partly covered, H–C(3')); 2.06 (*s* CH_3–C(2,6)). ^{13}C-NMR: see *Table 11*. MS: 250 (19, $[M + 1]^+$), 249 (100, M^+), 248 (18), 235 (85), 218 (9), 158 (27). Anal. calc. for $C_{18}H_{10}N$ (249.36): C 86.70, H 7.68, N 5.62; found: C 86.91, H 7.80, N 5.32.

2.39. *Rearrangement of* **43** (*Scheme 25*). Compound **43** (0.67 g, 2.4 mmol) was heated under N_2 in a mixture of 2.4 ml of 1N H_2SO_4, 5 ml of H_2O, 4 ml of EtOH, and 3 ml of PrOH at 85–90° during 30 min. The yellow mixture was subjected to CC (hexane/CH_2Cl_2 2:1 to 1:1) to yield (in the order of increasing polarity) 30 mg (9%) of 2,4,6-trimethylaniline, 40 mg (10%) of *(E)-4-methoxycinnamaldehyde* (**105**), and 110 mg (16%) of yellow N-*[3'-(4''-Methoxyphenyl)prop-2'-enylidene]-2,4,6-trimethylaniline* (**104**).

Aldehyde **105**: GC: 96%. IR (CCl_4): 2830*m*/2800*m* (CHO), 1670*s* (conj. CHO), 965*m* ((*E*)-CH=CH). ^{1}H-NMR (CCl_4). 9.56 (*d*, *J* = 7.5, CHO); 7.44 (*d*, *J* = 8.7, H–C(2',6')); 7.28 (*d*, *J* = 15.9, H–C(3')); 6.85 (*d*, *J* = 8.7, H–C(3',5')); 6.48 (*dd*, *J* = 15.9, 7.5, H–C(2)); 3.82 (*s*, CH_3O–C(4')).

Imine **104**: GC: 97%. IR: 1630*s* (C=N), 955 ((*E*)-CH=CH–). ^{13}C-NMR ($CDCl_3$): 164.6 (*d*, C(1')); 160.7 (*s*, C(4'')); 143.6 (*s*, C(1)); 143.1 (*d*, C(3')); 132.8 (*s*, C(1'')); 129.3 (*s*, C(4)); 128.9 (*d*, C(3,5)); 128.6 (*d*, C(2'',6'')); 127.1 (*s*, C(2,6)); 126.3 (*d*, C(2')); 114.3 (*d*, C(3'',5'')); 55.3 (*q*, CH_3O); 20.7 (*q*, CH_3–C(4)); 18.3 (*q*, CH_3–C(2,6)).

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