An upper limit to the oxidation potential is established in that $K_3[Fe(CN)_6]$, $E^\circ[\mathrm{Fe(III)/Fe(II)}] = 0.36$ V, may be used as the oxidant in the production of the Cu(III) species. The lack of electrode activity found in this system is a common occurrence; for example, at pH 7 the ethylenediaminetetraacetate complexes of cobalt(II), nickel(II), zinc(II), and manganese(II) show neither oxidative nor reductive waves in polarographic measurements ("Handbook of Analytical Chemistry", L. Meites, Ed., McGraw-Hill, San Francisco, Calif., 1963, pp 5-72).

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William E. Keyes, John B. R. Dunn, Thomas M. Loehr*
Department of Chemistry, Oregon Graduate Center
Beaverton, Oregon 97005

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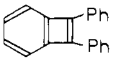
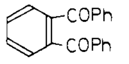
Oxidation of Tetraphenylbenzo[1,2:4,5]dicyclobutadiene with Molecular Oxygen in the Presence and Absence of Solvent to Afford Benzocyclobutadiene Oxide and *o*-Quinomethide, Respectively. Conversion of the Latter into Stable Methylenecyclohexa-1,3-diene

Sir:

Oxidation of 1,2-diphenylbenzocyclobutadiene (I) with molecular oxygen in boiling benzene to *o*-dibenzoylbenzene (II) and *o*-benzoylphenyl benzoate (III) has been reported.[1] The formation of III suggests that this reaction involves an oxidation process with one oxygen atom. Because 1,3-diphenylisobenzofuran peroxide (IV) of similar structure to **8**, which was prepared by photooxidation of 1,3-diphenylisobenzofuran (V), can easily be converted into II and III,[2] a possible pathway of the oxidation of I is that which proceeds successively via V and IV. To clarify the pathway of the oxidation of benzocyclobutadiene, we studied the oxidation of the title benzocyclobutadiene (**1**) and found that the oxidation of **1** with molecular oxygen in the presence of solvent affords benzocyclobutadiene oxide (**6**) and that **6** is further oxidized to its peroxide (**8**) which can easily be converted into tetrabenzoylbenzene (**7**) (Scheme I), tetrabenzoylphenol (**11**), and tribenzoylphenyl benzoate (**13**) (Scheme II). We also found that the oxidation of **1** with molecular oxygen in solid state affords *o*-quinomethide (**14**), which is easily converted into stable methylenecyclohexa-1,3-dienes (**15a–c**).



I



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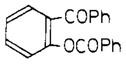
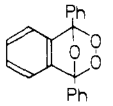
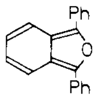


III



IV

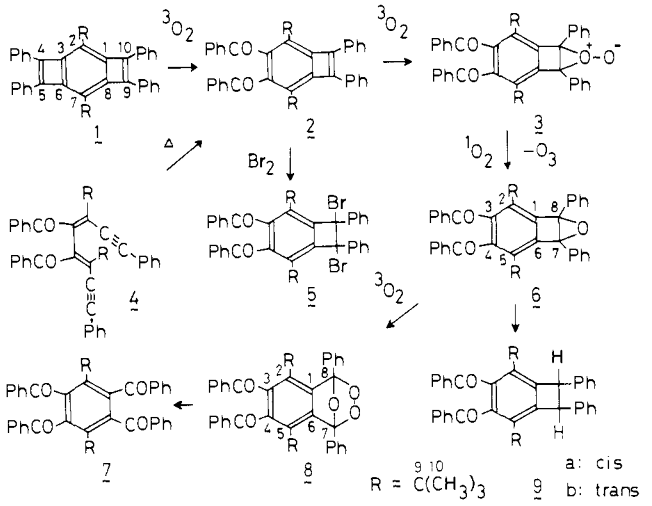


V

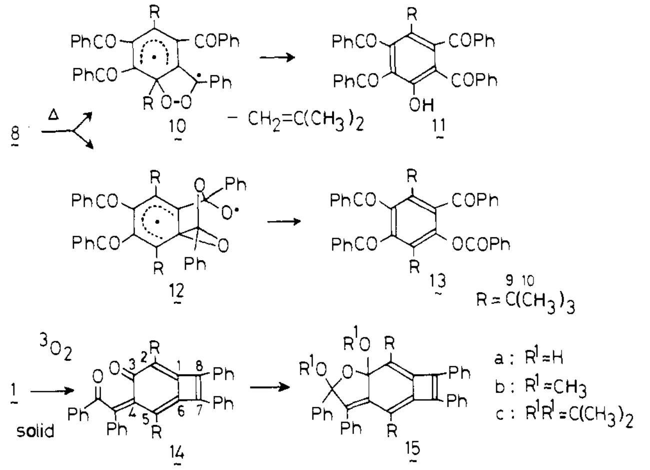
Stirring a suspension of **1**[3] in MeOH under O_2 atmosphere at room temperature for 1 h afforded **6** (96%): mp (N_2 atmosphere) 287–288 °C; ν_{max}[4] 1670 cm^{-1}; λ_{max} 266 nm (ϵ 43 700), 280 (sh) (33 800), 335 (sh) (4900); ^{1}H NMR δ 0.93 (s, 18 H), 6.8–7.9 ppm (m, 20 H); ^{13}C NMR[5] δ 32.6 (C_{10}), 35.3 (C_9), 57.7 (C_7), 131.9 (C_2), 137.6 (C_1), 152.3 ppm (C_3). No solvent effect for this oxidation was observed, and almost the same results were obtained when the oxidations were carried out in acetone, CCl_4, and petroleum ether. Hydrogenation of **6** over Pd/C afforded *cis*-diphenylbenzocyclobutane (**9a**) (46%): mp 204–206 °C; ^{1}H NMR δ 5.26 ppm (s, 2 H). $NaBH_4$ reduction of **6** gave **9a** (68%) and its trans isomer (**9b**, 12%): mp 206–207 °C; ^{1}H NMR δ 4.42 ppm (s, 2 H).

The oxidation of **1** to **6** probably proceeds via dibenzoylbenzocyclobutadiene (**2**), since **2** which was prepared (not isolated) by heating (*E,Z*)-4,5-dibenzoylocta-1,7-diyne-3,5-diene (**4**)[3b] under reflux in mesitylene under N_2 atmosphere for 1 h turned to **6** immediately by exposing to air. Although **2** was too air sensitive to isolate, it was isolated as dibromo derivative (**5**, 75%), mp 229–230 °C. Because the oxidation of **1** was also performed in the dark, triplet oxygen ($^3O_2$) would be the oxygenation reagent. A plausible pathway of the formation of **6** is as follows. Perepoxide of a triplet state, initially formed by the attack of $^3O_2$ to the 4,5 positions of **1**, turns to a singlet state by spin inversion.[6] This perepoxide of the singlet state gives **2** via a dioxethane intermediate.[6] Perepoxide **3** of a singlet state, which is formed by the same manner as described above, reacts with singlet oxygen ($^1O_2$) evolved during the oxidation process[6] to afford **6** and ozone.[7]

Scheme I



Scheme II



Although both the oxidation reactions of **1** and **2** were not quenched by a radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol, these reactions were quenched by a singlet oxygen scavenger, 1,4-diaza[2.2.2]bicyclooctane (Dabco).[8] The quenching results by Dabco are similar to those obtained for the oxidation of strained acetylene with molecular oxygen.[6]

Although **6** was stable in crystalline state at room temperature, a solution of **6** in benzene absorbed oxygen gradually even in the dark, affording, after 24 h, isobenzofuran peroxide (**8**, 50%). By photooxidation in tetrahydrofuran, however, **6** was converted into **8** in 72% yield within 1 h: mp 134–135 °C; ν_{max} 1670, 1650, 1220, 1070 cm^{-1}; λ_{max} 255 nm (ϵ 27 200), 263 (sh) (25 300); ^{1}H NMR δ 0.95 (s, 18 H), 7.50 ppm (br s, 20 H); ^{13}C NMR δ 32.9 (C_{10}), 37.6 (C_9), 112.5 (C_7), 134.3 (C_2), 138.5 (C_1), 142.7 ppm (C_3). A plausible pathway of the oxidation of **6** to **8** proceeds via the valence isomer of **6**, dibenzoyldiphenylisobenzofuran. Reduction of **8** with Ph_3P in benzene or KI in AcOH afforded **7** in good yield. This reduction is analogous to that of IV to II with the same reagents.[2a] Heating of **8** in benzene under reflux for 2 h afforded **7**[9] (7%) (mp 234.5–235.5 °C; ν_{max} 1670 cm^{-1}; λ_{max} 266 nm (ϵ 44 300); ^1H NMR δ 1.12 (s, 18 H), 7.1–7.7 ppm (br s, 20 H), **11** (48%) (mp 212–213 °C; ν_{max} 3350, 1670 cm^{-1}; ^1H NMR δ 1.30 (s, 9 H), 6.9–8.0 ppm (m, 20 H)), and **13** (3%) (mp 120 °C; ν_{max} 1740, 1670 cm^{-1}; ^1H NMR δ 1.15 and 1.25 (each s, 9 H), 7.0–8.3 ppm (m, 20 H)). This thermal reaction is contrasted with that of IV which affords III mainly in addition to II and some other products.[2a] A reasonable interpretation for this contrast is as follows. Intermediate **12**[2b] of the thermal conversion of **8** into **13** is unfavorable, because of steric crowding between *t*-Bu and Ph groups. Therefore, the pathway which proceeds via the sterically less hindered intermediate, **10**, and leads to **11** by the elimination of isobutylene from **10**, is favorable.

Very interestingly, however, oxidation of **1** in solid state gave **14** mainly. Keeping crystals of **1** in room for 5 days afforded **7** (13%) and **14** (50%): mp 250–251 °C; ν_{max} 1660, 1640 cm^{-1}; λ_{max} 253 nm (ϵ 26 700), 304 (27 400), 320 (sh) (25 900), 335 (sh) (18 500); ^1H NMR δ 0.81 and 0.82 (each s, 9 H), 7.1–8.1 ppm (m, 20 H); ^{13}C NMR δ 30.3 and 32.1 (C_{10}), 34.5 and 35.7 (C_9), 131.9 and 134.4 (C_2, C_5), 141.5 (C_4, C_6), 154.2 (C_1, $J_{16} = 35.2$ Hz), 192.4 ppm (C_3, $J_{34} = 50.8$ Hz). Because this oxidation was also performed in the dark, **14** would be produced by the attack of $^3O_2$ on the 3,4 positions of **1**, and **7** would be produced by the attack of two $^3O_2$s on the 4,5 and 9,10 positions. *o*-Quinomethide is unstable and only a few derivatives have been isolated.[10] Stability of **14** is probably due to the reason that the aromatization of its six-membered ring should produce an unfavorable benzocyclobutadiene system. However, acid-catalyzed reaction of **14** with nucleophile easily afforded **15**, stability of which would presumably be due to the same reason as above. Treatment of **14** with H_2SO_4 in aqueous acetone and MeOH at room temperature for 1 h afforded **15a** (80%) (mp 251–253 °C; λ_{max} 305 (sh) nm (ϵ 30 000), 315 (31 900), 330 (sh) (20 500)) and **15b** (83%) (mp 255–256 °C), respectively. Heating of **15a** and **15b** with H_2SO_4 in acetone under reflux for 2 h afforded **15c** (mp 267–268 °C) in 66 and 61% yields, respectively. UV spectra of **15b** and **15c** were comparable with that of **15a**.

It is not clear why oxygen attacks on the different positions of **1** depending on whether the oxidation is carried out in the presence or absence of solvent. Nonetheless, the present work would finally show that the oxidation of benzocyclobutadiene in solvent proceeds successively via cyclobutadiene oxide and isobenzofuran peroxide.

Acknowledgment. We are grateful to Dr. G. Rio for informing us of his unpublished spectral data of 1,3-diphenylisobenzofuran peroxide (IV) and to Drs. T. Oshima and M. Hatakenaka for the measurements of ^{13}C NMR spectra.

References and Notes

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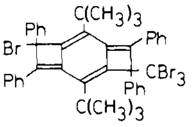
(3) (a) F. Toda and M. Ohi, *J. Chem. Soc., Chem. Commun.*, 506 (1975); (b) F. Toda and Y. Takahara, *Bull. Chem. Soc. Jpn.*, **49**, 2515 (1976).
(4) All the new compounds gave satisfactory elemental analyses and mass spectral data. IR, UV, and NMR spectra were measured in Nujol mill, $CHCl_3$, and $CDCl_3$, respectively.
(5) ^{13}C NMR signals of the six-membered ring carbons (C_1–C_6) of **6**, **8**, and **14** were assigned by measuring the spectra of each the two samples enriched by ^{13}C isotope (~40% each carbon) on 2,5 and 1,3,4,6 positions.
(6) N. J. Turro, V. Ramamurthy, K. C. Liu, A. Krebs, and R. Kemper, *J. Am. Chem. Soc.*, **98**, 6758 (1976).
(7) C. W. Jefford and C. G. Rimbault, *Tetrahedron Lett.*, 2479 (1976); M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *J. Am. Chem. Soc.*, **97**, 4439 (1975).
(8) Nonetheless, a thermally accessible triplet state is also considerable for **1**, because the heating of **1** and an equimolar amount of carbon tetrabromide in petroleum ether at 50 °C for 3 h in the dark afforded quinodimethane derivative i in 20% yield: mp 216–217 °C dec; λ_{max} 240 nm (ϵ 16 200), 358 (33 400)). The UV spectral data were comparable with those of analogous derivatives: F. Toda, K. Tanaka, and T. Yoshioka, *Chem. Lett.*, 657 (1976). This reaction probably proceeds via a radical chain process, because 2,6-di-*tert*-butyl-4-methylphenol quenched this reaction. Recently, similar reactions of tri-*tert*-butylcyclobutadiene with carbon tetrahalides have been reported: G. Maier and W. Sauer, *Angew. Chem., Int. Ed. Engl.*, **16**, 51 (1977). At present, however, no satisfactory interpretation for the difference of the behavior of **1** to carbon tetrabromide from that to molecular oxygen is available.



i

(9) Previously reported physical and spectral data for **7**[3] should be corrected to read as those described in this paper.
(10) L. Jurd, *Tetrahedron*, **33**, 163 (1977), and references cited therein.

Fumio Toda,* Nobuyuki Dan
Koichi Tanaka, Yoshikazu Takehira
Department of Chemistry, Faculty of Engineering
Ehime University, Matsuyama 790, Japan

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Structure of 1,4,8,11-Tetrathiacyclotetradecanecopper(I) Perchlorate: Comparative Geometries of Analogous Copper(I) and Copper(II) Complexes

Sir:

The geometry of copper complexes has been implicated as an important factor in copper redox chemistry.[1] Arguments involving the role of coordination geometry in copper protein chemistry have been especially prominent[1,2] even though only one copper protein structure has been reported to date.[3] A wide variety of structure types has been found for low molecular weight Cu(II)[4] and Cu(I)[5] complexes with Cu(II) favoring

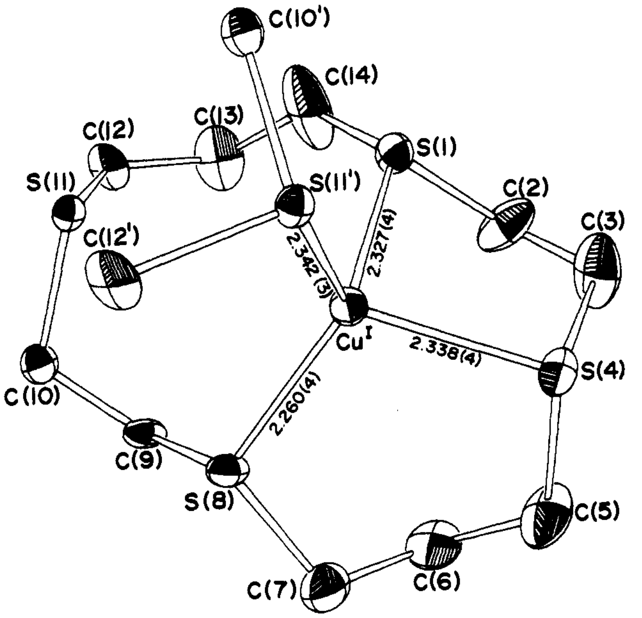

Figure 1. The Cu^I(14-ane-S_4)(ClO_4) subunit with atomic labeling. Atoms C(10′), S(11′), and C(12′) belong to the adjacent ligand molecule and atom S(11) is bonded to an adjacent Cu(I) ion.