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Radical Anions Derived from 4-Picrylimino-2,6-disubstituted-2,5-cyclohexadiene-1-one

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Synopsis. 4-Picrylimino-2,6-di-*t*-butyl (or bromo)-2,5-cyclohexadiene-1-ones were synthesized and radical anions were derived from them by one electron reduction with potassium metal. ESR measurement showed that an odd electron exists mainly on the quinone-imine moiety of the radical anion molecule.

A number of studies have been made on radical anions derived from quinones.[1] However, only one report[2] has appeared on radical anions derived from anils which are arylimino derivatives of *p*-benzoquinone. The title compounds are a new class of anils and are expected to give easily stable radical anions by one electron reduction since they have 2,6-disubstituted-*p*-benzoquinone and picryl moieties with known structures in the chemistry of stable radicals. In the present paper, we wish to report on the synthesis of the title compounds and some properties of radical anions derived from them.

Results and Discussion

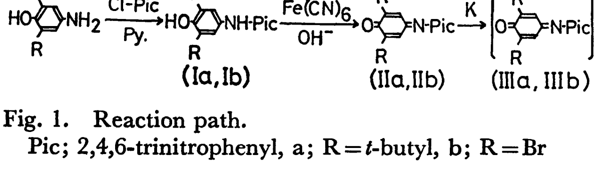

Fig. 1. Reaction path.
Pic; 2,4,6-trinitrophenyl, a; R=*t*-butyl, b; R=Br

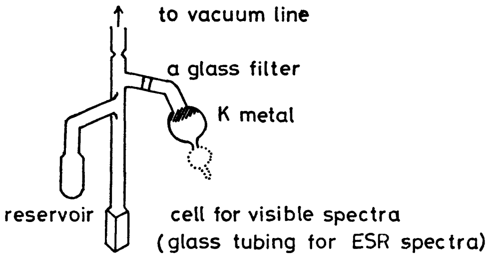

Fig. 2. An apparatus for reduction and spectral measurement.

Cyclohexadienones (II) were synthesized by ferricyanide oxidation of 4-*N*-picrylamino-2,6-disubstituted-phenols (I) prepared by the condensation of picryl chloride and 4-amino-2,6-disubstituted-phenol. The yield of each compound was moderate. One electron reduction of cyclohexadienone (II) (*ca.* 0.7 mg) in tetrahydrofuran (*ca.* 3 ml) with excess potassium metal was carried out *in vacuo* by using an apparatus shown in Fig. 2. The color of the reaction mixture turned immediately from yellow to violet (in case of *t*-butyl derivative), or to blue-violet (in case of bromo derivative). ESR measurement showed the presence of radical anions (III). Radical anions (III) were observed to change into some other species when they were in contact with excess potassium metal for some time, their color turning to brown in 20 min for the *t*-butyl derivative and in 3 min for the bromo derivative. Both radical anions (III) were found to be very stable in tetrahydrofuran when they were moved from excess potassium metal, remaining unchanged for a few days at room temperature *in vacuo*, though very unstable in air. ESR measurement for the decay of each radical anion (III) showed that radical anion (IIIa) was more stable than radical anion (IIIb). A solution of each radical anion (III) was therefore transferred to a cell from excess potassium metal before the color changed, and diluted to a suitable concentration for the spectral measurement with tetrahydrofuran condensed in a reservoir by chilling with liquid nitrogen. The absorption maxima in the electronic spectra of radical anions (III) is located at a greater wavelength (IIIa: 575 nm, IIIb: 583 nm) than the corresponding cyclohexadienones (IIa: 309 nm, IIb: 320 nm). These bathochromic shifts might be caused by the excitation of an odd electron in each radical anion molecule (III), as reported for many hydrocarbon radical anions.[3] The ESR spectrum of radical anion (IIIa) (Fig. 3) consists of a triplet (with hyperfine splitting of 4.38 G of an equal intensity) which might be due to an imino-nitrogen atom. The ESR spectrum of radical anion (IIIb) consists of a triplet (with hyperfine splitting of 6.25 G of an equal intensity) of a triplet (with hyperfine splitting of 1.88 G of intensity ratio=1: 2: 1) which might be due to an imino-nitrogen atom and two equivalent quinone-protons. The results suggest that unpaired electron distribution at an imino-nitrogen atom is maximal. The absence of the hyperfine splittings due to nitrogen atoms of picryl group suggests that an odd electron exists mainly on the quinone-imine moiety of the radical anion molecule (III). This may be explained by the fact that twisting of a picryl group disturbs the whole π-electron system of radical anion

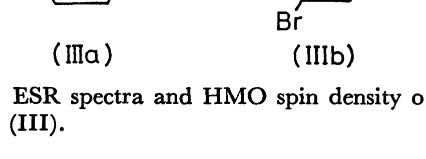

Fig. 3. ESR spectra and HMO spin density of radical anion (III).

(III),[4] and an odd electron exists on quinone-imine moiety which is considered to have greater electron affinity than a picryl group, since the electron affinity of 1,3,5-trinitrobenzene is 0.7 eV and that of 2,6-dibromo-*p*-benzoquinone is 1.2 eV.[5] The HMO unpaired electron distribution of each radical anion (III) was calculated by using parameters cited in the literature[6] for the π-electron system shown in Fig. 3, and the results are also shown in Fig. 3.

Experimental

*4-*N*-Picrylamino-2,6-di-*t*-butyl (or bromo)-phenol (I).* A saturated ethanol solution of 4-amino-2,6-di-*t*-butyl (or bromo)-phenol[7] (0.011 mol) containing pyridine (0.01 mol) was poured into a saturated ethanol solution of picryl chloride (0.01 mol). The reaction was continued for 3 h under refluxing in a stream of nitrogen. The solvent was distilled off as much as possible. The precipitates was filtered off, washed with cold hexane and water successively, and dried *in vacuo*. Recrystallization of each crude product from alcohol gave crystals of phenol (I). Phenol (Ia, R=*t*-butyl): red needles (1.4 g, 28%) from 1-propanol, mp 187—189 °C, Found: C, 55.76; H, 5.38; N, 12.96%; mol wt (MS) *m/e* 432 (M^+). Calcd for $C_{20}H_{24}O_7N_4$: C, 55.55; H, 5.59; N, 12.96%; mol wt 432.4. IR (KBr): 3640 (OH), 3350 (NH), 3070, 2960 (CH), 1625 (NH), 1590 (phenyl), 1530, 1340 (NO_2), 840 (CH) cm^{-1}; Phenol (Ib, R=Br): orange needles (3.0 g. 63%) from ethanol, mp 245—247 °C, Found: C, 30.32; H, 1.31; N, 12.02; Br, 33.41%; mol wt (MS) *m/e* 476 (M^+). Calcd for $C_{12}H_6O_7N_4Br_2$: C, 30.15; H, 1.27; N, 11.72; Br, 33.43%; mol wt 476.2, IR(KBr): 3400 (OH), 3300 (NH), 3070 (CH), 1615 (NH), 1590 (phenyl), 1525, 1355 (NO_2), 845 (CH) cm^{-1}.

*4-Picrylimino-2,5-di-*t*-butyl (or bromo)-cyclohexadiene-1-one (II).* The phenol (I) (0.001 mol) in benzene was oxidized with potassium ferricyanide (1.23 g, 0.004 mol) and potassium hydroxide (0.23 g, 0.0041 mol) in water (15 ml) by shaking the reaction mixture for 3 h at room temperature. The reaction mixture was then poured onto a large amount of water, and the organic layer was washed with water and dried over anhydrous sodium sulfate. A yellow powder was obtained after distilling off benzene from the organic layer, and each crude product was recrystallized from alcohol. Cyclohexadienone (IIa, R=*t*-butyl): yellow plates (0.37 g, 86%) from ethanol, mp 177—179 °C, Found: C, 54.29; H, 4.85; N, 13.53%; mol wt. (MS) *m/e* 430 (M^+). Calcd for $C_{20}H_{22}O_7N_4$: C, 55.81; H, 5.15, N, 13.02%; mol wt 430.4. IR (KBr) 3070, 2960 (CH), 1660 (C=N), 1640 (C=O), 1615 (C=C), 1550, 1345 (NO_2), 820 (CH) cm^{-1}. Cyclohexadienone (IIb, R=Br): yellow-brown plates (0.20 g, 42%) from ethanol, mp 220—221 °C. Found: C, 30.46; H, 0.92; N, 10.82; Br, 33.51%. Mol wt (MS) *m/e* 474 (M^+). Calcd for $C_{12}H_4O_7N_4Br_2$: C, 30.28; H, 0.85; N, 11.77; Br, 33.57%. Mol wt 474.2. IR (KBr); 3070 (CH), 1670 (C=O), 1615 (C=N), 1605 (C=C), 1535, 1350(NO_2), 825 (CH) cm^{-1}.

All the melting points were uncorrected. The infrared spectra were measured with a Shimadzu IR-27G grating spectrophotometer, the visible spectra with a Hitachi EPS-2U recording spectrophotometer and the ESR spectra with a Hitachi 771 electron spin resonance spectrometer.

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