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The 4.4′-benzidine rearrangement of 4-alkyl substituted hydrazobenzenes

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ABSTRACT

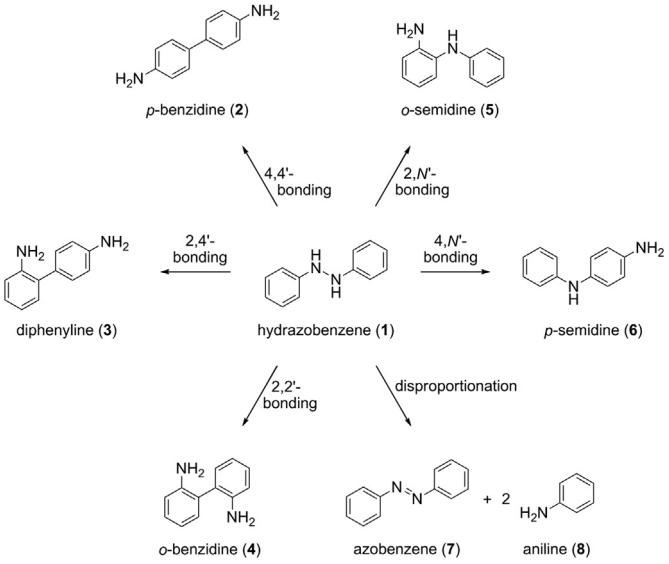
When treated with dilute inorganic acids *N*,*N*′-diarylhydrazines (hydrazobenzenes) with an alkyl substituent in the 4-position undergo [5,5]-sigmatropic rearrangement reactions to furnish 4-(4′-aminophenyl)-4-alkylcyclohexa-2,5-dienimines (*ipso*-benzidines) in moderate to excellent yields. Steric bulk of the 4-alkyl substituent in the starting material decreases the yield of the respective *ipso*-benzidine. Additional electron-donating alkyl substituents in the *ortho*- and/or *meta*-positions on both rings generally promote the reaction and consequently increase the yield of the 4.4′-benzidine rearrangement product. Described herein are our findings regarding the scope and limits of this unusual benzidine rearrangement.

1. Introduction

Acid-catalysed, intramolecular rearrangement reactions of *N*,*N*′-diarylhydrazines (hydrazobenzenes) affording diaminobiaryls (benzidines) and aminodiarylamins (semidines) are summarised under the term ‘benzidine rearrangement’. First described by August von Hofmann in 1863,[1] the eponymous reaction consists of the rearrangement of hydrazobenzene (**1**) to yield *para*-benzidine (**2**) and diphenyline (**3**) as the main products as well as *ortho*-benzidine (**4**), *ortho*-semidine (**5**) and *para*-semidine (**6**) as minor by-products (Scheme 1). Also formed are azobenzene (**7**) and 2 equivalents of aniline (**8**) due to the concurrently proceeding disproportionation reaction which is unavoidable under the usually employed reaction conditions.

Depending on the substitution pattern of the lead compound, some general rules for the benzidine rearrangement can be formulated:[2]

1. The 4.4′-rearrangement is usually the main reaction.
2. The *para*-benzidine rearrangement is eliminated for hydrazobenzenes in which the 4-position is blocked by a substituent.
3. The disproportionation is equal to the rearrangement, however, it can become the main reaction in cases where the 4.4′-rearrangement is impeded.
4. The *ortho*-semidine rearrangement prevails the *para*-semidine rearrangement.



Scheme 1. The benzidine rearrangement of hydrazobenzene.

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5. The *ortho*-benzidines are only minor by-products, however, in the case of naphthylhydrazo compounds they represent the main products.

Nevertheless, an exception of rule 2 for 4-alkyl substituted hydrazobenzenes is reported in this paper.

2. Results and discussion

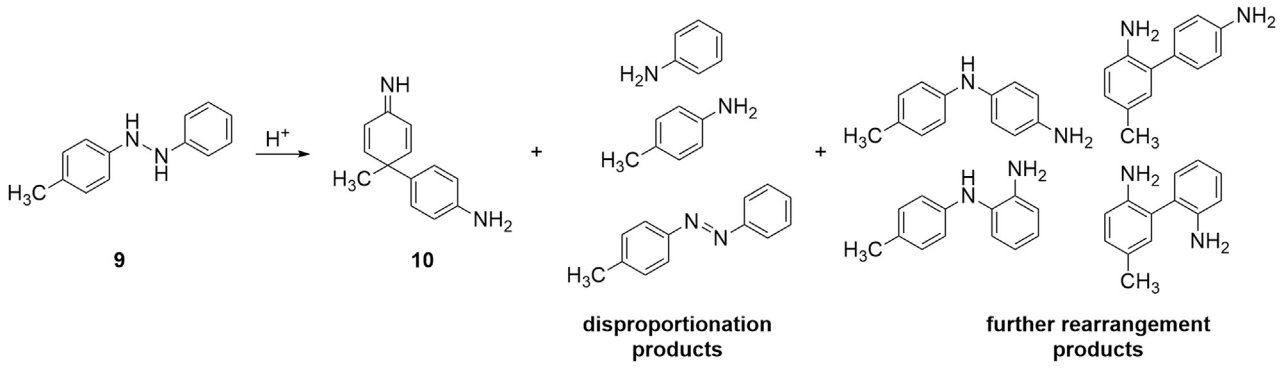
Contrary to the above stated second rule we discovered that benzidine rearrangements of 4-alkyl substituted hydrazobenzenes indeed do occur affording stabile 4-(4′-aminophenyl)-4-alkylcyclohexa-2,5-dienimines (*ipso*-benzidines) as products. In fact, such an unusual rearrangement reaction had already been reported by Badger, Drewer and Lewis in 1963[3] when they examined photochemical reactions of azo compounds in concentrated sulfuric acid. Nonetheless, Badger et al. did not realise that they had discovered a novel type of benzidine rearrangement and attributed their 'abnormal' observation to an indefinite photochemical effect. We therefore repeated the experiment of Badger and co-workers with 4-methylhydrazobenzene (**9**) in 22 N sulfuric acid, however, omitted the irradiation with a mercury lamp and obtained 4-(4′-aminophenyl)-4-methylcyclohexa-2,5-dienimine (**10**) in 28% yield accompanied by the regular rearrangement and disproportionation products (Table 1, entry 1). Encouraged by this result we then set out and investigated different reaction conditions to optimise the yield of the *ipso*-benzidine rearrangement product. The results are summarized in Table 1.

As evident from Table 1 the choice of the reaction conditions is essential for the outcome rearrangement reaction. In general, the conversion can be performed homogeneous in an organic solvent or heterogeneous in aqueous acidic medium, however, leading to different product distributions. In homogeneous methanolic solution under both, dry and wet reaction conditions, the 4.4′-benzidine rearrangement of hydrazobenzene **9** becomes only a minor side reaction that is dominated by the disproportionation of the starting material affording the *ipso*-benzidine **10** just as small by-product in 6% and 13% yield, respectively (Table 1, entries 2 and 3). On the other hand, under heterogeneous conditions in diluted aqueous hydrochloric acid, the 4.4′-benzidine rearrangement prevails the disproportionation providing the *ipso*-benzidine **10** as the major product in 46% yield (Table 1, entry 4). The combined yield of all other rearrangement products remained in all cases roughly the same in a range between 40% and 50%.

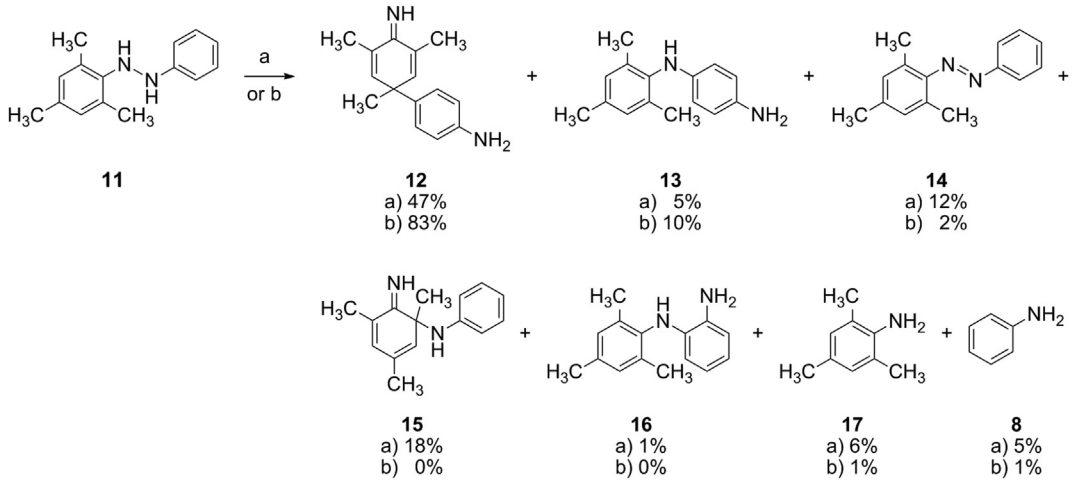
Next, we repeated the rearrangement reaction, this time however with mesitylphenylhydrazobenzene (1-mesityl-2-phenyl-hydrazine, **11**) as starting material. In the first experiment, **11** was treated under homogeneous reaction conditions with diluted sulfuric acid in a 75% methanolic solution to afford 4-(4′-aminophenyl)-2,4,6-trimethylcyclohexa-2,5-dienimine (**12**) as the major product in 47% yield accompanied by its isomer 2,4,6-trimethyl-6-(phenylamino)cyclohexa-2,4-dienimine (**15**) in 18% yield and the usual disproportionation products **8, 14** and **17** (23% combined yield). The also expected semidines **13** and **16** were only found in trace amounts of 5% and 1% yield, respectively (Scheme 2, conditions (a)). In a second experiment, we submitted **11** now to the optimised heterogeneous rearrangement conditions (Scheme 2, conditions (b)). Confirming our previous results, the dienimine **12** was now obtained in an improved yield of 83% accompanied by the *para*-semidine **13** in 10% yield. Other rearrangement products were not observed. This example once again emphasised the importance of the applied reaction conditions on the outcome of the reaction. Yet most importantly, the parallel proceeding disproportionation reaction was suppressed to the greatest possible extent producing the azobenzene **14** and anilines **8** and **17** only in trace amounts of 1% to 2%. A possible explanation for this reoccurring observation would be that in heterogeneous medium the intermolecular disproportionation reaction is less likely to occur due to the low concentration of the starting material in solution.

To verify the concept of the *ipso*-benzidine rearrangement as a general reaction type and to investigate its scope and limits, we then examined a wide range of differently substituted 4-alkyl hydrazobenzenes under the optimised heterogeneous reaction conditions. After complete conversion of the starting material, the reaction mixture was basified through the addition of aqueous sodium hydroxide solution and then exhaustively extracted with diethyl ether or dichloromethane. This easy to perform procedure allowed a quick and simple analysis of the product composition via quantitative ^{1}H NMR spectroscopy prior to the isolation and purification of the *ipso*-benzidines either via column chromatography or recrystallisation. Our results are summarized in Table 2.

Table 1
The rearrangement of 4-methylhydrazobenzene (**9**) under different reaction conditions



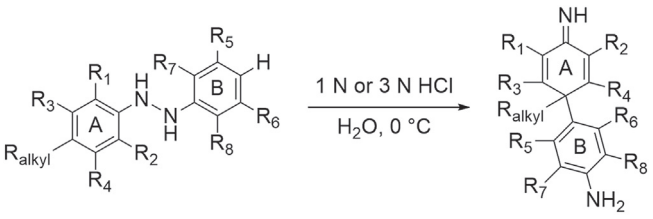
Entry	Reaction conditions	Yield of *ipso*-benzidine 10 [%]	Combined yield of the disproportionation products [%]	Combined yield of further rearrangement products [%]
1	22 N H_2SO_4	28	16	56
2	0.25 N H_2SO_4 in 100% MeOH	6	52	41
3	0.25 N H_2SO_4 in 75% MeOH	13	38	48
4	1 N HCl	46	4	50



Scheme 2. The benzidine rearrangement of 1-mesityl-2-phenylhydrazine **11** under (a) homogeneous and (b) heterogeneous reaction conditions. Reagents and conditions: a) 0.25 N H_2SO_4 in 75% MeOH, rt, 5 s; b) 1 N HCl in H_2O, rt, 0.5 h.

The simplest representative of the 4-alkyl substituted hydrazobenzenes, 4-methylhydrazobenzene (**9**), rearranged in 46% yield to the corresponding 2,5-cyclohexadienimine derivative **10** (Table 2, entry **18a**). Unsurprisingly, the yield of the rearrangement products then decreases with increasing steric hindrance of the alkyl substituent in the 4-position (Table 2, entries **18b**–**18e**). A *tert*-butyl group completely inhibits the 4.4′-rearrangement (Table

Table 2
The benzidine rearrangement of 4-alkyl substituted hydrazobenzenes.



18 19

Entry	Hydrazobenzene									Acid conc.	Time	Product	Yield[a]
18	R_{alkyl}	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	[mol/L]	[h]	19	[%]
a	Me	H	H	H	H	H	H	H	H	1.0	3.0	**a**	46
b	Et	H	H	H	H	H	H	H	H	1.0	3.0	**b**	38
c	*i*-Pr	H	H	H	H	H	H	H	H	1.0	2.0	**c**	27
d	*c*-Pr	H	H	H	H	H	H	H	H	1.0	0.33	**d**	22
e	*n*-Bu	H	H	H	H	H	H	H	H	1.0	0.8	**e**	17
f	*t*-Bu	H	H	H	H	H	H	H	H	1.0	2.0	**f**	0
g	Vinyl	H	H	H	H	H	H	H	H	1.0	0.75	**g**	0
h	Allyl	H	H	H	H	H	H	H	H	1.0	0.75	**h**	0
i	Me	H	Cl	H	H	H	H	H	H	3.0	2.0	**i**	53
j	Me	H	H	H	H	Cl	H	H	H	3.0	6.0	**j**	59
k	Me	H	H	H	H	H	H	H	Cl	3.0	3.0	**k**	53
l	Me	Me	H	H	H	H	H	H	H	1.0	3.0	**l**	61
m	Me	H	H	Me	H	H	H	H	H	1.0	3.0	**m**	55
n	Me	H	H	H	H	Me	H	H	H	1.0	3.0	**n**	53
o	Me	Me	Me	H	H	H	H	H	H	1.0	1.0	**o**	83
p	Et	Et	Et	H	H	H	H	H	H	1.0	1.5	**p**	74
q	*i*-Pr	*i*-Pr	*i*-Pr	H	H	H	H	H	H	1.0	2.0	**q**	47
r	Me	Me	*t*-Bu	H	H	H	H	H	H	1.0	18.0	**r**	86
s	Me	Me	Me	H	H	Cl	H	H	H	1.0	2.0	**s**	70
t	Me	Me	Me	H	H	H	H	H	Cl	1.0	1.0	**t**	70
u	Me	H	Me	Me	H	H	H	H	H	1.0	1.0	**u**	82
v	Me	H	H	Me	Me	H	H	H	H	1.0	0.5	**v**	72
w	Me	H	H	H	H	Me	Me	H	H	1.0	0.3	**w**	0
x	Me	H	H	H	H	H	H	Me	Me	1.0	0.1	**x**	71
y	Me	Me	Me	Me	Me	H	H	H	H	1.0	0.1	**y**	82
z	Me	H	H	Me	Me	Me	Me	H	H	1.0	0.5	**z**	0

[a] Assigned by quantitative ^{1}H NMR analysis. The yield of the other rearrangement and disproportionation by-products was not determined.

2, entry **18f**). The possible elimination of the *tert*-butyl substituent was not observed.

We then investigated the effect of additional alkyl substituents on both rings. In most cases, alkyl substituents in the *ortho*- and/or *meta*-positions promoted the reaction and increased the yields of the *ipso*-benzidines. Exceptions of this general observation occurred when the 3′- and 5′-positions in the hydrazobenzene precursor were both substituted with methyl groups (B-Ring; R_5, R_6=Me). In these cases, strong steric interactions inhibited the 4.4′-rearrangement (Fig. 1) so that the respective *ipso*-benzidines **19w** and **19z** did not form. On the other hand, in case of just one methyl substituent in *ortho*-position to the hydrazo group the rearrangement proceeded as usual giving the dienimine **19n** in 53% yield.

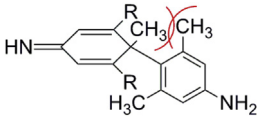


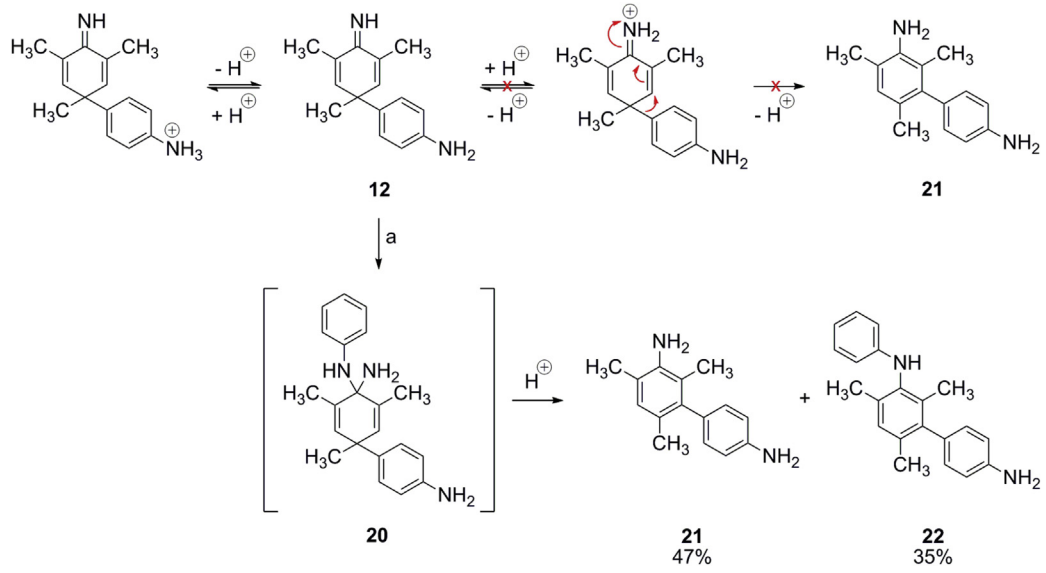
Fig. 1. Steric hindrance in dienimines **19w** (R=H) and **19z** ($R=CH_3$).

Increasing steric bulk of the *ortho*-alkyl substituents also had a decreasing effect on the yields (see entries **18o**–**18q**). The yield dropped from 83% for the trimethyl-substituted derivative **12** (entry **18o**) via 74% for the triethyl-substituted congener **19p** to 47% for the tri-*iso*-propyl substituted dienimine **19q**. Deactivating chloro-substituents required a higher acid concentration (3 mol/L) for the rearrangement to proceed (entries **18i**–**18k**). Nevertheless, this effect could be compensated via additional electron-donating methyl substituents (entries **18s**, **18t**). The 2-*tert*-butyl derivative **18r** reacted only very slowly due to low wettability. The corresponding dienimine **19r**, though, is a stabile compound that was obtained in 86% yield despite the long reaction time of 18 h.

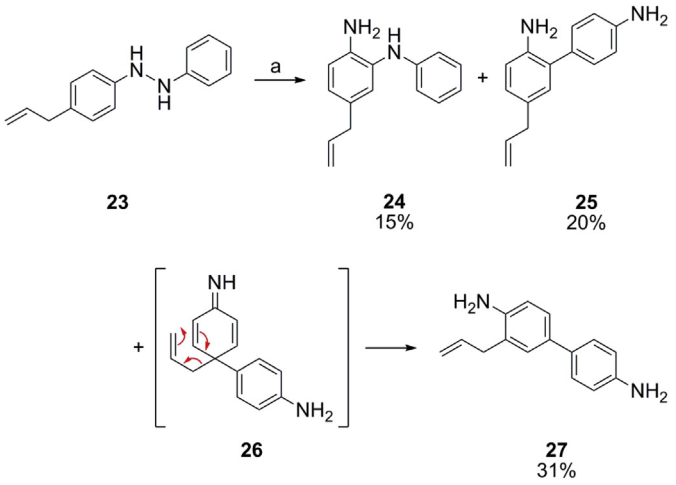
The obtained *ipso*-benzidines exhibit an extraordinary stability towards acid hydrolysis of their imino functionality and, more importantly, display no tendency to re-aromatise the cyclohexa-2,5-dienimine system neither via the elimination of the 4-alkyl substituent nor in a dienimine-aniline rearrangement even under strong acid conditions (see Scheme 3). At first, these properties may appear rather surprising, yet, they can be rationalised by a simple explanation. The protonation of the *ipso*-benzidines in acidic medium occurs at the more basic nitrogen of the 4-aminophenyl moiety which is the wrong position for subsequent rearrangement reactions. This protects the molecule from further electrophilic attack. On the other hand, when treated with aniline under mild acid catalysis (pH 3.8), these compounds indeed do slowly undergo a dienimine-aniline rearrangement yielding *meta*-benzidines. As shown in Scheme 3 the reaction proceeds via the initial addition of aniline to the imino group affording the aminal **20**. The now stronger basic aminal group is then protonated resulting in the migration of the 4-aminophenyl moiety to the *meta*-position and the elimination of one amino group to yield the two *meta*-benzidines **21** and **22**. Hence, the reaction sequence of a 4.4′-benzidine rearrangement and a subsequent dienimine-aniline rearrangement simulates the *meta*-benzidine rearrangement of 4-alkyl substituted hydrazobenzenes.

4-vinyl (**28**) and 4-allyl substituted hydrazobenzenes (**23**) represent special cases in the 4.4′-benzidine rearrangement (Table 2, entries **18g** and **18h**). In the event of 4-allylhydrazobenzene, the intermediate 4-allyldienimine **26** is an unstable compound that, although present in the crude reaction mixture as observed by ^{1}H NMR analysis, could not be isolated. Driven by the potential to stabilise the dienimine system via re-aromatisation of the A-ring, the allyl substituent migrated in a 3.3′-rearrangement to afford the allylbenzidine **27** as the major product in 31% yield (Scheme 4). The *ortho*-semidine **24** as well as the diphenyline **25** were also isolated in 15% and 20% yield, respectively.

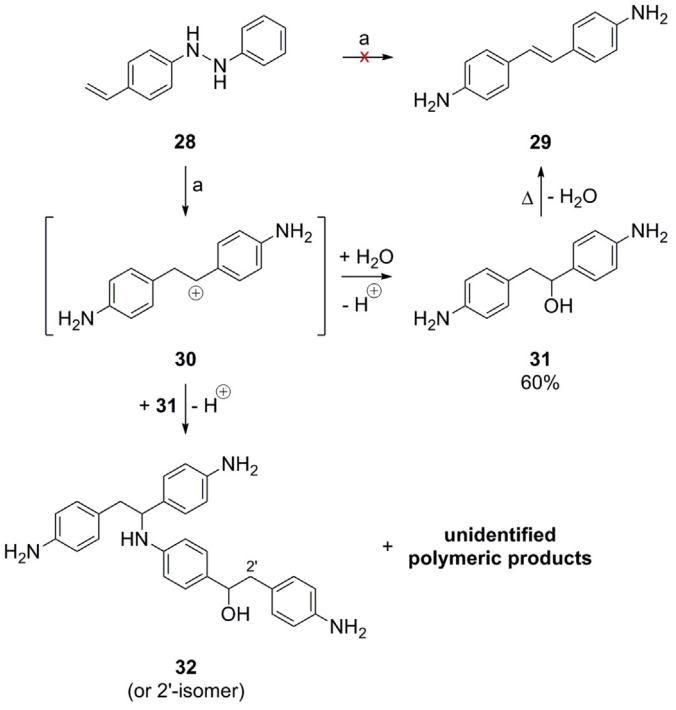
4-vinylhydrazobenzene (**28**) did not react according to the general scheme of the *ipso*-benzidine rearrangement either. Instead, the vinyl substituent was incorporated into the rearrangement reaction initially leading to the intermediate carbenium ion **30** (Scheme 5). Addition of water to **30** then provided 1,2-bis(4-aminophenyl)ethan-1-ol (**31**) in 60% yield as the main product. Furthermore, a number of insoluble polymeric products were also isolated from the reaction mixture. The structures of these compounds could not be elucidated but we assume they arose from the polymerisation of carbenium ion **30**. Clues to the possible composition of these polymers could be deduced from the dimer **32** which was obtained as a side product in trace amounts. Nevertheless, the originally expected product of a formal vinylogous benzidine rearrangement, 4,4′-diaminostilbene (**29**), was not observed. The stilbene **29** was only obtained via the elimination of



Scheme 3. The aniline-promoted dienimine-aniline rearrangement of *ipso*-benzidines. Reagents and conditions: (a) aniline, 6 N HCl, pH 3.8, rt, 12 d.



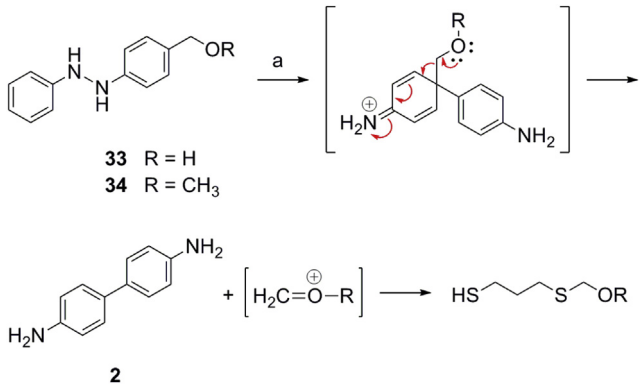
Scheme 4. The benzidine rearrangement of 4-allylhydrazobenzene (**23**). Reagents and conditions: (a) 1 N HCl in H_2O, 0 °C, 45 min.



Scheme 5. The benzidine rearrangement of 4-vinylhydrazobenzene (**28**). Reagents and conditions: (a) 1 N HCl in H_2O, 0 °C, 45 min.

water when pure alcohol **31** was heated above its melting point of 115 °C.

4-oxymethyl and 4-acetyl substituents further limit the synthetic applications of the *ipso*-benzidine rearrangement. When we employed 4-hydroxymethyl- (**33**) and 4-methoxymethylhydrazobenzene (**34**) in the 4.4′-rearrangement reaction we found that these compounds also do not produce stable *ipso*-benzidines. Instead, the dieniminium intermediates re-aromatise via the elimination of the 4-oxymethyl substituent to give benzidine (**2**) as depicted in Scheme 6. The addition of 1,3-propanedithiol prevented the polymerisation reaction of formaldehyde with the amine rearrangement products by scavenging the intermediate occurring oxonium cation. **2** was subsequently separated from the crude reaction mixture as its insoluble diacetyl derivative in 47% and 41% yield, respectively.

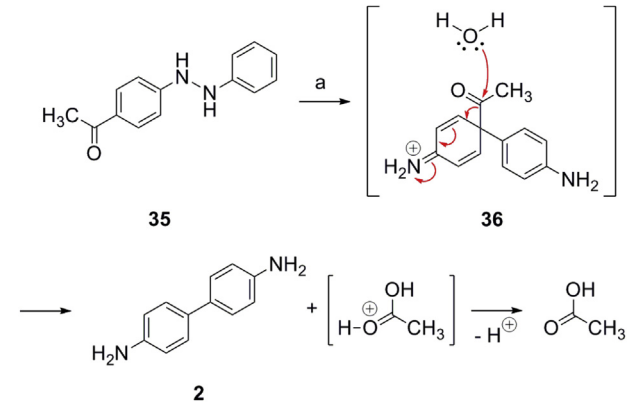


Scheme 6. Elimination of 4-hydroxymethyl and 4-methoxymethyl substituents during the benzidine rearrangement. Reagents and conditions: (a) 1 N HCl in H_2O, 1,3-propanedithiol rt, 45 min.

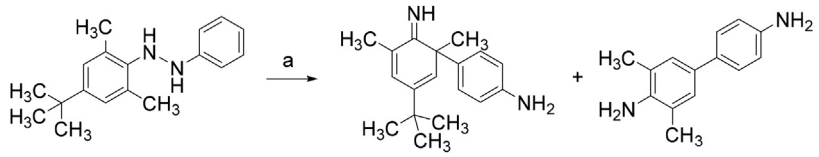
In the rearrangement reaction of 4-acetylhydrazobenzene (**35**) we observed a similar loss of the 4-substituent. In this case the dieniminium intermediate **36** stabilised through the elimination of acetic acid via the initial addition of water to give once again benzidine (**2**) as the major product (Scheme 7). As in the previous example, **2** was precipitated from the crude reaction mixture as its insoluble bisacetamide in 53% yield. The usual disproportionation products and further rearrangement compounds were obtained in 12% and 35% yield, respectively (not shown in Scheme 7).

As seen from entry **18f** in Table 2, 4-*tert*-butylhydrazobenzene does not undergo the 4.4′-rearrangement due to the steric hindrance of the bulky *tert*-butyl substituent. Yet, when we submitted 4-*tert*-butyl-2,6-dimethylhydrazobenzene (**37**) to our heterogeneous reaction conditions (Scheme 8), we obtained the *ipso*-diphenyline **38** and the benzidine **39** in 17% and 18% yield besides and the anticipated usual disproportionation products (not shown). In this case the 4.4′-arrangement with subsequent elimination of the *tert*-butyl substituent competed with the 2.4′-rearrangement of **37** yielding the observed products **38** and **39**.

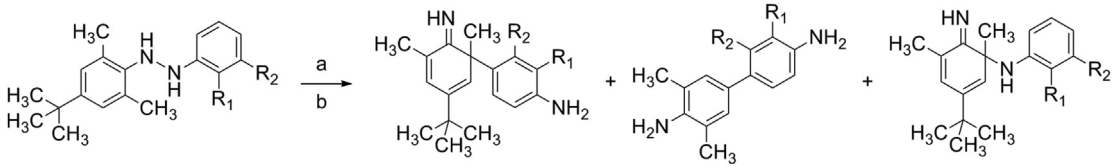
Thereupon, the rearrangement of two further 4-*tert*-butyl-2,6-dimethylhydrazobenzenes with chloro-substituents on the B-ring in the *ortho*- and *meta*-position were also examined (Scheme 9). Both compounds afforded the respective 2.4′-rearrangement products, *ipso*-diphenylines **41a** and **41b**, in 10% and 14% yield. Interestingly, in the case of 1-(4-*tert*-butyl-2,6-dimethylphenyl)-2-(3-chlorophenyl)hydrazine (**40b**) the usually also formed elimination product, benzidine **42b**, was not observed, possibly due to steric hindrance of the chloro substituent in the *meta*-position. Instead, a trace amount of the unusual *ortho*-semidine **43b** was also obtained.



Scheme 7. The benzidine rearrangement of 4-acetylhydrazobenzene under heterogeneous reaction conditions. Reagents and conditions: (a) 3 N HCl in H_2O, rt, 6 h.



Scheme 8. The *ipso*-diphenyline rearrangement of 4-*tert*-butyl-2,6-dimethylhydrazobenzene under heterogeneous reaction conditions. Reagents and conditions: (a) 1 N HCl in H_2O, rt, 45 min.



Scheme 9. The *ipso*-diphenyline rearrangement of chlorinated 4-*tert*-butyl-2,6-dimethylhydrazobenzenes under heterogeneous reaction conditions. Reagents and conditions: (a) 2 N HCl in H_2O, rt, 2 h; (b) 1 N HCl in H_2O, rt, 1.5 h.

3. Conclusions

Contrary to previous beliefs the 4.4′-rearrangement of 4-alkyl substituted hydrazobenzenes is possible and represents a novel and general type of rearrangement reaction further expanding the classic benzidine rearrangement. This new reaction gives access to 4-(4′-aminophenyl)-4-alkylcyclohexa-2,5-dienimines ('*ipso*-benzidines'), a widely unknown class of compounds.[4] Due to their resistance towards hydrolysis and the deficiency to re-aromatise via a dienimine-aniline rearrangement or the elimination of the 4-alkyl substituent, these compounds display a remarkable stability. Depending on the substitution pattern of the initial hydrazobenzene these *ipso*-benzidines can be isolated in moderate to excellent yields. Hydrazobenzenes with bulky substituents in the 4-position, however, undergo 2.4′- rather than 4.4′-rearrangements due to the sterically hindrance yielding stable *ipso*-diphenylines. Exceptions of this general reaction scheme include 4-oxymethyl and 4-acetyl substituted hydrazobenzenes which do not yield stable *ipso*-benzidines. Incited by the possibility to re-aromatise the intermediate cyclohexa-2,5-dienimine system these compounds eliminate the 4-substituent to give benzidine (**2**) as the major product. Applications of this new rearrangement reaction in the synthesis of more complex molecules will be reported in a future publication.

4. Experimental

NMR spectra were recorded on Varian EM 360, Bruker HX 90, WH 90 (^{1}H) as well as Bruker WP 200 and WH 270 (^{1}H and ^{13}C) spectrometers. IR spectra were recorded with a Perkin–Elmer 580 IR spectrometer in $CHCl_3$ and CCl_4 solutions or as KBr pellet. Mass spectra (EI) were obtained with Varian CH 5 and Finnigan MAT 312 mass spectrometers operating at an ionisation potential of 70 eV. Quoted are the relative masses and their intensity in relation to the base peak [%]. Elemental analyses were performed with the Heraeus elemental analyser CHN-Rapid. Melting points were obtained using a Büchi 510 capillary melting point apparatus according to Tottoli and are uncorrected. Column chromatography was carried out on silica gel from Machery-Nagel (50–200 μm) using mixtures of petrol ether (boiling range 40–65 °C), diethyl ether and methanol. Analytical thin-layer chromatography was performed on Machery-Nagel and Riedel-de Haen aluminium TLC plates precoated with silica gel and fluorescence indicator F254. For analytical gas chromatography a Varian Aerograph 1400 was employed.

4.1. General methods

4.1.1. Syntheses of ipso-benzidines (4-(4′-aminophenyl)-4-alkylcyclohexa-2,5-dienimines) and ipso-diphenylines.

General procedure for benzidine rearrangements under heterogeneous reaction conditions in dilute aqueous hydrochloric acid: The respective hydrazobenzene (200 mg) was suspended in aqueous hydrochloric acid (20 mL) and stirred under ice-cooling at 0–5 °C under N_2 atmosphere until its full conversion (see Table 2). The reaction mixture was then mixed with diethyl ether or dichloromethane (20–50 mL) and neutralised via the addition of 2 N aqueous sodium hydroxide solution until strong basic pH. The phases were subsequently separated, and the aqueous phase extracted until quantitative recovery of all products (TLC control). The combined extracts were dried over Na_2SO_4 or $MgSO_4$, filtered and concentrated under reduced pressure. Examination of the obtained residue (95–100% recovery) by ^{1}H NMR spectroscopy afforded the composition of the product mixture. The substituents at the dienimine ring of the *ipso*-benzidines (ring A) possess characteristic chemical shifts compared to the substituents at the aromatic rings of all other reaction products allowing the quantification via ^{1}H NMR spectroscopy. The following purification by column chromatography or recrystallisation yielded the pure *ipso*-benzidines.

The rearrangement products are relative nonpolar compounds generally enabling a separation by column chromatography with diethyl ether/petrol ether mixtures (e.g., 1:9 or 1:1). The polarity increases in the following order: diazene (least polar) via hydrazobenzene, *ortho*-semidine, aniline, *para*-semidine, *ipso*-semidines, diphenyline, *para*-benzidine to *ipso*-benzidine (most polar) (see diagram in Supplementary data). The *ipso*-benzidines (and *ipso*-diphenylines) are comparatively polar compounds that require ether/methanol mixtures (e.g., 4:1) for complete elution. A quick and easy elution of the *ipso*-benzidine with ether can be achieved by deactivating the silica gel with up to 30 wt % water prior to the chromatography.

*4.1.1.1. 4-(4-Aminophenyl)-4-methylcyclohexa-2,5-dienimine (**10**/**19a**).* 46%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.54 (s, CH_3), 3.7 (s, NH_2), 6.19 (d, J=11 Hz, 2×CH), 6.34 (d, J=11 Hz, 2×CH), 6.62 (d, J=8 Hz, 2×Ar−H), 6.8 (br s, NH) 7.07 (d, J=8 Hz, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3380 (br), 3250 (br), 3000, 2970, 2930, 2870, 1665, 1620, 1575, 1510, 1455, 1430, 1340, 1280, 1185, 1165, 1085, 890, 825; MS (EI, 70 eV) m/z (%) 198 (98, M^+), 197 (80), 183 (100), 182 (23), 171 (23), 156 (34); calcd for $C_{13}H_{14}N_2$: C 78.75, H 7.12, N 14.13; found: C 78.70, H 7.01, N 14.03.

*4.1.1.2. 4-(4-Aminophenyl)-4-ethylcyclohexa-2,5-dienimine (**19b**).* 38%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.85 (t, J=7.5 Hz, CH_3), 2.00 (q, J=7.5 Hz, CH_2), 3.6 (br s, NH_2), 6.27 (d, J=10 Hz, 2×CH), 6.40 (d, J=10 Hz, 2×CH), 6.67 (d, J=8.5 Hz, 2×ArH), 7.12 (d, J=8.5 Hz, 2×ArH), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3460 (br), 3400 (br), 3250 (br), 3020, 3000, 2960, 2940, 2880, 1660, 1620, 1570, 1510, 1430, 1280, 1190, 1160, 1090, 905, 895, 825; MS (EI, 70 eV) m/z (%) 212 (50, M^+), 211 (12), 197 (29), 184 (27), 183 (100), 156 (24), 140 (12), 77 (24); calcd for $C_{14}H_{16}N_2$: C 79.21, H 7.60, N 13.20; found: C 79.16, H 7.58, N 13.11.

*4.1.1.3. 4-(4-Aminophenyl)-4-isopropylcyclohexa-2,5-dienimine (**19c**).* 27%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.87 (d, J=7 Hz, 2×CH_3), 2.40 (sept, J=7 Hz, CH), 4.0 (br s, NH_2), 6.40 (br s, 4×CH), 6.62 (d, J=9 Hz, 2×Ar−H), 7.05 (d, J=9 Hz, 2×Ar−H), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3250 (br), 3020, 3000, 2960, 2880, 1660, 1620, 1600 (w), 1570, 1510, 1430, 1380, 1280, 1190, 1160, 890, 820; MS (EI, 70 eV) m/z (%) 226 (16, M^+), 211 (11), 184 (36), 183 (100), 168 (22), 167 (19), 156 (20), 149 (15); calcd for $C_{15}H_{18}N_2$: C, 79.61, H, 8.02, N, 12.38; found: C, 79.69, H, 8.07, N, 12.34.

*4.1.1.4. 4-(4-Aminophenyl)-4-cyclopropylcyclohexa-2,5-dienimine (**19d**).* 22%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.2−0.7 (m, 2×CH_2), 1.1−1.5 (m, CH), 3.2−5.0 (br s, NH, NH_2), 6.14 (d, J=11 Hz, 2×CH), 6.30 (d, J=11 Hz, 2×CH), 6.68 (d, J=9 Hz, 2×Ar−H), 7.24 (d, J=9 Hz, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}]:3400 (br), 3250 (br), 3000, 2960, 1670, 1625, 1570, 1520, 1515, 1430, 1340, 1280, 1185, 1165, 1025, 900, 830, 660; MS (EI, 70 eV) m/z (%) 224 (100, M^+), 222 (17), 191 (20), 190 (26), 181 (91), 168 (18), 159 (31), 133 (54), 93 (24), 77 (30), 63 (20); calcd for $C_{15}H_{16}N_2$: C 80.32, H 7.19, N 12.49; found: C 80.24, H 7.17, N 12.38.

*4.1.1.5. 4-(4-Aminophenyl)-4-butylcyclohexa-2,5-dienimine (**19e**).* 17%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.88 (t, J=7 Hz, CH_3), 1.28 (m, 2×CH_2), 1.94 (m, CH_2), 3.7 (br s, NH_2), 6.31 (s, 4×CH), 6.61 (d, J=9 Hz, 2×Ar−H), 7.08 (d, J=9 Hz, 2×Ar−H), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3200 (br), 3020, 3000, 2960, 2930, 2860, 1660, 1620, 1570, 1510, 1475, 1440, 1340, 1280, 1185, 1160, 1100, 890, 825; MS (EI, 70 eV) m/z (%) 240 (22, M^+), 197 (16), 184 (31), 183 (100), 156 (18), 85 (46), 83 (61); calcd for $C_{16}H_{20}N_2$: C 79.96, H 8.39, N 11.66; found: C 79.79, H 8.25, N 11.51.

*4.1.1.6. 4-(4-Aminophenyl)-2-chloro-4-methylcyclohexa-2,5-dienimine (**19i**).* 53%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.60 (s, CH_3), 3.72 (br s, NH_2), 6.35 (dd, J_1=9.5 Hz, J_2=2 Hz, CH), 6.49 (d, J=9.5 Hz, CH), 6.56 (d, J=2 Hz, CH), 6.65 (d, J=8 Hz, 2×Ar−H), 7.06 (d, J=8 Hz, 2×Ar−H), 9.7 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3260 (br), 3030, 3000, 2970, 2940, 2870, 2840, 1650, 1620, 1610, 1580, 1510, 1410, 1375, 1280, 1185, 1010, 980, 900, 820; MS (EI, 70 eV) m/z (%) 234 (8, M^+), 233 (10), 232 (25), 231 (19), 219 (15), 217 (47), 197 (100), 196 (38), 195 (23), 192 (6), 190 (19), 182 (71), 181 (30), 180 (27), 170 (17), 154 (26); calcd for $C_{13}H_{13}ClN_2$: C 67.09, H 5.63, N 12.04; found: C 66.96, H 5.57, N 12.04.

*4.1.1.7. 4-(4-Amino-2-chlorophenyl)-4-methylcyclohexa-2,5-dienimine (**19j**).* 59%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.61 (s, CH_3), 3.4 (s, NH_2), 6.24 (d, J=11 Hz, 2×CH), 6.40 (d, J=11 Hz, 2×CH), 6.53 (dd, J_1=8 Hz, J_2=2 Hz, Ar−H), 6.65 (d, J=2 Hz, Ar−H), 7.1 (br s, NH) 7.16 (d, J=8 Hz, Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3500 (br), 3400 (br), 3260 (br), 3040, 2980, 2930, 2870, 1655, 1620, 1605, 1570, 1490, 1460, 1430, 1280, 1250, 1160, 1085, 1050, 890, 850, 825; MS (EI, 70 eV) m/z (%) 234 (17, M^+), 233 (16), 232 (47), 231 (17), 219 (13), 217 (38), 207 (11), 205 (31), 197 (100), 196 (52), 195 (20), 192 (13), 190 (29), 182 (48), 170 (17), 154 (21), 140 (12), 127 (26); calcd for $C_{13}H_{13}ClN_2$: C 67.09, H 5.63, N 12.04; found: C 67.00, H 5.65, N 12.03.

*4.1.1.8. 4-(4-Amino-3-chlorophenyl)-4-methylcyclohexa-2,5-dienimine (**19k**).* 53%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.52 (s, CH_3), 4.1 (br s, NH_2), 6.26 (s, 4×CH), 6.68 (d, J=8 Hz, Ar−H), 6.96 (dd, J_1=8 Hz, J_2=2 Hz, Ar−H), 7.15 (d, J=2 Hz, ArH), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3500 (br), 3400 (br), 3200 (br), 3030, 3000, 2970, 2880, 1660, 1620, 1600, 1570, 1500, 1460, 1430, 1400, 1300, 1160, 1090, 890, 840, 820; MS (EI, 70 eV) m/z (%) 234 (23, M^+), 233 (35), 232 (68), 231 (70), 219 (37), 218 (29), 217 (100), 207 (18), 205 (43), 197 (39), 196 (37), 192 (23), 190 (56), 182 (61), 181 (35), 154 (41), 127 (45); calcd for $C_{13}H_{13}ClN_2$: C 67.09, H 5.63, N 12.04; found: C 66.81, H 5.71, N 11.99.

*4.1.1.9. 4-(4-Aminophenyl)-2,4-dimethylcyclohexa-2,5-dienimine (**19l**).* 61%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.52 (s, CH_3), 1.95 (d, J=1 Hz, CH_3), 3.8 (br s, NH_2), 6.17 (dt, J_1=2 Hz, J_2=1 Hz, CH), 6.18 (d, J=10 Hz, CH), 6.33 (dd, J_1=10 Hz, J_2=2 Hz, CH), 6.59 (d, J=9 Hz, 2×Ar−H), 7.05 (d, J=9 Hz, 2 Ar−H), 7.2 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3250 (br), 3020, 3000, 2970, 2930, 2870, 1660, 1620, 1570, 1510, 1455, 1430, 1375, 1305, 1280, 1185, 900, 880, 830; MS (EI, 70 eV) m/z (%) 212 (44, M^+), 211 (47), 198 (20), 197 (100), 196 (30), 195 (18), 185 (11), 182 (72), 181 (19), 180 (27), 170 (24), 168 (14), 152 (15), 143 (21); calcd for $C_{14}H_{16}N_2$: C 79.20, H 7.60, N 13.20; found: C 79.10, H 7.60, N 13.14.

*4.1.1.10. 4-(4-Aminophenyl)-3,4-dimethylcyclohexa-2,5-dienimine (**19m**).* 55%; colourless, crystalline solid; mp 116−120 °C (ether); ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.52 (s, CH_3), 1.62 (d, J=1 Hz, CH_3), 3.7 (br s, NH_2), 6.11 (m, CH), 6.18 (s, 2×CH), 6.59 (d, J=8 Hz, 2×ArH), 6.77 (d, J=8 Hz, 2×ArH), 8.2 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3250 (br), 3040, 3000, 2970, 2940, 2880, 1660, 1620, 1570, 1510, 1430, 1375, 1280, 1180, 1170, 1140, 1010, 900, 870, 825; MS (EI, 70 eV) m/z (%) 212 (70, M^+), 211 (78), 197 (100), 196 (34), 195 (19), 185 (34), 182 (30), 181 (15), 180 (18), 170 (56), 169 (15), 168 (17), 167 (13); calcd for $C_{14}H_{16}N_2$: C 79.20, H 7.60, N 13.20; found: C 79.01, H 7.55, N 13.12.

*4.1.1.11. 4-(4-Amino-2-methylphenyl)-4-methylcyclohexa-2,5-dienimine (**19n**).* 53%; colourless, vitreous solid; ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.54 (s, CH_3), 2.10 (s, CH_3), 3.4 (br s, NH_2), 6.27 (s, 4×CH), 6.40 (d, J=2.5 Hz, Ar−H), 6.52 (dd, J_1=8 Hz, J_2=2.5 Hz, Ar−H) 7.0 (br s, NH), 7.15 (d, J=8 Hz, Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3250 (br), 3040, 3000, 2970, 2930, 2880, 1650, 1620, 1600 (w), 1570, 1500, 1460, 1430, 1265, 1080, 1020, 890, 860, 830; MS (EI, 70 eV) m/z (%) 212 (100, M^+), 211 (26), 197 (75), 196 (24), 195 (20), 182 (23), 181 (19), 180 (24), 170 (22), 143 (31); calcd for $C_{14}H_{16}N_2$: C 79.20, H 7.60, N 13.20; found: C 79.02, H 7.53, N 13.08.

*4.1.1.12. 4-(4-Aminophenyl)-2,4,6-trimethylcyclohexa-2,5-dienimine (**12**/**19o**).* 83%; colourless, crystalline solid; mp 132−133 °C (ethyl acetate/petrol ether); ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.50 (s, CH_3), 1.98 (s, 2×CH_3), 3.6 (br s, NH_2), 6.19 (s, 2×CH), 6.60 (d, J=8 Hz, 2×Ar−H), 7.05 (d, J=8 Hz, 2×Ar−H), 8.3 (br s, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm] 167.90 (s), 145.31 (s), 144.51 (d),

132.71 (s), 128.96 (s), 127.17 (d), 115.00 (d), 42.95 (s), 25.15 (q), 17.80 (q); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3380 (br), 3200 (br), 3000, 2970, 2870, 1670, 1620, 1560, 1510, 1450, 1430, 1370, 1280, 1180, 1165, 1050, 1010, 905, 890, 845, 825; UV (MeOH) λ_{max} (ε) 245 nm (24,500); MS (EI, 70 eV) *m/z* (%) 226 (100, M^+), 225 (65), 212 (15), 211 (71), 210 (18), 209 (8), 196 (27), 195 (18), 194 (8), 184 (13), 180 (7), 118 (27), 93 (10), 91 (6); calcd for $C_{15}H_{18}N_2$: C 79.60, H 8.02, N 12.38; found: C 79.86, H 8.13, N 12.38.

*4.1.1.13. 4-(4-Aminophenyl)-2,4,6-triethylcyclohexa-2,5-dienimine (**19p**).* 74%; colourless, crystalline solid; mp 110–111 °C (ether/pentane); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.79 (t, *J*=7 Hz, CH_3), 1.19 (t, *J*=7 Hz, 2×CH_3), 1.96 (q, *J*=7 Hz, CH_2), 2.42 (q, *J*=7 Hz, 2×CH_2), 3.7 (br s, NH_2), 6.06 (s, 2×CH), 6.62 (d, *J*=8 Hz, 2×ArH) 7.06 (d, *J*=8 Hz, 2×ArH), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3300 (br), 3000, 2970, 2940, 2880, 1665, 1625, 1565, 1510, 1455, 1430, 1280, 1190, 1150, 900, 870, 825; MS (EI, 70 eV) *m/z* (%) 268 (34, M^+), 267 (7), 253 (9), 240 (31), 239 (100), 211 (16), 210 (51), 195 (14); calcd for $C_{18}H_{24}N_2$: C 80.55, H 9.01, N 10.44; found: C 80.42, H 9.12, N 10.55.

*4.1.1.14. 4-(4-Aminophenyl)-2,4,6-triisopropylcyclohexa-2,5-dienimine (**19q**).* 47%; colourless, vitreous solid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 0.83 (d, *J*=7 Hz, 2×CH_3), 1.13 (d, *J*=7 Hz, 2×CH_3), 1.15 (d, *J*=7 Hz, 2×CH_3), 2.15 (sept, *J*=7 Hz, CH), 3.11 (sept, *J*=7 Hz, 2×CH), 5.0 (br s, NH_2), 6.22 (s, 2×CH), 6.59 (d, *J*=8 Hz, 2×Ar–H) 7.04 (d, *J*=8 Hz, 2×Ar–H), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3380 (br), 3200 (br), 2960, 2930, 2870, 1670, 1620, 1560, 1510, 1460, 1420, 1385, 1360, 1275, 1190, 1130, 900, 870, 830; MS (EI, 70 eV) *m/z* (%) 310 (17, M^+), 295 (5), 268 (48), 267 (100), 253 (20), 225 (12), 224 (11), 209 (7), 183 (8); calcd for $C_{21}H_{30}N_2$: C 81.24, H 9.74, N 9.02; found: C 81.20, H 9.64, N 9.05.

*4.1.1.15. 4-(4-Aminophenyl)-2-tert-butyl-4,6-dimethylcyclohexa-2,5-dienimine (**19r**).* 86%; colourless, crystalline solid; mp 122 °C (ether/petrol ether); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.33 (s, 3×CH_3), 1.48 (s, CH_3), 1.89 (d, *J*=1 Hz, CH_3), 4.7 (br s, NH_2), 6.08 (m, CH), 6.21 (d, *J*=2.5 Hz, CH) 6.57 (d, *J*=8 Hz, 2×Ar–H), 7.01 (d, *J*=8 Hz, 2×Ar–H), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3460 (br), 3400 (br), 3280 (br), 3050, 2980, 2930, 2880, 1670, 1625, 1565, 1515, 1455, 1420, 1375, 1360, 1290, 1190, 1140, 1120, 1050, 1010, 900, 835; MS (EI, 70 eV) *m/z* (%) 268 (25, M^+), 267 (13), 253 (53), 213 (100), 212 (33), 197 (18); calcd for $C_{18}H_{24}N_2$: C 80.55, H 9.01, N 10.44; found: C 80.54, H 8.93, N 10.44.

*4.1.1.16. 4-(4-Amino-2-chlorophenyl)-2,4,6-trimethylcyclohexa-2,5-dienimine (**19s**).* 70%; colourless, vitreous solid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.55 (s, CH_3), 1.99 (s, 2×CH_3), 3.7 (br s, NH_2), 6.24 (s, 2×CH), 6.50 (dd, J_1=8 Hz, J_2=2.5 Hz, Ar–H), 6.64 (d, *J*=2.5 Hz, Ar–H), 7.17 (d, *J*=8 Hz, Ar–H), 7.6 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3500 (br), 3400 (br), 3250 (br), 3020, 2980, 2920, 2870, 1670, 1620, 1600, 1560, 1490, 1450, 1430, 1370, 1280, 1170, 1050, 1025, 890, 850; MS (EI, 70 eV) *m/z* (%) 262 (12, M^+), 260 (33), 225 (16), 210 (27), 209 (17), 197 (9), 195 (28), 180 (15), 167 (25), 135 (33), 134 (39), 120 (77), 105 (41), 91 (100). calcd for $C_{15}H_{17}ClN_2$: C 69.09, H 6.57, N 10.74; found: C 68.81, H 6.73, N 10.63.

*4.1.1.17. 4-(4-Amino-3-chlorophenyl)-2,4,6-trimethylcyclohexa-2,5-dienimine (**19t**).* 70%; colourless, vitreous solid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.49 (s, CH_3), 1.99 (s, 2×CH_3), 4.0 (br s, NH_2), 6.16 (s, 2×CH), 6.66 (d, *J*=8 Hz, Ar–H), 6.94 (dd, J_1=8 Hz, J_2=2 Hz, Ar–H), 7.12 (d, *J*=2 Hz, Ar–H), 8.0 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3480 (br), 3400 (br), 3280 (br), 2970, 2920, 2870, 1670, 1620, 1595, 1565, 1500, 1450, 1430, 1375, 1300, 1285, 1180, 1165, 1050, 895, 845, 815; MS (EI, 70 eV) *m/z* (%) 262 (35, M^+), 261 (34), 260 (100), 259 (50), 247 (17), 246 (13), 245 (50), 244 (11), 210 (25), 209 (20), 195 (11), 152 (12); calcd for $C_{15}H_{17}ClN_2$: C 69.09, H 6.57, N 10.74; found: C 69.01, H 6.61, N 10.75.

*4.1.1.18. 4-(4-Aminophenyl)-2,4,5-trimethylcyclohexa-2,5-dienimine (**19u**).* 82%; colourless, crystalline solid, mp 138 °C (ether); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.51 (s, CH_3), 1.62 (d, *J*=1.5 Hz, 5-CH_3), 1.93 (d, *J*=1.5 Hz, 2-CH_3), 3.6 (br s, NH_2), 6.06 (q, *J*=1.5 Hz, 6-H), 6.13 (q, *J*=1.5 Hz, 3-H), 6.60 (d, *J*=9 Hz, 2×ArH), 6.98 (d, *J*=9 Hz, 2×ArH), 7.3 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3420 (br), 3380 (br), 3200 (br), 2970, 2920, 2870, 1670, 1620, 1570, 1510, 1450, 1430, 1375, 1310, 1280, 1180, 1135, 1010, 900, 890, 840, 825; MS (EI, 70 eV) *m/z* (%) 226 (100, M^+), 225 (75), 212 (14), 211 (76), 210 (20), 199 (15), 196 (28), 195 (16), 184 (20), 118 (25); calcd for $C_{15}H_{18}N_2$: C 79.60, H 8.02, N 12.38; found: C 79.41, H 8.14, N 12.22.

*4.1.1.19. 4-(4-Aminophenyl)-3,4,5-trimethylcyclohexa-2,5-dienimine (**19v**).* 72%; colourless, crystalline solid; mp 126–127 °C (ether); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.53 (s, CH_3), 1.61 (s, 2×CH_3), 3.7 (br s, NH_2), 6.11 (s, 2×CH), 6.60 (d, *J*=8 Hz, 2×Ar–H), 6.95 (d, *J*=8 Hz, 2×Ar–H), 7.4 (s, NH, broad); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3460 (br), 3380 (br), 3200 (br), 2980, 2950, 2920, 2880, 2860, 1665, 1620, 1570, 1510, 1455, 1430, 1405, 1370, 1330, 1290, 1275, 1180, 1165, 1010, 900, 880, 820; MS (EI, 70 eV) *m/z* (%) 226 (100, M^+), 225 (29), 211 (52), 199 (24), 196 (17), 184 (26); calcd for $C_{15}H_{18}N_2$: C 79.60, H 8.02, N 12.38; found: C 79.52, H 8.02, N 12.32.

*4.1.1.20. 4-(4-Amino-3,5-dimethylphenyl)-4-methylcyclohexa-2,5-dienimine (**19x**).* 71%; colourless, vitreous solid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.53 (s, CH_3), 2.14 (s, 2×CH_3), 3.6 (br s, NH_2), 6.19 (d, *J*=10 Hz, 2×CH), 6.34 (d, *J*=10 Hz, 2×CH), 6.83 (s, 2×Ar–H), NH (not observed); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3500 (br), 3420 (br), 3250 (br), 3040, 2980, 2940, 2880, 1660, 1625, 1605, 1580, 1490, 1465, 1450, 1435, 1380, 1370, 1345, 1320, 1300, 1190, 1165, 1110, 1090, 1000, 925, 910, 900, 875, 840, 820; MS (EI, 70 eV) *m/z* (%) 262 (92, M^+), 225 (28), 212 (19), 211 (100), 210 (15), 199 (10), 196 (17), 195 (10), 194 (9), 184 (13); calcd for $C_{15}H_{18}N_2$: C 79.60, H 8.02, N 12.38; found: C 79.64, H 7.92, N 12.41.

*4.1.1.21. 4-(4-Aminophenyl)-2,3,4,5,6-pentamethylcyclohexa-2,5-dienimine (**19y**).* 82%; colourless, crystalline solid; mp 159–160 °C; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.47 (s, CH_3), 1.55 (d, *J*=1 Hz, 2×CH_3), 1.96 (d, *J*=1 Hz, 2×CH_3), 3.6 (br s, NH_2), 4.9 (br s, NH), 6.57 (d, *J*=8 Hz, 2×Ar–H), 6.88 (d, *J*=8 Hz, 2×Ar–H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450 (br), 3400 (br), 3300 (br), 3030, 3000, 2990, 2940, 2880, 1660, 1620, 1550, 1510, 1470, 1425, 1380, 1280, 1200, 1185, 1160, 1120, 1065, 1015, 860, 840; MS (EI, 70 eV) *m/z* (%) 254 (100, M^+), 253 (16), 239 (48), 224 (37), 209 (17), 137 (15), 136 (48), 119 (19), 118 (37), 112 (12), 104 (10); calcd for $C_{17}H_{22}N_2$: C 80.27, H 8.72, N 11.01; found: C 80.15, H 8.82, N 10.86.

*4.1.1.22. (4-Aminophenyl)-2,4,6-trimethylphenylamine (**13**).* Oily liquid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 2.15 (s, 2×CH_3), 2.28 (s, CH_3), 3.9 (br s, NH_2), 5.1 (br s, NH), 6.37 (d, *J*=8 Hz, 2×Ar–H), 6.56 (d, *J*=8 Hz, 2×Ar–H), 6.89 (s, 2×Ar–H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3400 (br), 3360 (br), 3000, 2940, 2920, 2860, 1610, 1510, 1480, 1400, 1375, 1310, 1290, 1250, 1150, 1125, 1010, 850, 825; MS (EI, 70 eV) *m/z* (%) 226 (100, M^+), 225 (15), 209 (9), 208 (7), 135 (10), 134 (13); calcd for $C_{15}H_{18}N_2$: C 79.60, H 8.02, N 12.38; found: C 79.85, H 8.11, N 12.46.

*4.1.1.23. 2,4,6-Trimethyl-6-(phenylamino)cyclohexa-2,4-dien-1-imine (**15**).* Colourless, crystalline solid; mp 83 °C (ether/pentane); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.31 (s, CH_3), 1.84 (d, *J*=1.5 Hz, CH_3), 2.12 (d, *J*=0.5 Hz, CH_3), 4.1 (s, NH), 5.64 (m, CH), 6.2–6.4 (m, CH & 2×ArH), 6.5–6.8 (m, ArH), 6.9–7.2 (m, 2×ArH), 9.5 (br, s, NH); IR (CCl_4) $\tilde{\nu}$ [cm^{-1}] 3420 (br), 3250 (br), 3060, 3020, 2980, 2920, 2890, 2870, 1605, 1500, 1450, 1425, 1365, 1315, 1280, 1260, 1205,

1170, 1010, 900, 870, 690; MS (EI, 70 eV) *m/z* (%) 226 (42, M^+), 135 (29), 134 (100), 119 (22), 118 (22), 117 (87), 93 (34), 91 (22), 77 (46), 66 (19), 51 (16), 40 (21); calcd for $C_{15}H_{18}N_2$: C 79.61, H 8.02, N 12.38; found: C 79.51, H 8.09, N 12.28.

4.1.2. Aniline-promoted dienimine-aniline rearrangement of ipso-benzidine ***12****.* Procedure: 4-(4-aminophenyl)-2,4,6-trimethylcycl ohexa-2,5-dienimine (**12**) (226 mg, 1.0 mmol) was treated with a mixture of aniline (1863 mg, 20.0 mmol) and 6 N aqueous HCl (0.06 mL) (aniline reagent pH 3.8) and stirred for 12 days at room temperature. The reaction mixture was then diluted with diethyl ether (20 mL) and neutralised via the addition of 2 N aqueous NaOH solution until basic pH. The phases were subsequently separated, and the aqueous phase extracted until quantitative recovery of all products (TLC control). The combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Residual aniline was subsequently evaporated in high vacuum yielding 297 mg crude product. Separation und purification of the reaction products was achieved via column chromatography (1×18 cm, Et_2O: PE=3:7→1:1) over silica gel affording the two *meta*-benzidines **21** and **22** in 47% and 35% yield, respectively.

*4.1.2.1. 2,4,6-Trimethyl-[1,1′-biphenyl]-3,4′-diamine (****21****).* 47%; colourless, crystalline solid; mp 138 °C (ethanol/water); ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.89 (s, CH_3), 1.93 (s, CH_3), 2.20 (s, CH_3), 3.6 (s, 2×NH_2), 6.70 (d, *J*=8 Hz, 2×Ar−H), 6.84 (s, Ar−H), 6.89 (d, *J*=8 Hz, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3450, 3380, 3000, 2920, 2860, 1620, 1520, 1475, 1375, 1315, 1275, 1180, 1170, 1010, 980, 870, 835; MS (EI, 70 eV) *m/z* (%) 266 (100, M^+), 225 (14), 211 (16), 210 (18), 209 (9), 196 (10), 195 (11), 194 (8); calcd for $C_{15}H_{18}N_2$: C 79.61, H 8.02, N 12.38; found: C 79.52, H 7.99, N 12.48.

*4.1.2.2. 2,4,6-Trimethyl-N^3-phenyl-[1,1′-biphenyl]-3,4′-diamine (****22****).* 35%; colourless, crystalline solid; mp 172 °C (ether/pentane); ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.91 (s, CH_3), 2.03 (s, CH_3), 2.20 (s, CH_3), 3.6 (s, NH_2), 5.1 (s, NH), 6.4−6.8 (m, 3×Ar−H), 6.71 (d, *J*=8 Hz, 2×Ar−H), 6.90 (d, *J*=8 Hz, 2×Ar−H), 7.00 (s, Ar−H), 7.0−7.3 (m, 2×ArH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}]: 3420, 3080, 3050, 2960, 2930, 2860, 1625, 1605, 1525, 1500, 1475, 1405, 1320, 1300, 1280, 1180, 1155, 1125, 1080, 1030, 1015, 1000, 985, 875, 835; MS (EI, 70 eV) *m/z* (%) 302 (100, M^+), 301 (17); calcd for $C_{21}H_{22}N_2$: C 83.40, H 7.33, N, 9.26; found: C 83.40, H 7.33, N 9.26.

*4.1.3. The benzidine rearrangement of 4-allylhydrazobenzene (****23****).* Procedure: 4-allylhydrazobenzene (**23**) (200 mg) was treated with 1 N aqueous hydrochloric acid (20 mL) at 0 °C for 45 min. Basic work-up with 2 N aqueous sodium hydroxide solution followed by column chromatography (2×20 cm, ether/petrol ether 1: 1) afforded *ortho*-semidine **24** in 15%, diphenyline **25** in 20% and *para*-benzidine **27** in 31% yield, respectively. Furthermore, the disproportionation product 1-(4-allylphenyl)-2-phenyldiazene was obtained in 4% yield.

*4.1.3.1. 5-Allyl-2-amino-diphenylamine (****24****).* 15%; oily liquid. ^{1}H NMR (270 MHz, $CDCl_3$) δ [ppm] 3.26 (br d, *J*=7 Hz, CH_2), 3.64 (s, NH_2), 5.02 (dm, *J*=10 Hz, CH), 5.03 (dm, *J*=18 Hz, CH), 5.19 (s, NH), 5.92 (ddt, J_1=18 Hz, J_2=10 Hz, J_3=7 Hz, CH), 6.70−6.78 (m, 3×Ar−H), 6.80−6.88 (m, 2×Ar−H), 6.98 (br s, Ar−H), 7.17−7.26 (m, 2×ArH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3400 (br), 3080, 3060, 3000, 2920, 2840, 1640, 1625, 1600, 1515, 1500, 1440, 1420, 1310, 1260, 1150, 1000, 920, 825; MS (EI, 70 eV) *m/z* (%) 224 (100, M^+), 223 (22), 209 (30), 206 (17), 197 (20), 195 (10), 182 (14), 181 (13), 145 (12), 133 (24), 132 (54), 130 (27); calcd for $C_{15}H_{18}N_2$: C 80.32, H 7.19, N 12.49; found C 80.07, H 7.18, N 12.45.

*4.1.3.2. 5-Allylbiphenyl-2,4′-diamine (****25****).* 20%; oily liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ [ppm] 3.30 (br d, *J*=7 Hz, CH_2), 3.66 (s, 2×NH_2), 5.02 (dm, *J*=10 Hz, CH), 5.06 (dm, *J*=18 Hz, CH), 5.98 (ddt, J_1=18 Hz, J_2=10 Hz, J_3=7 Hz, CH), 6.67 (d, *J*=8 Hz, Ar−H), 6.74 (d, *J*=8 Hz, 2×Ar−H), 6.95 (m, 2×Ar−H), 7.24 (d, *J*=8 Hz, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3480 (br), 3400 (br), 3080, 3060, 3000, 2920, 2860, 1625, 1520, 1500, 1440, 1415, 1280, 1185, 1155, 1000, 920, 835; MS (EI, 70 eV) *m/z* (%) 224 (100, M^+), 223 (35), 209 (15), 208 (17), 197 (21), 195 (14), 182 (13), 180 (14); calcd for $C_{15}H_{18}N_2$: C 80.32, H 7.19, N 12.49; found: C 80.23, H 7.15, N 12.45.

*4.1.3.3. 3-Allylbiphenyl-4,4′-diamine (****27****).* 31%; oily liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ [ppm] 3.35 (dm, *J*=7 Hz, CH_2), 3.66 (s, 2×NH_2), 5.15 (2m, 2×CH), 5.99 (ddt, J_1=17 Hz, J_2=10 Hz, J_3=7 Hz, CH), 6.72 (2d, J_1=8 Hz, Ar−H, J_2=8 Hz, 2×Ar−H), 7.24 (br s, Ar−H), 7.26 (dd, J_1=8 Hz, J_2=2 Hz, Ar−H), 7.36 (d, *J*=8 Hz, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3400 (br), 3090, 3060, 3010, 2990, 2910, 2840, 1640, 1615, 1605, 1515, 1500, 1475, 1435, 1310, 1180, 1000, 920, 830; MS (EI, 70 eV) *m/z* (%) 224 (100, M^+), 223 (16), 209 (21), 197 (15), 180 (14); calcd for $C_{15}H_{18}N_2$: C 80.32, H 7.19, N 12.49; found: C 80.23, H 7.06, N 12.49.

*4.1.4. The benzidine rearrangement of 4-vinylhydrazobenzene (****28****).* Procedure: 4-vinylhydrazobenzene (**28**) (50 mg) was treated with 1 N aqueous hydrochloric acid (5 mL) and stirred at 0 °C for 45 min. Basic work-up with 2 N aqueous sodium hydroxide solution was followed by extraction of the crude product into chloroform. Upon concentration of the chloroform extract to approx. 1 mL, 1,2-bis(4-aminophenyl)ethan-1-ol (**31**) slowly crystallised from the solution as a colourless solid in 60% yield.

*4.1.4.1. 1,2-Bis(4-aminophenyl)ethan-1-ol (****31****).* 60%; colourless, crystalline solid; ^{1}H NMR (90 MHz, CD_3OD) δ [ppm] 2.78 (dd, J_1=7 Hz, J_2=14 Hz, CH), 3.07 (dd, J_1=7 Hz, J_2=14 Hz, CH), 4.61 (t, *J*=7 Hz, CHOH), 4.85 (s, 2×NH_2, OH), 6.57 (d, *J*=8 Hz, 2×Ar−H), 6.63 (d, *J*=8 Hz, 2×Ar−H), 6.81 (d, *J*=8 Hz, 2×Ar−H), 7.00 (d, *J*=8 Hz, 2×Ar−H); IR (KBr) $\tilde{\nu}$ [cm^{-1}] 3600−3000 (br), 3040, 3010, 2940, 2920, 2860, 1620, 1520, 1440, 1270, 1260, 1180, 1060, 830; MS (EI, 70 eV) *m/z* (%)n228 (3, M^+), 211 (10), 210 (50), 195 (12), 193 (11), 165 (16), 122 (86), 107 (100), 106 (47), 94 (41), 85 (21), 83 (33), 77 (42); calcd for $C_{14}H_{16}N_2O$: C 73.66, H 7.06; N 12.27; found C 73.75, H 7.06, N, 12.15.

4.1.5. ipso-Diphenyline rearrangements

4.1.5.1. Procedure*:* 4-tert-Butyl-2,6-dimethylhydrazobenzene (**37**) (200 mg) was treated with 2 N aqueous hydrochloric acid (20 mL) and stirred at 0 °C for 45 min. Basic aqueous work-up with 2 N NaOH and extraction with ether was followed by separation of the product mixture and purification of the products via two consecutive column chromatographies (CC 1: 1×15 cm, Et_2O: PE=3: 1→1: 0; CC 2: 1×15 cm, Et_2O: PE=1: 9→1: 0) affording the *ipso*-diphenyline (**38**) and the diaminobiphenyl (**39**) in 17% and 18% yield, respectively.

*4.1.5.1.1. 6-(4′-Aminophenyl)-4-(tert-butyl)-2,6-dimethylcyclohexa-2,4-dienimine (****38****).* 17%; colourless, crystalline solid; mp 132 °C (ether); ^{1}H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.12 (s, 3×CH_3), 1.45 (s, CH_3), 2.03 (d, *J*=1 Hz, CH_3) 3.5 (br s, NH_2 & NH), 5.69 (d, *J*=2 Hz, H-5), 6.57 (m, H-3), 6.62 (d, *J*=8 Hz, 2×Ar−H), 6.99 (d, *J*=8 Hz, 2×Ar−H); ^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm] 183.53 (s), 145.37 (s), 138.59 (s), 134.56 (s), 133.08 (d),

131.43 (d), 131.43 (s), 128.00 (d), 115.13 (d), 49.52 (s), 33.69 (s), 29.02 (q), 26.68 (q), 17.94 (q); IR (CCl_4) $\tilde{\nu}$ [cm^{-1}] 3480 (br), 3400 (br), 3250 (br), 3040, 2970, 2940, 2880, 1625, 1580, 1515, 1480, 1455, 1365, 1350, 1280, 1190, 1180, 1140, 1120, 910, 870, 850, 830; MS (EI, 70 eV) *m/z* (%) 268 (16, M^+), 253 (47), 212 (78), 211 (100), 197 (19), 119 (52); calcd for $C_{18}H_{24}N_2$: C 80.55, H 9.01, N 10.44; found: C 80.45, H 9.15, N 10.38.

*4.1.5.1.2. 4,4′-Diamino-3,5-dimethylbiphenyl (**39**).* 18%; oily liquid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 2.21 (s, 2×CH_3), 3.6 (br s, 2×NH_2), 6.68 (d, *J*=8 Hz, 2×Ar−H), 7.12 (s, 2×Ar−H) 7.34 (d, *J*=8 Hz, 2×Ar−H); IR (CCl_4) $\tilde{\nu}$ [cm^{-1}] 3480 (br), 3400 (br), 3020, 2980, 2930, 2910, 2860, 1625, 1525, 1485, 1445, 1435, 1265, 1215, 1195, 1180, 1085, 880, 670; MS (EI, 70 eV) *m/z* (%) 212 (100, M^+), 211 (12), 106 (12), 105 (13), 95 (39), 94 (23), 93 (59), 69 (16), 57 (27), 56 (40), 55 (24); calcd for $C_{14}H_{16}N_2$: C 79.21, H 7.60, N 13.20; found: C 79.10, H 7.57, N 13.10.

4.1.5.2. Procedure: 1-(4-tert-Butyl-2,6-dimethylphenyl)-2-(2-chlorophenyl)hydrazine (**40a**) (200 mg) was treated with 2 N aqueous hydrochloric acid (20 mL) and stirred at 0 °C for 2 h. Basic aqueous work-up with 2 N NaOH and extraction with ether was followed by separation and purification of the products via a single column chromatography (1×15 cm, Et_2O) affording the *ipso*-diphenyline (**41a**) in 10% yield.

*4.1.5.2.1. 6-(4′-Amino-3′-chlorophenyl)-4-(tert-butyl)-2,6-dimethylcyclohexa-2,4-dienimine (**41a**).* 10%; colourless, crystalline solid; mp 143 °C (ether); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.12 (s, 3×CH_3), 1.47 (s, CH_3), 2.02 (d, *J*=1 Hz, CH_3), 4.0 (s, NH_2), 5.66 (d, *J*=2 Hz, H-5), 6.56 (dq, J_1=1 Hz, J_2=2 Hz, H-3), 6.68 (d, *J*=8 Hz, Ar−H), 6.89 (dd, J_1=2 Hz, J_2=8 Hz, Ar−H), 7.10 (d, *J*=2 Hz, Ar−H), 6.1 (br s, NH); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3500 (br), 3400 (br), 3340 (br), 2960, 2870, 1655, 1620, 1590, 1575, 1500, 1480, 1450, 1400, 1360, 1290, 1265, 1005, 900, 865, 820; MS (EI, 70 eV) *m/z* (%) 304 (14, M^+), 302 (37), 289 (21), 287 (56), 248 (34), 247 (44), 246 (97), 245 (100), 231 (14), 230 (9), 211 (10), 210 (23), 209 (12), 196 (10), 195 (10), 154 (10), 152 (26), 136 (12), 135 (10); calcd for $C_{18}H_{23}ClN_2$: C 71.39, H 7.65, N 9.25; found: C 71.42, H 7.65, N 9.34.

4.1.5.3. 1-(4-tert-Butyl-2,6-dimethylphenyl)-2-(3-chlorophenyl)hydrazine (**40b**) (200 mg) was treated with 2 N aqueous hydrochloric acid (20 mL) and stirred at 0 °C for 90 min. Basic aqueous work-up with 2 N NaOH and extraction with ether was followed by separation of the crude product mixture and purification of the products via two consecutive column chromatographies (CC 1: 1×5 cm, Et_2O: MeOH=1: 0→49: 1; CC 2: 1×15 cm, Et_2O) affording the *ipso*-diphenyline (**41b**) and the *ortho*-semidine (**43b**) in 14% and 3% yield, respectively.

*4.1.5.3.1. 6-(4′-Amino-2′-chlorophenyl)-4-(tert-butyl)-2,6-dimethylcyclohexa-2,4-dienimine (**41b**).* 14%; colourless, vitreous solid; ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.10 (s, 3×CH_3), 1.40 (s, CH_3), 2.10 (d, *J*=1 Hz, CH_3), 4.2 (br s, NH_2), 5.55 (d, *J*=2 Hz, H-5), 6.58 (dd, J_1=2.5 Hz, J_2=8 Hz, Ar−H), 6.58 (m, H-3), 6.69 (d, *J*=2.5 Hz, Ar−H), 7.28 (d, *J*=8 Hz, Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3480 (br), 3400 (br), 3340 (br), 2960, 2860, 1620, 1605, 1580, 1490, 1480, 1455, 1360, 1285, 1270, 1050, 1005, 905, 865, 840; MS (EI, 70 eV) *m/z* (%) 304 (16 M^+), 302 (43), 289 (22), 287 (55), 267 (16), 251 (32), 248 (28), 247 (22), 246 (79), 245 (29), 211 (100), 210 (80), 209 (38), 194 (37), 152 (34), 86 (39), 84 (58), 57 (20); calc for $C_{18}H_{23}ClN_2$: C 71.39, H 7.65, N 9.25; found: C 71.38, H 7.78, N 9.30.

*4.1.5.3.2. 4-(tert-Butyl)-6-((3′-chlorophenyl)amino)-2,6-dimethylcyclohexa-2,4-dienimine (**43b**).* 3%; colourless, crystalline solid; mp 150 °C (ether); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 1.10 (s, 3×CH_3), 1.31 (s, CH_3), 2.14 (d, *J*=1 Hz, CH_3), 4.3 (s, NH), 5.65 (d, *J*=2 Hz, H-5), 6.17 (ddd, J_1=1.5 Hz, J_2=2 Hz, J_3=8 Hz, Ar−H), 6.27 (t, *J*=2 Hz, Ar−H), 6.62 (m, H-3), 6.63 (ddd, J_1=1.5 Hz, J_2=2 Hz, J_3=8 Hz, Ar−H), 6.96 (t, *J*=8 Hz, Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3430 (br), 3350 (br), 2960, 2870, 1595, 1495, 1480, 1365, 1320, 1270, 1175, 1100, 1010, 990, 910, 860, 840; MS (EI, 70 eV) *m/z* (%) 304 (11, M^+), 302 (32), 289 (4), 287 (13), 252 (10), 248 (8), 246 (22), 177 (32), 176 (100), 162 (65), 161 (34), 154 (33), 152 (99), 146 (24), 127 (27), 106 (18), 91 (14), 77 (11), 65 (13); calcd for $C_{18}H_{23}ClN_2$: C 71.39, H 7.65, N 9.25; found: C 71.31, H 7.41, N 9.18.

4.1.6. N-Acetylation of rearrangement products. Procedure: To the solution of the respective amino compound in glacial acetic acid (0.2 mol/L) is slowly added an excess amount of acetic anhydride (200 wt % of the starting material) at 10 °C under cooling. The mixture is stirred for 30 min and then quenched with a small amount of water to hydrolyse unreacted anhydride. The acetic acid is removed under reduced pressure and the crude product is subsequently purified by recrystallization or column chromatography. Under the employed reaction conditions, only primary amino groups are acetylated giving the *N*-acetylated compounds usually in quantitative yield.

*4.1.6.1. N-(4-(mesitylamino)phenyl)acetamide (**Ac-13**).* Colourless, crystalline solid; mp 181 °C (ethanol/water); ^1H NMR (90 MHz, DMSO-d_6) δ [ppm] 1.97 (s, CH_3), 2.09 (s, 2×CH_3), 2.24 (s, Ac-CH_3), 6.32 (d, *J*=8 Hz, 2×Ar−H), 6.91 (s, 2×Ar−H), 7.02 (s, NH), 7.23 (d, *J*=8 Hz, 2×Ar−H), 9.53 (s, Ac-NH); IR (KBr) $\tilde{\nu}$ [cm^{-1}] 3380 (br), 3280 (br), 3080, 2950, 2920, 1655, 1625, 1610, 1550, 1510, 1485, 1370, 1310, 1285, 1250; MS (EI, 70 eV) *m/z* (%) 268 (100, M^+), 227 (14), 226 (57), 225 (54), 209 (12), 208 (8); calcd for $C_{17}H_{20}N_2O$: C 76.09, H 7.51; N 10.44; found: C 76.06, H 7.59, N, 10.40.

*4.1.6.2. N-(2-(mesitylamino)phenyl)acetamide (**Ac-16**).* Colourless, crystalline solid; mp 189 °C (ethanol/water); ^1H NMR (90 MHz, $CDCl_3$) δ [ppm] 2.12 (s, 2×CH_3), 2.22 (s, Ac-CH_3), 2.30 (s, CH_3), 3.42 (s, 2×NH), 6.29 (dd, J_1=8 Hz, J_2=2 Hz, Ar−H), 6.6–7.3 (m, 3×Ar−H), 6.9 (s, 2×Ar−H); IR ($CHCl_3$) $\tilde{\nu}$ [cm^{-1}] 3410 (br), 3300 (br), 3000, 2960, 2920, 2860, 1750, 1710, 1675, 1600, 1505, 1480, 1435, 1415, 1365, 1310, 1090; MS (EI, 70 eV) *m/z* (%) 268 (100, M^+), 253 (20), 251 (42), 227 (29), 226 (13), 210 (46), 209 (47), 208 (59), 194 (13), 193 (17); calcd for $C_{17}H_{20}N_2O$: C 76.06, H 7.51, N 10.44; found: C, 75.96, H 7.51, N 10.44.

*4.1.6.3. 4,4′-Diacetamide-3,5-dimethylbiphenyl (**DiAc-39**).* Colourless, crystalline solid; mp 313 °C (acetic acid/water); ^1H NMR (90 MHz, DMSO-d_6) δ [ppm] 2.07 (s, 2×CH_3), 2.20 (s, 2×Ac-CH_3), 7.40 (s, 2×Ar−H), 7.67 (s, 4×Ar−H), 9.37 (s, NH), 10.03 (s, NH). IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3280 (br), 3100, 3030, 2920, 2850, 1660, 1600, 1520, 1480, 1420, 1370, 1315, 1290, 1260, 1190, 830; MS (EI, 70 eV) *m/z* (%): 296 (82, M^+), 254 (72), 253 (36), 213 (34), 212 (100), 211 (60), 197 (18), 196 (22); calcd for $C_{18}H_{20}N_2O_2$: C 72.95, H 6.80, N 9.45; found: C 72.83, H 6.75, N 9.46.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.03.103. This material contains further experimental procedures for the syntheses of all starting materials and analytical data of all new compounds.

References and notes

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4. Except Badger *et al.* only Rieker and Speiser reported the synthesis of a 4-(4′-aminophenyl)-4-alkylcyclohexa-2,5-dienimine. However, their synthesis (via the anodic oxidation of 3,5-di-*tert*-butyl-substituted diaminobiphenyl) did not involve a 4.4′-benzidine rearrangement as described in this paper, see Rieker, A.; Speiser, B. *J. Org. Chem.* **1991**, *56*, 4664–4671.