CHEMISTRY LETTERS, pp.789-792, 1977. Published by the Chemical Society of Japan

THE SYNTHESIS OF HIGHLY STABLE *o*- AND *p*-QUINONE METHIDES

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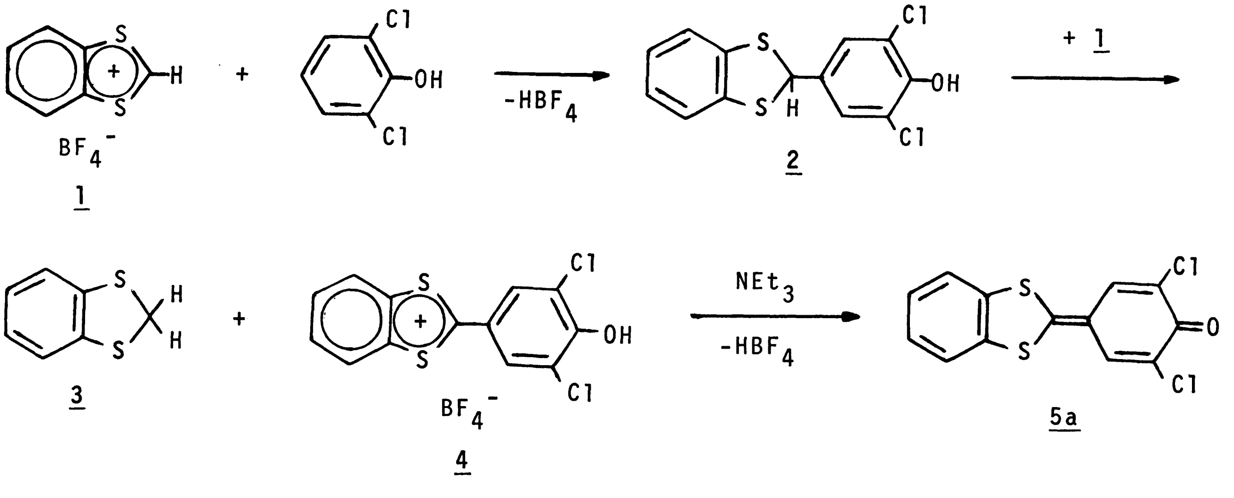
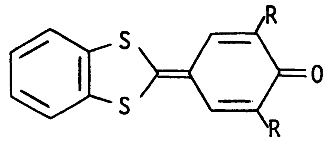
The reactions of 2,4- and 2,6-disubstituted phenols with two molar amounts of 1,3-benzodithiolylium tetrafluoroborate in acetonitrile at room temperature followed by treatment with triethylamine afforded the highly stable quinone methides, 2-(1,3-benzodithiol-2-ylidene)-3,5-cyclohexadien-1-ones and 4-(1,3-benzodithiol-2-ylidene)-2,5-cyclohexadien-1-ones, respectively, in good yields.

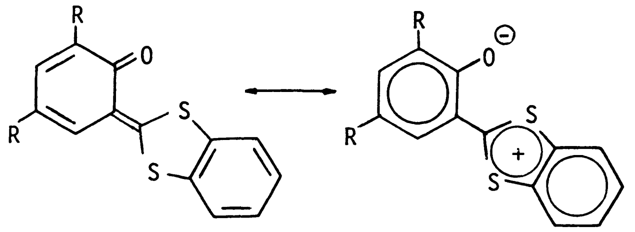
The chemistry of quinone methides has attracted considerable attention in recent years because of their intriguing chemical and physical properties.[1)] *o*-Quinone methides are especially very reactive[1c)] and are never isolated under normal conditions except a few cases.[2)] We wish to report the synthesis of highly stable *o*-quinone methides as well as *p*-quinone methides.

The reaction of 2,6-dichlorophenol with an equimolar amount of 1,3-benzodithiolylium tetrafluoroborate (1)[3)] in acetonitrile in the presence of pyridine at room temperature overnight afforded compound 2, mp 88-89°C, quantitatively. However, when two equivalents of 1 was allowed to react with 2,6-dichlorophenol under the same conditions and the resulting mixture was treated with triethylamine, the stable *p*-benzoquinone methides 5a, mp 277-280°C (from DMF), was obtained in 91% yield as deep red crystals along with 1,3-benzodithiole (3) (70%), bp 105°C/3 mmHg (lit.,[3)] bp 103-104°C/3 mmHg). As illustrated in the scheme, a second molecule of 1

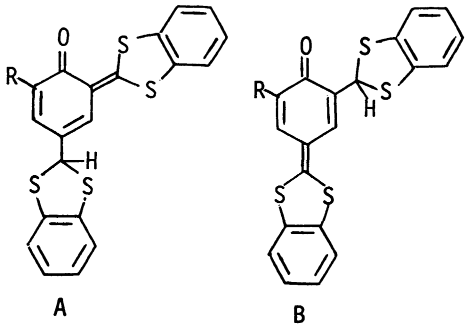




5b; R = *i*-Pr
5c; R = *t*-Bu

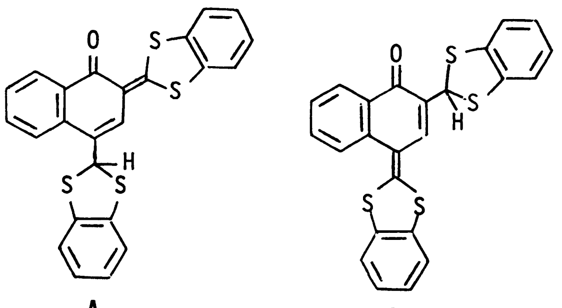


6a; R = Me
6b; R = *t*-Bu
6c; R = Cl

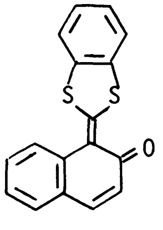


A B

7a; R = Me
7b; R = Cl



A 8 B



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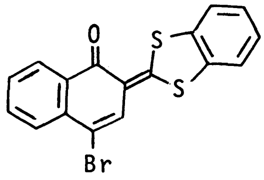

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abstracts a hydride from the initial product 2 to yield the dithiole 3 and the dithiolylium salt 4, which is then converted into the final product 5a by treatment with triethylamine. Similarly, the reactions of 2,6-diisopropyl- and 2,6-di-*t*-butylphenols with two equivalents of 1 gave rise to the quinone methides 5b (51%), mp 161-162°C (from cyclohexane) and 5c (96%), mp 179-180°C (from cyclohexane) (lit.,[2b] mp 184-185°C), respectively.

The reaction of 2,4-dimethylphenol with two equivalents of the dithiolylium salt 1 in acetonitrile at room temperature and the subsequent treatment with triethylamine also afforded the deeply colored stable *o*-benzoquinone methide 6a, mp 240-241°C (from benzene), in 85% yield. Similarly, 2,4-di-*t*-butyl- and 2,4-dichlorophenols reacted with two equivalents of 1 to give the *o*-quinone methides 6b (80%), mp 156-157°C (from hexane) and 6c (43%), mp 284-285°C (from benzene), respectively.

The reactions of *o*-methyl- and *o*-chlorophenols with three equivalents of 1 gave the quinone methides 7a (35%), mp 223-224°C (from benzene) and 7b (32%), mp 254-257°C (from DMF), respectively. Similarly, 1-naphthol and three equivalents of

Spectroscopic Data of Quinone Methides

Compounds	IR (KBr)	UV ($CHCl_3$)	H NMR (δ)	
	$\nu_{C=O}$ (cm^{-1})	λ_{max} (nm) (log ε)	$CDCl_3$ as solvent	CF_3CO_2D as solvent
5a	1604	512 (4.31), 381 (4.22), 456 sh (3.87)	a)	8.17 (2H, s), 7.9-8.7 (4H, AA'BB' m)
5b	1606	480 sh (4.54), 460 (4.64), 436 sh (4.51)	1.16 (12H, d), 3.23 (2H, heptet), 7.07 (2H, s), 7.1-7.6 (4H, AA'BB' m)	1.45 (12H, d), 3.35 (2H, heptet), 8.07 (2H, s), 7.8-8.6 (4H, AA'BB' m)
5c	1600	474 sh (4.52), 452 (4.67)	1.31 (18H, s), 7.08 (2H, s), 7.1-7.6 (4H, AA'BB' m)	1.64 (18H, s), 8.20 (2H, s), 7.8-8.6 (4H, AA'BB' m)
6a	1620	540 sh (4.02), 507 (4.19), 364 (4.09)	2.18 (3H, s), 2.21 (3H, s) 7.02 (2H, broad s), 7.2-8.0 (4H, m)	2.49 (3+3H, s), 7.65 (1H, broad s), 7.92 (1H, braod s), 7.8-8.7 (4H, AA'BB' m)
6b	1614	528 sh (4.08), 498 (4.23), 360 (4.09)	1.30 (9H, s), 1.44 (9H, s), 7.0-7.9 (4+2H, m)	1.50 (9H, s), 1.67 (9H, s), 8.20 (1+1H, s), 7.8-8.6 (4H, AA'BB' m)
6c	1595	546 sh (4.21), 521 (4.30), 362 (4.03)	a)	7.9-8.3 (2+2H, m), 8.4 8.8 (2H, half of an AA'BB' pattern)
7a	1620	526 sh (4.19), 498 (4.28), 362 (4.07)	a)	2.42 (3H, s), 5.95 (1H, s), 6.9-7.3 (4H, AA'BB' m), 7.7-8.7 (4+2H, m)
7b	1605	540 sh (4.18), 509 (4.28), 364 (3.98)	a)	5.96 (1H, s), 6.9-7.4 (4H, m), 7.8-8.6 (4+2H, m)
8	1595	506 (4.38), 479 (4.40), 340 (4.08)	a)	6.52 (1H, s), 6.9-7.5 (4H, m), 7.5-8.7 (4+4+1H, m)
9	1619	471 (4.10), 446 sh 4.00), 370 (3.35)	6.6-8.6 (10H, m)	7.1-9.1 (10H, m)

a) A well-defined spectrum could not be obtained owing to the insolubility of the sample.

1 gave the quinone methide 8, mp 267-269°C (from DMF), in 92% yield. 2-Naphthol reacted with two equivalents of 1 to give the quinone methide 9 (83%), mp 164-165°C (from acetone) (lit.,2a,b) mp 165°C). Of particular interest is the reaction of 4-bromo-1-naphthol with two equivalents of 1 which gave a 96% yield of 8, the expected quinone methide 10 not being obtained.4) Phenol itself failed to react with 1, product isolated being dibenzotetrathiafulvalene3) (51%), mp 237-238°C.

The success of the present method in the synthesis of quinone methides consists in the fact that the aryl substituent of 2-aryl-1,3-benzodithiolylium ions stabilizes these cations to such an extent that the methine hydrogen atom of the initial products, 2-aryl-1,3-benzodithioles, can be easily abstracted by the 2-unsubstituted 1,3-benzodithiolylium ion.

The spectroscopic properties of quinone methides5) thus obtained are summarized in the Table.

o-Benzoquinone methides 6 are thermally very stable; for example, 6c melts at 284-285°C without decomposition. The unusually high stability of 6 may be attributed to the conjugation between an electron-donating 1,3-benzodithiol-2-ylidene group and an electron-withdrawing carbonyl group. The same holds for *p*-benzoquinone methides 5. This is reflected in their carbonyl frequencies, which appear as low as 1595-1620 cm^{-1}. Some of the quinone methides are scarcely soluble in ordinary organic solvents, but are easily soluble in trifluoroacetic acid, in which their NMR spectra were recorded. As is evident from the dramatic low-field shift of their NMR spectra observed in changing the solvent from deuterochloroform to deuterotrifluoroacetic acid, these quinone methides are protonated at their carbonyl oxygen atoms in trifluoroacetic acid and hence, they exist in the positively-charged 1,3-dithiolylium forms in this solvent; for example, the signal due to the benzene ring protons of 1,3-benzodithiole nucleus of 6a appears at δ 7.8-8.7 as a typical AA'BB' pattern in deuterotrifluoroacetic acid, thus indicating that the free rotation about the pinch bond can occur in this solvent, whereas it appears as a complex multiplet at δ 7.2-8.0 in deuterochloroform. It is noteworthy here that the UV spectra of 7 closely resemble those of 6 and differ much from those of 5, suggesting that the quinone methides 7 exist in the *o*-quinone methide type of tautomeric form A rather than *p*-quinone methide type of tautomeric form B. It is not clear as to whether compound 8 exists in the form A or B.

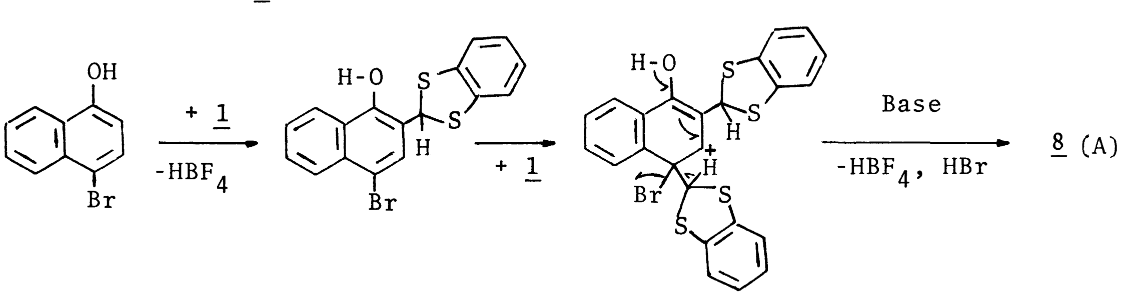
References and Notes

1) For recent reviews, see a) H. U. Wagner and R. Gompper, "The Chemistry of Quinoid Compounds," ed. by S. Patai, John and Wiley, Chapter 18, 1974; b) R. Okazaki, Yuki Gosei Kagaku Kyokai-shi, 34, 439 (1976); c) J. Colonge and G. Descotes, "1,4-Cycloaddition Reactions," ed. by H. Hammer, Academic Press, p. 217 (1967).

2) a) W. R. H. Hurtley and S. Smiles, J. Chem. Soc., 534 (1927); b) R. Gompper and E. Kutter, Chem. Ber., 98, 1365 (1965); c) D. L. Coffen and P. E. Garrett, Tetrahedron Lett., 2043 (1969); d) F. Effenberger and R. Niess, Angew. Chem., 79, 474 (1967); e) M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr., 2074 (1967).

3) J. Nakayama, K. Fujiwara, and M. Hoshino, Chem. Lett., 1099 (1975); J. Nakayama K. Fujiwara, and M. Hoshino, Bull. Chem. Soc. Jpn., 49, 3567 (1976).

4) The formation of 8 is tentatively explained as follows:



5) Satisfactory elemental analyses were obtained for all new quinone methides.

(Received May 26, 1977)