# Oxidation of 4-Alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes: Formation of 4-Alkyl-2,6-di-*t*-butylnitrobenzenes *via* Iminoxyl Radical

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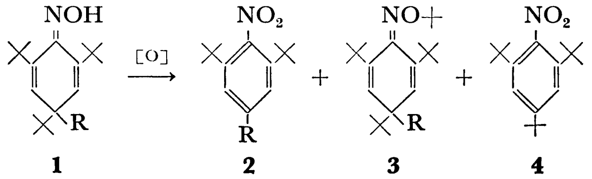
Reactions of 4-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**1**) with silver(I) oxide afforded 4-alkyl-2,6-di-*t*-butylnitrobenzenes (**2**) mainly, which were found to be formed *via* an iminoxyl radical on the base of the ESR spectra and by-products, 4-alkyl-1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**3**). This reaction is a novel oxidative decomposition of iminoxyl radical and provides a practical preparative method for the nitrobenzenes (**2**). Oxidation of **1** with other reagents (nickel peroxide and *m*-chloroperbenzoic acid) and oxidation of 6-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,4-cyclohexadienes (**5**) have also been described.

Although many iminoxyl radicals have been studied by means of ESR, there have been only two examples of iminoxyl radicals which were so stable as to be isolated.[1,2] We attempted to prepare and isolate another type of stable iminoxyl radicals by hydrogen abstraction from highly sterically hindered oximes, 4-alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**1**) which were prepared from 2,4,6-tri-*t*-butylnitroso-[3a] and -nitrobenzenes.[3b] Intermediary iminoxyl radical was observed by ESR, but could not be isolated because of further reaction. We describe here the novel oxidative decomposition of the iminoxyl radical found during this attempt and the usefulness of this reaction as a preparative method for 4-alkyl-2,6-di-*t*-butylnitrobenzenes (**2**).[4]

*Oxidation with Silver(I) Oxide or Nickel Peroxide.* The reaction of the oxime (**1**) with excess silver(I) oxide or nickel peroxide[5] in benzene at room temperature gave 4-alkyl-2,6-di-*t*-butylnitrobenzene (**2**) mainly, along with 4-alkyl-1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**3**) and 2,4,6-tri-*t*-butylnitrobenzene (**4**) as minor products. The yields of the products and reaction conditions are summarized in Table. The products were isolated by means of thin layer chromatography (TLC) and characterized by their spectral and analytical data except for **2d** where the pure specimen free from **4** has not been obtained owing to the similar $R_f$ value of **2d** and **4**, and the yield was determined by means of high speed liquid chromatography with a UV detector assuming that both **2d** and **4** have the same molar extinction coefficient at 254 nm.



**a**: R=Et; **b**: R=*i*-Pr; **c**: R=PhCH$_2$; **d**: R=1-Ad

There has been no practical method for the synthesis of 1-substituted 4-alkyl-2,6-di-*t*-butylbenzenes except for phenols and their derivatives:[6] the preparation of nitrobenzenes (**2**) by nitration of the corresponding hydrocarbons is very difficult owing to the bulky *t*-butyl groups, and for example, Mhyre *et al.* reported that nitration of 3,5-di-*t*-butyltoluene affords the corresponding 2- and 4-nitro derivatives in 98.5 and 1.5% yields respectively.[7] Therefore, the present reaction provides a convenient method for the synthesis of **2**. Furthermore, in view of a key role of a nitro group in synthetic chemistry, this reaction might also give an access to other various derivatives.

Similar oxidation of 1-hydroxyimino-6-methyl-2,4,6-tri-*t*-butyl-2,4-cyclohexadiene (**5**) with silver(I) oxide afforded 2,4-di-*t*-butyl-6-methylnitrobenzene (**6**), the corresponding nitrosobenzene (**7**), and 1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**8**) (see Table).

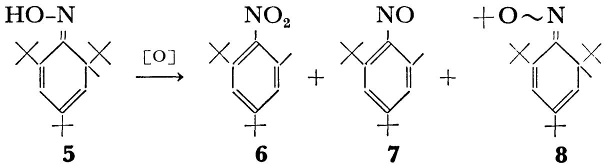


TABLE. YIELDS OF THE PRODUCTS

| No. | Oxime | R | Oxidizing agent | Reaction time (h) | **2** (%) | Other product (%) |
|---|---|---|---|---|---|---|
| 1 | **1a** | Et | $Ag_2O$ | 24.5 | 56 | **3a**(17) |
| 2 | **1b** | *i*-Pr | $Ag_2O$ | 24 | 96 | |
| 3[a] | **1b** | *i*-Pr | $Ag_2O$ | 24.5 | 56 | **3b**(13) |
| 4 | **1b** | *i*-Pr | Ni-PO | 22.3 | 37 | |
| 5 | **1c** | $PhCH_2$ | $Ag_2O$ | 24.5 | 55 | **3c**(9), **4**(10) |
| 6 | **1c** | $PhCH_2$ | MCPBA[b] | 24 | 37 | |
| 7 | **1d** | 1-Ad[c] | $Ag_2O$ | 21 | 48 | **4** (26) |
| 8 | **1d** | 1-Ad[c] | MCPBA[b] | 22.5 | 10 | **4** (28) |
| 9 | **5** | | $Ag_2O$ | 0.5 | | **6**(14), **7**(14), **8**(16) |

a) Reaction in a degassed system. b) *m*-Chloroperbenzoic acid. c) 1-Adamantyl group.

*ESR Study of the Reaction.* During the reactions of **1** with a defficient amount of nickel peroxide (Ni-PO), lead(IV) dioxide ($PbO_2$), or silver(I) oxide ($Ag_2O$), a strong ESR signal (Type A; $a_N=32$ G, $a_H=4$ G, $g=2.006$) was recorded irrespective of the 4-substituent (Fig. 1). This signal was identical with that observed in the reaction of **1** with photo-excited benzophenone,[8] which has been reported to be an excellent reagent for the formation of an iminoxyl radical from an oxime.[9] Therefore, Type A signal is assignable to the corresponding iminoxyl radical (**9**). The signal was so stable that the intensity was not reduced even after a day at room temperature under air. The line shape varied reversibly with temperature (Fig. 2), and this may be ascribed to a conformational change. The line shape was also changed by the solvent (Fig. 2).

When an excess amount of Ni-PO, $PbO_2$, or $Ag_2O$, was used, Type A signal was recorded at first, but the signal rapidly decreased in its intensity and changed into a signal due to another iminoxyl radical (Type B; $a_N=32$ G, $g=2.006$) (Fig. 3), whose structure remains unknown.

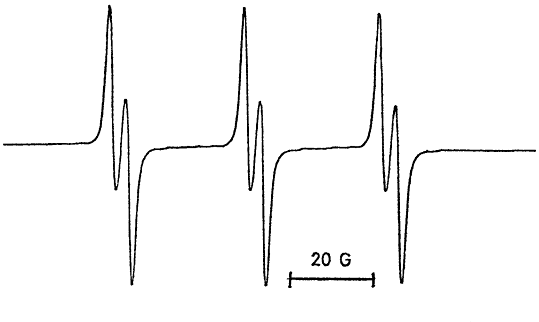


Fig. 1. Type A signal obtained by the reaction of **1b** with Ni-PO in benzene at room temperature.

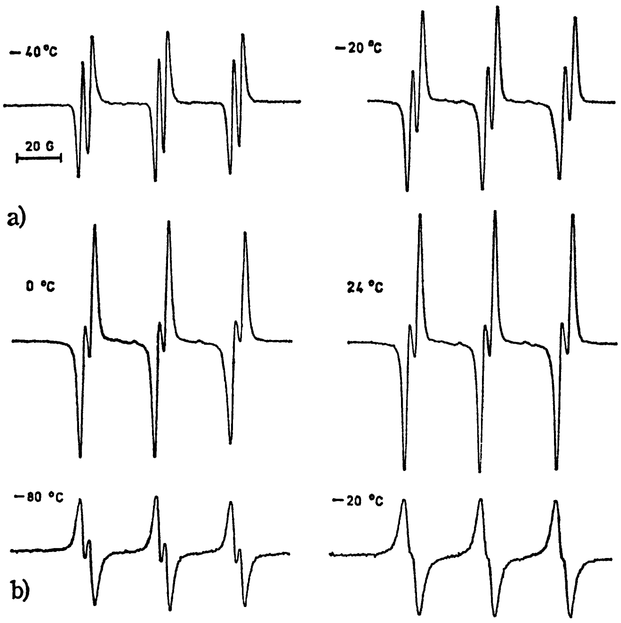


Fig. 2. Temperature and solvent dependence of the line shape of Type A signal: a) **1b**+photoexcited benzophenone in $CH_2Cl_2$, b) **1b**+photoexcited benzophenone in hexane.

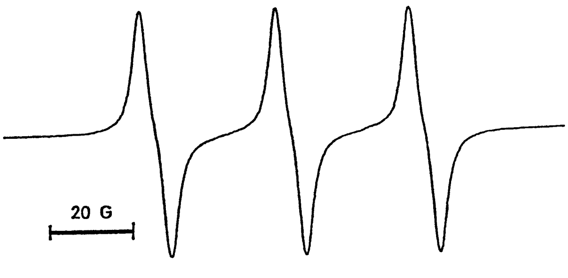


Fig. 3. Type B signal obtained by the reaction of **1c** with an excess amount of Ni-PO in hexane at room temperature.

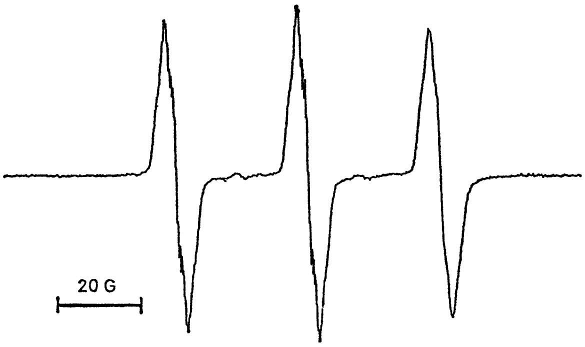
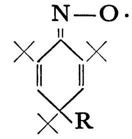


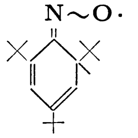
Fig. 4. Type C signal obtained by the reaction of **5** with photoexcited benzophenone in $CH_2Cl_2$ at −84 °C.

On the other hand, Type C signal ($a_N=32$ G, $g=2.006$) (Fig. 4) was observed during the oxidation of oxime (**5**) with photo-excited benzophenone and this may be assigned to the iminoxyl radical (**10**). Reaction of oxime (**5**) with excess Ni-PO, $PbO_2$, or $Ag_2O$ gave a signal similar to Type B signal ($a_N=32$ G, $g=2.006$).

The iminoxyl radical (**9**) showed a splitting due to one of the protons on the 3- or 5-position; such a long range coupling is characteristic of iminoxyl radicals[10] and often observed in $\sigma$-radicals.[11] It is interesting that the iminoxyl radical (**10**) did not show any such splitting due to the ring proton.

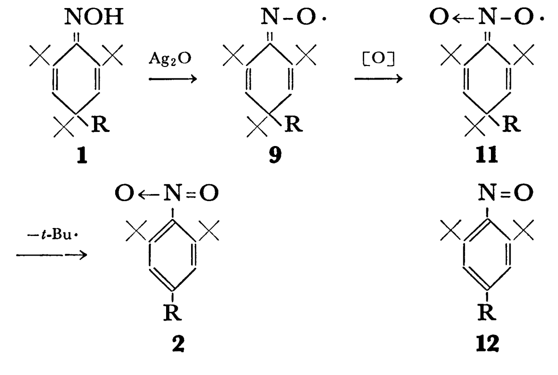


**9**



**10**

*Reaction Mechanism.* The nitrobenzenes (**2**) are considered to be formed *via* the initially produced iminoxyl radicals (**9**) in the following manner.



This pathway is supported by the observation of a strong ESR signal due to **9**, which was destroyed by excess oxidizing agents, and the formation of the oxime ether (**3**) by the combination between **9** and *t*-butyl radical.

An alternative route *via* 4-alkyl-2,6-di-*t*-butylnitrosobenzene (**12**), which might be formed by the elimination of a *t*-butyl radical from **9** can be ruled out, because 2,4,6-tri-*t*-butylnitrosobenzene was never oxidized into **4** by Ni-PO or $Ag_2O$ at room temperature even after a day.

We consider a similar mechanism can also be applied to the oxidation of **5**. In this case, however, elimination of *t*-butyl radical from the initially formed iminoxyl radical (**10**) also took place as suggested by the formation of a considerable amount of 2,4-di-*t*-butyl-6-methylnitrosobenzene (**7**).

The source of the oxygen which is responsible for the oxidation of **1** into **2** remains obscure: although involvement of stubbornly adsorbed oxygen may be possible, the oxygen seems to stem from the silver(I) oxide, because **9** is fairly stable even under air as suggested by before-mentioned ESR spectroscopy, also because the formation of **2** was still observed even in the degassed solvent and with degassed silver(I) oxide. The reaction of **1b** in a degassed system (No. 3 in Table) afforded also **3b** besides **2b** in contrast to the reaction under air. This formation of **3b** is probably ascribed to the prolonged life times of **9b** and the eliminated *t*-butyl radicals in the absence of oxygen. Therefore, it seems preferable to carry out the reaction in the presence of atmospheric oxygen in order to obtain **2** in a high yield.

This reaction is a novel type of fragmentation of iminoxyl radicals and the first example of the formation of nitro compound in silver(I) oxide oxidation of oximes. This unusual reaction is ascribable to the following two reasons: first, the bulky *t*-butyl groups on **9** make a barrier against intermolecular coupling which is a main decomposition pathway in usual iminoxyl radicals; secondly, an inclination of the cyclohexadienone oxime system to aromatize by an elimination of the bulky *t*-butyl group favours the reaction energetically.

In the cases of **1a** and **1b**, the selective elimination of the *t*-butyl group took place, while in the cases of **1c** and **1d**, a considerable amount of **4** which represents the elimination of benzyl or 1-adamantyl group, respectively, was obtained. These facts imply that the elimination of 1-adamantyl radical which is less stable than *t*-butyl radical$^{12)}$ competed with that of *t*-butyl radical, and that the elimination of *t*-butyl radical was favorable over that of benzyl radical although the latter is more stable than the former. Therefore, it is concluded that the more bulky group is selectively eliminated, although elimination of a small group can competitively occur if it is more stable as a free radical than a bulky group.

*Oxidation with* m-*Chloroperbenzoic Acid.* The reaction of **1** with *m*-chloroperbenzoic acid is interesting, because it is expected that the reaction is initiated by heterolytic oxidation of the nitrogen of the oxime, suggesting elimination of *t*-butyl group as a cation. Thus there must be some differences in the reaction products compared with the silver(I) oxide oxidation. The reaction afforded similar products to those obtained in the silver(I) oxide oxidation (Table), but the product ratio **2d**/**4** was inversed. Although the yields of the nitro compounds were relatively low, this inversion seems to imply the mechanistic difference between the two reactions.

## Experimental

All melting points were not corrected. The IR and UV spectra were recorded with Hitachi EPI-G2 and 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. The ESR spectra were recorded with a JEOL JES-ME spectrometer and *g* values were determined on the basis of $Mn^{2+}$ marker. Solvents were not degassed unless otherwise noted.

*Materials.* 4-Alkyl-1-hydroxyimino-2,4,6-tri-*t*-butyl-2,5-cyclohexadienes (**1**),$^{3)}$ 1-hydroxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**5**),$^{3)}$ 2,4,6-tri-*t*-butylnitrosobenzene,$^{13)}$ 2,4-di-*t*-butyl-6-methylnitrosobenzene (**7**),$^{13)}$ 2,4,6-tri-*t*-butylnitrobenzene (**4**),$^{14)}$ and 2,4-di-*t*-butyl-6-methylnitrobenzene (**6**)$^{14)}$ were prepared by the reported methods.

*Oxidation of 1-Hydroxyimino-2,4,6-tri-*t*-butyl-4-ethyl-2,5-cyclohexadiene (**1a**) with Silver(I) Oxide.* To a suspension of a few hundred miligrams of silver(I) oxide in 2 ml of benzene was added a benzene solution (2 ml) of 40.4 mg (0.132 mmol) of **1a**. After the mixture was stirred for 24.5 h at room temperature, the insoluble part was filtered off. After removal of the solvent from the filtrate, the residue was treated with TLC (silica gel, hexane–benzene (4 : 1)), and each fraction was eluted with ether. The first fraction ($R_f$=0.83) gave 8.0 mg (17%) of 1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-4-ethyl-2,5-cyclohexadiene (**3a**) as a tarry material, which was purified by TLC (silica gel, hexane) followed by molecular distillation. IR (neat): 965 $cm^{-1}$ (NO); NMR ($CCl_4$): $\delta$ 0.65 (t, $J$=7 Hz, 3H), 0.82 (s, 9H), 1.22 (s, 9H), 1.28 (s, 9H), 1.32 (s, 9H), 1.65 (q, $J$=7 Hz, 2H), and 5.75 (ABq, $\Delta\delta$=0.13, $J$=2 Hz, 2H); $\lambda_{max}$ (hexane): 258 nm ($\varepsilon$ 5940); MS: *m*/*e* 304 (M−57, 32%) and 57 (100%).

The second fraction ($R_f$=0.67) gave 19.3 mg (56%) of **2a** which was recrystallized four times from aqueous methanol, mp 100.5—101.5 °C; IR (KBr): 1525 and 1375 $cm^{-1}$ ($NO_2$); NMR ($CCl_4$): $\delta$ 1.31 (t, $J$=7 Hz, 3H), 1.42 (s, 18H), 2.70 (q, $J$=7 Hz, 2H), and 7.23 (s, 2H); $\lambda_{max}$ (hexane): 247 ($\varepsilon$ 960) and 348.5 nm (180); MS: *m*/*e* 263 ($M^+$, 19%) and 248 (100).

Found: C, 72.84; H, 9.43; N, 5.51%. Calcd for $C_{16}H_{25}NO_2$: C, 73.00; H, 9.51; N, 5.32%.

Another reaction under similar conditions afforded 64% of **2a**.

*Oxidation of 1-Hydroxyimino-2,4,6-tri-*t*-butyl-4-isopropyl-2,5-cyclohexadiene (**1b**) with Silver(I) Oxide.* Reaction of 50.0 mg (0.156 mmol) of **1b** and a large excess of silver(I) oxide in 4.5 ml of benzene for 24 h followed by treatment with TLC (silica gel, hexane–benzene (4 : 1)), afforded 41.6 mg (96%) of 2,6-di-*t*-butyl-4-isopropylnitrobenzene (**2b**) as white crystals ($R_f$=0.78—0.61), which were recrystallized twice from aqueous methanol, mp 101—103 °C; IR (KBr): 1525 and 1370 $cm^{-1}$ ($NO_2$); NMR ($CCl_4$): $\delta$ 1.25 (d, $J$=7 Hz, 6H), 1.35 (s, 18H), 2.88 (sep, $J$=7 Hz, 1H), and 7.21 (s, 2H); $\lambda_{max}$ (hexane): 246 sh ($\varepsilon$ 1740) and 340 nm (350); MS: *m/e* 277 ($M^+$, 17%) and 262 (100). Crude material showed a peak at *m/e* 291 (trace) which indicates the contamination of trace of 2,4,6-tri-*t*-butylnitrobenzene (**4**).

Found: C, 73.68; H, 9.68; N, 4.98%. Calcd for $C_{17}H_{27}NO_2$: C, 73.65; H, 9.75; N, 5.05%.

*Reaction of **1b** with Silver(I) Oxide in Degassed System.* A few hundred miligrams of silver(I) oxide in 3.5 ml of dry benzene was degassed four times, and a solution of 44.3 mg (0.139 mmol) of **1b** in 0.5 ml of dry benzene was added under argon atmosphere. After the mixture was stirred for 24.5 h at room temperature, the insoluble part was filtered off. The filtrate was evaporated *in vacuo* and treated with TLC (silica gel, hexane–benzene (4 : 1)). A fraction with $R_f$ of 0.78 gave 6.8 mg (13%) of 1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-4-isopropyl-2,5-cyclohexadiene (**3b**) as colorless oil, IR (neat): 975 cm$^{-1}$ (NO); NMR ($CCl_4$): $\delta$ 0.90 (s, 9H), 1.22 (s, 9H), 1.29 (s, 9H), 1.32 (s, 9H), 5.89 (ABq, $\Delta\delta=0.15$, $J=2$ Hz, 2H), and the signals due to the isopropyl group were obscure; $\lambda_{max}$ (hexane): 259 nm ($\varepsilon$ 7590); MS: *m/e* 318 (M−57, 23%) and 57 (100),

Found: C, 80.00; H, 12.36; N, 3.69%. Calcd for $C_{25}H_{45}NO$: C, 79.93; H, 12.08; N, 3.92%.

A fraction with $R_f$ of 0.5 gave 21.6 mg (56%) of **2b**, which was identified by the IR and NMR spectra.

*Reaction of **1b** with Nickel Peroxide.* Reaction of **2b** (60.7 mg, 0.190 mmol) with a large excess of nickel peroxide in 5 ml of benzene for 22.3 h at room temperature followed by treatment with TLC (silica gel, hexane–benzene (4 : 1)) gave 18.6 mg (37%) of **2b**.

*Reaction of 1-Hydroxyimino-4-benzyl-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**1c**) with Silver(I) Oxide.* Reaction of **1c** (46.2 mg, 0.126 mmol) and a large excess of silver(I) oxide in 4 ml of benzene for 24.5 h at room temperature followed by TLC (silica gel, hexane–benzene (4 : 1)) afforded the following compounds. The first fraction ($R_f$=0.89) gave 5.0 mg (9%) of 1-*t*-butoxyimino-4-benzyl-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**3c**) as white crystals, which were recrystallized from aqueous methanol, mp 107—109 °C; IR (KBr): 750 cm$^{-1}$ (NO); NMR ($CCl_4$): $\delta$ 0.91 (s, 9H), 0.98 (s, 9H), 1.19 (s, 9H), 1.27 (s, 9H), 2.93 (s, 2H), 5.89 (s, 2H), and 7.12 (s, 5H); $\lambda_{max}$ (hexane): 259 nm ($\varepsilon$ 9540); MS: *m/e* 366 (M−57, 21%) and 57 (100).

Found: C, 82.34; H, 11.09; N, 3.34%. Calcd for $C_{29}H_{45}NO$: C, 82.21; H, 10.71; N, 3.30%.

A fraction with $R_f$ of 0.72 gave 3.9 mg (10%) of **4**. A fraction with $R_f$ of 0.56 afforded 22.7 mg (55%) of 4-benzyl-2,6-di-*t*-butylnitrobenzene (**2c**) as white crystals, mp 110—112 °C (from aqueous methanol); IR (KBr): 1525 and 1375 cm$^{-1}$ ($NO_2$); NMR ($CCl_4$): $\delta$ 1.32 (s, 18H), 3.95 (s, 2H), and 7.1—7.3 (m, 7H); $\lambda_{max}$ (hexane): 249 ($\varepsilon$ 1380), 254.5 (1380), 259 (1330), 262 sh (1250), 265 sh (1140), 269.5 (1202), and 345 nm (200); MS: *m/e* 325 ($M^+$, 29%) and 310 (100).

Found: C, 77.40; H, 8.58; N, 4.41%. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.37; N, 4.31%.

Another reaction under similar condition afforded **2c** (68) and **3c** (16%).

*Reaction of 1-Hydroxyimino-4-(1-adamantyl)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**1d**) with Silver(I) Oxide.* Reaction of **1d** (21.9 mg, 0.053 mmol) with a large excess of silver(I) oxide in benzene (2 ml) for 21 h at room temperature followed by treatment with TLC (silica gel, hexane–benzene (4 : 1)) gave 13.5 mg of white crystalline material, which was a mixture of **4** and 4-(1-adamantyl)-2,6-di-*t*-butylnitrobenzene (**2d**). The molar ratio was determined to be 1 : 2.3 (**4**; 26%, **2d**; 48%) by means of high speed liquid chromatography (styrene–divinylbenzene copolymer, methanol–aqueous ammonia (1%)) with a UV detector assuming that both **4** and **2d** have the same molar extinction coefficient at 254 nm. The spectral data of the mixture were as follows, IR (KBr): 1525 and 1380 cm$^{-1}$ ($NO_2$); NMR ($CCl_4$): $\delta$ 1.37 (s, 18H), 1.78 (m, 15H), 7.32 (s, 2H), and signals due to **4**; MS: *m/e* 369 ($M^+$ of **2d**, 13%), 354 (53), 291 ($M^+$ of **4**, 8), 276 (55), 135 ($Ad^+$, 32), and 57 (100).

*Reaction of 1-Hydroxyimino-4-benzyl-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**1c**) with m-Chloroperbenzoic Acid.* A dichloromethane solution (4 ml) of **1c** (50.0 mg, 0.14 mmol) and 98.1 mg (0.74 mmol) of *m*-chloroperbenzoic acid was stirred for 24 h at room temperature. Subsequently, the reaction mixture was shaken with an aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extract was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was treated with TLC (silica gel, hexane–benzene (4 : 1)). A fraction with $R_f$ of 0.63—0.51 gave 14.8 mg (37%) of consumed **1c** of **2c**. From a fraction with $R_f$ of 0.26—0.17, 5.8 mg (11.6%) of **1c** was recovered.

*Reaction of 1-Hydroxyimino-4-(1-adamantyl)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene (**1d**) with m-Chloroperbenzoic Acid.* A dichloromethane solution (4 ml) of *m*-chloroperbenzoic acid (132 mg, 0.765 mmol) and **1d** (48.2 mg, 0.117 mmol) was stirred for 22.5 h at room temperature. Usual work-up afforded 13.5 mg of white crystals, which were a mixture of **4** and **2d** according to the NMR and IR spectra, and the yields were calculated to be 28 and 10% respectively.

*Reaction of 1-Hydroxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**5**) with Silver(I) Oxide.* A mixture of **5** (134.4 mg, 0.46 mmol) and a large excess of silver(I) oxide in 8 ml of benzene was stirred for 35 min at room temperature. The mixture was worked up as usual and treated with TLC (silica gel, hexane–benzene (4 : 1)). A fraction with $R_f$ of 0.86–0.72 afforded 26.1 mg (16%) of 1-*t*-butoxyimino-2,4,6-tri-*t*-butyl-6-methyl-2,4-cyclohexadiene (**8**) as white crystals, mp 76—79 °C (from aqueous methanol); IR (KBr): 970 cm$^{-1}$ (NO); NMR ($CCl_4$): $\delta$ 0.86 (s, 9H), 1.09 (s, 9H), 1.31 (s, 18H), 1.55 (s, 3H), 5.20 (d, $J=2$ Hz, 1H), and 6.13 (d, $J=2$ Hz, 1H); $\lambda_{max}$ (hexane): 314 nm ($\varepsilon$ 6400); MS: *m/e* 290 ($M^+$−*t*-Bu, trace), 204 (75%), 57 (94), and 41 (100). Fraction ($R_f$=0.50—0.56) and a fraction ($R_f$=0.39—0.47) afforded 14.8 mg (14%) of 2,4-di-*t*-butyl-6-methylnitrosobenzene (**7**) and 15.9 mg (14%) of 2,4-di-*t*-butyl-6-methylnitrobenzene (**6**) respectively, which were identified by comparing the spectral data with those of the authentic samples.

*ESR Measurements.* An oxime and an oxidizing agent were mixed in a solvent and transferred into a sample tube directly or in a pyrex capillary just before a measurement. A procedure for a reaction between an oxime and photoexcited benzophenone was as follows: a mixed solution of an oxime and a carbonyl compound whose concentration was controlled to be *ca.* 0.1 mol/l for the oxime and *ca.* 0.05 mol/l for benzophenone, was placed in a pyrex capillary, which was transferred into a sample tube and irradiated with a high pressure mercury lamp in a cavity of ESR spectrometer.

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