Reactions of 2,4,6-Tri-*t*-butylnitrosobenzene with Grignard Reagents

Yoshio INAGAKI, Renji OKAZAKI, and Naoki INAMOTO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received November 27, 1974)

Reactions of 2,4,6-tri-*t*-butylnitrosobenzene (**1**) with alkylmagnesium halides afforded 6-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,4-cyclohexadienes (**2**), 4-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**3**), and *N*-alkyl-2,4,6-tri-*t*-butylanilines (**4**) depending on the Grignard reagents used. The distribution of the reaction products indicated that the oximes were formed *via* an attack of the anionic species on the *ortho*- and the *para*-carbons, respectively, to the nitroso group, but that the *N*-alkylanilines *via* a free radical mechanism involving an electron transfer from the Grignard reagent to **1**. The free radical mechanism was confirmed in the case of *t*-butylmagnesium chloride by trapping the *t*-butyl radicals as 1-*t*-butoxyimino-2,4,4,6-tetra-*t*-butyl-2,5-cyclohexadiene (**8**). Such a mechanistic difference has been explained in terms of the difference in electron affinities of the free radicals derived from Grignard reagents.

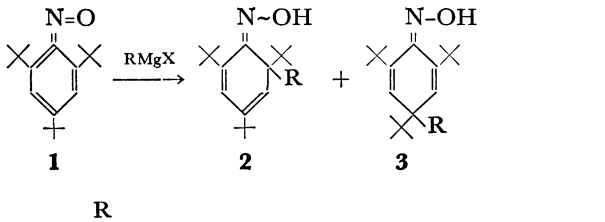
As part of studies on the steric effects in the reactions of 2,4,6-tri-*t*-butylaniline (**6**) and 2,4,6-tri-*t*-butylnitrosobenzene (**1**),[1-4] we investigated the reaction of **1** with Grignard reagents.

In the reactions of nitrosobenzenes with Grignard reagents, the formation of *N*,*N*-disubstituted hydroxylamines, secondary amines, and azobenzenes has been demonstrated,[5-9] and the free radical mechanism has been proposed for the formation of the hydroxylamines.[10]

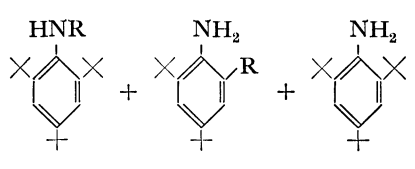
We have preliminarily communicated, in the reactions of **1**, Grignard reagents attack not only the nitrogen atom but also the *ortho*- and *para*-positions of the nitroso group.[11] This paper describes detailed accounts of these reactions and discuss the factors influencing the products distribution and the reaction mechanism.

Results and Discussion

Reaction Products. Reactions of 2,4,6-tri-*t*-butylnitrosobenzene (**1**) with a large excess of Grignard reagents (RMgX) in ether under nitrogen for *ca.* 1 hr at 0 °C, in which an ethereal solution of **1** was added dropwise into a solution of the Grignard reagent, gave 6-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,4-cyclohexadienes (**2**), 4-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**3**), *N*-alkyl-2,4,6-tri-*t*-butylanilines (**4**), 6-alkyl-2,4-di-*t*-butylanilines (**5**), and 2,4,6-tri-*t*-butylaniline (**6**) depending on the R group. The yields of the products are shown in Table 1.



R	
a	Me
b	Et
c	*i*-Pr
d	*t*-Bu
e	$PhCH_2$
f	1-Ad*



* Ad represents adamantyl group.

TABLE 1. YIELD (%) OF THE REACTION PRODUCTS

	RMgX	2	3	4	5	6
a	MeMgI	46	4	—	—	2
b	EtMgBr	26	30	—	—	8
c	*i*-PrMgBr	2	54	6	3	—
d	*t*-BuMgCl	—	trace	43	—	38
e	$PhCH_2MgCl$	29	44	—	—	6
f	1-AdMgBr	—	55	—	—	3

The structures of the products were confirmed by their analytical and spectral data. Two isomeric oximes (**2** and **3**) were distinguished each other by the UV spectra: isomers with absorption maxima at longer wave length (304—313 nm) were identified as **2**, whereas those with absorption maxima at shorter wave length (243—251 nm) as **3**. There are also some differences between the NMR spectra of the two isomers: a typical spectrum of **2** consists of three singlets due to the three *t*-butyl groups and a pair of doublets due to the two olefinic protons, but a typical spectrum of **3** consists of two singlets with intensity of 2 : 1 due to the *t*-butyl groups and an AB quartet due to the two olefinic protons. However, in the case of **3e** the three *t*-butyl groups appeared as three singlets with equal intensity and the two olefinic protons were equivalent. The abnormality may be ascribed to magnetic anisotropy of the phenyl group.

The oximes **2** and **3** correspond to the 1,4- and 1,6-conjugate addition products of the Grignard reagents to the nitrosobenzene (**1**) respectively, and this is the first example of conjugate addition to the nitrosobenzene system in marked contrast with a great many examples of conjugate addition in carbonyl compounds.[12]

The formation of **4c** and **4d** is noteworthy in view of difficult preparation of the corresponding methyl and ethyl derivatives,[13] the only known *N*-alkylated 2,4,6-tri-*t*-butylanilines; this reaction might provide a synthetic method for 2,4,6-tri-*t*-butylanilines with a bulky alkyl group on the nitrogen.

Mass Spectra of the Reaction Products. The oxime (**2**) was characterized by the four outstanding peaks at *m/e* M−56, M−73, M−87, and M−89, but the oxime (**3**) by the three peaks at *m/e* M−56, M−73, and M−89. The oximes (**2** and **3**) showed very weak molecular ion peaks, which were often obscure

in the oxime (**3**), but the metastable ion peak corresponding to loss of isobutylene (56 mass units) from the molecular ion was observed.

Two outstanding peaks M^+ (23—47%) and $(M-15)^+$ (100%) were characteristic of the anilines **4a**, **4b**, **4c**, **5c**, and **6**. Namely, loss of a methyl radical from the molecular ion was the predominant process, and the corresponding metastable ion peak was observed.

In contrast with those five anilines, the aniline **4d** showed a weak peak at *m/e* 302 (M−15) but outstanding peaks at *m/e* 317 (M^+, 11%), 261 (M−56, 33%), and 246 (M−71, 100%). A metastable ion peak corresponding to loss of 56 mass units from the molecular ion was observed. Therefore the pronounced feature of aniline **4d** is loss of isobutylene (56 mass units) from the molecular ion. Radical cation of **6** thus produced readily loses a methyl radical, as mentioned above, to exhibit the base peak.

Reaction Mechanism. The yields of the products changed systematically depending on the R group. As the bulkiness of the R group increases from methyl to 1-adamantyl (1-Ad), the yield of oxime **2** with a longer conjugate system decreased, while the yield of sterically less hindered oxime **3** increased. The yield ratios of the oximes (**2**/**3**) were alike each other in the reactions of the ethyl and the benzyl Grignard reagents with primary anionic centers, but much different in other cases. Thus the yields of **2** or **3** seem to be dependent mainly on a steric factor.

On the other hand, formation of the secondary amine **4** seems to be independent of the steric factor. Namely, the reaction with *t*-butylmagnesium chloride produced **4d** as a major product along with **3d** only a trace amount. whereas 1-adamantylmagnesium bromide which has also a tertiary anionic center afforded the oxime (**3f**) in a high yield. Moreover, the reactions with methyl, ethyl, and benzyl Grignard reagents did not afford **4**, although they should be sterically much more favorable in the attack onto the nitrogen.

These facts suggest the difference in the formation mechanisms of the oximes (**2** and **3**) and the secondary amine (**4**); the oximes were produced *via* attack of the anionic species on the *ortho*- and *para*-carbons to the nitroso group, while the secondary amine (**4**) *via* the following pathway involving an electron transfer from the Grignard reagent to the nitrosobenzene (**1**)

$$\mathrm{Ar\text{-}N{=}O + RMgX \rightarrow [Ar\text{-}\dot{N}\text{-}O\text{-}MgX + R\cdot]} \quad \mathbf{7}$$
$$\rightarrow \mathrm{ArN(R)OMgX} \xrightarrow{\mathrm{RMgX}} \mathrm{ArN(R)MgX} \xrightarrow{\mathrm{H_2O}} \mathbf{4}$$
(Ar: 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$)

Such a mechanistic difference can be interpreted as the difference in electron affinitiy of a free radical (R·). The relation between the electron affinities of free radicals and the yields of reaction products is shown in Table 2, in which the order of electron affinities of methyl, ethyl, and isopropyl radicals suggests that the electron affinity of *t*-butyl radical is smaller than that of isopropyl radical. Since 1-adamantyl radical is not so much stabilized as *t*-butyl radical because of its rigid structure,[17] the electron affinity should be much higher than that of *t*-butyl radical. Hence the easiness of the oxidation of the alkyl anion into the corresponding free radical is in the following order:

$$\mathrm{Me} < \mathrm{Et},\ \mathrm{PhCH_2} < i\text{-Pr} < t\text{-Bu} \gg \text{1-Ad}$$

A similar order has recently been reported also for the rates of electron transfer reactions from Grignard reagents to di-*t*-butyl peroxide.[16]

In the case of isopropyl and *t*-butyl Grignard reagents, isopropyl and *t*-butyl anions are so easily oxidized into the corresponding free radicals by **1** that the free radical mechanism which produces **4** is predominant. However, in other cases the anions are not easily oxidized into the corresponding free radicals, so that the anionic mechanism which produces oximes **2** and **3** is predominant. Consequently the Grignard reagents containing an anionic center which is more easily oxidized than isopropyl anion are expected to afford the secondary amine **4** in the reaction with **1**.

If such a free radical mechanism is actually operative, the *t*-butyl radicals derived from the Grignard reagent, in the reaction system composed of *t*-butylmagnesium chloride and an excess of the nitrosobenzene **1**, are expected to attack **1** itself on the oxygen atom, because tertiary alkyl radicals are trapped by **1** on the oxygen atom.[4,18]

This possibility was examined by the following inverse Grignard reaction. To a solution of **1** in ether, an ethereal solution of *t*-butylmagnesium chloride was added dropwise, but the total amount of the Grignard reagent added was a large excess in order to attain a similar final condition. This reaction resulted in the formation of 1-*t*-butoxyimino-2,4,4,6-tetra-*t*-butyl-2,5-cyclohexadiene (**8**) at the expense of **4d**; **8** is the same type of compound as **9** produced by the reaction of **1** with 1-cyano-1-methylethyl radicals.[4]

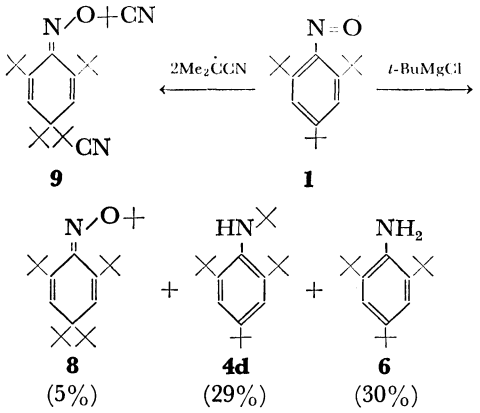
Thus, this result shows the existence of *t*-butyl radicals in the reaction system, and therefore substantiate the free radical mechanism mentioned above.

The reaction of **1** with *t*-butylmagnesium chloride

Table 2. Relation between yields of reaction products and electron affinities of alkyl radicals

R	Me	Et	*i*-Pr	*t*-Bu	$PhCH_2$	1-Ad
4 (%)	—	—	6	43	—	—
2 + **3** (%)	50	56	56	trace	73	55
Electron affinities of R· (eV)	1.1[a]	0.9[a]	0.6[a]	—	1.8[a], 0.9[b]	—
$-\log k$[c] (l. mol^{-1} sec^{-1})	5.4	3.8	2.8	2.3	—	—

a) Data from electrode reactions.[14] b) Data in gas phase.[15] c) *k* denotes the rate constants of the reaction of Grignard reagents with di-*t*-butyl peroxide.[16]



gave a considerable amount of **6** in contrast with the reactions with the other five Grignard reagents. Considering the facility of an electron transfer from *t*-butylmagnesium chloride mentioned above, the following pathway appears to be the most probable for the formation of the aniline (**6**): the radical **7** initially formed by an electron transfer from *t*-butylmagnesium chloride as in the formation of **4** is further reduced by the Grignard reagent to give **10**, hydrolysis of which afford **6**.[19]

$$\underset{\mathbf{1}}{Ar\text{-}N{=}O} \xrightarrow{RMgX} \underset{\mathbf{7}}{ArNOMgX} \xrightarrow{2RMgX} \underset{\mathbf{10}}{ArN(MgX)_2} \xrightarrow{H_2O} \underset{\mathbf{6}}{ArNH_2}$$

(Ar: 2,4,6-(t-Bu)$_3$C$_6$H$_2$)

The formation mechanism of **5c** is obscure. Since a nucleophilic substitution on the aromatic ring of **1** is improbable, it was presumably formed by reduction of oxime **2c** accompanied by elimination of *t*-butyl group.

Experimental

All melting points were not corrected. The IR and UV spectra were recorded with Hitachi EPI-G2 and Hitachi EPS-3 spectrophotometers respectively. The NMR spectra were measured with a Hitachi R-24 (60 MHz) spectrometer using tetramethylsilane as an internal standard. The mass spectra were recorded with a Hitachi RMU-6L mass spectrometer. All reactions were carried out under nitrogen. Chromatographic separations were performed using dry column chromatography method (Woelm silica gel for dry column chromatography) unless otherwise noted.

Materials. 2,4,6-Tri-*t*-butylnitrosobenzene (**1**),[1] (mp 166.0—166.5 °C; lit, 166—168 °C), 2,4,6-tri-*t*-butylaniline (**6**), (mp 135.5—138.6 °C; lit, 147—148 °C),[13] 2,4,6-tri-*t*-butyl-*N*-methylaniline (**4a**), (mp 109.5—111.0 °C; lit, 111—112 °C),[13] and 2,4,6-tri-*t*-butyl-*N*-ethylaniline (**4b**), (mp 79.5—81.0 °C; lit, 77.78 °C)[13] were prepared by the reported methods.

*Reaction of 2,4,6- Tri- t- butylnitrosobenzene (**1**) with Methylmagnesium Iodide.* To an ice-cold ethereal solution (25 ml) of methylmagnesium iodide (31 mmol), 2 g (7.3 mmol) of **1** in 30 ml of ether was added with stirring. After stirring at 0 °C for 3.5 hr, the reaction mixture was poured into cold aqueous ammonium chloride, extracted with ether, washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent *in vacuo*, the residue (1.9 g) was chromatographed on silica gel. Elution with carbon tetrachloride gave 147 mg of white crystals, which were submitted to dry column chromatography with carbon tetrachloride to give 30 mg (2%) of 2,4,6-tri-*t*-butylaniline (**6**), the IR and NMR spectra of which were identical with those of an authentic sample, and 83 mg (4%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-4-methyl-2,5-cyclohexadiene (**3a**), which was recrystallized three times from aqueous methanol, mp 119.5—120 °C; IR (KBr): 3250 (νOH) and 960 cm^{-1} (νNO); NMR (CCl_4): δ 0.83 (s, 9H), 1.05 (s, 3H), 1.21 (s, 18H), 5.77 (ABq, $\Delta\delta$=0.11, J=2 Hz, 2H), and 7.68 (broad s, 1H); λ_{max} (*n*-hexane): 243 nm (ε 10300); MS: *m/e* 291 (M$^+$, trace), 235 (34%), 218 (43), 202 (46), and 57 (100).

Found: C, 78.29; H, 11.06; N, 5.03%. Calcd for $C_{19}H_{33}NO$: C, 78.28; H, 11.42; N, 4.80%.

Elution with benzene gave 915 mg (46%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**2a**), which was recrystallized three times from *n*-hexane, mp 160.8—161.5 °C; IR (KBr): 3250 (νOH) and 960 cm^{-1} (νNO); NMR ($CDCl_3$): δ 0.96 (s, 9H), 1.08 (s, 9H), 1.32 (s, 12H), 5.42 (d, J=2 Hz, 1H), 6.15 (d, J=2 Hz, 1H), and 9.30 (broad s, 1H); λ_{max} (*n*-hexane): 304 nm (ε 4400); MS: *m/e* 291 (M$^+$, trace), 235 (42%), 218 (60), 204 (46), 202 (41), and 57 (100).

Found: C, 78.29; H, 11.06; N, 5.03%. Calcd for $C_{19}H_{33}NO$: C, 78.28; H, 11.42; N, 4.80%.

Further elution with dichloromethane afforded only tarry mass which could not be identified.

*Reaction of **1** with Ethylmagnesium Bromide.* To an ice-cold ethereal solution (30 ml) of ethylmagnesium bromide (73 mmol), 2 g (7.3 mmol) of **1** in 25 ml of ether was added dropwise during 15 min with stirring. After additional stirring at 0 °C for 1 hr, the reaction mixture was worked up as usual to give 1.79 g of the residue, which was chromatographed with carbon tetrachloride. The column could be divided into six fractions, each of which was eluted with ether, and the solvent was removed. From the first fraction a trace of **1** was recovered. The second fraction gave white crystals (129 mg), which were tentatively assigned as an isomer of 1-hydroxyimino-2,4,6-tri-*t*-butyl-6-ethyl-2,4-cyclohexadiene (**2b**) from the spectral data, but not purified, IR (KBr): 3300 (νOH) and 970 cm^{-1} (νNO); NMR (CCl_4): δ 0.83 (t, J=7 Hz, 3H), 0.84 (s, 9H), 1.05 (s, 9H), 1.23 (s, 9H), 2.50 (m, 2H), 5.15 (d, J=2 Hz, 1H), and 6.13 (d, J=2 Hz, 1H, and the signal of OH proton was obscure); λ_{max} (*n*-hexane): 311 nm (ε 3400); MS: *m/e* 305 (M$^+$, 2%), 249 (46), 232 (79), 218 (41), 216 (59), and 57 (100).

The third fraction afforded 143 mg (8%) of **6**. The fourth fraction afforded 692 mg (30%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-4-ethyl-2,5-cyclohexadiene (**3b**), which was recrystallized five times from methanol, mp 120.2—121.1 °C; IR (KBr): 3300 (νOH) and 970 cm^{-1} (νNO); NMR ($CDCl_3$): δ 0.67 (t, J=7 Hz, 3H), 0.85 (s, 9H), 1.27 (s, 18H), 1.65 (q, J=7 Hz, 2H), 5.75 (ABq $\Delta\delta$=0.14, J=2 Hz, 2H), and 8.24 (broad s, 1H): λ_{max} (*n*-hexane): 246 nm (ε 8800); MS: *m/e* 305 (M$^+$, trace), 249 (49%), 232 (63), 216 (58), and 57 (100).

Found: C, 78.56; H, 11.36; N, 4.52%. Calcd for $C_{20}H_{35}NO$: C, 78.63; H, 11.55; N, 4.58%.

The fifth fraction gave 589 mg (26%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-6-ethyl-2,4-cyclohexadiene (**2b**), which was recrystallized four times from methanol, mp 123.5—124.5 °C; IR (KBr): 3400 (νOH) and 970 cm^{-1} (νNO); NMR ($CDCl_3$): δ 0.75 (t, J=7 Hz, 3H), 0.93 (s, 9H), 1.10 (s, 9H), 1.33 (s, 9H), 1.4—2.3 (m, 2H), 5.33 (d, J=1.5 Hz, 1H), 6.22 (d, J=1.5 Hz, 1H), and 9.75 (broad s, 1H); λ_{max} (*n*-hexane): 308 nm (ε 4400); MS: *m/e* 305 (M$^+$, 0.5%),

249 (37), 232 (62), 218 (37), 216 (43), and 57 (100).

Found: C, 78.69; H, 11.20; N, 4.74%. Calcd for $C_{20}H_{35}NO$: C, 78.63; H , 11.55; N, 4.58%.

Reaction of **1** *with Isopropylmagnesium Bromide.* To an ice-cold ethereal solution (30 ml) of isopropylmagnesium bromide (73 mmol), 2 g (7.3 mmol) of **1** in 23 ml of ether was added dropwise during 15 min with stirring. After additional stirring at 0 °C for 30 min, the reaction mixture was worked up as usual to give 1.95 g of a tarry material, which was chromatographed with carbon tetrachloride. The column could be divided into six fractions. The first fraction gave 129 mg (6%) of 2,4,6-tri-*t*-butyl-*N*-isopropylaniline (**4c**), which was recrystallized three times from methanol, mp 80.5—81.0 °C; IR (KBr): 3440 cm^{-1} (νNH); NMR (CCl_4): δ 0.94 (d, J=7 Hz, 6H), 1.28 (s, 9H), 1.43 (s, 18H), 3.42 (sep, J=7 Hz, 1H), 3.90 (broad s, 1H), and 7.07 (s, 2H); λ_{max} (*n*-hexane): 256.5 (ε 7500) and 292 nm (1400); MS: *m/e* 303 (M^+, 41%) and 288 (100).

Found: C, 83.04; H, 12.27; N, 4.90%. Calcd for $C_{21}H_{37}N$: C, 83.10; H, 12.29; N, 4.61%.

The second fraction afforded 308 mg of a mixture of **2c** and **3c** (by NMR). Further twice dry column chromatography with carbon tetrachloride gave 53 mg (2%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-6-isopropyl-2,4-cyclohexadiene (**2c**), which was recrystallized three times from methanol, mp 117—120 °C; IR (KBr): 3300 (νOH) and 975 cm^{-1} (νNO); NMR (CCl_4): δ 0.71 (d, J=7 Hz, 6H), 1.07 (s, 9H), 1.13 (s, 9H), 1.24 (s, 9H), 3.72 (sep, J=7 Hz, 1H), 5.62 (d, J=2 Hz, 1H), and 6.12 (d, J=2 Hz, 1H, and the signal of OH proton was obscure); λ_{max} (*n*-hexane): 311 nm (ε 4900); MS: *m/e* 319 (M^+, trace), 263 (19%), 246 (63), 232 (56), 230 (70), and 57 (100).

Found: C, 78.53; H, 11.67; N, 4.20%. Calcd for $C_{21}H_{37}NO$: C, 78.94; H, 11.67; N, 4.38%.

The third fraction gave 1.24 g (54%) of 1-hydroxyimino-2,4,6-tri-*t*-butyl-4-isopropyl-2,5-cyclohexadiene (**3c**) as a tarry material, which crystallized on cooling and was recrystallized five times from cold methanol at −78 °C, mp 73.5—74.5 °C; IR (neat): 3330 (νOH) and 975 cm^{-1} (νNO); NMR ($CDCl_3$): δ 0.96 (d, J=7 Hz, 6H), 0.93 (s, 9H), 1.27 (s, 18H), 1.95 (sep, J=7 Hz, 1H), 5.90 (ABq, $\Delta\delta$=0.16, J= 2 Hz, 2H, and the signal of OH proton was obscure, but in carbon tetrachloride solution observed at 8.60 as a broad singlet); λ_{max} (*n*-hexane): 246.5 nm (ε 8800); MS: *m/e* 319 (M^+, trace), 263 (41%), 246 (54), 230 (61), and 57 (100).

Found: C, 79.04; 11.75; N, 4.56%. Calcd for $C_{21}H_{37}NO$: C, 78.94; H, 11.67; N, 4.38%.

The fourth fraction afforded 50 mg (3%) of 2,4-di-*t*-butyl-6-isopropylaniline (**5c**), which was recrystallized twice from methanol and identical with an authentic sample obtained from the reaction of 2,4,6-tri-*t*-butylnitrobenzene with isopropylmagnesium bromide[22] with respect to the spectral data, mp 84—85 °C; IR (KBr): 3485 and 3405 cm^{-1} (νNH_2); NMR (CCl_4): δ 1.20 (d, J=7 Hz, 6H), 1.26 (s, 9 H), 1.43 (s, 9H), 2.89 (sep, J=7 Hz, 1H), 3.54 (broad s, 2H), and 7.00 (ABq, $\Delta\delta$=0.08, J=2 Hz, 2H); MS: *m/e* 247 (M^+, 23%) and 232 (100).

Reaction of **1** *with* t-*Butylmagnesium Chloride.* To an ice-cold ethereal solution (40 ml) of *t*-butylmagnesium chloride (73 mmol), 2 g (7.3 mmol) of **1** in 15 ml of ether was added dropwise during 10 min with stirring. After additional stirring at 0 °C for 50 min, the reaction mixture was worked up as usual to give 1.79 g of crystals, which were chromatographed with carbon tetrachloride. The column was divided into four fractions. The first fraction gave 993 mg (43%) of 2,4,6,*N*-tetra-*t*-butylaniline (**4d**), which was recrystallized four times from methanol, mp 63—64.5 °C; IR (KBr): 3045 cm^{-1} (νNH); NMR ($CDCl_3$): δ 0.93 (s, 9H), 1.28 (s, 9H), 1.42 (s, 18H), 3.00 (broad s, 1H), and 7.14 (s, 2H); λ_{max} (*n*-hexane): 223 (ε 1680) and 260 nm (4200); MS: *m/e* 317 (M^+, 11%), 302 (4), 261 (33), and 246 (100).

Found: C, 83.33; H, 12.22; N, 4.21%. Calcd for $C_{22}H_{39}N$: C, 83.21; H, 12.38; N, 4.41%.

The second fraction afforded 714 mg (38%) of **6**. The third fraction gave 84 mg of a colorless tarry substance, which was again chromatographed with carbon tetrachloride. On the basis of the spectral data (IR and NMR) the resulting material was identified as 1-hydroxyimino-2,4,4,6-tetra-*t*-butyl-2,5-cyclohexadiene (**3d**), but failed to be isolated in pure state, IR (neat): 3300 (νOH) and 955 cm^{-1} (νNO); NMR (CCl_4): δ 1.01 (s, 18H), 1.25 (s, 18H), 6.17 (ABq, $\Delta\delta$=0.12, J=2 Hz, 2H, and the signal of OH proton was obscure).

Reaction of **1** *with Benzylmagnesium Chloride.* To an ice-cold ethereal solution (30 ml) of the Grignard reagent (73 mmol), 2 g (7.3 mmol) of **1** in 15 ml of ether was added dropwise during 20 min with stirring. After additional stirring at 0 °C for 30 min, the reaction mixture was worked up as usual to give 4.2 g of partly crystalline substance, which was chromatographed with carbon tetrachloride. The column could be divided into five fractions. The first and the second fractions gave 1.4 g of bibenzyl and 150 mg (6%) of **6** respectively. The third fraction gave 1.16 g (44%) of 1-hydroxyimino-4-benzyl-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**3e**), which was recrystallized four times from methanol, mp 169.7—170.8 °C; IR (KBr): 3280 cm^{-1} (νOH); NMR ($CDCl_3$): δ 0.98 (s, 9H), 1.09 (s, 9H), 1.21 (s, 9H), 3.04 (s, 2H), 5.95 (s, 2H), 7.12 (s, 5H), and 7.55 (broad s, 1H); λ_{max} (*n*-hexane): 247 nm (ε 9200); MS: *m/e* 367 (M^+, trace), 311 (34%), 294 (32), 278 (28), 91 (79), and 57 (100).

Found: C, 81.88; H, 10.38; N, 4.01%. Calcd for $C_{25}H_{37}NO$: C, 81.69; H, 10.15; N, 3.81%.

The fourth fraction gave 776 mg (29%) of 1-hydroxyimino-6-benzyl-2,4,6-tri-*t*-butyl-2,4-cyclohexadiene (**2e**), which was recrystallized four times from methanol, mp 158—158.5 °C; IR (KBr): 3280 cm^{-1} (νOH); NMR ($CDCl_3$): δ 0.89 (s, 9H), 0.99 (s, 9H), 1.28 (s, 9H), 2.85 (d, J=15 Hz, 1H), 3.78 (d, J=15 Hz, 1H), 5.47 (d, J=2 Hz, 1H), 6.20 (d, J=2 Hz, 1H), 7.14 (s, 5H), and 8.75 (broad s, 1H); λ_{max} (*n*-hexane): 313 nm (ε 4000); MS: *m/e* 367 (M^+, 1.5%), 311 (32), 294 (100), 276 (15), 278 (26), 91 (43), and 57 (82).

Found: C, 81.91; H, 10.33; N, 3.85%. Calcd for $C_{25}H_{37}NO$: C, 81.74; H, 10.08; N, 3.81%.

Reaction of **1** *with 1-Adamantylmagnesium Bromide.* To an ice-cold ethereal solution (31 ml) of the Grignard reagent (42 mmol), 1.76 g (6.4 mmol) of **1** in 24 ml of ether was added dropwise during 1 hr with stirring. The reaction mixture was worked up as usual to give 7.9 g of light green tar, which was chromatographed with carbon tetrachloride as eluent. The column could be divided into four fractions. The first fraction gave 5 g of a light green crystalline material, which was composed mainly of decomposition product of the Grignard reagent, but contained 300 mg of unchanged **1** according to the signal intensity on the NMR spectra. Yields were calculated on the base of **1** consumed. The second fraction, colorless tarry mass, was a mixture of **6** (36 mg, 3%) and 1-hydroxyimino-4-(1-adamantyl)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**3f**, 1.2 g, 55%) according to the signal intensity on the NMR spectra. By further chromatography with carbon tetrachloride, **3f** was isolated, but **6** could not be isolated in pure state. **3f**: mp 135—136 °C

(five times from methanol); IR (KBr): 3300 (νOH) and 960 cm^{-1} (νNO); NMR (CCl_4): δ 1.05 (s, 9H), 1.28 (s, 18H), 1.60 (broad s, 6H), 1.82 (broad s, 9H), 6.15 (ABq, $\Delta\delta$=0.1, J=2 Hz, 2H), and 7.86 (s, 1H); λ_{max} (*n*-hexane): 251 nm (ε 9300); MS: *m/e* 411 (M^+, trace), 355 (2%), 354 (3), 339 (6), 338 (3), 324 (5), 322 (3), 244 (23), 135 (100), and 57 (31).

Found: C, 81.72; H, 10.71; N, 3.36%. Calcd for $C_{28}H_{45}NO$: C, 81.69; H, 11.03; N, 3.40%.

The subsequent fractions afforded about 700 mg of unidentified materials, which could not be isolated in pure state.

Reaction of **1** *with* t-*Butylmagnesium Chloride (Inverse Addition).* To an ice-cold solution of 1.5 g (5.5 mmol) of **1** in 10 ml of ether, an ethereal solution (43 ml) of the Grignard reagent (55 mmol) was added dropwise with stirring during 30 min. After additional stirring at 0 °C for 30 min, the reaction mixture was worked up as usual to give 1.5 g of pale yellow, partly crystalline material, which was chromatographed with *n*-hexane. The column could be divided into three fractions. The first fraction gave 110 mg (5%) of 1-*t*-butoxyimino-2,4,4,6-tetra-*t*-butyl-2,5-cyclohexadiene (**8**) as colorless oil, which was purified by TLC (silica gel, *n*-hexane) and distilled once *in vacuo*, IR (neat): 960 cm^{-1} (νNO); NMR (CCl_4): δ 1.00 (s, 18H), 1.21 (s, 9H), 1.29 (s, 18H), and 6.15 (ABq, $\Delta\delta$=0.1, J=2 Hz, 2H); λ_{max} (*n*-hexane): 260 nm (ε 6700); MS: *m/e* 332 (38%), 276 (88), 244 (43).

Found: C, 80.26; H, 11.81; N, 3.89%. Calcd for $C_{26}H_{47}NO$: C, 80.14; H, 12.16; N, 3.59%.

The second fraction gave 477 mg (29%) of **4d**. The third fraction was again chromatographed with a mixture of *n*-hexane and dichloromethane (2 : 1) as eluent. The column could be divided into three fractions. The first fraction gave 421 mg (30%) of **6**. The second fraction afforded 49 mg (3%) of 1-hydroxyimino-2,4,4,6-tetra-*t*-butyl-2,5-cyclohexadiene (**3d**) as white crystals, which were recrystallized three times from aqueous methanol, mp 123—127 °C. Although satisfactory elemental analysis could not be obtained, the following spectral data suggested the structure **3d**; IR (KBr): 3300 (νOH) and 955 cm^{-1} (νNO); NMR (CCl_4): δ 1.02 (s, 18H), 1.26 (s, 18H), 6.17 (ABq, $\Delta\delta$=0.12, J=2 Hz, 2H), and 8.0 (broad s, 1H); λ_{max} (*n*-hexane): 249 nm (ε 9700); MS: *m/e* 277 (16%), 276 (14), 260 (28), 246 (30), 244 (43), and 57 (100).

The subsequent fractions gave 82 mg of partly crystalline substance, which could not be purified.

Mass Spectra of Anilines ***4a***, ***4b***, *and* ***6a***. **4a**; *m/e* 275 (M^+, 30%) and 260 (100). **4b**; *m/e* 239 (M^+, 47%) and 224 (100). **6**; *m/e* 261 (M^+, 27%) and 246 (100).

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19) The possibility of the reduction of **1** into **6** with magnesium metal, probably in combination with magnesium halides or impurities in the metal, cannot be ruled out completely.[20,21] If **6** is formed in such a way, the yield of **6** should be constant irrespective of the Grignard reagents used, but this is not the case. Therefore the reduction with magnesium metal may not be a predominant pathway leading to **6**.

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