(1974); P. S. Braterman and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 657 (1972); and P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).

(5) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).

(6) In solution, the complex yields a proton NMR spectrum fully consistent with a cis stereochemistry.[5] However, since there is a very slight asymmetry in the Co–H mutliplet, a very small amount of the trans may be present. Cis–trans interconversion should be very fast in the solution state.[5,7] Thus, although experiments show a cis dihydride to be formed in the reverse of reaction 1, this does not prove that a concerted cis oxidative addition prevails.

(7) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 75 (1973).

(8) Mineral acids decompose the complex.

(9) An analogous hydride, $H_2Co[P(OC_2H_5)_3]_4^+$, was obtained from the HCo-$[P(OC_2H_5)_3]_4$.

(10) The dihydrides were fully characterized by NMR and elemental analysis.

(11) In vacuum, thermolysis of the salt begins above ~150° as signaled by a measurable rate of hydrogen evolution.

(12) Another cobalt species must be formed (stoichiometry considerations). This species is probably $Co[P(OCH_3)_3]_6^{3+}$ but characterization data are not as yet unequivocal. The overall reaction would be: $9Co[P(OCH_3)_3]_4^+ \rightarrow 6Co[P(OCH_3)_3]_5^+ + 2Co^0 + Co[P(OCH_3)_3]_6^{3+}$. The trigonal bipyramidal $Co[P(OCH_3)_3]_5^+$ is in a virtual thermodynamic sink and invariably forms in these reductive eliminations. For this reason, extended studies to $Y_2CoL_4^+$ systems with $L = P(CH_3)_3$ or $P(O\text{-}i\text{-}C_3H_7)_3$ may simplify mechanistic studies because of the expected stability of these CoL_4^+ cations.

(13) Reaction conditions were 25° and ~700 mm D_2 pressure in dichloromethane solution.

(14) (a) The H_2–D_2 exchange reaction is substantially faster than the slow "decomposition" of $H_2Co[P(OCH_3)_3]_4^+$ through the intermediate Co-$[P(OCH_3)_3]_4^+$ to $Co[P(OCH_3)_3]_5^+$, $Co[P(OCH_3)_3]_6^{3+}$, and Co^0. (b) Coordinated deuterium was favored.

(15) Proton exchange between $H_2Co[P(OCH_3)_3]_4^+$ and $HCo[P(OCH_3)_3]_4$ is moderately fast in solution especially if the solvent is capable of solvating the proton.

(16) The multiline ^1H spectrum of the cis dihydride broadens to a single resonance as temperature increases and then the single resonance sharpens on further temperature increase to 70° (thermal decomposition at 80° and above is of sufficient consequence that spectral studies above this temperature were not feasible). There was no evidence of the expected fast exchange *intramolecular* limiting spectrum of a binominal quintet. Fast dissociation of phosphite ligands in this upper temperature range is consistent with the DNMR data.

(17) Protonation of the methyl complex is a substantially faster step than the complimentary alkylation [typically $(CH_3)_3O^+PF_6^-$ was used] of the hydride, an observation consistent with the relatively congested cobalt coordination sphere in these complexes (close approach of H^+ to cobalt should be less hindered than that of CH_3^+ in for example $(CH_3)_3O^+$).

(18) Elemental analysis and NMR characterization. AB_3 ^{31}P spectrum.

(19) This ammonia complex reacted with H_2 and with $P(OCH_3)_3$ to form H_2Co-$[P(OCH_3)_3]_4^+$ and $Co[P(OCH_3)_3]_5^+$, respectively. The first step in these reactions is dissociation of the ammonia ligand.

(20) These included ethylene, propylene, 1-hexene, and diphenylacetylene. The acetylene complex was more stable than the ethylene complex; both these complexes showed the expected A_2B_2 ^{31}P NMR spectrum.

(21) This complex gave a low temperature AB_2 ^{31}P pattern which is that expected for a square pyramidal form with an apical phosphite ligand (analogous to that established for the isoelectronic η^4-$C_4H_6Fe(CO)_3$).

(22) The yellow propylene complex was prepared and isolated as a PF_6^- salt at −78°. Evacuation of this salt at 25° led to complete propylene removal to give the blue $Co[P(OCH_3)_3]_4^+PF_6^-$ salt.

(23) Reaction of the solid at 25°

(24) NH_3, $P(OCH_3)_3$, and C_2H_4.

(25) In dichloromethane, the green solution of the complex rapidly precipitated Co^0. Acetonitrile formed a red, weak complex with $Co(P(OCH_3)_3]_4^+$. This complexation stabilized such solutions; decomposition occurred over a several hour period.

(26) F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975).

(27) $C_3H_5CoH_2[P(OCH_3)_3]_3$ in the absence of a reducible substrate slowly eliminates propylene. The stability of this intermediate is ~1–2 orders of magnitude greater than that of $C_3H_5(H)Co[P(OCH_3)_3]_3^+$.

(28) Methane formation was never quantitative. For example, in dichloromethane the yield of methane was about 70–75% with a 1:1 stoichiometry. Reactivity of the cobalt intermediate complex towards the solvent may partly account for this result. Extensive dissociation of $(CH_3)_2Co[P(OCH_3)_3]_4^+$ to $(CH_3)_2Co[P(OCH_3)_3]_3^+$ is expected on steric grounds. Liberated phosphite ligand should then react rapidly with the oxonium salt. In fact, a higher yield of methane was obtained when the ratio of oxonium salt to CH_3Co-$[P(OCH_3)_3]_4$ was raised to 2:1.

(29) Analysis based on high resolution mass spectral data. We are indebted to Dr. J. Henion for obtaining these data.

(30) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 4545 (1972).

(31) Steric factors may also tend to favor the elimination step in cobalt vis a vis iron since the metal radius is smaller in the former.

(32) For evidence that charge plays an important role see R. Ettore, *Inorg. Nucl. Chem. Lett.*, **5**, 45 (1969).

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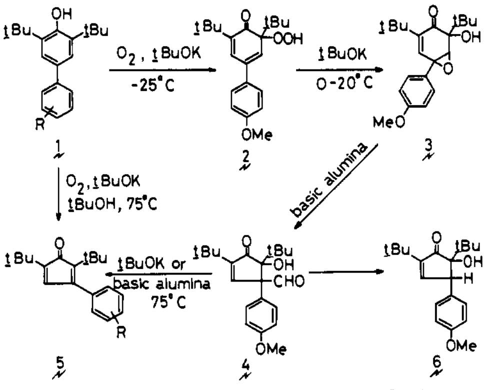
Mechanism of the Formation of Cyclopentadienone Derivatives from 4-Aryl-2,6-di-*tert*-butylphenols by Base-Catalyzed Oxygenation

Sir:

Recently it has been shown that 4-aryl-2,6-di-*tert*-butylphenols (**1**) are easily oxygenated in the presence of *t*-BuOK in *t*-BuOH to give antiaromatic 3-aryl-2,5-di-*tert*-butylcyclopentadienones (**5**) in good yields.[1] The reaction provides a novel and convenient method for the synthesis of such antiaromatic compounds.[2] We now wish to report the mechanism of this interesting reaction, clarified with the aim of isolation of intermediates employing **1** (R = 4-OMe) which quantitatively gives the cyclopentadienone **5** (R = 4-OMe).

It has been found that modification of the reaction conditions makes it possible to isolate the intermediates. Thus, oxygen was bubbled through a solution of **1** (R = 4-OMe) (15 mmol) in *t*-BuOH/petroleum ether (1:1) (100 ml) containing *t*-BuOK (75 mmol) at −25 °C for 40 min. Acidification of the reaction mixture with aqueous NH_4Cl solution and evaporation of the solvent afforded hydroperoxide **2** in 85% yield; yellow needles; mp 99–101°; ir (KBr) 3340 (OOH), 1665 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.03 (9, H, s, *t*-Bu), 1.28 (9 H, s, *t*-Bu), 3.84 (3 H, s, OMe), 6.61 (1 H, d, vinyl H, *J* = 2.8 Hz), 7.05 (1 H, d, vinyl H, *J* = 2.8 Hz), 6.7–7.6 (4 H, m, ArH), 9.00 (1 H, s, OOH, exchangeable with D_2O).[3] Treatment of this hydroperoxide with *t*-BuOK in *t*-BuOH at 75 °C quantitatively gave **5** (R = 4-OMe), while the treatment at room temperature resulted in the formation of **3** and **5** (R = 4-OMe) in 75 and 25% yields, respectively. The ratio of **3** to **5** (R = 4-OMe) depends on the reaction temperature: the higher temperature causes the higher yield of **5** (R = 4-OMe).[1] As was shown by separate experiments,[1] the cyclopentadienones **5** are formed in high yields upon heating the epoxy-*o*-quinols of type **3** with *t*-BuOK in *t*-BuOH at 75 °C. It is, therefore, obvious that the formation of **5** (R = 4-OMe) on the oxygenation of **1** (R = 4-OMe) proceeds by a mechanism involving these intermediates. All attempts to isolate any intermediate between **3** and **5** (R = 4-OMe) in this reagent system were unsuccessful. However, adsorption of **3** on activated basic alumina (activity I) in CH_2Cl_2 followed by elution with MeOH afforded isomeric ring contracted product **4** in 50% yield: colorless needles; mp 158–160°; ir (KBr) 3460 (OH), 1730 (CHO), 1710 cm^{-1} (ring C=O); NMR ($CDCl_3$): δ 0.63 (9 H, s, *t*-Bu), 1.33 (9 H, s, *t*-Bu), 3.39 (1 H, s, OH, exchangeable with D_2O), 3.85 (3 H, s, OMe, 7.24 (1 H, s, vinyl H), 6.9–7.4 (4 H, m, ArH), 9.17 (1 H, s, CHO); together with **5** (R = 4-OMe) (25%). In addition, treatment of **3** with the same basic alumina in *t*-BuOH at 75 °C quantitatively afforded **5** (R = 4-OMe). The compound **4** was also obtained by treatment of **3** with silica gel or CF_3COOH at room temperature. Taking account of the conclusions by Hart et al.[8] for the acid-catalyzed

Scheme I



R; 4-OMe, 3-OMe, 2-OMe, 4-Me, 3-Me, 2-Me, 4-Cl, H rearrangement of cyclohexadienone monoepoxides, these results are indicative of the structure of the ring contracted product to be **4**. Structure **4** is further supported by the fact that elution of **4** through a nonactivated basic alumina column with MeOH gave deformylated product **6** in 95% yield: liquid; bp 145° 1 mm; ir (KBr) 3540 (OH), 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.67 (9 H, s, *t*-Bu), 1.25 (9 H, s, *t*-Bu), 2.95 (1 H, s, OH, exchangeable with D_2O), 3.76 (3 H, s, OMe), 4.08 (1 H, d, methine H, J = 2.0 Hz), 7.28 (1 H, d, vinyl H, J = 2.0 Hz), 6.7-7.3 (4 H, m, ArH). Elution of **3** through a column of nonactivated basic alumina with MeOH also gave **6** in 70% yield, which gave no **5** on heating with *t*-BuOK. Compound **4** rapidly and quantitatively gave **5** (R = 4-OMe) in the *t*-BuOK/*t*-BuOH solution at 75 °C. Neither CO nor CO_2 was liberated in all the cases where **5** (R = 4-OMe) was formed, suggesting the lost carbon atom being expelled as formic acid or its ester. Accordingly, neither Favorskii type rearrangement widely seen in the base-catalyzed ring contraction of cyclohexene epoxides[9-13] nor the mechanism similar to that observed in the one-electron oxidation of 2,4,6-tri-*tert*-butylresorcinol[14] is applicable for the present reaction.

From these results, the mechanism by which the cyclopentadienones **5** are formed on the base-catalyzed oxygenation of the phenols **1** is depicted as shown in the scheme.[15] The exclusive ortho hydroperoxylation of **1** can be rationalized by assuming that the carbanion electron distribution of the phenoxide prefers the 2-position because the carbanion at 4-position is destabilized by electronic repulsion with the aromatic substituent and because the potassium ion seems to be complexed coming close to the O-C_2-C_6 area of the phenoxide (association of ion pair within solvent cage).

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References and Notes

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(2) W. Schafer, A. Schweig, G. Maier, and T. Sayrac, *J. Am. Chem. Soc.*, **96**, 279 (1974).
(3) This provides the first example of isolation and characterization of *o*-hydroperoxide obtained on the oxygenation of phenols.[4] It has been demonstrated that the oxygenation of 2,4-di-*tert*-butylphenols in the *t*-BuOK/*t*-BuOH system takes place exclusively at the ortho position.[5] The yield of **2** refers to isolated product. The NMR spectrum of the reaction mixture, on the other hand, showed **2** being obtained nearly quantitatively accompanied with only small amounts of **3** and **5** (R = 4-OMe). Further evidences for the structure **2**: the reduction with Me_2S gave the corresponding *o*-quinol which was easily converted to 3-*tert*-butyl-5-(4-methoxyphenyl)catechol, and quantitative formation of 3-*tert*-butyl-5-(4-methoxyphenyl)-*o*-benzoquinone by acid catalysis.
(4) There is a report describing the formation of *o*-hydroperoxide from 2,4,6-tri-*tert*-butylphenol but without evidence: A. F. Bickel and H. R. Gersmann, *Proc. Chem. Soc., London*, 231 (1957).
(5) A. Nishinaga, T. Itahara, and T. Matsuura, *Tetrahedron Lett.*, 4481 (1974).
(6) The transformation of **2** into **3** would involve the intramolecular asymmetric decomposition of dioxetane intermediate caused by interaction between the peroxy anion and π-system of the molecule as suggested for analogous reactions.[5,7]
(7) A. Nishinaga, T. Itahara, and T. Matsuura, *Chem. Lett.*, 667 (1974).
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(10) G. W. K. Cavill and C. D. Hall, *Tetrahedron*, **23**, 1119 (1967).
(11) W. Reusch and P. Mattison, *Tetrahedron*, **23**, 1953 (1967).
(12) R. W. Mouk, K. M. Patel, and W. Reusch, *Tetrahedron*, **31**, 13 (1975).
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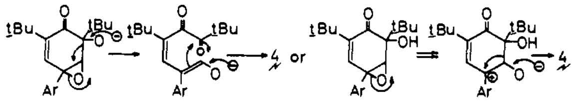
(14) W. H. Starnes, Jr., D. A. Plank, and C. Floyd, *J. Org. Chem.*, **40**, 1124 (1975).
(15) The following two possible mechanisms of the ring contraction may be considered:



Another possibility involving symmetrical decomposition of dioxetane intermediate such as generating an excited carbonyl group can be ruled out because no chemiluminescence was observed on the conversion of **2** to **5**.

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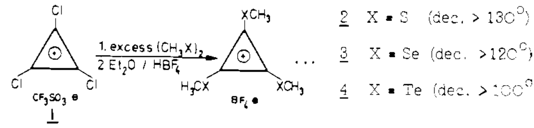
Toward Metallocyclopropenium Ions: Redox Cleavage of Diorganyldichalcogenides by Trichlorocyclopropenium Salts

Sir:

By virtue of their sp-hybridized carbon-to-ligand bonds and the availability of two orthogonal acceptor-π-orbitals, cyclopropenium ions can with some justification be regarded as "sesquiacetylenes" in which the acetylene bonding principle is extended to a second dimension. The idea of connecting the extremely versatile bonding and reactivity patterns of acetylene chemistry with the trifunctionality and strain potential of cyclopropenium ions has led us to explore synthetic pathways which would yield (organo-)metallocyclopropenium systems, conceivable analogues of metal acetylides.

In this paper we report on the unprecedented redox cleavage of diorganyldichalcogenides by the trichlorocyclopropenium cation as a general and convenient route to triorganylchalcogenocyclopropenium salts. Furthermore, as part of a preliminary mechanistic study of this reaction type, we outline a method which permits a controlled and high-yield synthesis of 1,2-dimethylthiocyclopropenthione, **11**, the first derivative of thiodeltic acid. Except for the case of **2**[1,2] all compounds in this paper are novel[3] and should not be easily accessible by conventional techniques.[4] The title reaction can be effected in CH_2Cl_2 under mild conditions (3 h at room temperature) according to eq 1 with yields around 40%:



(1)

The triflates were converted to the less hygroscopic and better crystallizing fluoborates **2–4**. These salts are colorless needles which develop an obnoxious odor through partial hydrolysis when exposed to the air.

Just as with **2**[1,2] spectroscopic data of **3** and **4** are indicative of the high symmetry (D_{3h}) of these systems. The NMR spectra ($CDCl_3$) consist of one sharp singlet (**2**, τ 7.15; **3**, τ 7.28; **4**, τ 7.62) which moves upfield as the electronegativity of X decreases.

The ir spectra are very simple and are entirely dominated by an intense broad band around 1200 cm^{-1} which, according to Yoshida's analysis of triheteroatom substituted cyclopropenium systems,[4] must arise from coupling of the degenerate ring deformation modes (E′) with the corresponding carbon-to-ligand vibration modes ("characteristic ring vibration"): ir (KBr),[5] **2**, 1350 (m), 1245 (s, broad), 1050 (m); **3**, 1440 (m), 1220 (s, broad), 1060 (m); **4**, 1435 (m), 1175 (s, broad), 1050 cm^{-1} (m).

Longest wavelength uv absorption exhibit a pronounced red shift on going from **2** to **4**: uv (CH_3CN) nm, **2**, 275 (ϵ 16 800); **3**, 297 (ϵ 20 100); **4**, 342 (ϵ 14 200). This is the expected trend for an intramolecular charge-transfer band and is in line with