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).

Acknowledgment. This research was supported by the Japan Society for the Promotion of Science. We wish to thank Professor T. Matsuura for helpful discussions.

References and Notes

(1) A. Nishinaga, T. Itahara, T. Matsuura, A. Rieker, and D. Koch, *Angew. Chem.*, **88**, 154 (1976).

(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).

(8) H. Hart, I. Huang, and P. Lavrik, *J. Org. Chem.*, **39**, 999 (1974); H. Hart and E. M. Shih, *ibid.*, **40**, 1128 (1975).

(9) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3972 (1961).

(10) G. W. K. Cavill and C. D. Hall, *Tetrahedron*, **23**, 1119 (1967).

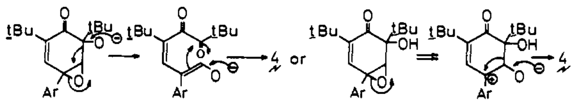
(11) W. Reusch and P. Mattison, *Tetrahedron*, **23**, 1953 (1967).

(12) R. W. Mouk, K. M. Patel, and W. Reusch, *Tetrahedron*, **31**, 13 (1975).

(13) W. Herz and M. G. Nair, *J. Org. Chem.*, **34**, 4016 (1969); W. Herz, V. S. Iyer, and M. G. Nair, *ibid.*, **40**, 3519 (1975).

(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**.

Akira Nishinaga*
Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Kyoto, Japan

Anton Rieker
Institut für Organische Chemie der Universität
74 Tübingen Auf der Morgenstelle, Germany

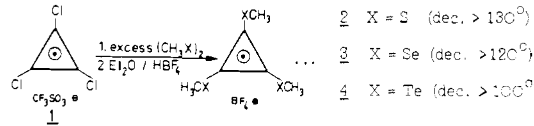
Received April 12, 1976

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.

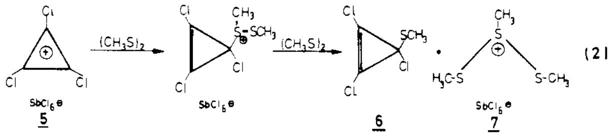
The ir spectra are very simple and are entirely dominated by an intense broad band around 1200 cm^{-1} which, according to Yoshida's analysis of triheteroatom substituted cyclopropenium systems,[4] must arise from coupling of the degenerate ring deformation modes (E′) with the corresponding carbon-to-ligand 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).

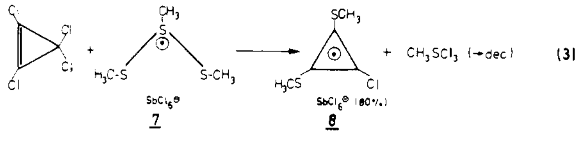
Longest wavelength uv absorption exhibit a pronounced red shift on going from **2** to **4**: uv (CH_3CN) nm, **2**, 275 (ϵ 16 800); **3**, 297 (ϵ 20 100); **4**, 342 (ϵ 14 200). This is the expected trend for an intramolecular charge-transfer band and is in line with theoretical predictions for triheteroatom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

Viewing the spectroscopic data in context it becomes apparent that **3** much more closely resembles **2** than **4**. This is paralleled by the thermal behavior of these salts: while **2** and **3** are thermally stable beyond 110°, **4** rapidly eliminates elemental tellurium above 90 °C and gradually during standing in diffuse daylight.[6] Mass spectroscopic behavior of **2–4** reflects the same trend: while trimethylthio- and trimethylselenocyclopropenium ions appear as a parent peak in the spectra (70 eV, 110°) of **2** and **3**, respectively, no such peak is observed in the spectrum of **4**.

Together with a recently synthesized trialkoxycyclopropenium salt[7] compounds **2–4** complete the set of triheteroatom-substituted cyclopropenium salts involving group 6b elements. Whereas trialkoxycyclopropenium cations are stabilized by the +M effect of the substituents (and destabilized by their −I effect); trimethyltellurocyclopropenium cations on the other extreme must receive what stabilization there is predominantly via the pronounced +I effect of tellurium. This follows from the poor π-overlap between the diffuse 5p orbitals of tellurium and 2p orbitals of carbon. In fact, tellurium is the most electropositive element (electronegativity 2.01) to have been attached to the cyclopropenium cation as yet. Therefore **4** represents the best model so far available for the study of triorganylmetallocyclopropenium cations which might be expected to reflect some of the properties of organometal acetylides.

Reaction 1 can be extended to the synthesis of triarylthio- and triarylselenocyclopropenium salts (average yields: 60–80%) but fails for the corresponding ditellurides which obviously are too stable. Replacement of **1** in eq 1 by $C_3Cl_3^+SbCl_6^-$, **5**, gives the corresponding trimethylchalcogenocyclopropenium hexachloroantimonates in high yield (80–90%) for X = S, Se as very insoluble, yellow (X = S) and yellow-orange (X = Se) salts. $C_3(TeCH_3)_3^+SbCl_6^-$, however, could not be prepared by this route as CH_3-Te-Te-CH_3 was oxidatively destroyed by $SbCl_6^-$. The structure of salts **2–4** indicates that a redox cleavage of the dichalcogenides must have taken place. Although one could in principle formulate a repeated 4-center exchange process yielding RXCl as the other reaction product in eq 1, we have so far been unable to confirm the presence of these unstable compounds in the complex reaction mixtures. On the other hand we made observations which point to a more complex mechanism: (1) A search for further reaction products in the mother liquor of the reaction of **5** with CH_3SSCH_3 yielded small amounts of methyl(bismethylthio)sulfonium hexachlorantimonate (**7**), indentical with an independently synthesized sample.[8] The most obvious way how **7** could have been formed is shown in eq 2. (2) While **7** is unreactive towards **5** (two positively charged species.) it does undergo a highly specific exchange reaction with tetrachlorocyclopropene according to eq 3:

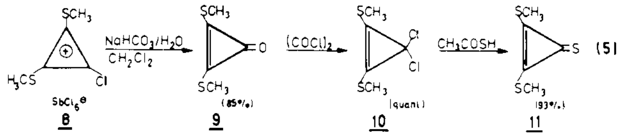




Thus hitherto unknown dimethylthiochlorocyclopropenium salt **8** is precipitated in pure form from the homogeneous reaction mixture as white microcrystalline material with mp 219° dec: ir (KBr),[5] cm^{-1}, 1865 (m), 1330 (m), 1280 (s), 1235 (s); uv (CH_3CN), nm, 266 (ϵ 17 900); NMR (CD_3CN) τ 6.93 (s, 3 H), 7.08 (s, 3 H). The lower symmetry of **8** as compared to **2** is evidenced by the occurrence of the A_1-band[4] at 1865 cm^{-1}, the splitting of the characteristic ring vibration (E_1 at 1280, 1235 cm^{-1}), and the 1:1 splitting of the $-SCH_3$ signal in NMR. The latter observation is compatible with C_s-symmetry, e.g., a rigid exo-endo alignment of SCH_3 groups due to hindered rotation at room temperature, as indicated in **8**. The following points concerning eq 3 are noteworthy: (a) the very yield of **8** indicates that **7** must be capable of *twofold CH_3S transfer;* (b) in the course of this exchange reaction free $(CH_3S)_2$ does not intervene. According to control experiments $(CH_3S)_2$ instantaneously converts **8** into $C_3(SCH_3)^+SbCl_6^-$; (c) so far the formation of CH_3SCl_3 is a postulate. This unstable compound could not be observed directly in NMR, rather a variety of signals which may result from its expected decomposition.[9] Equation 3 can be taken as a reasonable model for the presumable further reaction of **6** with **7** to yield $C_3(SCH_3)_3^+SbCl_6^-$. The overall process could then be written as eq 4:

$$5 + 2(CH_3S)_2 \longrightarrow C_3(SCH_3)_3^+SbCl_6^- + CH_3SCl_3 \qquad (4)$$

We are still actively searching for further support of this mechanism and its generalization for the higher homologues of $(RS)_2$. Finally, **8** deserves mention as a key intermediate in the first synthesis of thiodeltic acid dimethyl ester, **11**, via **9** and **10**, according to eq 5:



All these reactions proceed very cleanly at room temperature. The new compounds had the following characteristics: **9**, colorless needles from CH_2Cl_2/n-hexane with mp 114° dec; ir (KBr), cm^{-1}, 1860 (s), 1760 (m), 1520 (s), 1430 (m), 1325 (m), 1085 (s), 985 (w), 725 (m), 695 (m); uv (CH_2Cl_2), nm, 264 (ϵ 18 100); NMR ($CDCl_3$) τ 7.24 (s); **10**, thermally unstable yellow oil, characterized by its conversion to **11** and reconversion to **8** with $SbCl_5$, NMR ($CDCl_3$) τ 7.31 (s); **11**, light brown needles from cyclohexane, mp 126° dec; ir (KBr), cm^{-1}, 1685 (w), 1430 (w), 1280 (s), 1140 (s), 980 (m), 750 (s), 700 (w); uv (CH_2Cl_2), nm, 271 (ϵ 18 800); NMR ($CDCl_3$) τ 7.08 (s); mass spectrum *m/e* (assignment, rel intensity) 162 (M^+, 100%), 147 ($M^+ - CH_3$, 23%) 115 ($M^+ - SCH_3$, 81%), 100 ($C_3S_2^+$, 59%), 88 ($C_2S_2^+$, 14%).

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) R. Gompper and U. Jersak, *Tetrahedron Lett.*, 3409 (1973).
(2) Z. Yoshida, S. Miki, and S. Yoneda, *Tetrahedron Lett.*, 4731 (1973).
(3) All new compounds gave satisfactory elemental analysis.
(4) For a recent review see Z. Yoshida, *Top. Curr. Chem.*, **40**, 47 (1973).
(5) Only the most prominent bands are listed.
(6) Products of this decomposition are still being investigated.
(7) E. V. Dehmlow, *Angew. Chem.*, **86**, 203 (1974).
(8) R. Weiss and C. Schlierf, *Synthesis*, in press; cf. also G. Capozzi, V. Cucchini, S. Modena, and F. Rivetti, *J. Chem. Soc., Perkin Trans. 2*, 900 (1975).
(9) J. B. Douglass, R. V. Norton, R. C. Weichmann, and R. B. Clarkson, *J. Org. Chem.*, **34**, 1803 (1969).
(10) Only one member of this class of compounds has so far been synthesized: di-*tert*-butylthiocyclopropenone (a) in 4% yield via a carbene addition pathway: E. V. Dehmlow, *Chem. Ber.*, **101**, 410 (1968); (b) in unspecified yield via alkaline hydrolysis of a tri-*tert*-butylthiocyclopropenium salt together with ring-opening products: Z. Yoshida, S. Yoneda, T. Miyamoto, and S. Miki, *Tetrahedron Lett.*, 813 (1974).

R. Weiss,* C. Schlierf, K. Schloter
Institut für Organische Chemie der Universität München
8000 München 2, Germany

Received March 24, 1976