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Synthesis of Disubstituted Benzoquinones by the Photochemical Reaction of Acetylenes with $Fe(CO)_5$

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Synopsis. Internal acetylenes substituted with alkyl groups and terminal acetylenes substituted with alkyl, aryl, and functionallized alkyl groups are converted to disubstituted quinones by the photochemical reaction with $Fe(CO)_5$ followed by treatment with Ce(IV).

In the course of our investigations on quinonoid compounds,[1] we required a new synthetic methodology for disubstituted benzoquinone derivatives. Indirect methods,[2] whereby two substituents are introduced stepwise into benzoquinone, suffer from several difficulties, such as low yields and frequent need for long reaction steps. Direct conversion can be achieved by the photochemical reaction of acetylenes with $Fe(CO)_5$.[3] It appeared that this procedure would provide an attractive route to disubstituted benzoquinones because of a simple operation and a satisfactory yield. However, a curious thing was that any systematic investigations had not been performed and the ratio of products (2,5- and 2,6-isomers) had not been established. Consequently, we decided to explore the reaction of various types of acetylenes with $Fe(CO)_5$ in hopes of developing a practical procedure and establishing the scope and limitations.

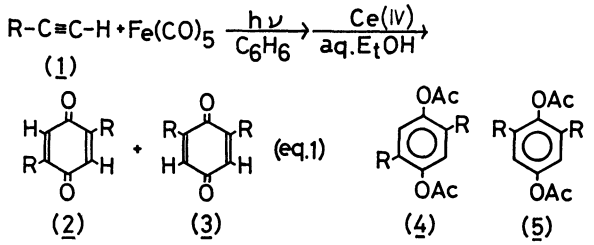
Results and Discussion

A benzene solution of an acetylene and $Fe(CO)_5$ was irradiated by a high pressure Hg lamp under N_2, and the reaction was followed by GLPC. After most of the starting acetylene was consumed, treatment of the reaction mixture with ceric ammonium nitrate produced the desired quinones. The results are summarized in Table 1. The structure of 2,5-(**2**) and 2,6-isomers (**3**) was determined by the ^1H NMR spectra of their acetyl derivatives. Reductive acetylation of **2** and **3** produced **4** and **5**, respectively, in a good yield. Since the two acetyl groups of **4** possess an identical chemical shift and those of **5** two different chemical shifts, two isomers could be easily discriminated.

TABLE 1. REACTION OF VARIOUS ACETYLENES WITH $Fe(CO)_5$[a]

Acetylene **1** R		Products, % (isold) **2**	**3**	Conversion %
$-(CH_2)_5CH_3$	(**1a**)	28	22	94
$-(CH_2)_3Cl$	(**1b**)	11	9	96
$-(CH_2)_8CO_2CH_3$	(**1c**)	22	16	93
$-C_6H_5$	(**1d**)	22	9	96
$-C_6H_4CH_3$	(**1e**)	18	9	96
$-C_6H_4Cl$	(**1f**)	17	10	85

a) Conversion indicates the amounts of acetylene consumed after 2 h irradiation.



As is apparent from Table 1, the terminal acetylenes can be converted to the corresponding quinones and the functional groups can be introduced into the side chain. Normally, 2,5-isomer (**2**) is obtained predominantly, presumably owing to the steric reason. However, diphenylacetylene does not give the desired quinone, though dimethylacetylene can be converted to duroquinone.[3] Since the reaction of phenylacetylene, *p*-methylphenylacetylene, and *p*-chlorophenylacetylene proceeds in a similar fashion and the product distributions are nearly identical, it seems that the electronic circumstances around the triple bond do not influence the reaction cource. Other acetylenes such as 2-propyn-1-ol, 3-bromo-1-propyne, 3-methoxy-1-propyne, and 1-butyne-3-one, where the functional groups are involved in the alpha-position, did not produce the desired quinones.

We next examined the reaction of acyclic alkadiynes with $Fe(CO)_5$ in hopes of obtaining cyclophanes bearing quinonoid structure.[4] Unfortunately, however, similar treatment of 1,9-decadiyne with $Fe(CO)_5$ did not produce the desirable methylene bridged benzoquinone but afforded the normal intermolecular cyclization products. Other diynes such as 1,7-octadiyne and 1,11-dodecadiyne gave the similar results. Consequently, the intramolecular cyclization is an unfavorable reaction at least in the above three diynes.

Finally the reaction of trimethylethynylsilane was examined to explore a possibility of obtaining quinone metalloids bearing a silyl group. Such a metalloid may be converted further to a number of functionallized quinone derivatives, since the transformation of C–Si bond to various C–Hetero bonds and C–C bond is well established.[5] Unexpectedly, the reaction took an entirely different course. Cyclopentadienone derivative was isolated from among tarry materials. Although the structure was assigned as the cyclopentadienone–Fe complex (**6** or **7**), the discrimination between both isomers

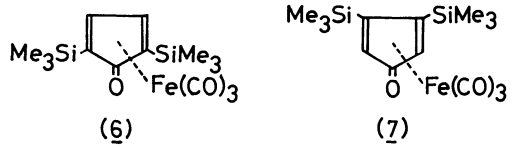
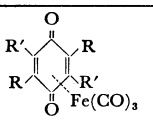
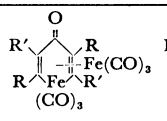
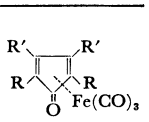


Table 2. The relationship between the substituents of acetylenes and the reaction products[a)]

R–C≡C–R′ R	R′			
$-(CH_2)_mX$	H[b)]	Yes	No	No
$-C_6H_4-Y$	H[b)]	Yes	No	No
$-C_6H_5$	C_6H_5[6)]	No	Yes	Yes
$-SiMe_3$	H[b)]	No	No	Yes
cyclo-C_3H_4-	H[7)]	Yes	No	No
Me–	Me[3)]	Yes	No	No

a) Yes indicates that the product is obtained, and No means the reverse.
b) Our own works.

was not possible. The reaction of trimethylpropynylsilane or trimethyl-1-hexynylsilane was quite sluggish, and these acetylenes were recovered even after irradiation for 24 h.

In conclusion, the course of the reaction highly depends upon the structure of acetylenes. The results of our own experiments and others are summarized in Table 2. The requirement for obtaining quinone derivatives is that i) internal acetylenes are substituted not with aryl groups but with alkyl groups, and that terminal acetylenes are substituted with ii) alkyl groups, iii) aryl groups, and with iv) functionallized alkyl groups where the functional groups are separated from the quinone moiety at least by two methylene units.

Experimental

General Procedure for the Reaction of Acetylenes with $Fe(CO)_5$. Oxygen-free dry benzene solution of an acetylene (0.025 mol) and $Fe(CO)_5$ (4.9 g, 0.025 mol) was irradiated by a high pressure Hg lamp under N_2 at 20 °C. GLPC examination revealed that generally the acetylene was almost consumed after 2 h. Then, the solvent was removed under reduced pressure, giving black oil. To an acetone solution of this oil was added an ethanol–water (72:25) solution of $(NH_4)_2Ce(NO_3)_6$ (13.7 g, 0.025 mol) with stirring and the resulting mixture was stirred overnight at room temperature. The organic materials were extracted with benzene and dried over anhyd. Na_2SO_4. The products were filtered through the column of silica, and benzene eluted the desired quinones in substantially pure form. These quinones (a mixture of 2,5- and 2,6-isomers) were further filtered through the column of silica to separate the isomers, and to obtain analytically pure materials. **2a** (yellow needles); mp 83—83.5 °C; NMR (CCl_4) 0.89 (t, 6H), 1.70—1.10 (m, 16H), 2.40 (t, 4H), 6.50 (s, 2H); IR (KBr) 1652, 1615 cm^{-1}; Mass *m/e* 276; Found; C, 78.38; H, 10.24%. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21%. **3a** (brown oil); NMR (CCl_4) 0.90 (t, 6H), 1.80—1.10 (m, 16H), 2.45 (t, 4H), 6.52 (s, 2H); IR (neat) 1659, 1615 cm^{-1}; Mass *m/e* 276; Elemental analysis was not performed since the pattern of mass spectra was identical with **2a**. **2b** (yellow crystal): mp 66—69 °C; NMR ($CDCl_3$) 2.08 (m, 4H), 2.62 (t, 4H), 3.56 (t, 4H), 6.57 (s, 2H); IR (KBr) 1649 cm^{-1}; MS *m/e* 260.040. Calcd for $C_{12}H_{14}O_2Cl_2$; 260.037079. **3b** (brown oil); NMR ($CDCl_3$) 1.99 (m, 4H), 2.61 (t, 4H), 3.55 (t, 4H), 6.50 (s, 2H); IR (neat) 1655, 1616 cm^{-1}. **2c** (pale yellow needles); mp 94—94.5 °C; NMR ($CDCl_3$) 1.60—1.20 (m, 28H), 2.40 (t, 4H), 3.67 (s, 6H), 7.16 (s, 2H); IR (KBr) 1733, 1651 cm^{-1}; Found; C, 69.52; H, 9.01%. Calcd for $C_{26}H_{40}O_6$; C, 69.61; H, 8.99%. **3c** (yellow oil); NMR ($CDCl_3$) 1.60—1.20 (m, 28H), 2.30 (t, 4H), 3.68 (s, 6H), 6.50 (s, 2H); IR (neat) 1740, 1665 cm^{-1}; Found; C, 69.52; H, 9.01%. Calcd for $C_{26}H_{40}O_6$; C, 69.61; H, 8.99%. **2d** (orange-yellow plates); mp 214—215 °C (lit,[8)] 214 °C); NMR ($CDCl_3$) 6.84 (s, 2H), 7.36 (m, 10H); IR (KBr) 1646 cm^{-1}. **3d** (reddish needles); mp 137—138 °C (lit,[9)] 135 °C); NMR ($CDCl_3$) 6.82 (s, 2H), 7.36 (m, 10H); IR (KBr) 1652 cm^{-1}. **2e** (orange-yellow plates); mp 222—223 °C (lit,[10)] 220 °C); NMR ($CDCl_3$) 2.42 (s, 6H), 6.88 (s, 2H), 7.50—7.10 (m, 8H); IR (KBr) 1657 cm^{-1}. **3e** (orange-red needles); mp 150—155 °C (lit,[9)] 161 °C); NMR ($CDCl_3$) 2.40 (s, 6H), 6.84 (s, 2H), 7.30—7.00 (m, 8H); IR (KBr) 1668 cm^{-1}. **2f** (orange needles); mp 223—224 °C; NMR ($CDCl_3$) 6.94 (s, 2H), 7.50—7.20 (m 8H); IR (KBr) 1652 cm^{-1}; Found; C, 65.59; H, 2.89; Cl, 21.43%. Calcd for $C_{18}H_{10}O_2Cl_2$; C, 65.67; H, 3.07; Cl, 21.54%. **3f** (orange crystal); mp 112—116 °C; NMR ($CDCl_3$) 6.82 (s, 2H), 7.50—7.20 (m, 8H); IR (KBr) 1660 cm^{-1}; Found; C, 65.59; H, 2.89; Cl, 21.43%. Calcd for $C_{18}H_{10}O_2\ Cl_2$; C, 65.67; H, 3.07; Cl, 21.54%.

The reductive acetylation was carried out by the reported procedure.[11)] The reaction proceeded quite smoothly, and the reaction product was directly analyzed by ^1H NMR spectra without further purification. **4a**; NMR (CCl_4) 0.88 (t, 6H), 1.70—1.10 (m, 16H), 2.19 (s, 6H), 2.43 (t, 4H), 6.77 (s, 2H). **5a**; NMR (CCl_4) 0.90 (t, 6H), 1.70—1.10 (m, 16H), 2.19 (s, 3H), 2.24 (s, 3H), 2.40 (t, 4H), 6.75 (s, 2H). **4d**; NMR ($CDCl_3$) 2.07 (s, 6H), 7.16 (s, 2H), 7.50—7.30 (m, 10H). **5d**; NMR ($CDCl_3$) 2.05 (s, 3H), 2.10 (s, 3H), 7.00 (s, 2H), 7.50—7.30 (m, 10H). **4e**; NMR ($CDCl_3$) 2.08 (s, 6H), 2.36 (s, 6H), 7.12 (s, 2H), 7.40—7.20 (m, 7H). **5e**; NMR ($CDCl_3$) 2.06 (s, 3H), 2.11 (s, 3H), 2.35 (s, 6H), 7.05 (s, 2H), 7.40—7.20 (m, 8H). Other isomers (**2b** and **3b**, **2c** and **3c**, **2f** and **3f**) were determined by their carbonyl stretching frequencies.

The reaction of ethynylsilane with $Fe(CO)_5$ was performed similarly. After irradiation for 4 h, evaporation of the solvent followed by filtration through the column of florisil gave the complex (**6** or **7**); pale yellow needles (mp 135—138 °C); yield 2%; NMR ($CDCl_3$) 0.32 (s, 18H), 5.52 (s, 2H); IR KBr) 2055, 1993, 1960, 1606 cm^{-1}; UV ($CHCl_3$) λ_{max} 302 nm, log ε=3.5; Mass *m/e* 364; Found; C, 45.39; H, 5.54%. Calcd for $C_{13}H_{20}O_4Si_2Fe$; C, 46.15; H, 5.53%.

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