(*E*/*Z*) Equilibria, 16[1]

Lone Electron Pair Donor Quality of the Imino Function: Synthesis and Reactivity of Sterically Strongly Congested Iminocyclopentanes

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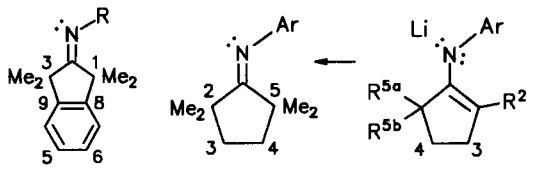
Received June 9, 1992

Key Words: Imines / Permethylation / Substitution, electrophilic aromatic / Steric shielding

2,6-Dimethyl-*N*-(2,2,5,5-tetramethylcyclopentylidene)aniline (**4h**) is obtained by permethylation; it forms salts (**5**) by *N*-protonation. Its CN double bond is strongly shielded against nucleophilic attack and cannot be hydrolyzed. Nitration and bromination occur smoothly in the aromatic *p*-position (**12**, **13**), showing the directing power of the lone electron pair of the imino function. This π-donor quality is assessed by probing weaker electrophiles and by qualitative competition experiments.

The plans to construct sterically strongly hindered Schiff bases arose from projects to develop suitable isoelectronic and isosteric model substances for the non-observable carbanions of vinyllithium compounds. We also hoped that the emerging structural system would allow an unequivocal elucidation of the mechanism of *anti*/*syn* stereomutation[2] for both classes of compounds. Such stereomutation is sterically accelerated[2] in the tetramethyl-2-indanylidene series **1**; it was expected that increased front strain along the CN double bond[3] should cause a larger acceleration in the system **2**. This was indeed observed[4] and explained by increased internal pressure of the 5,5-dimethyl group against the *N*-aryl moiety, because the 3,4-single bond[3] of **2** is longer than the C-8/C-9 bond of **1**. For easier interpretation of such data, we had chosen the *N*-cyclopentylidene derivatives **2** rather than the corresponding *N*-cyclohexylidene analogues in order to avoid stereodynamic complications by chair inversion. Our synthetic route involves permethylation of lithiated imines **3**, as described in Section A.

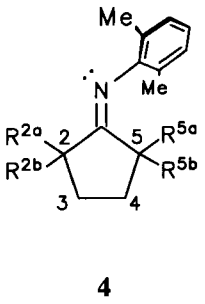


1 **2** **3**

Increased congestion about the C-1 terminus of the CN double bond was also expected to render the system **2** even more stable towards nucleophiles (Section B), whereas compounds of type **1** are still slowly hydrolyzed by aqueous acid[2]. Therefore, plans to determine at a later time the basicities of such imines in aqueous media provided a final motivation for their preparation. The present investigation concludes with a study (Section C) of the distinctive reactivity in electrophilic aromatic substitution at the *N*-aryl group of **2**, providing chemical evidence for the donor quality of the imino function.

A. α,α′-Permethylation of Schiff Bases

2,2,5,5-Tetramethylcyclopentanone[5] does not react below its boiling temperature with 2,6-dimethylaniline under the conditions[6] of the $TiCl_4$-mediated condensation. This amine was therefore first condensed with plain cyclopentanone by $ZnCl_2$ catalysis in refluxing benzene to give **4a**, accompanied by the aldol condensation product **4b** which was formed exclusively in boiling toluene as a solvent[7].



4

4	R^{2a}	R^{2b}	R^{5a}	R^{5b}
a	H	H	H	H
b	$(CH_2)_4C$		H	H
c	Me	H	H	H
d	H	H	Me	H
e	Me	Me	H	H
f	Me	H	Me	H
g	Me	Me	Me	H
h	Me	Me	Me	Me
i	Et	Et	Me	Me

Owing to their high kinetic acidity, *N*-(cyclopentylidene)imines may be deprotonated with *n*-butyllithium or methyllithium in the presence of less than stoichiometric (down to catalytic)[8] amounts of diisopropylamine, without any addition to the C=N bond (General Procedure, see Experimental). Interconversion of the lithium compound **3** (Ar = 2,6-dimethylphenyl) with its precursor **4a** is slow on the NMR time scale. Methylation of **4a** gives an (*E*/*Z*) equilibrium mixture **4c**/**d** with ca. 90% of the (*E*) isomer **4c**; this yield is very roughly in accord with the 65% calculated from empirical substituent parameters[9]. Further deprotonation and methylation of **4c**/**d** according to the General Procedure leads to a 1:2 mixture of regioisomers **4e** and **4f**. Since **4e** has been independently prepared[6] before, analysis of the mixture is easy even though the α,α′-dimethyl isomer **4f** is present in the *cis* and *trans* forms (ca. 1:1). The latter are recognized by their widely separated pairs of 5- and 2-methyl proton doublets which on heating coalesce due to

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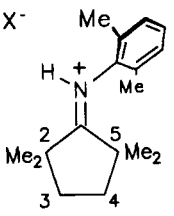
(*E*,*Z*) diastereotopomerization, requiring $\Delta G^{\neq} = 17.1(3)$ kcal/mol (see Experimental).

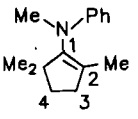
The regioselectivity **4e/f** cannot be efficiently controlled even though a *tert*-CH group has to compete with a CH_2 site[10]. The (*E*,*Z*) equilibrium **4c/d** should be established within a few min at −20°C (in analogy with the stereomutation of **4f**), which is much faster than the (*E*,*Z*) isomerization of 2-butanone anil[11]. Therefore, the role[10] of the CN double-bond configuration in the methylation of **4c/d** is difficult to predict, but the **4e/f** product ratio changes very little anyway, from 30:70 at +70°C to 50:50 at −20°C.

The third deprotonation/methylation step is convergent with formation of the single product **4g** from the **4e/f** mixture. Empirical substituent parameters[9] predict at least 99% of (*E*)-**4g**. The fourth (and any further attempted) deprotonation and methylation produce only **4h** without any indication of *N*-methylation. Hence, this 2,2,5,5-tetramethyl compound is most easily prepared in a one-pot synthesis, and the residual and stronger auxiliary bases may be extracted with very dilute acid. However, **4h** is soluble in 2 N HCl solution, in contrast to **4i**[6]. Its stable salts **5a**−**c** exhibit either C_{2v} or C_s symmetry on the NMR time scale (see Experimental), depending on their equilibration with the free base **4h** which is in or above the coalescence region (C_{2v}) at room temperature.



5a - c

5a: X = ClO_4^-
5b: X = BF_4^-
5c: X = Cl^-

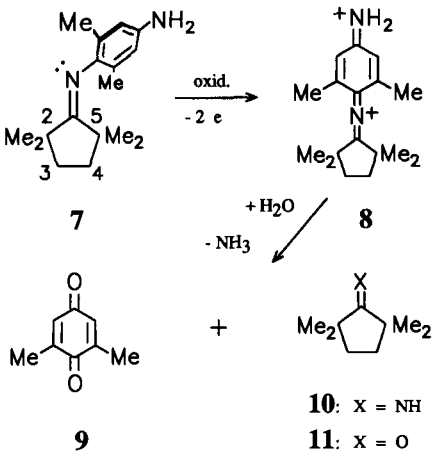


6

The two *ortho*-methyl groups in the aniline part of **4g** and **h** are synthetically essential: Application of the General Procedure to simple cyclopentanone anil[7,12,13] introduces the first three methyl groups into the 2- and 5-positions, as intended, but the fourth one is attached to nitrogen to yield exclusively the enamine **6**.

B. Stability to Nucleophiles and Redox Reagents

The *N*-(dimethylcyclopentylidene)anilines **4e** and **f** are hydrolyzed by hot dilute acid, whereas complete cleavage of **4g** to 2,6-dimethylaniline and 2,2,5-trimethylcyclopentanone requires at least 11 days in boiling concentrated hydrochloric acid. But not even traces of the amine or of tetramethylcyclopentanone[5] **11** are liberated from **4h** in conc. HCl after three days at reflux. Pure **4h** is also recovered from boiling acetic acid containing aqueous sodium acetate (8 h at 130°C), a reagent recommended[14] for recalcitrant cases like this one. Since *N*-protonation as the first step of hydrolysis is not impeded, as shown by the isolation of the salts **5a**−**c**, only the nucleophilic attack at C-1 of **5** is sterically hindered. Accordingly, **4h** does not react with 2,4-dinitrophenylhydrazine in conc. sulfuric acid nor with $LiAlH_4$ (2 h in refluxing THF). In an attempt of electron transfer to **4h**, metallic lithium will be shown[4] to have no stereodynamical influence.



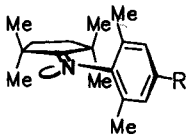
7 **8** **9** **10**: X = NH **11**: X = O

Since their CN double bond is so well protected, disintegration of such imines should aim at the cleavage of the *N-aryl* bond after conversion to a quinone imine intermediate. Aqueous hydrogen peroxide or sodium dichromate do not react with **4h**, but the *p*-amino derivative **7** (described in Section C) is sufficiently reactive toward sodium dichromate in acid to be cleaved to the known fragments **9**−**11**, probably via the quinone imine dication **8**. This implies constitutional evidence for **7** and hence also for its precursor **4h**.

C. Electrophilic Aromatic substitution, Activated by sp^2-Nitrogen of the Imino Function

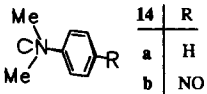
The hydrolytic stability of the sterically congested imine **4h** allows to work under conditions which an unprotected CN double bond would not survive. The treatment with a nitration mixture affords the single *p*-nitrated product **12**, demonstrating that the imino function can override the directing influence of two methyl groups. Subsequent reduction of **12** to the primary amine **7** is a matter of routine. NMR spectra of these and the following imines are assigned with reference to those of **4h**[6] and correspond to effective C_{2v} symmetry at room temperature due to coalescence.

It is obvious from molecular models (and verified by X-ray analysis[3]) that the aryl group of **4h** has to prefer a nearly orthogonal arrangement with respect to the CN double bond, as shown in **12**/**13**. This is also the most suitable conformation for the lone electron pair to interact with the aromatic π system. However, this formally sp^2-hybridized lone pair must be a weaker π donor than the lone pair of *N*,*N*-dimethylaniline (**14a**) which has more *p* character and hence better overlap with the π system of its phenyl group. Weaker electrophilic agents are therefore unreactive toward **4h**: Aqueous nitrous acid does not react with **4h** if the formation of nitrous gases is avoided (which would give NO_2^+ and again **12**). Equimolar amounts of **4h** and **14a** in dilute acid treated with potassium nitrite (sufficient for both compounds) afford **14b** together with unchanged **4h**. Likewise, **4h** is recovered after treatment with benzenediazonium chloride in aqueous ethanol at room temperature or with acetyl chloride/$AlCl_3$ in 1,2-dichloroethane at +50°C (2 h). The Vilsmeier formylation of **4h** fails under conditions (see Experimental) which produce the aldehyde **14c** from **14a**.



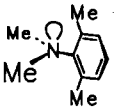
	R
4h	H
7	NH_2
12	NO_2
13	Br

4h, 7, 12, 13



14	R
a	H
b	NO
c	CHO
d	Br

14



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On the other hand, bromination of **4h** proceeds instantaneously to yield only **13**, whereas no trace of **13** is formed in a competition experiment of **4h** and **14a** for bromine which affords only **14d**. Hence, the lone electron pair is a poorer π donor in **4h** than in **14a**. Nevertheless, electrophilic bromination is clearly activated in **4h** (without a catalyst) as compared to benzene or *N*,*N*,2,6-tetramethylaniline (**15**): The latter is brominated in the 3-position with some difficulty[15] and not susceptible to nitrosation[16] or azo coupling[16,17], because steric repulsions in **15** force the lone electron pair out of conjugation.

D. Conclusion

Permethylation of the cyclopentylidene fragment appears to occur with particular ease, compared with *N*-(cyclohexylidene)amines[18], but is not as efficacious as CH-methylation in acyclic[10] systems. The product **4h** is sterically more shielded than *N*-(1,1,3,3-tetramethyl-2-indanylidene)amines[6] (**1**). An appreciable *p*-directing substituent effect becomes evident from the formation of the products **12** and **13** which provide the entries to a series of further derivatives[4] with additional evidence for the π donor quality of the lone electron pair of the imino function. At present we can give a first quantification of this substituent effect for the ground state of **4h** by NMR spectroscopy in the following manner.

The quality of aryl conjugation with the lone electron pair is best assessed by the *p*-carbon atom ^{13}C-NMR shift, because disturbing short-range effects should not act over this distance. When **15** (δ = 124.7)[19] and 2,6-dimethylaniline (δ = 117.8)[19] are taken as the references for no and for maximal conjugation, respectively, the *p*-carbon shifts of **4h** (δ = 121.8)[6] and of **4i** (δ = 121.7)[6] indicate 58% of the π donor quality found for 2,6-dimethylaniline. This figure agrees well with previous estimates[20,21].

We gratefully acknowledge the support obtained from the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*.

Experimental

The syntheses of **4e** and **4i** and the spectrometric equipment are described[6].

N-(1-Cyclopenten-1-yl)-N-lithio-2,6-dimethylaniline [**3**, all R = H and Ar = $C_6H_3(CH_3)_2$-(2,6)]: A 5-mm NMR test tube was charged with 75 mg (0.4 mmol) of **4a**, 0.052 ml (0.37 mmol) of diisopropylamine, and 0.20 ml of dry THF under argon. Methane evolution was noticed during the slow addition at −20°C of 0.28 ml of methyllithium (1.6 M in ether). – ^{1}H NMR (THF/ether, 3:2): δ = 2.15 (s, 2 *o*-CH_3), 6.40 and 6.73 (AB_2 system, *p*- and *m*-H). – After treatment with 0.008 ml (0.2 mmol) of dry methanol, the ^{1}H-NMR absorptions of imine **4a** were observed in addition to those of **3** at 32°C.

N-Cyclopentylidene-2,6-dimethylaniline (**4a**): 2,6-Dimethylaniline (123.5 ml, 1 mol), cyclopentanone (110 ml, 1.24 mol), and $ZnCl_2$ (1.0 g, dehydrated) in benzene (300 ml) were refluxed for 6–10 h by using a water separator to yield 12 ml (67%) of water. The solution was concentrated and the dark-red oil (190 g) distilled with a Vigreux column (20 cm). After a fore-run of 2,6-dimethylaniline (71 g), the almost colourless liquid **4a** was recovered at 89–92°C/0.001 Torr, leaving a residue of crude **4b** (10.6 g, 4%). Allowing for 10% contamination of the distillate (71.1 g) by 2,6-dimethylaniline (which did not interfere with further processing), the actual yield of **4a** was 63.9 g (34%). The analytical sample was obtained by repeated fractionating distillation, b.p. 144–147°C/15 Torr, and stored under N_2 in a refrigerator. – IR (film or cyclohexane): $\tilde{\nu}$ = 1690 and 1675 cm^{-1} (CN), 1470, 1182, 760. – UV (cyclohexane): λ_{max} (lg ε) = 273 nm (3.470). – ^{1}H NMR (CCl_4): δ = 1.73 (unresolved, 2 CH_2), 1.92 (s covering m, 2 *o*-CH_3 and CH_2), 2.46 (pseudo-t, CH_2-2), 6.57 and 6.73 (AB_2 system, *p*- and *m*-H). – ^{13}C NMR: Ref.[6] – Prolonged heating during the preparation of **4a** resulted in higher proportions of **4b**, which could not be suppressed by modifications like slow continuous addition of cyclopentanone.

$C_{13}H_{17}N$ (187.3) Calcd. C 83.37 H 9.15 N 7.48
Found C 83.35 H 8.72 N 7.34

N-[2-(Cyclopentylidene)cyclopentylidene]-2,6-dimethylaniline (**4b**): The non-distilled residue from **4a** was recrystallized from methanol to yield ca. 30% of slightly yellow, small needles with m.p. 75–76°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2938, 2870, 1622, 1593, 1467, 1205, 1191, 763. – ^{1}H NMR (CCl_4): δ = 1.72 (mc, 2 CH_2), 1.91 (mc, 2 CH_2), 1.95 (s, 2 *o*-CH_3), 2.35 (mc, 2 CH_2), 2.84 (mc, 1 CH_2), 6.60 and 6.78 (AB_2 system, *p*- and *m*-H). – ^{13}C NMR ($CDCl_3$): δ = 18.1 (q, 2 CH_3); 22.1, 27.2, 31.1, 33.3, 33.6, and 34.4 (all t, 7 CH_2); 122.0 (d, *p*-C), 125.2 (s, 2 *o*-C), 127.7 (d, 2 *m*-C), 127.9 (s, C-2), 150.1 (s, *ipso*-C), 151.4 (s, olefinic C), 174.1 (s, C-1).

$C_{18}H_{23}N$ (253.4) Calcd. C 85.32 H 9.15 N 5.53
Found C 85.05 H 9.15 N 5.41

General Procedure (GP) for Methylation of Imines: A strong stirring rod, the imine (**4a** or **4c–g**, 100 mmol), and 3.50 ml (25 mmol) or 1.40 ml (10 mmol) of diisopropylamine in ca. 400 ml of dry THF were placed in a 2-l three-necked flask fitted with two dropping funnels and a reflux condensor carrying a nitrogen bubbler. The mixture was cooled with magnetic stirring under N_2 in an ice bath, and 100 mmol of *n*-butyllithium (1.3 M in hexane, 77 ml) was added dropwise within 10 min. A subsequent period at room temp. is not necessary for the first stages of methylation (see below). Methyl iodide (6.22 ml, 100 mmol) was introduced from the second dropping funnel within 10 min and the mixture warmed up to room temp. for workup or for completion at the later stages of methylation. Depending on the desired degree of methylation, the alternating addition of *n*-butyllithium and methyl iodide was repeated as required (up to six times for difficult cases).

After quenching the reaction with 10 ml of methanol, part of the THF solvent may be removed on a rotating evaporator. The product was distributed between 500 ml of ether and 800 ml of dist. water. Before washing, the ethereal extracts may be shaken with 0.2 N HCl to remove basic contaminants from the less basic prod-

ucts **4g** and **4h** (not recommended for **4c** or **4f**). After drying with Na_2SO_4, the crude material was distilled in vacuo.

2,6-Dimethyl-N-(2-methylcyclopentylidene)aniline (**4c**): A sample (no yield) drawn from a continuing run of the GP (see above) had b.p. 137–140°C/12 Torr. – ^{1}H NMR (CCl_4): δ = 0.65 [d, ^3J = 7 Hz, 2-CH_3 of (*Z*) isomer **4d**], 1.27 (d, ^3J = 6.5 Hz, 2-CH_3), 1.76 (mc, 2 CH_2), 1.93 (s, 2 *o*-CH_3), 2.42 (very br m, CH-2 and CH_2), 6.60 and 6.78 (AB_2 system, *p*- and *m*-H).

$C_{14}H_{19}N$ (201.3) Calcd. C 83.53 H 9.51
Found C 83.19 H 9.69

N-(2,5-Dimethylcyclopentylidene)-2,6-dimethylaniline (**4f**): Two methylations according to the GP yielded 44% of **4f** as a liquid mixture (2:1) with **4e**[6], b.p. 135–145°C/12 Torr. – IR (film): ṽ = 2945 cm^{-1}, 2865, 1678, 1460, 761. – ^{1}H NMR (CCl_4): δ = 0.65 and 0.67 (2 d, ^3J = 7 Hz, 5-CH_3 of *cis* and *trans* isomers), ca. 1.27 (2 part. hidden d, 2-CH_3 of *cis* and *trans*), 1.92 and 1.98 (2 s, 2 *o*-CH_3 of *cis* and *trans*), 6.63 and 6.77 (AB_2 system, *p*- and *m*-H). – ^{1}H NMR (anisole, from −30 up to +121°C): Δδ = 0.68 (2,5-CH_3), T_c = +70(5)°C at δ = 0.95 (d, ^3J = 7 Hz).

$C_{15}H_{21}N$ (215.3) Calcd. C 83.67 H 9.83 N 6.51
Found C 83.55 H 9.87 N 6.83

2,6-Dimethyl-N-(2,2,5-trimethylcyclopentylidene)aniline (**4g**): Following the GP with three sequential deprotonations and methylations, 20.60 g (110 mmol) of **4a** was converted into 15.38 g (61%) of colourless, liquid **4g**, b.p. 156–159°C/18 Torr. – ^{1}H NMR (CCl_4): δ = 0.68 (d, ^3J = 7 Hz, 5-CH_3), 1.20 and 1.24 (2 s, 2-CH_3), 1.72 (mc, CH_2-3 and -4), 1.92 and 1.98 (2 s, 2 *o*-CH_3), ca. 2.17 (br, CH-5), 6.63 and 6.80 (AB_2, *p*- and *m*-H). – ^{13}C NMR: Ref.[6]

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**4h**): Permethylation of **4a** by the GP consistently yielded 53–66% of purified **4h** in batches up to 250 mmol. Typically, 10.3 g (55 mmol) of **4a** gave 7.75 g (58%) of colourless, liquid **4h** boiling at 157–167°C/12 Torr or 90–93°C/0.01 Torr. Since the fourth deprotonation was sluggish, the mixture should be allowed to stand at least for 30 min at room temp. before the fourth addition of methyl iodide. This last step may be accelerated by addition of a larger proportion of CH_3I. It is of course possible to append additional cycles of the GP. – IR (film): ṽ = 2955 cm^{-1}, 2870, 1682, 1460, 760. – UV (cyclohexane or ethanol): λ_{max} (lg ε) = 281 nm (3.184), 237 (4.007). – ^{1}H NMR (CCl_4 at +30°C): δ = 1.06 (s, 4 CH_3), 1.63 (s, 2 CH_2), 1.96 (s, 2 *o*-CH_3), 6.57 and 6.75 (AB_2, *p*- and *m*-H). – ^{1}H and ^{13}C NMR ($CDCl_3$): Ref.[6]

$C_{17}H_{25}N$ (243.4) Calcd. C 83.89 H 10.35 N 5.76
Found C 83.88 H 10.20 N 5.81

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)anilinium Perchlorate (**5a**): A solution of 2.30 ml of $HClO_4$ (70%) in 4.5 ml of dist. water was slowly added to 2.00 g (8.2 mmol) of crude **4h**. The spontaneously precipitating needles were washed with water to neutrality and finally with ether; crude yield 1.29 g (46%), m.p. 211.5–213°C (from 1-propanol). – IR (KBr): ṽ = 2967 cm^{-1}, 2930, 2880, 2470 (br), 1658, 1120 (vs). – UV (methanol): λ_{max} = 272 nm. – ^{1}H NMR (methanol): δ = 1.12 and 1.58 (2 broadened s, 2- and 5-CH_3), 1.98 (s, 2 CH_2), 2.26 (s, 2 *o*-CH_3), 7.25 (mc, 3 arom. H). – ^{1}H NMR (2 N HCl): δ = 1.11 and 1.65 (2 s, 2- and 5-CH_3), 2.00 (s, 2 CH_2), 2.26 (s, 2 *o*-CH_3), 7.38 (mc, 3 arom. H).

$C_{17}H_{26}ClNO_4$ (343.9) Calcd. C 59.38 H 7.62 N 4.07
Found C 59.59 H 7.59 N 3.74

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)anilinium Tetrafluoroborate (**5b**): A cold sample of **4h** (1.95 g, 8.03 mmol) was combined with 2.80 ml of aqueous HBF_4 (50%) and scratched for crystallization, yielding 2.28 g (86%) of **5b**; colourless needles from 2-propanol, m.p. 203–205°C. – IR (KBr): ṽ = 2965 cm^{-1}, 2925, 2870, 2450 (br), 1664, 1124, 1083. – UV ($CHCl_3$): λ_{max} (lg ε) = 272 nm (sh 3.036). – ^{1}H NMR ($CDCl_3$): δ = 1.32 (br, 4 CH_3), 1.88 (s, 2 CH_2), 2.22 (s, 2 *o*-CH_3), 7.15 (s, 3 arom. H).

$C_{17}H_{26}BF_4N$ (331.2) Calcd. C 61.65 H 7.91 N 4.23
Found C 61.57 H 7.78 N 4.34

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)anilinium Chloride (**5c**): 500 mg (2.05 mmol) of **4h** was mixed with 2.0 ml of conc. HCl. The mixture was concentrated and the residue dried in vacuo, the viscous oil slowly transforming into colourless platelets. From 1-propanol 200 mg (35%) of **5c** with m.p. 185–187.5°C. – IR (KBr): ṽ = 2960 cm^{-1}, 2875, 2470 (br), 1965 (br), 1661, 1463. – UV ($CHCl_3$): λ_{max} (lg ε) = 273 nm (sh 2.962). – ^{1}H NMR ($CDCl_3$): δ = 1.02 and 1.89 (2 s, 2- and 5-CH_3), 1.85 (s, 2 CH_2), 2.28 (s, 2 *o*-CH_3), 7.15 (s, 3 arom. H).

$C_{17}H_{26}ClN$ (279.9) Calcd. C 72.96 H 9.36 N 5.01
Found C 73.72 H 9.41 N 5.16

N-Methyl-N-(2,5,5-trimethyl-1-cyclopenten-1-yl)aniline (**6**): *N*-(Cyclopentylidene)aniline was prepared (33%) from cyclopentanone diethyl acetal[13] and aniline in the presence of anhydrous $ZnCl_2$ according to the literature method[13]; b.p. 120–124°C/12 Torr (ref.[12] 120–121°C/10 Torr). It was then subjected to four deprotonation and methylation cycles according to the GP to yield exclusively the crude enamine **6**, which was not basic and was not further purified; b.p. ca. 130°C/12 Torr. – IR (film): ṽ = 2960 cm^{-1}, 2865, 1603, 1502. – ^{1}H NMR (CCl_4): δ = 1.05 (s, 2 5-CH_3), 1.40 (t, ^3J = ca. 1 Hz, 2-CH_3), 1.73 and 2.27 (2 pseudo-t, CH_2-3 and -4), 3.02 (s, NCH_3), 6.43 (mc, *p*-H), 6.52 (d, ^3J = 7 Hz, 2 *o*-H), 7.00 (pseudo-t, ^3J = 7 Hz, 2 *m*-H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (2-CH_3), 27.7 (2 5-CH_3), 32.4 (CH_2-3), 38.9 (CH_2-4 and NCH_3), 46.7 (C-5), 112.1 (2 *o*-C), 115.8 (*p*-C), 128.7 (2 *m*-C), 133.2 (C-2), 147.0 and 149.3 (C-1 and *ipso*-C).

2,6-Dimethyl-4-nitro-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**12**): 12 ml of conc. H_2SO_4 was dissolved in 23 ml of conc. HNO_3, the solution cooled in an ice bath and added dropwise within 15 min to 24.3 g (100 mmol) of the ice-cooled imine **4h** with stirring. The mixture was kept at room temp. for 1 h and poured into 500 ml of an ice/water mixture. After extracting with ether or CH_2Cl_2 the combined extracts were washed with 2 N Na_2CO_3 and water, then dried with Na_2SO_4, and the solvent was evaporated. 25.3 g (88%) of crude **12** was isolated and recrystallized from 400 ml of ethanol to give 20.2 g (70%) of yellow needles, m.p. 160–161.5°C. – IR (KBr): ṽ = 2960 cm^{-1}, 2870, 1688 (CN), 1509 and 1330 (NO_2). – UV (cyclohexane): λ_{max} (lg ε) = 333 nm (4.132). – ^{1}H NMR ($CDCl_3$ at +25°C): δ = 1.11 (s, 4 CH_3), 1.74 (s, 2 CH_2), 2.13 (t, ^3J = 0.6 Hz, 2 *o*-CH_3), 7.87 (sept, ^3J = 0.6 Hz, 2 arom. H). – ^{1}H NMR (CCl_4): δ = 1.08, 1.72, 2.10, 7.80. – ^{13}C NMR ($CDCl_3$ at +25°C): δ = 18.6 (qm, ^1J = 127.7 Hz, *o*-CH_3), 26.5 (qq, ^1J = 127.0, ^3J = 4.6 Hz, 2- and 5-CH_3), 37.5 (tm, ^1J = 130.5, ^3J = 4.4 Hz, C-3,4), 45.7 (> sept, ^2J or ^3J = 3.8 Hz, C-2,5), 123.3 (dq, ^1J = 165, ^3J = 5.2 Hz, *m*-C), 125.3 (q, ^2J = 5.9 Hz, *o*-C), 142.2 (t, ^2J = 3.6 Hz, *p*-C), 154.3 (m, ^3J = 3.9 Hz, *ipso*-C), 187.8 (m, ^3J = 3.3 Hz, C-1).

$C_{17}H_{24}N_2O_2$ (288.4) Calcd. C 70.80 H 8.39 N 9.71
Found C 70.50 H 8.54 N 9.92

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]aniline (**7**): 3.50 g (12.1 mmol) of **12** and 1.0 g of Raney-Ni in 100 ml of ethanol consumed ca. 1 l of hydrogen gas within 1 h. The filtrate was evaporated and the remainder (2.90 g, 93%) crystallized from low-boiling petroleum ether to afford 2.20 g (70%) of pale yellow needles, m.p. 99–100.5°C. – IR (KBr): = 3460, 3418, 3320, and

3210 cm^{-1} (NH); 2950, 2870, 1669 (CN), 1618 (NH), 1460, 1205. – UV (cyclohexane): λ_{max} (lg ε) = 246 nm (4.019), 308 (3.450). – ^1H NMR (CCl_4): δ = 1.07 (very br s, 4 CH_3), 1.63 (s, 2 CH_2), 1.85 (s, 2 *o*-CH_3), 3.03 (br s, NH_2), 6.15 (s, 2 arom. H).

$C_{17}H_{26}N_2$ (258.4) Calcd. C 79.02 H 10.14 N 10.84
Found C 79.04 H 10.17 N 10.91

Oxidative Cleavage of **7**: Solid sodium dichromate dihydrate (700 mg, 2.35 mmol) was slowly added to a stirred solution of 1.00 g (3.87 mmol) of the *p*-amino derivative **7** in 15 ml of 2 N H_2SO_4 with intermittent cooling. After 2 d of further stirring and subsequent addition of CH_2Cl_2 (20 ml), the mixture was filtered and the filter cake thoroughly washed several times with CH_2Cl_2. The combined CH_2Cl_2 phases were extracted with 2 N H_2SO_4 and washed to neutrality, then dried with Na_2SO_4 and distilled in a bridge to leave a remainder consisting of 164 mg (31%) of 2,6-dimethyl-1,4-quinone[22,23] (**9**) and 42 mg (8%) of 2,2,5,5-tetramethylcyclopentanone[5] (**11**). 50 mg of **9** was recovered by sublimation at 110°C/50 Torr; rapidly decomposing, long yellow needles, m.p. 55–62°C (ref.[22] 72–73°C, ref.[23] 74–75°C). – ^1H NMR (CCl_4): δ = 2.02 (s, 2 CH_3), 6.44 (s, 2H).

The united H_2SO_4 phases were made alkaline with 2 N NaOH and repeatedly extracted with CH_2Cl_2. The extracts were washed neutral (causing[24] loss of material) and dried with Na_2SO_4. The distillation residue as above contained 48 mg (9%) of the imine **10**[24].

Attempted Vilsmeier Formylation of **4h**: *N,N*-Dimethylformamide (300 mg, 4.1 mmol) was slowly added to an ice-cooled, stirred solution of 0.200 ml (2.1 mmol) of oxalyl chloride in 3.0 ml of chloroform. After further stirring at room temp. for 30 min 243 mg (1 mmol) of **4h** in 1 ml of chloroform was added slowly and the mixture heated to reflux for 4 h. A sample showed only the ^1H-NMR absorptions of the cation **5**. Therefore, 122 mg (1 mmol) of *N,N*-dimethylaniline (**14a**) was added and refluxing continued for 3 h. The solution was hydrolyzed with ice/water, then 2 N NaOH, and extracted with ether to yield 350 mg of a crude oil which contained **14a** and the aldehyde **14c** in roughly equal amounts and **4h**.

4-Bromo-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**13**): Bromine (0.90 ml, 17.4 mmol) was added dropwise within 5 min to the ice-cooled solution of 3.75 g (15.4 mmol) of **4h** in 20 ml of tetrachloromethane. The red and viscous mass was kept at room temp. for 1 h, dissolved in 20 ml of 2 N NaOH and 50 ml of CH_2Cl_2, the organic phase was separated and washed with NaOH and water. After drying with Na_2SO_4 and evaporation of the solvent, the crude material (5.80 g, 117%) was recrystallized from ethanol: 2.50 g (50%) of colourless rhombohedra, m.p. 111.5–112.5°C, b.p. 130–135°C (bath temp.)/0.5 Torr. – IR (KBr): ν ≙ 2950 cm^{-1}, 2870, 1680 (CN), 1457, 1198, 865, 855. – UV (cyclohexane or $CDCl_3$): λ_{max} (lg ε) = 244 nm (4.123), 288 (3.247). – ^1H NMR (CCl_4): δ = 1.07 (s, 4 CH_3), 1.67 (s, 2 CH_2), 1.97 (s, 2 *o*-CH_3), 6.94 (s, 2 arom. H).

$C_{17}H_{24}BrN$ (322.3) Calcd. C 63.36 H 7.51 N 4.35
Found C 63.32 H 7.66 N 4.12

Competitive Bromination of **4h** *and N,N-Dimethylaniline* (**14a**): A solution of 0.028 ml (0.55 mmol) of bromine in 2 ml of chloroform was added dropwise to a stirred solution of 300 mg (1.23 mmol) of **4h** and 0.160 ml (1.26 mmol) of **14a** in 2.5 ml of chloroform. The bromine was immediately consumed, and some HBr evolved. After 45 min at 25°C, the suspension of hydrobromides was concentrated and the residue dissolved in ether with the help of sufficient 2 N NaOH. The crude, brown oil (490 mg, 99%) isolated from the ethereal extracts consisted of **14a**, **14b** and **4h** in a 24:37:39 ratio.

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CAS Registry Numbers

3 [all R = H, Ar = $C_6H_3(CH_3)_2$ 2,6]: 143171-46-4 / **4a**: 85385-01-9 / **4b**: 143171-38-4 / **4c**: 143171-39-5 / **4d**: 143191-07-5 / **4e**: 142294-70-0 / *cis*-**4f**: 143171-40-8 / *trans*-**4f**: 143171-47-5 / **4g**: 142294-72-2 / **4h**: 142294-73-3 / **5a**: 143171-42-0 / **5b**: 143171-43-1 / **5c**: 143171-44-2 / **6**: 143171-45-3 / **7**: 143142-54-5 / **9**: 527-61-7 / **11**: 4541-35-9 / **12**: 143142-55-6 / **13**: 143142-53-4 / **14a**: 121-69-7 / **14b**: 138-89-6 / 2,6-dimethylaniline: 87-62-7 / cyclopentanone: 120-92-3