

2,5- AND 2,6-DICYCLOPROPYLBENZOQUINONES FROM PHOTOREACTION OF CYCLOPROPYLACETYLENE
WITH $\text{Fe}(\text{CO})_5$

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Our study of the photochemical reactions of vinylcyclopropane systems indicated that the vinylic π -electrons serve as the initial site of coordination to iron from which involvement of the cyclopropane ring; i.e., ring opening, follows (Scheme I).¹

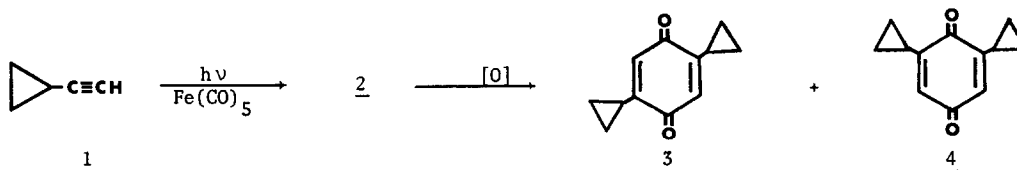
Scheme I



The question whether acetylenic π -electrons might play a similar role in reactions of cyclopropylacetylene systems was the initial point of interest in the present study.

From the outset, however, it was apparent that on irradiation of cyclopropylacetylene (1)² with $\text{Fe}(\text{CO})_5$ in solution (hexane or CH_2Cl_2),³ only the acetylenic portion of the molecule is involved. From the reaction mixture a black organometallic material (2) obtained directly as a precipitate (in hexane) or on evaporation of the solution (CH_2Cl_2) yielded on oxidative degradation 2,5- and 2,6-dicyclopropylbenzoquinones (3 and 4, Scheme II) in overall yield ~70%.

Scheme II



Though complete analysis of 2 has so far been restricted by its relative instability, the available chemical and spectral data point to an iron carbonyl complex into which two acetylene units, bound to metal and not directly to carbonyl, are incorporated. I.r. analysis (nujol)

showed the presence of terminal metal carbonyl ($2100\text{-}1900\text{ cm}^{-1}$) and bridging carbonyl ($\sim 1800\text{ cm}^{-1}$) in addition to C-C and C-H absorption. The highest ionic weight fragment in the mass spectrum of 2 corresponds to M^+ of the benzoquinones 3 and 4 (m/e 188), and further fragmentation parallels that of 3 and 4.

The benzoquinones were obtained in pure form from the oxidation mixture by chromatography (florisil, petroleum ether eluent) and recrystallization: ⁴ 3, m.p. $130\text{-}131^\circ$, yellow needles (pentane); $\nu_{\text{CO}} \approx 1640\text{ cm}^{-1}$; m/e 188 (M^+); nmr (CCl_4) τ : 3.99 (s, 2H), 7.98 (m, 2H), 8.75-9.42 (m, 8H); 4, m.p. $70\text{-}71^\circ$, yellow plates (pentane); $\nu_{\text{CO}} \approx 1654\text{ cm}^{-1}$; m/e 188 (M^+); nmr (CCl_4) τ : 4.10 (s, 2H), 7.95 (m, 2H), 8.78-9.43 (m, 8H). The isomers could be differentiated on the basis of their m.p.s (the 2,6-isomers in this series melt much below their 2,5-counterparts) and from p.m.r. ^{13}C -H satellites of the quinone ring protons: 3, $J_{13\text{C-H}} \sim 163\text{ Hz}$, $J_{\text{HH}} \sim 0$; 4, $J_{13\text{C-H}} \sim 164\text{ Hz}$, $J_{\text{HH}} \sim 2.8\text{ Hz}$.

The nonparticipation of the cyclopropyl group in the photoreaction of 1 with $\text{Fe}(\text{CO})_5$ suggests that production of benzoquinone derivatives should be general for a series of substituted acetylenes when no competing reaction pathway is involved under these conditions. An early study⁵ reported the direct formation of benzoquinone- $\text{Fe}(\text{CO})_3$ complexes on irradiation of neat solutions of $\text{Fe}(\text{CO})_5$ with both terminal and disubstituted alkynes; e.g., 2-butyne \longrightarrow duroquinone- $\text{Fe}(\text{CO})_3$, though it was not indicated whether the two isomers possible from terminal acetylenes were obtained.⁶ When we irradiated the disubstituted acetylene, 3-hexyne, with $\text{Fe}(\text{CO})_5$ in CH_2Cl_2 , tetraethylbenzoquinone- $\text{Fe}(\text{CO})_3$ ⁸ was isolated as a reaction product in addition to the black material analogous to 2 and the free benzoquinone, the latter two products constituting the major portion.⁹

On the other hand, similar irradiation of the terminal alkynes, phenylacetylene and 1-hexyne, was comparable to that of 1, where the only significant product was the black material analogous to 2, which on oxidative degradation afforded a mixture of the 2,5- and 2,6-disubstituted benzoquinones in good yield.¹⁰

Competitive reactions were involved in the photolyses of diphenylacetylene¹¹ and t-butylacetylene with $\text{Fe}(\text{CO})_5$ in solution and several products could be isolated, of which precursors of quinone systems¹² constituted only a part.

An extreme case is represented in the irradiation of dicarbomethoxyacetylene under these conditions. A single product, a black organometallic species lacking terminal metal carbonyl, was formed from which the trimer hexacarbomethoxybenzene was obtained on degradation.¹³

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2. Prepared according to C.E. Hudson and N.L. Bauld, J.Am.Chem.Soc., 94, 1158 (1972).
3. Irradiations were carried out on solutions ~0.05M in 1 and ~0.07M in $\text{Fe}(\text{CO})_5$ in a pyrex vessel (70 watt Hg-arc lamp) under nitrogen for 3 to 5 hours.
4. Elemental analyses of 3 and 4 were satisfactory.
5. H.W. Sternberg, R. Markby and I. Wender, J.Am.Chem.Soc., 80, 1009 (1958).
6. On thermal reaction of terminal acetylenes with $\text{Fe}(\text{CO})_5$ in basic medium, hydroquinone products obtained are only those of 2,5-disubstitution.⁷
7. W. Reppe and H. Vetter, Ann., 582, 133 (1953).
8. Tetraethylbenzoquinone- $\text{Fe}(\text{CO})_3$: orange needles (pentane), m.p. 57°; ir (hexane) $\nu_{\text{CO}(\text{terminal})} \sim 2098, 2039, 2020 \text{ cm}^{-1}$, $\nu_{\text{CO}(\text{quinone})} \sim 1650 \text{ cm}^{-1}$; nmr (CDCl_3) τ : 7.08 (q, 2H 8.93 (t, 3H); m/e 220 $[\text{M}-\text{Fe}(\text{CO})_3]^+$.
9. When the evaporated product mixture was treated directly with Ce(IV) in aq. ethanol, a 94% yield of tetraethylquinone was obtained.
10. It was generally observed that on going from hexane to CH_2Cl_2 irradiation solutions, the relative amount of the 2,5-isomer increased.
11. Our results of the photoreaction of toluene in CH_2CH_2 -hexane were similar to those reported for reaction in benzene: G.W. Schrauzer, J.Am.Chem.Soc., 81, 5307 (1959).
12. For reviews of reactions of acetylenes with iron carbonyl reagents from which benzoquinone derivatives are observed, see W. Hubel in "Organic Syntheses via Metal Carbonyls", Vol. I, I. Wender and P. Pino, Eds., Interscience Publishers, N.Y., pp 273-342 (1968), and C.W. Bird, "Transition Metal Intermediates in Organic Synthesis", Logos Press, London, pp 205-238 (1967).

13. The production of benzene compounds from thermal reactions of acetylenes with metal catalysts (including iron carbonyls) is well-documented; cf., C.W. Bird, "Transition Metal Intermediates in Organic Synthesis", Logos Press, London, pp 1-29 (1967).