Syntheses of Stable *N*-*tert*-Alkoxyarylaminyl Mono- and Diradicals by the Reaction of the Lithium Salts of 2,4,6-Trisubstituted Anilines with *tert*-Alkyl Mono- and Diperoxybenzoates[1]

Yozo Miura* and Toshiyuki Nishi

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

miura@a-chem.eng.osaka-cu.ac.jp

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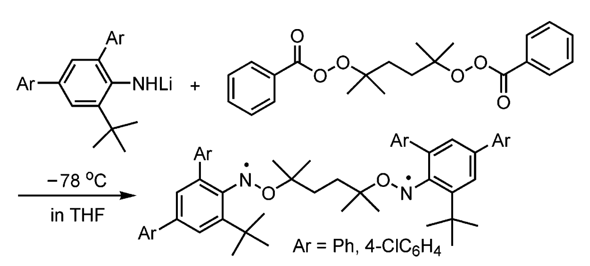
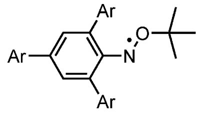


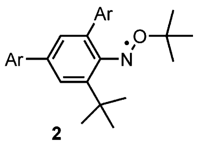
The reaction of the lithium salts of 2,4,6-triaryl- and 2-*tert*-butyl-4,6-diarylanilines with *tert*-alkyl mono- and diperoxybenzoates gave isolable *N*-*tert*-alkoxyarylaminyl mono- and diradicals. The substituent effects of *tert*-alkyl peroxybenzoates on the yields of *N*-*tert*-alkylarylaminyls were studied.

Although a variety of *N*-alkoxyaminyls ($R\dot{N}OR'$) have been widely studied by ESR spectroscopic methods,[2] their isolation has been unsuccessful for a long period. However, quite recently, we succeeded in the first isolation of *N*-alkoxyarylaminyls as radical crystals.[3−5] Typical isolated *N*-alkoxyarylaminyls were *N*-*tert*-butoxy-2,4,6-triarylphenylaminyls (**1**) and *N*-*tert*-butoxy-2-*tert*-butyl-4,6-diarylphenylaminyls (**2**), which were prepared by the reaction of the corresponding lithium salts of 2,4,6-triaryl- and 2-*tert*-butyl-4,6-diarylanilines with *tert*-butyl peroxybenzoate in THF at −78 °C. Interestingly, this family of radicals showed no reaction with atmospheric oxygen and were thermally very stable even in solution. In recent years, isolable stable free radicals have attracted increasing attention as a spin source or building blocks in the field of molecule-based magnetism[6] and as mediators in the living radical polymerization.[7] As a continuing work on the syntheses of isolable stable free *N*-alkoxyarylaminyls, we carried out the reactions of the lithium salts of 2,4,6-triaryl- and 2-*tert*-butyl-4,6-diarylanilines with a variety of *tert*-alkyl mono- and diperoxybenzoates, and it was found that a vaiety of *tert*-alkoxyarylaminyl mono- and diradicals can be obtained by using a variety of *tert*-alkyl mono- and diperoxybenzoates. Furthermore, to clarify the substituent effect of *tert*-alkyl peroxybenzoates on the yields of *N*-alkoxyarylaminyls, we performed the reaction of the lithium salt of 2-*tert*-butyl-4,6-diphenylaniline with 4-mono- and 3,5-disubstituted *tert*-butyl peroxybenzoates. We herein report the results.



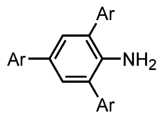
1

a: Ar = Ph
b: Ar = 4-ClC$_6$H$_4$



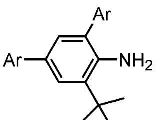
2

a: Ar = Ph
b: Ar = 4-ClC$_6$H$_4$



3

a: Ar = Ph
b: Ar = 4-ClC$_6$H$_4$



4

a: Ar = Ph
b: Ar = 4-ClC$_6$H$_4$

Results and Discussion

Substituent Effects of *tert*-Butyl Peroxybenzoates on the Yields of *N*-Alkoxyarylaminyls. The reaction of the lithium salt of 2,4-diphenyl-6-*tert*-butylaniline (**4a**) with nonsubstituted and substituted *tert*-butyl peroxybenzoates, **5a**−**e**, were carried out to discuss the substituent effects of *tert*-butyl peroxybenzoates (**5**) on the yields of **2a**[3,4] (Scheme 1). The results are summarized in Table 1. Upon addition of **5** to the lithium salt of **4a** in THF at −78 °C, the mixtures immediately turned red, indicating that **2a** was formed. Only one exception was the reaction with a nitro-substituted peroxybenzoate, **5d**. In this case, the mixture turned black upon addition of **5d**, and TLC analysis of the reaction mixture showed no formation of **2a**. Table 1 indicates that the yields of **2a** are approximately constant (∼30%), regardless of the peroxybenzoates used, except for the reaction with **5d**. This result demonstrates that the substituent effects of **5** on the yields of **2a** are negligibly small. No formation of **2a** in the reaction of the lithium salt of **4a** with **5d** suggests that the lithium salt reacts predominantly with the nitro group. Since **5b** is commercially available, use of **2b** is advised for the syntheses of **1** and **2** via the above reaction.

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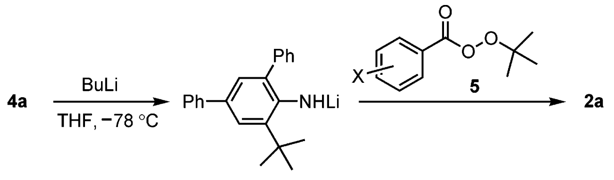
10.1021/jo0402881 CCC: \$30.25

SCHEME 1



a: X = 4-OMe, **b**: X = H, **c**: X = 4-Cl, **d**: X = 4-NO_2, **e**: X = 3,5-Cl_2

TABLE 1. Substituent Effects of 5 on the Yield of 2a

peroxybenzoate (substituent)	yield of **2a**[a] (%)
5a (4-MeO)	31
5b (H)	30
5c (4-Cl)	28
5d (X = 4-NO_2)	0
5e (3,5-Cl_2)	32

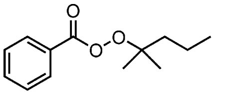
[a] Isolated yield.

TABLE 2. Preparation of 7 and 8 by the Reaction of the Lithium Salts of 3 and 4 with 6[a]

aniline[b]	*N*-alkoxyphenylaminyl	yield[c](%)
3a	**7a**	13
3b	**7b**	12
4a	**8a**	24
4b	**8b**	20

[a] **6**, 3.30 mmol; THF, 55 mL; butyllithium, 2.2 mmol; −78 °C. [b] 1.65 mmol. [c] Isolated yield.

Preparation of Monoradicals 7 and 8 Using Perbenzoate 6. If *tert*-alkyl peroxybenzoates can be used instead of *tert*-butyl peroxybenzoate in the reaction shown in Scheme 1, a variety of *N*-*tert*-alkoxyarylaminyls can be obtained via the reaction. To confirm this point, we carried out the reactions of the lithium salts of **3** and **4** with 1,1-dimethylbutyl peroxybenzoate (**6**) under the same conditions as above. The results are summarized in Table 2. The reaction of the lithium salts of **3** with **6** gave *N*-(1,1-dimethylbutoxy)-2,4,6-triarylphenylaminyls (**7**) in 12−13% yields, and the reaction of the lithium salt of **4** with **6** gave *N*-(1,1-dimethylbutoxy)-2-*tert*-butyl-4,6-diarylphenylaminyls (**8**) in 20−24% yields. The spin concentrations of **7** and **8** determined by ESR were more than 90%. Since **7b** and **8b** were obtained as crystals, their structures were confirmed by elemental analyses and ESR spectra. On the other hand, since **7a** and **8a** were obtained as a red oil, their structures were confirmed by high-resolution FAB mass spectra and ESR spectra. To ascertain that **7** and **8** are not nitroxides, their ESR spectra were measured. All ESR spectra showed a 1:1:1 triplet spectru from which the a_N and g values were determined to be 0.979−0.984 mT and 2.0041−2.0043 (in benzene), respectively. These ESR parameters are very similar to the previously reported ones for **1** and **2** (a_N = 0.984−1.05 mT, g = 2.0038−2.0043),[3,4] but they are quite different from those for nitroxides (a_N = 1.27 mT, g = 2.0062),[4] clearly indicating that the isolated radicals **7** and **8** are not nitroxides.



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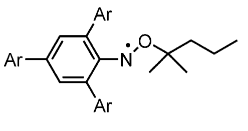
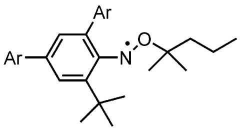


7

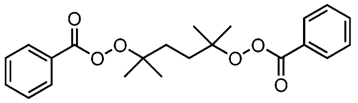
a : Ar = Ph
b: Ar = 4-ClC_6H_4



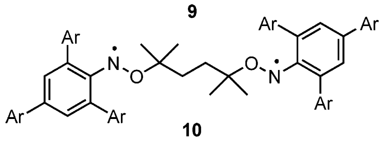
8

a : Ar = Ph
b: Ar = 4-ClC_6H_4

Preparation of Diradicals by the Reaction with Diperoxybenzoate. Based on the above results, it is expected that if *tert*-alkyl diperoxybenzoates are used instead of *tert*-alkyl monoperoxybenzoates one may be able to obtain *N*-*tert*-alkoxyarylaminyl diradicals. We carried out the above reaction using 2,5-bis(benzoyldioxy)-2,5-dimethylhexane (**9**) as diperoxybenzoate. When **9** was added to THF solutions of the lithium salts of **3** and **4**, the mixtures immediately turned to red, similar to the reactions with monoperoxybenzoates. Although isolation of diradical **10** was unsuccessful despite much effort, diradical **11** could be isolated in 3.3−4.9% yields as red crystals, together with small amounts of monoradical, after chromatography. We assume that the failure in the isolation of **10** is due to the gradual decomposition of **10** during the isolation procedure. This assumption is based on the previous observation that 2,4,6-triaryl-substituted *N*-*tert*-butoxyphenylaminyls are less stable than 2,4-diaryl-6-*tert*-butyl-substituted ones. The spin concentrations of the isolated diradicals were determined to be 182 (**11a**) and 168% (**11b**), respectively, by ESR. The ESR spectra of the diradicals in benzene at 25 °C were split into an incomplete 1:2:3:2:1 quintet due to the spin exchange interaction between the two nitrogen radical centers.

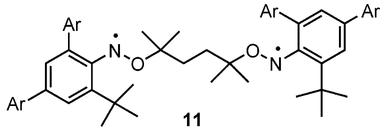


9



10

a : Ar = Ph
b: Ar = 4-ClC_6H_4



11

a : Ar = Ph
b: Ar = 4-ClC_6H_4

To determine the zero-field splitting parameters, |D| and |E|, of diradical **11**, ESR spectra of **11a** were measured at 77 K using toluene as the glass matrix, and |D| and |E| were determined to be 6.80 and 0.51 mT, respectively. From the |D| value the average distance between the two radical centers was calculated to be 7.43 Å using the point-dipole approximation (g = 2.00). This distance shows a reasonable agreement with that (8.33 Å) between N and N in the structure of **11a** optimized using the AM1 method.

Conclusions

We carried out the reaction of the lithium salts of 2,4,6-triaryl- and 2,4-diaryl-6-*tert*-butylanilines with *tert*-alkyl mono- and diperoxybenzoates and obtained *N*-*tert*-alkoxyarylaminyl mono- and diradicals as crystals or oil. From the results we showed that a variety of isolable 2,4,6-trisubstituted *N*-*tert*-alkoxyarylaminyl mono- and diradicals can be prepared from a variety of *tert*-alkyl mono- and diperoxybenzoates.

Experimental Section

tert-Butyl peroxybenzoate, 2,4,6-triphenylaniline, 2,4,6-tris-(4-chlorophenyl)aniline, 2-*tert*-butyl-4,6-diphenylaniline, and 2-*tert*-butyl-4,6-bis(4-chlorophenyl)aniline were prepared according to the previously reported methods.[8,9] *tert*-Butyl 4-methoxy- (**5b**), 4-chloro- (**5c**), 4-nitro- (**5d**), and 3,5-dichloroperoxybenzoates (**5e**) were prepared by the reaction of *tert*-butyl hydroperoxide with the corresponding benzoyl chloride in NaOH aqueous solution according to the reported procedure.[10] *tert*-Butyl peroxybenzoate (**5a**), 1,1-dimethylbutyl peroxybenzoate (**6**), and 2,5-bis(benzoyldioxy)-2,5-dimethylhexane (**9**) were kind gifts from the Japan Oil Company, Co. Ltd. Silica gel column chromatography was carried out on Kanto Chemical silica gel 60 N, while alumina column chromatography was carried out on Merck aluminum oxide 90.

Reaction of the 2-*tert*-Butyl-4,6-diphenylanilines with *tert*-butyl Peroxybenzoates (5). A solution of 2-*tert*-butyl-4,6-diphenylaniline (500 mg, 1.66 mmol) in anhydrous THF (50 mL) was charged with N_2 and cooled to −78 °C. A hexane solution of butyllithium (1.56 M) (1.38 mL, 2.15 mmol) was added with a syringe through a double septum with stirring, and the resultant mixture was stirred for 15 min at the same temperature. A solution of **5** (3.3 mmol) in anhydrous THF (5 mL) was then added with a syringe through a double septum, and after being stirred for 1 h at the same temperature, the mixture was gradually warmed to room temperature and water (ca. 100 mL) was added. The mixture was extracted with benzene, and the benzene solusion was dried, evaporated, and chromatographed on alumina with 1:5 benzene−hexane to give **2a** as red crystals. Yields are summarized in Table 1.

Reaction of 2,4,6-Triarylphenylanilines and 2-*tert*-Butyl-4,6-diarylphenylanilines with 1,1-Dimethylbutyl Peroxybenzoate (6). In the same manner as above, the reaction of the lithium salts of **3** and **4** with 1,1-dimethylbutyl peroxybenzoate **6** was carried out. Thus, a solution of 2-*tert*-butyl-4,6-diphenylaniline (1.65 mmol) in anhydrous THF (50 mL) was cooled to −78 °C and a hexane solution of butyllithium (1.56 M) (1.38 mL, 2.15 mmol) was added with stirring under N_2. After the resultant mixture was stirred for 15 min at the same temperature, a solution of **6** (0.37 g, 3.3 mmol) in anhydrous THF (5 mL) was added and the resultant mixture was stirred for 1 h at the same temperature. After the mixture was gradually raised to room temperature, water (ca 100 mL) was added, and the mixture was extracted with benzene. The benzene extract was dried, evaporated, and chromatographed on alumina with 1:9 benzene−hexane to give **7** or **8** as a red or purple oil or red crystals.

***N*-(1,1-Dimethylbutoxy)-2,4,6-triphenylaminyl (7a):** yield 13% (89 mg, 0.21 mmol); purple oil (the spin concentration determined by ESR 93%); UV−vis (benzene) λ_{max} 335.5 nm (ϵ 25600) and 537 (718 L mol^{-1} cm^{-1}); ESR (benzene) $a_N = 0.986$ mT (*g* 2.0041); HRFABMS *m*/*z* calcd for $C_{30}H_{30}NO$ 420.2327, found 420.2344.

***N*-(1,1-Dimethylbutoxy)-2,4,6-tris(4-chlorophenyl)aminyl (7b):** yield 12% (105 mg, 0.20 mmol); red powdery crystals (from MeOH) (the spin concentration determined by ESR 94%); mp 102−104 °C; UV−vis (benzene) λ_{max} 344 (ϵ 30100) and 546 nm (1260 L mol^{-1} cm^{-1}); ESR (benzene) $a_N = 0.979$ mT (*g* 2.0042). Anal. Calcd for $C_{30}H_{27}Cl_3NO$: C, 68.78; H, 5.19; N, 2.67. Found: C, 68.64; H, 5.05; N, 2.50.

***N*-(1,1-Dimethylbutoxy)-2-*tert*-butyl-4,6-diphenylaminyl (8a):** yield 24% (160 mg, 0.40 mmol); purple oil (the spin concentration determined by EPR 94%); UV−vis (benzene) λ_{max} 336 (ϵ 26800) and 542 nm (1370 L mol^{-1} cm^{-1}); ESR (benzene) $a_N = 0.979$ mT (*g* 2.0041); HRFABMS *m*/*z* calcd for $C_{28}H_{34}NO$ 400.2640, found 400.2635.

***N*-(1,1-Dimethylbutoxy)-2-*tert*-butyl-4,6-tris(4-chlorophenyl)aminyl (8b):** yield 20% (152 mg, 0.32 mmol); purplish red powdery crystals (from MeOH) (the spin concentration determined by ESR 96%); mp 96−98 °C; UV−vis (benzene) λ_{max} 345 (ϵ 36800) and 548 nm (1060 L mol^{-1} cm^{-1}); ESR (benzene) $a_N = 0.979$ mT (*g* 2.0043). Anal. Calcd for $C_{28}H_{32}Cl_2NO$: C, 71.63; H, 6.87; N, 2.98. Found: C, 71.46; H, 6.68; N, 2.79.

Reaction of 2-*tert*-Butyl-4,6-diarylanilines with 2,5-Bis(benzoyldioxy)-2,5-dimethylhexane (9). A solution of 2-*tert*-butyl-4,6-diphenylaniline (2.32 mmol) in anhydrous THF (50 mL) was charged with N_2 and cooled to −78 °C. A hexane solution of butyllithium (1.56 M) (1.92 mL, 3.0 mmol) was added with a syringe through a double septum with stirring, and the resultant mixture was stirred for 15 min at the same temperature. A solution of **9** (0.53 g, 1.38 mmol) in anhydrous THF (10 mL) was then added via syringe through a double septum after the mixture was stirred for 1 h at the same temperature. After the temperature was gradually raised to room temperature, water (ca. 100 mL) was added, and the mixture was extracted with benzene. The benzene solution was dried, evaporated, and chromatographed on silica gel with 1:3 or 1:4 benzene−hexane to give **11** as red crystals.

***N,N′*-(2,2,5,5-Tetramethyltetramethylenedioxy)bis[2-*tert*-butyl-4,6-diphenylphenylaminyl] (11a):** yield 4.9% (42 mg, 0.057 mmol); red needles (from MeOH−ethyl acetate) (the spin concentration determined by ESR 182%); mp 190−191 °C; UV−vis (benzene) λ_{max} 336 (ϵ 59100) and 545 nm (3020 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{52}H_{58}N_2O_2$: C, 84.06; H, 7.89; N, 3.77. Found: C, 83.47; H, 7.46; N, 3.71.

***N,N′*-(2,2,5,5-Tetramethyltetramethylenedioxyl)bis[2-*tert*-butyl-4,6-bis(4-chlorophenyl)phenylaminyl] (11b):** yield 3.3% (34 mg, 0.038 mmol); red powdery crystals (from MeOH−ethyl acetate)(the spin concentration determined by ESR 164%); mp 188−189 °C; UV−vis (benzene) λ_{max} 345 (ϵ 63000) and 548/ nm (2750/L mol^{-1} cm^{-1}). Anal. Calcd for $C_{52}H_{54}Cl_4N_2O_2$: C, 70.19; H, 6.18; N, 3.18. Found: 70.65; H, 6.31; N, 2.92.

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