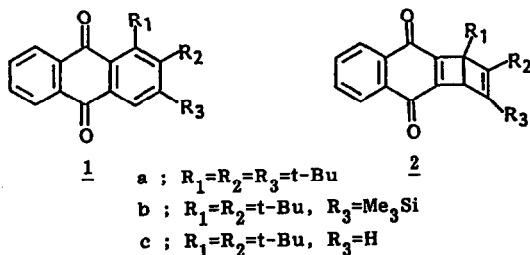


NOVEL ANTHRAQUINONE DERIVATIVES UNDERGOING
PHOTOCHEMICAL VALENCE ISOMERIZATION

Sadao Miki, Kohji Matsuo, Masahiro Yoshida and Zen-ichi Yoshida*
Department of Synthetic Chemistry, Kyoto University, Yoshida Kyoto 606 Japan

Summary : 1,2,3-Tri-*t*-butylanthraquinone (1a), 1,2-di-*t*-butyl-3-trimethylsilylanthraquinone (1b) and 1,2-di-*t*-butylanthraquinone (1c) have been synthesized. Upon irradiation, 1a and 1b underwent valence isomerization to produce the corresponding Dewar-type isomers 2a and 2b, whereas 1c gave photoreduction products via abstraction of the *t*-butyl hydrogen by the quinone carbonyl oxygen.

In this paper we wish to report our finding on novel anthraquinone derivatives, 1,2,3-tri-*t*-butylanthraquinone (1a) and 1,2-di-*t*-butyl-3-trimethylsilylanthraquinone (1b) which underwent valence isomerization photochemically to give the corresponding hemi-Dewar anthraquinones (2a,b). The derivatives and the reaction are extremely interesting from the following points of view. (1) Photochemical reactions of anthraquinones known so far are mostly limited to the reactions on the quinone carbonyl group such as hydrogen abstraction and photoaddition¹⁾ or photoinduced electron transfer, and the present valence isomerization reaction of 1a,b is a new type of photochemistry of anthraquinone molecule. (2) The reaction can be placed in the category of valence isomerization of arenes, the area of which has been having an enormous potential both for the synthesis of novel compounds and the provision of experimental supports for theories on chemical reactions.²⁾ (3) The reaction is closely relevant to the photoresponse of organic molecules involving photochromism.

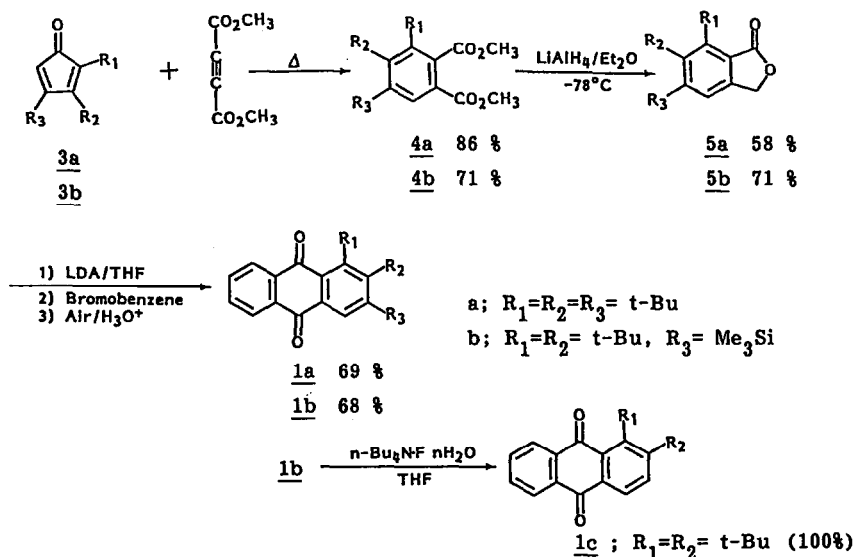


The anthraquinones 1a, 1b and 1,2-di-*t*-butylanthraquinone (1c) were synthesized according to Scheme 1 starting from 2,3,4-tri-*t*-butylcyclopenta-2,4-dien-1-one (3a)³⁾ and 2,3-di-*t*-butyl-4-trimethylsilylcyclopenta-2,4-dien-1-one (3b).⁴⁾ In the Scheme the LAH reduction of dimethyl phthalate derivatives (4a,b) at -78 °C gave 5,6,7-tri-substituted phthalides (5a,b) selectively over 4,5,6-tri-substituted derivatives. The reaction of the phthalides with bromobenzene in the presence of lithium di-isopropylamide followed by air oxidation afforded 1.⁵⁾ The anthraquinone 1a was also accessible by oxidative aromatization of the Diels-Alder adduct of butadiene with 5,6,7-tri-*t*-butyl-1,4-naphthoquinone, which was obtained by the Diels-Alder reaction of 3a with dehydrobenzoquinone generated by the

Pb(OAc)₄ oxidation⁶⁾ of N-aminotriazolohydroquinone. Spectroscopic data for the new anthraquinone derivatives are summarized in Table 1.

Irradiations of the degassed solutions of 1a and 1b in acetonitrile (5 mM) by a 100 W high-pressure Hg-lamp through a combination of filters (aqueous solutions of K₂CrO₄, CoSO₄ and NiSO₄) gave the photostationary mixtures with the compositions 1a/2a = 2.5/1 and 1b/2b = 4/1, respectively. The formations of 2a and 2b were chemically quantitative, and the quantum yields at 313 nm were 0.03 for both the cases. The products 2a,b were isolated by chromatography on silicagel (hexane/CH₂Cl₂ = 1/2) at -15 °C followed by recrystallization from acetonitrile. Their spectroscopic data are shown in Tabel 1 and Figure 2. The half lives for the thermal cycloreversions of 2a and 2b in CDCl₃ were 17 hr at 48 °C and 6 hr at 24 °C, respectively. Irradiations of 2a and 2b in the same conditions as above gave the

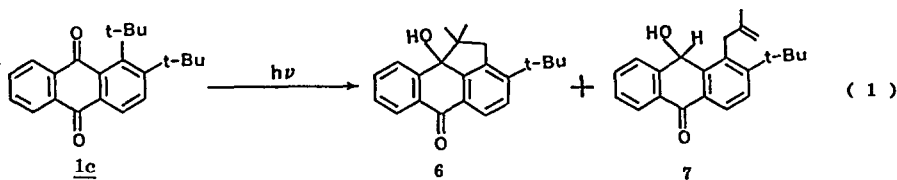
Scheme 1

Table 1 ¹H-NMR, IR and Mass spectroscopic data of 1 and 2.

Compounds	Mp °C	IR (KBr) cm ⁻¹	¹ H-NMR(CDCl ₃)	Exact Mass m/e(M ⁺), (Calcd.)
			δ ppm(TMS)	
<u>1a</u>	116	1660, 1280	8.24-8.05(m, 2H) 7.90(s, 1H) 7.79-7.60(m, 2H) 1.50(s, 18H), 1.44(s, 9H)	376.2415 (376.2402)
<u>1b</u>	100	1670, 1295	8.21-7.64(m, 5H) 1.47(s, 9H), 1.46(s, 9H) 0.47(s, 9H)	392.2145 (392.2171)
<u>1c</u>	150	1670, 1320 1290	8.24-7.62(m, 6H) 1.54(s, 9H), 1.52(s, 9H)	320.1758 (320.1776)
<u>2a</u>	105 (dec.)	1660, 1600 1590	8.15-7.56(m, 4H) 3.85(s, 1H), 1.20(s, 9H) 1.19(s, 9H), 1.12(s, 9H)	376.2382 (376.2402)
<u>2b</u>	68 (dec.)	1662, 1600 1592	8.11-7.59(m, 4H) 3.93(s, 1H), 1.13(s, 18H) 0.19(s, 9H)	392.2158 (392.2171)

photostationary mixtures with the same compositions as the respective above reactions. Quantum yields for the photocycloreversions at 313 nm were 0.7 and 0.6 for 2a and 2b, respectively. When irradiation was performed with a high-pressure Hg-lamp coupled with a Toshiba L-39 filter (> 350 nm) the compositions of the photostationary mixtures were $\underline{1a}/\underline{2a} = 2/1$ and $\underline{1b}/\underline{2b} = 5/1$. Thus, the anthraquinones 1a,b undergo photochemical valence-isomerization to produce the corresponding hemi-Dewar anthraquinones 2a,b in quantitative chemical yields, and the isomerization is photochemically reversible.

On the other hand, photochemical reaction of 1c was quite different from those of 1a,b, and irradiations of 1c in degassed acetonitrile, ethanol or carbon tetrachloride afforded many products. At the early stage of low conversion, however, only two products, 6 and 7,⁷⁾ were observed in the reaction mixtures (eq. 1) with a ratio of $\underline{6}/\underline{7} = 2/1$ in carbon tetrachloride.



The formation of 6 and 7 can be reasonably explained based on a mechanism⁸⁾ starting from the abstraction of the t-butyl hydrogen by the carbonyl oxygen. This reaction is usual photoreduction for carbonyl compounds involving their $n\pi^*$ triplet states. However, the valence isomerization of 1a,b to 2a,b seems quite unusual if the excited state responsible for the reaction is $n\pi^*$ in nature. In connection with this anomaly of 1a,b in photochemical reaction behavior, their electronic spectra are suggestive. As is seen in Figure 1, compared with the electronic spectrum of parent anthraquinone, the spectra 1a and 1b are characteristic revealing longest wavelength absorption bands with large extinction coefficients of $3530 \text{ cm}^{-1}\text{M}^{-1}$ and $3280 \text{ cm}^{-1}\text{M}^{-1}$, respectively, whereas extinction coefficient for the longest wavelength absorption band for the parent molecule is below $100 \text{ cm}^{-1}\text{M}^{-1}$ due to the spin-forbidden $n\pi^*$ nature of the absorption band. Judging from the large extinction coefficients

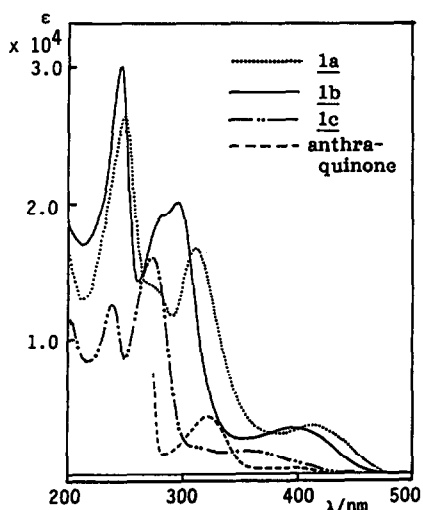


Figure 1 Electronic Spectra of 1a,b,c and anthraquinone in acetonitrile.

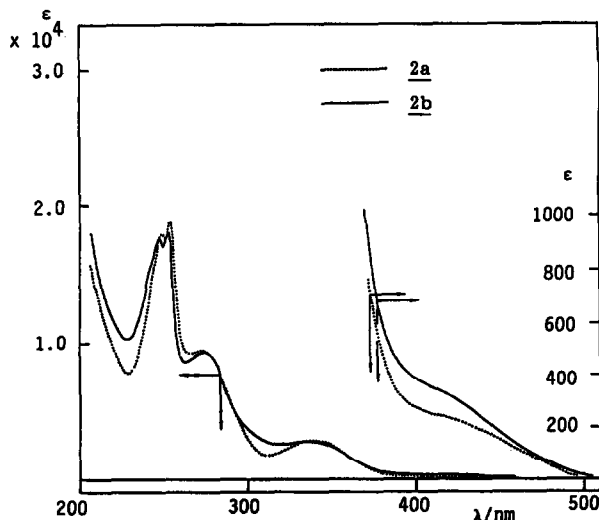


Figure 2 Electronic Spectra of 2a,b in acetonitrile.

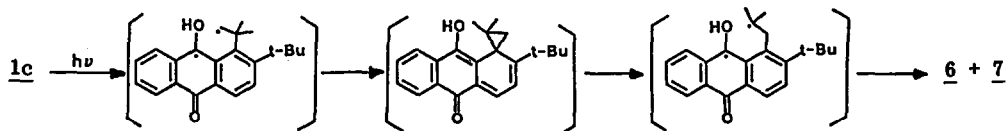
for the longest absorption bands for 1a,b, the lowest excited singlet states of 1a,b should bear $\pi\pi^*$ nature significantly. Although all of the photochemical valence isomerizations of benzenes known so far generally involve singlet states and not triplet states,⁹⁾ there remains possibility for the isomerization of 1a,b to proceed via their lowest triplet states. It seems likely that the change in excited electronic configuration relating to $n\pi^*/\pi\pi^*$ nature by the substitutional modification in 1a,b may occur in their lowest triplet states.

The nature of the excited states of 1 has been under investigation and will be communicated.¹⁰⁾

References and Notes

- (1) For example, H. J. Hagemann, "Methoden Der Organischen Chemie, Photochemie" Band IV/5b, Teil II, P.941-985, Georg Thieme Verlag, Stuttgart (1975).
- (2) G. Kaupp, Angew. Chem. Int. Ed. Engl., 19, 243-275 (1980).
- (3) G. Maier, S. Pfriem, U. Schäfer, K. D. Malsch and R. Matusch, Chem. Ber., 114, 3965 (1981).
- (4) The use of phthalide anions for the preparation of substituted anthraquinones has been described by Sammes; P. G. Sammes and D. J. Dodsworth, J. Chem. Soc. Chem. Comm., 1979, 33-34.
- (5) 2,3-Di-*t*-butyl-4-trimethylsilylcyclopenta-2,4-dien-1-one (3b) was prepared by the similar manner as the preparation of 3a by Maier³⁾ using *t*-butyl-trimethylsilylacetylene in place of di-*t*-butylacetylene. 3b: reddish yellow viscous oil, Exact Mass Calcd. for $C_{16}H_{28}OSi$ 264.1909, found 264.1927. IR(neat film) 1705, 1635, 850 cm^{-1} . 1H -NMR ($CDCl_3$) δ ppm 5.70(s, 1H), 1.35(s, 9H), 1.34(s, 9H), 0.28(s, 9H).
- (6) C. W. Rees and D. E. West, J. Chem. Soc. (C), 1970, 583.
- (7) Structure assignments for 6 and 7 were done based on the following spectroscopic data coupled with the NOE technique in the 1H -NMR measurements.
6; IR(CCl_4 soln.) 3600 (free HO), 1677, 1315 cm^{-1} , 1H -NMR($CDCl_3$) δ ppm 8.30 (d, 1H), 7.89(d, 1H), 7.82(d, 1H), 7.62(t, 1H), 7.49(t, 1H), 7.48(d, 1H), 3.22(center of AB quartet, 2H), 1.76(s, 3H), 1.40(s, 9H), 0.87(s, 3H). Exact Mass Calcd. for $C_{22}H_{24}O_2$; 320.1776. found 320.1762. 7; IR(CCl_4 soln.) 3600, 1672, 1320, 900 cm^{-1} . 1H -NMR($CDCl_3$) δ ppm 8.23(d, 1H), 8.14(d, 1H), 7.67-7.47(m, 4H), 5.82(d, 1H, upon treatment with D_2O the doublet turned to a singlet), 4.79(broad s, 1H), 4.03(broad s, 1H), 4.01(center of AB quartet, 2H), 2.01(s, 3H), 1.43(s, 9H). Exact Mass Calcd. for $C_{22}H_{24}O_2$; 320.1776, found 320.1806.

(8)



- (9) N. J. Turro, "Modern Molecular Photochemistry", Chapter 12, The Benjamin/Cummings Publishing Co., Inc., California (1978).
- (10) T. Nakayama, T. Yamaguchi, K. Ushida, K. Hamanoue, S. Miki, K. Matsuo and Z. Yoshida, Chem. Phys. Lett., submitted.