

Cyclic Voltammetric Characteristics of Some Carbenium Salts Having Methoxyphenyl Groups

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It is of interest to construct stable multistep redox system by combining some redox centers, and to examine how the redox properties would be changed. But, it is not easy even to control the redox potential of some redox centers over the wide range. We have recently reported the synthesis of di- and triarylcarbenium salts, and mono- and diaryl(ferrocenyl)carbenium salts having some methoxy substituents on the phenyl group, and have revealed that methoxyphenyl and ferrocenyl groups could stabilize the carbenium salts and the wide range of the cathodic shift in the reduction potentials could be observed as the number of *o*- and *p*-methoxy groups increased (1, 2). We will report here the effect of methoxy substituents on some arylbis(2,6-dimethoxyphenyl)-carbenium salts on the redox potentials and on the absorption maxima, prior to construction of the multistep redox system.

These compounds as shown in upper right column were synthesized and dissolved in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate. Cyclic voltammetric measurements were done at 25°C in a conventional three electrodes cell with Pt wire working electrode. UV-vis spectra were measured in 1,2-dichloroethane.

All of these salts except **5c** showed a reversible one electron, diffusion-controlled redox wave based on carbenium-methyl radical redox couple. The reduction peak potentials of **4** and **5** varied in the range from +260 ~ +70 mV vs. Ag/AgCl, and from +300 ~ -370 mV vs. Ag/AgCl, respectively, depending on the aryl substituent (Table 1). The cathodic shift in the redox potentials could be again observed, owing to the electron donation from the *p*-methoxy substituents on aryl group rather than that from *o*-methoxy group. In addition, the resulting methyl radicals seem to be stabilized by the steric effect of these aryl groups.

The longest absorption maxima of these salts were shifted from 530 to 800 nm for **4**, and from 520 to 600 nm for **5**, with about 4 of log ϵ (Table 2). Apparent LUMO and HOMO levels were estimated using these E^0 and λ_{\max} values. Both the LUMO and HOMO levels of **5** were shifted depending on the aryl substituent, whereas the LUMO level of **4** rather than the HOMO was shifted. The dependence of LUMO level on the substituent constant (σ_p^+) was also examined. Linear relationship was observed for compounds, **4** and **5**. These results indicate that the LUMO is almost localized on the central cationic carbon.

References

- M. Wada et al., *Bull. Chem. Soc. Jpn.*, **68**, 243 (1995); *Bull. Chem. Soc. Jpn.*, **68**, 3233 (1995); *Bull. Chem. Soc. Jpn.*, **70**, 2737 (1997); *Bull. Chem. Soc. Jpn.*, **71**, 1667 (1998); *J. Organometal. Chem.*, **574**, 86 (1999).
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Abbreviations

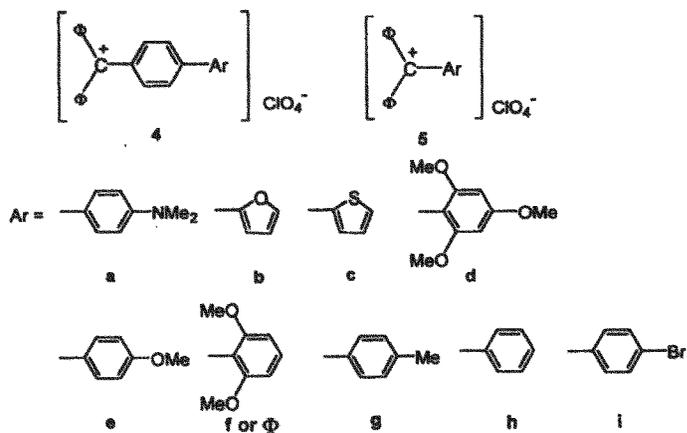


Table 1. CV data of **4** and **5**.

Compounds	E _{pc} *	E _{pa} *	E ⁰ *	ipa/ipc
4a	70	160	115	1.02
4b	230	320	275	0.92
4c	233	325	279	0.94
4d	175	260	218	0.98
4e	210	290	250	0.96
4f	210	290	250	1.00
4g	228	308	268	0.93
4h	248	327	288	0.95
4i	260	340	300	0.98
5a	-370	-290	-330	0.94
5c	270	—	—	—
5d	-160	-80	-120	0.98
5e	-22	72	25	0.99
5f	-23	65	21	0.97
5h	150	245	198	0.97
5i	300	380	340	1.00
5j	47	147	97	0.97

Abbreviations are the same as above, except 2-methoxyphenyl as j.

* All potentials are in mV referred against aq. Ag/AgCl.

Table 2. UV-vis data of **4** and **5**.

Compounds	Color of solution	λ_{\max} / nm (log ϵ)
4a	green	797 (4.88)
4b	blue	777 (3.71)
4c	blue	750 (3.62)
4d	blue	677 (4.45)
4e	blue	642 (4.66)
4f	purple	595 (4.23)
4g	purple	593 (4.29)
4h	purple	545 (4.60)
4i	purple	532 (4.44)
5a	red	504 (4.43)
5c	reddish-purple	569 (4.17)
5d	reddish-purple	530 (4.17)
5e	purple	540 (4.44)
5f	purple	589 (4.12)
5h	reddish-purple	522 (4.25)
5i	purple	554 (4.26)
5j	purple	602 (4.03)