BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1852—1854 (1972)

Studies on Stable Free Radicals. XII.[1] ESR Spectra of 2-*t*-Butylaminotropone *N*-Oxyl Radicals

Toshimasa TODA, Eiko MORI, and Keisuke MURAYAMA
Central Research Laboratories, Sankyo Co., Ltd., Shinagawa-ku, Tokyo

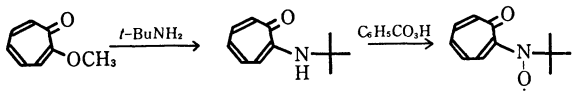
(Received November 15, 1971)

We observed a well resolved ESR spectrum of 2-*t*-butylaminotropone *N*-oxyl radical generated by the oxidation of the corresponding amine with perbenzoic acid, and assigned the values of hyperfine coupling constants of protons in the tropone ring by a comparison with the ESR spectra of deuterium substituted 2-*t*-butylaminotropone *N*-oxyl radicals: $a_N = 12.7$ gauss, $a_H{}^3 = a_H{}^5 = a_H{}^7 = 1.86$ gauss and $a_H{}^4 = a_H{}^6 = 0.93$ gauss for protons on tropone ring.

ESR spectra of arylnitroxide radicals, such as diphenylnitroxide radical[2] or *t*-butylphenylnitroxide radical[3] have been reported. However, the ESR spectrum of the nitroxide radical having aromatic seven-membered ring has not yet been reported. We observed the ESR spectrum of 2-*t*-butylaminotropone *N*-oxyl radical (IIa) and assigned the values of hyperfine splitting constants of protons on the tropone ring in IIa by a comparison with the ESR spectra of deuterium substituted 2-*t*-butylaminotropone *N*-oxyl radicals.

Results

We prepared 2-*t*-butylaminotropone (Ia) by the reaction[4] of 2-methoxytropone[5] with *t*-butylamine and obtained the corresponding nitroxide radical (IIa) by the oxidation of Ia with perbenzoic acid.[6]



(Ia) (IIa)

Since the nitroxide radical IIa is unstable and unisolable, we measured the ESR spectrum of IIa obtained by mixing a solution of Ia in benzene and perbenzoic acid in the ESR sample tube directly at room temperature.

The ESR spectrum of IIa is presented in Fig. 1-a. Triplet lines due to the interaction of a ^{14}N (12.7 gauss) and nine lines (0.93 gauss, the intensity ratio is 1 : 2 : 4 : 6 : 6 : 6 : 4 : 2 : 1) of each component of the triplet were observed. Further splittings in each component of the triplet would be caused by the interaction with protons on the tropone ring, because no interaction with protons of *t*-butyl group in *t*-butylphenylnitroxide radical have been observed in the ESR spectrum.[3]

1) Part XI: T. Toda, E. Mori, and K. Murayama, This Bulletin, **45**, 1764 (1972).

2) a) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961). b) Y. Deguchi, This Bulletin, **35**, 260 (1962).

3) H. Lamaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, **1965**, 372.

4) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *Chem. Pharm. Bull.* (Tokyo), **13**, 819 (1965).

5) T. Nozoe, S. Seto, T. Ikemi, and T. Arai, *Proc. Jcpan Acad.*, **27**, 102 (1959).

6) a) K. Tokumaru, H. Sakuragi, and O. Simamura, *Tetrahedron Lett.*, **1964**, 3945. b) T. Toda, E. Mori, and K. Murayama, This Bulletin, **45**, 1904 (1972).

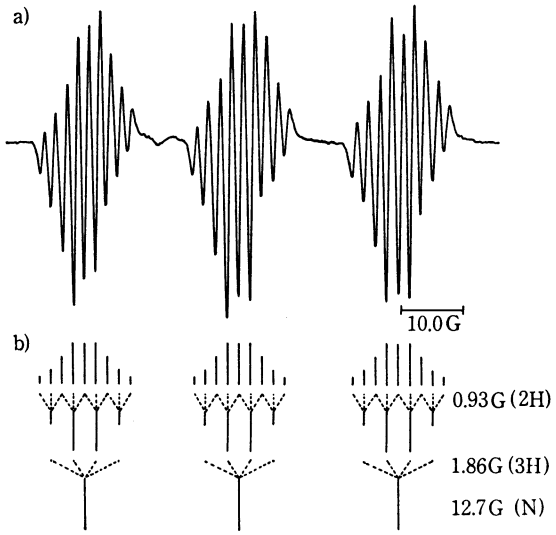


Fig. 1. ESR spectra of 2-*t*-butylaminotropone *N*-oxyl radicals (IIa).
a): Spectrum observed in benzene at room temperature.
b): Stick spectrum consisting of the values of the assigned splitting constants.

To assign the values of coupling constants of protons on the tropone ring in IIa, we prepared deuterium substituted 2-*t*-butylaminotropones (Ib, Ic, and Id) as shown in Chart 1 and measured the ESR spectra of the corresponding nitroxide radicals (IIb, IIc, and IId).

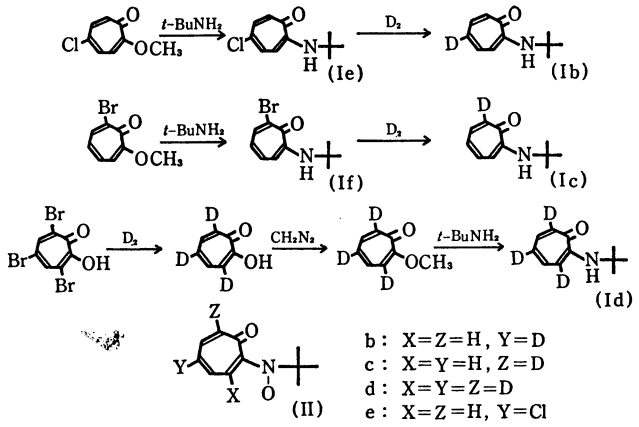


Chart 1

The nitroxide radical IIb gave the spectrum shown in Fig. 2, in which seven lines (splitting at 0.93 gauss, 1 : 3 : 3 : 4 : 3 : 3 : 1) were observed in each component of the triplet. Radical IIc also showed a spectrum (each component of the triplet was split into seven lines at 0.93 gauss) similar to that of IIb. Similarity of both spectra of IIb and IIc suggests that each value for the coupling constants of protons at the 5- and 7-positions on the ring in IIa is the same.

We observed slightly broadened triplet lines (a_N= 12.7 gauss) in the spectrum of IId as shown in Fig. 3. Each component of the triplet lines would not be resolved in the ESR spectrum because of small coupling constant values of the protons at the 4- and 6-

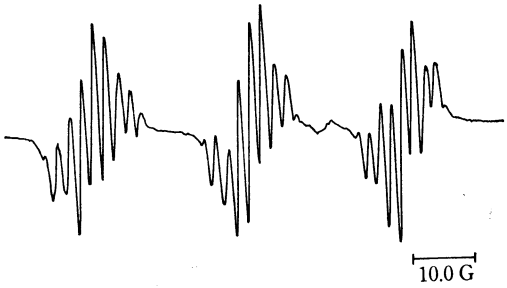


Fig. 2. ESR spectrum of 2-*t*-butylamino-5-*d*-tropone *N*-oxyl radical (IIb).

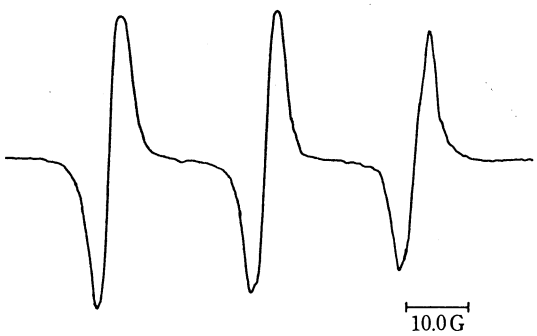


Fig. 3. ESR spectrum of 2-*t*-butylamino-3,5,7-tri-*d*-tropne *N*-oxyl radical (IId).

positions and of deuterium at the 3-, 5- and 7-positions on the ring in IId.

From the results, we assigned the values of the coupling constants of protons on the tropone ring and of nitrogen in IIa as follows: $a_H^3=a_H^5=a_H^7=$ 1.86 gauss, $a_H^4=a_H^6=0.93$ gauss and $a_N=12.7$ gauss. The stick spectrum consisting of these values is shown in Fig. 1-b and agrees with the observed spectrum of IIa.

The results obtained for IIa are comparable with those for *t*-butylphenylnitroxide radical ($a_H^4=a_H^2=a_H^6=2\cdot a_H^3=2\cdot a_H^5=1.9$ gauss and $a_N=13.4$ gauss).[3]

We obtained the following values for the coupling constants of nitrogen and the protons in 2-*t*-butylamino-5-chlorotropone *N*-oxyl radical, IIe : $a_N=12.4$ gauss and $a_H^3=a_H^7=2\cdot a_H^4=2\cdot a_H^6=1.98$ gauss. The spectrum is given in Fig. 4. The values are also comparable to those of the *t*-butyl-*p*-chlorophenylnitroxide radical ($a_N=13$ gauss and $a_H^2=a_H^6=2\cdot a_H^3=2\cdot a_H^5=2.01$ gauss).[3]

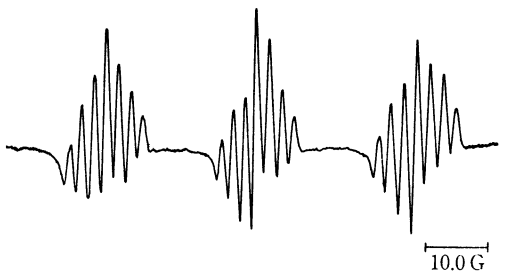


Fig. 4. ESR spectrum of 2-*t*-butylamino-5-chlorotropone *N*-oxyl radical (IIe).

The results indicate that the distribution of an unpaired electron at the 3—7 positions on the tropone

ring in IIa is similar to that at the 2—6 positions on the phenyl ring in the *t*-butylphenylnitroxide radical.

Experimental

Melting points and boiling points are uncorrected.

ESR Measurements. ESR spectra were obtained with a Hitachi MES 4001 type X-band spectrometer employing 100 kHz modulation. The samples prepared by mixing the solution of the amines (*ca.* 3%) in benzene and perbenzoic acid (*ca.* 5 mg) in an ESR sample tube were fully degassed and sealed. The splitting constants were measured relative to the aqueous solution of Fremy's salt.

2-t-Butylaminotropone (Ia). A solution of 13.6 g (0.1 mol) of 2-methoxytropone[5] and 14.6 g (0.2 mol) of *t*-butylamine in 100 m*l* of ethanol was heated under reflux for 24 hr. After removal of ethanol, the resulting oil was distilled: bp 122—133°C/2 mmHg. Yield, 12.7 g (68.3%). The distilled oil solidified on standing. Recrystallization from cyclohexane gave an analytically pure sample: mp 61—62°C. Found: C, 74.28; H, 8.56; N, 7.78%. Calcd for $C_{11}H_{15}ON$: C, 74.54; H, 8.53; N, 7.90%. IR (cm^{-1}) (Nujol): 3250, 1604 and 1597. UV (mμ): λ_{max}^{EtOH} 248, 338 and 407. NMR (τ) (in CCl_4): 2.95—3.50(5H) and 8.50 (9H).

2-t-Butylamino-5-chlorotropone (Ie). A solution of 8.0 g (45 mmol) of 2-methoxy-5-chlorotropone[7] and 6.6 g (90 mmol) of *t*-butylamine in 100 m*l* of ethanol was heated under reflux for 24 hr. After removal of ethanol, the redidue was chromatographed on an alumina column. Eluting with ethanol afforded 6.2 g (65.0%) of Ie. Recrystallization from petroleum ether gave a pure sample: mp 81.5—83°C. Found: C, 62.42; H, 6.68; N, 6.67; Cl, 16.75%. Calcd for $C_{11}H_{14}ONCl$: C, 62.40; H, 6.66; N, 6.64; Cl, 16.74%.

2-t-Butylamino-7-bromotropone (If). A solution of 8.6 g (40 mmol) of 2-methoxy-7-bromotropone[5] and 6.0 g (83 mmol) of *t*-butylamine in 100 m*l* of ethanol was refluxed for 27 hr. After ethanol was removed under reduced pressure, the resulting crystalline solid was recrystallized from methanol to give 6.1 g (59.5%) of If: mp 138.5—140°C. Found: C, 51.35; H, 5.52; N, 5.41; Br, 30.90%. Calcd for $C_{11}H_{14}ONBr$: C, 51.57; H, 5.51; N, 5.49; Br, 31.19%.

2-t-Butylamino-5-d-tropone (Ib). A solution of 4.3 g (20 mmol) of Ie and 3.0 g of triethylamine in dry dioxane was shaken with 1.0 g of anhydrous palladium chloride and 6 m*l* of deuterium oxide in an atmosphere of deuterium. After about 130 m*l* of deuterium was absorbed, the reaction mixture was filtered to separated a precipitate. The filtrate was concentrated under reduced pressure and the residue was distilled: bp 126—130°C/2 mmHg. The distilled oil solidified on standing. Recrystallization from cyclohexane furnished a pure sample: mp 61.0—62.5°C. Yield, 2.1 g (59.0%). Found: C, 74.20; H(D), 9.19; N, 7.85%. Calcd for $C_{11}H_{14}DON$: C, 74.12; H(D), 9.07; N, 7.89%.

2-t-Butylamino-7-d-tropone (Ic). By a method similar to the above, 2.6 g (73.0%) of Ic was obtained from 5.1 g (20 mmol) of If: mp 61.5—62.5°C. Found: C, 73.91; H(D), 9.05; N, 7.81%. Calcd for $C_{11}H_{14}DON$: C, 74.12; H(D), 9.07; N, 7.89%.

2-t-Butylamino-3,5,7-tri-d-tropone (Id). A solution of 35.8 g (0.1 mol) of 3,5,7-tribromotropolone[8] and 40.0 g of triethylamine in 300 m*l* of dry dioxane was shaken with 5.0 g of anhydrous palladium chloride and 30 m*l* of deuterium oxide in an atmosphere of deuterium. After about 7 *l* of deuterium was absorbed during 4 hr, the reaction mixture was filtered to separate a precipitate. The precipitate was dissolved in 60 m*l* of aqueous sodium hydroxide (50%) and extracted with 200 m*l* of chloroform. The filtrate and the chloroform layer were combined, dried over sodium carbonate and concentrated under reduced pressure. The residue was distilled to give 6.5 g of 3,5,7-tri-*d*-tropolone: bp 106—110°C/12 mmHg. The oil solidified on standing. Recrystallization from benzene gave a pure sample: mp 51.5—53°C. Found: C, 66.99; H(D), 7.75%. Calcd for $C_7H_3D_3O_2$: 67.19; H(D), 7.25%. NMR (τ) (in CCl_4): 1.50(1H) and 2.78(2H). To a solution of 2.9 g (23 mmol) of 3,5,7-tri-*d*-tropolone in 50 m*l* of ether was added a solution of diazomethane (3 g) in 100 m*l* of ether dropwise with ice bath cooling. The solution was allowed to stand overnight at room temperature. After removal of ether, the resulting oil was distilled to give 2.0 g (57.5%) of 2-methoxy-3,5,7-tri-*d*-tropone: bp 138—142°C/5 mmHg. By a similar procedure used for Ia, 1.6 g (61.4%) of Id was obtained from 2.0 g (14 mmol) of 2-methoxy-3,5,7-tri-*d*-tropone: mp 60.0—62°C. Found: C, 73.07; H(D), 10.36; N, 7.59%. Calcd for $C_{11}H_{12}D_3ON$: C, 73.28; H(D), 10.05; N, 7.78%.

Perbenzoic Acid. Perbenzoic acid was prepared by the usual way[9] and purified by sublimation under reduced pressure: 35—40°C/4 mmHg.

The authors are grateful to Dr. Nobuo Soma for his helpful suggestions in the preparation of the amines, and to Dr. Genshun Sunagawa, the director, for his encouragement.

7) T. Sato, *Nippon Kagaku Zasshi*, **80**, 1171 (1959).

8) T. Nozoe, Y. Kitahara, K. Yamane, and A. Yoshikoshi, *Proc. Japan Acad.*, **27**, 18 (1959).

9) G. Braun, "Organic Syntheses", Coll. Vol. I, p. 431 (1956).