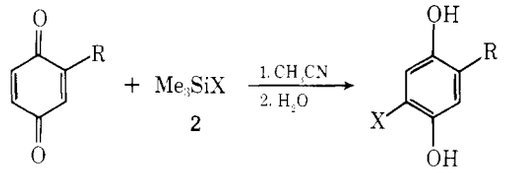
Communications

Catalyzed Addition of Trimethylsilyl Halides to Quinones. Direct Preparation of Halohydroquinones and Their Silyl Ethers

Summary: A new method for the regiospecific preparation of halohydroquinones is presented.

Sir: In the course of recent electrochemical studies we have observed that the catalyzed addition of trimethylsilyl halides to 1,4-benzoquinones, followed by hydrolysis of the initially formed adducts, give rise to the halogenated hydroquinones. Because there is considerable current interest in functionalized quinones[1,2] we have investigated some aspects of this reaction and report our preliminary results here.



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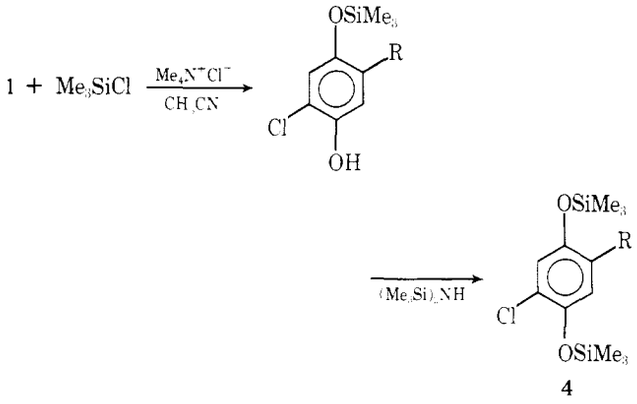
In acetonitrile, trimethylsilyl halides do not give adducts with quinones. Curiously, however, the addition of a small amount of tetraethylammonium fluoroborate initiates a visible reaction and, upon hydrolytic workup, a good yield of the chlorohydroquinone is obtained. A suitable procedure for the preparation of chlorohydroquinones involved stirring 2 mmol of sublimed quinone, 3 mmol of trimethylsilyl halide, and 0.2 mmol of tetraethylammonium fluoroborate in 3 mL of carefully dried acetonitrile overnight, at which time the quinone color was discharged. The solution was reduced in vacuo and stirred with 5 mL of water and 15 mL of dichloromethane. The aqueous layer was separated and extracted with two 15-mL portions of dichloromethane. The organic layers were combined and rinsed with 5 mL of water followed by 5 mL of saturated sodium chloride solution and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo yielded the solid product, which was recrystallized. This reaction has been performed with four *p*-quinones, one *o*-quinone, and also using trimethylsilyl bromide as shown in Table I. With these compounds the reaction is quite regioselective, producing mainly the 2,5-disubstituted product.

Although the role played by fluoroborate is not entirely clear, it seemed that chloride might catalyze the reaction and, indeed, comparable yields of chlorohydroquinone were produced using the above procedure with tetraethylammonium chloride replacing tetraethylammonium fluoroborate. A further adaptation of the procedure involves treatment of the unhydrolyzed reaction product with hexamethyldisilazane.



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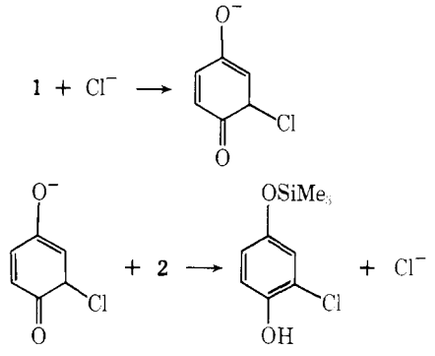
Careful workup then gave good yields of the disilyl ethers[3] (Table I). The utility of this reaction can be enhanced by coupling it to an oxidation step. Thus treatment of 4-methylcatechol with mercuric oxide[4] in acetonitrile containing anhydrous magnesium sulfate followed by filtration gave a solution containing the corresponding *o*-quinone. Treatment of this solution with chlorotrimethylsilane, tetraethylammonium chloride, and then hexamethyldisilazane gave after workup and distillation a 68% yield of 1,2-bis(trimethylsiloxy)-4-chloro-5-methylbenzene. This provides a method for halogenating catechols without isolating the unstable *o*-quinones.

A probable mechanism for chloride catalysis involves Michael addition of chloride followed by trapping of the anion with trimethylsilyl chloride. These two steps propogate a chain.



Halohydroquinones have recently been touted[2] as useful starting materials for the synthesis of more complex materials and it would appear that this reaction will have utility. It seems to be the method of choice for the reductive halogenation of quinones as it proceeds under mild conditions, is regiospecific, and gives consistently high yields. Hydrogen halides add similarly, but the yields are often low and polyhalogenation is a common problem.[4,5] The Michael addition observed is in marked contrast to the addition of trimethylsilyl cyanide to quinones, which is typically catalyzed by anionic initiation or triphenylphosphine, but gives exclusively 1,2 addition.[6]

In the present case soluble halide salts seem to be specific catalysts. Thus, we have found that other salts, i.e., tetraethylammonium perchlorate, sodium hexafluoroantimonate,

Table I. Products from 1,4-Benzoquinones with Trimethylsilyl Halides[a]

1R	2X	product (% yield)[b]
H	Cl	**3** (95)
CH_3	Br	**3** (92)
CH_3	Cl	**3** (75)
OCH_3	Cl	**3** (79)
H	Br	**4** (64)
Cl	Cl	**4** (72)
H	Cl	**4** (98)
CH_3	Cl	**4** (77)

[a] **3** from reaction catalyzed by fluoroborate; **4** from reaction catalyzed by chloride. [b] Yield of hydroquinones, **3**, by isolation. Yields of **4** by GLC.[3]

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sodium cyanide, and lithium perchlorate, are not catalysts, but sodium fluoroborate, boron trifluoride etherate, and triphenylphosphine do catalyze the reaction. The mechanism by which these compounds initiate addition deserves further study.

Acknowledgment. This work was supported by the National Institutes of Health and the National Science Foundations.

Supplementary Material Available: Complete experimental details and spectroscopic data (6 pages) are available. Ordering information is given on any current masthead page.

References and Notes

(1) See, for example, L. S. Hegedus and E. L. Waterman, *J. Am. Chem. Soc.*, **96**, 6789 (1974); K. Sato, S. Inoue, and K. Saito, *J. Chem. Soc., Perkin Trans. 1*, 2289 (1973); C. D. Snyder and H. Rappaport, *J. Am. Chem. Soc.*, **96**, 8046 (1974); A. S. Kende, T. Tsay, and J. E. Mills, *ibid.*, **98**, 1967 (1976).
(2) M. S. Manning, P. W. Raynolds, and J. S. Swenton, *J. Am. Chem. Soc.*, **98**, 5008 (1976); M. J. Manning, D. R. Henton, and J. S. Swenton, *Tetrahedron Lett.*, 1679 (1977).
(3) All new compounds possessed NMR, IR, and high resolution mass spectra in accord with the assigned structures. See paragraph at the end of the paper about supplementary material.
(4) This is an adaptation of the method of A. McKillop and D. Young, who recently reported the oxidation of *p*-hydroquinone via mercuric oxide in methanol. A. McKillop and D. Young, *Synth. Commun.*, **7**, 467 (1977).
(5) J. Cason, R. E. Harman, S. Goodwin, and C. F. Allen, *J. Org. Chem.*, **15**, 860 (1950); A. R. Ling, *J. Chem. Soc.*, **61**, 558 (1892).
(6) For a general discussion of the substitution chemistry of quinones, see K. T. Finley in "The Chemistry of Quinonoid Compounds", Interscience, New York, N.Y., 1974, pp 877–1144.
(7) D. A. Evans, J. M. Huffman, and L. K. Truesdale, *J. Am. Chem. Soc.*, **95**, 5822 (1973); D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); W. Lidy and W. Sundermeyer, *Chem. Ber.*, **106**, 587 (1973).

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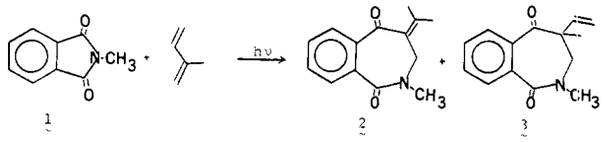
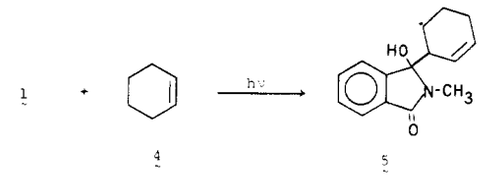
Photochemical Addition of Alkenes to *N*-Methylphthalimides. Formation of 3,4-Benzo-6,7-dihydroazepine-2,5-diones

Summary: The photochemical reactions of *N*-methylphthalimide with a number of alkenes in acetonitrile solution to give substituted 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-diones is described.

Sir: Recently there has been a great deal of interest in the photochemistry of cyclic imides. It has been shown that appropriately N-substituted phthalimides[1–13] and succinimides[14] undergo type II processes involving *N*-alkyl or -aryl chains and that *N*-alkenylsuccinimides afford intramolecular Paterno–Buchi products.[15] We recently reported[16] that dienes efficiently add to *N*-methylphthalimide (**1**) to give 6-methylene (**2**) or 6-vinyl (**3**) substituted 3,4-benzo-6,7-dihydro-



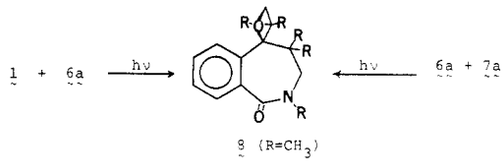
1-methylazepine-2,5-diones in an essentially unprecedented reaction that is formally a $[\pi^2 + \sigma^2]$ photochemical cycloaddition. During our investigation of the scope of this reaction with respect to acceptable variations in the π^2 component we confirmed the report of Kanaoka and Hatanaka[17] that cyclohexene undergoes photochemical reaction with **1** to afford only the photoreduction product **5** in poor yield.



However, when **1** (2 g) was irradiated in the presence of a 50-fold molar excess of 2-methylpropene (**6a**) in acetonitrile

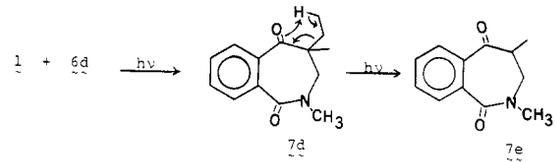
6a, $R_1=R_2=CH_3$, $R_3=R_4=H$ — **7a**, $R_1=R_2=CH_3$
b, $R_1=CH_2CH_3$, $R_2=R_3=R_4=H$ — **b**, $R_1=CH_2CH_3$, $R_2=H$
c, $R_1=(CH_2)_3CH_3$, $R_2=R_3=R_4=H$ — **c**, $R_1=(CH_2)_3CH_3$, $R_2=H$
d, $R_1=CH_2CH_3$, $R_2=CH_3$, $R_3=R_4=H$ — **d**, $R_1=CH_2CH_3$, $R_2=CH_3$
e, $R_1=R_2=R_3=CH_3$, $R_4=H$ — **e**, $R_1=CH_3$, $R_2=H$
f, $R_1=CH_2CH_3$, $R_2=R_3=CH_3$ $R_4=H$ — **f**, $R_1=R_2=H$
g, $R_1=R_2=R_3=R_4=CH_3$

solution with an unfiltered (quartz) 450-W Hanovia lamp for a period of 6 h, workup[18] of the reaction mixture gave two products identified as **7a** and **8** in 32 and 12% yields, respec-



tively. The structure of the major product 3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione (**7a**, mp 88–89 °C) was based on the following spectroscopic evidence: NMR ($CDCl_3$) δ 1.28 (s, 6 H), 3.22 (s, 3 H), 3.55 (s, 2 H), 7.32–7.94 (m, 4 H); IR (CCl_4) 1695 and 1660 cm^{-1}; *m/e* 217 (15). The minor product was identified as the oxetane **8**: NMR ($CDCl_3$) δ 0.74 (s, 6 H), 1.41 (s, 3 H), 1.70 (s, 3 H), 3.17 and 2.74 (AB pattern, J = 14 Hz, 2 H), 3.20 (s, 3 H), 4.39 and 3.98 (AB pattern, J = 5 Hz, 2 H), 7.13–7.70 (m, 4 H); IR ($CHCl_3$) 1630 cm^{-1}; *m/e* 273 (37). The structure and mode of formation of **8** was confirmed by irradiating **7a** in the presence of 2-methylpropene (**6a**). The product **8** was obtained in 17% yield.

In a similar manner irradiation of 2-methyl-1-butene and **1** afforded a 43% yield of **7e** (mp 75–76 °C): NMR ($CDCl_3$) δ



1.21 (d, J = 7 Hz, 3 H), 3.02–2.80 (m, 1 H), 3.20 (s, 3 H), 3.66 (m, 2 H), 7.38–8.00 (m, 4 H); IR ($CHCl_3$) 1690 and 1635 cm^{-1}; *m/e* 203 (30). Compound **7e** is presumably a secondary photoproduct of **7d**.[19]

The parent 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione (**7f**) was obtained in 60% yield from 1-butene and in 46% yield from 1-hexene via **1** → **7b** → **7f** and **1** → **7c** → **7f** sequences.

Table I. Ionization Potentials of Olefins and Benzazepindione Yields

alkene	**6b**	**6c**	**6a**	**6d**	2-butene	cyclopentene	cyclohexene	**6e**	**6f**
yield (%)	60	46	44	43	~32[24]	0[17]	0[17]	0	0
IP (EV)	9.58[21]	9.46[21]	9.23[21]	9.12[22]	9.13[21]	9.01[22]	8.95[22]	8.68[21]	8.53[23]