Table I. Polarographic Data for Neutral Complexes and Electron Spin Resonance Data for Cations

No.	Compound	E_p^{ox},[a] V	$\langle g \rangle$	$\langle A_{^{31}P} \rangle$, G
1	$Pd(o\text{-}O_2C_6Cl_4)(PPh_3)_2$	+0.73	2.006	<6[b]
2	$Pt(o\text{-}O_2C_6Cl_4)(PPh_3)_2$	+0.89	2.004	<8[b]
3	$Ir(o\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	+0.92	2.002	<8[b]
4	$Rh(o\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	+0.92	2.003	19.3
5	$Ru(o\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$	+0.65	2.004	24.5
6	$Ru(o\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$	+0.65	2.007	24.7

[a] In dichloromethane solution with $(C_4H_9)_4NPF_6$ as supporting electrolyte *vs.* an aqueous saturated calomel electrode. [b] Peak to peak line width.

hexafluorophosphate. For example treatment of an orange dichloromethane solution of **6** (λ_{max} 440 nm (ϵ 3.1 × 10^3), 330 (4.9 × 10^3); $\nu_{C\equiv O}$ 2046, 1994 cm^{-1}) with silver hexafluorophosphate produces a purple solution of the cation **6**$^+$ (λ_{max} 595 nm (ϵ 4.1 × 10^3), 518 (4.5 × 10^3), 415 (4.2 × 10^3), 385 (4.3 × 10^3), 335 sh (5.7 × 10^3); $\nu_{C\equiv O}$ 2074, 2023 cm^{-1}). The reaction to form **6**$^+$ is chemically reversible; reduction of a dichloromethane solution of **6**$^+$ with zinc quantitatively regenerates the electronic spectrum of **6**. Solutions of **6**$^+$ exhibit an esr spectrum consistent with a doublet ground state. Similar data have been obtained for the other complexes. However, because of the strongly oxidizing nature of the cations, no attempts have been made to isolate them. Due to the lower stability of the bonding between first-row transition metals and dioxylene ligands, the electron-transfer reactions of complexes of the type $M(o\text{-}O_2C_6Cl_4)_2{}^{2-}$ (M = Co, Ni, Cu) are significantly less well delineated.[11]

The formulation of the cations with the unpaired electron residing primarily on the dioxylene ligand rather than the metal is based on the following observations. The presence of a dioxylene ligand is necessary in order to observe reversible one-electron oxidations in such complexes (*e.g.*, $Pt(o\text{-}O_2C_6Cl_4)(PPh_3)_2$ undergoes this oxidation whereas $(Ph_3P)_2PtCl_2$, $(Ph_3P)_2Pt(PhC\equiv CPh)$, and $(Ph_3P)_2Pt(CS_2)$ do not). The isotropic *g* values for the various cations (Table I) are all quite similar with little dependence on the metal and are close to the isotropic value of 2.0054 reported[12] for a number of chlorinated *p*-quinones. Additionally the *g* tensor anisotropy for these cations is quite small; **5**$^+$ in dichloromethane at 77°K exhibits axial symmetry with $g_\perp$ = 2.020 and $g_\parallel$ = 2.000. These values contrast sharply with those observed for ruthenium(III)–phosphine compounds and other low-spin d^5 complexes which typically exhibit rhombic symmetry with $g_1 \sim 2.8$, $g_2 \sim 2.0$ and $g_3 \sim 1.6$.[13] Moreover spin-lattice relaxation is generally rapid for low-spin d^5 ions and consequently esr spectra of Ru(III), Ir(IV), and Rh(IV) species are generally only observable at low temperatures, whereas the esr spectra set out in Table I were obtained in solution at 25°.

Additionally these cations exhibit hyperfine coupling to the phosphine ligands which is sensitive to and diagnostic of the coordination geometry. Complexes **1**, **2**, and **3** have been shown to possess phosphine ligands which are trans to the dioxylene ligand.[2,6] No hyperfine splitting due to phosphorus is seen in the corresponding cations **1**$^+$, **2**$^+$, or **3**$^+$. However **4** has phosphines which are trans to one another and which lie above and below the dioxylene plane.[6] The esr spectrum of **4**$^+$ exhibits hyperfine splitting due to two equivalent phosphorus nuclei. The coordination geometry of **5** and **6** have not previously been determined. However, the observation of two infrared active carbonyl stretching frequencies in the neutral complexes[7] and in their respective cations indicates that the carbon monoxide ligands are cis to one another. The presence of hyperfine splitting by two equivalent phosphorus nuclei in the esr spectra of **5**$^+$ and **6**$^+$ along with the observation of two carbonyl stretching vibrations for each requires that the phosphines in these two complexes lie trans to each other and consequently the geometry of **5** and **6** is as depicted. The pattern of phosphorus hyperfine coupling is also consistent with the localization of the odd electron in these cations in a π orbital of the dioxylene ligand. When a phosphine lies trans to the dioxylene ligand the phosphorus s orbitals lie in the nodal plane of molecular orbital containing the odd electron. Consequently first-order theory of hyperfine coupling predicts that there should be no splitting from such phosphines. However, phosphines which lie above and below the dioxylene plane do not lie on a nodal plane of the crucial ligand molecular orbital. Therefore spin density may be transmitted to the phosphorus either through the metal or *via* a direct, through space interaction.

The cations described herein are unusually clear cut examples of species containing radical ligands, although it should be noted that coordination of semiquinones and semidiones by nontransition metal ions has also been detected.[14] A direct comparison of these complexes with their thio counterparts—the dithiolenes, which undergo extensive series of redox reactions[15]—cannot be made at this time since analogous dithiolene complexes of the heavier transition metals have not been synthesized. In general, however, the dithiolenes exhibit more extensive mixing of ligand and metal orbitals than observed here.

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(12) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2441 (1955).

(13) A. Hudson and M. J. Kennedy, *J. Chem. Soc. A*, 1116 (1969).

(14) D. R. Eaton, *Inorg. Chem.*, **3**, 1268 (1964); G. A. Russell and D. F. Lawson, *J. Amer. Chem. Soc.*, **94**, 1699 (1972).

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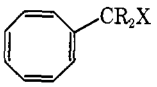
[8]Annulene as a Neighboring Group. I. Multiple Rearrangement Attending the Solvolysis of Cyclooctatetraenylcarbinyl Chlorides

Sir:

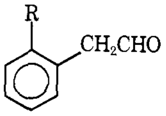
Although cyclooctatetraene (**1**) occupies a central position as the smallest stable member of the nonaromatic annulenes, the literature fails to record a single experiment designed specifically to assess the capability of **1** to function as a neighboring group in solvolytic processes. The present study, an outgrowth of our interest in this question, provides relevant data that the ionization of cyclooctatetraenylcarbinyl derivatives proceeds to a substantial degree with positionally specific valence isomerization and generation of a bicyclic homocyclopropenium cation intermediate. To the extent that this conversion operates, these results provide intriguing insight into the exceptional maneuverability of the π bonds in COT, despite the marked tendency of this polyolefinic system to reside in the thermodynamically more stable but π-overlap disruptive boat conformation. A companion paper[1] reports on yet a different deep-seated rearrangement which occurs with β-cyclooctatetraenylethyl systems.

Reaction of alcohol **2**–OH[2] with thionyl chloride and pyridine in $CHCl_3$ led readily to **2**–Cl.[3] Hydrolysis of this chloride at room temperature for 5 days in aqueous ethanol (1:1) buffered with 2,6-lutidine gave **2**–OH (37%), **2**–OCH_2CH_3 (17%), and *o*-tolylacetaldehyde (**3**, 46%). The identity of **3** was established by independent synthesis involving sequential lithium aluminum hydride reduction and Collins oxidation of commercially available *o*-tolylacetic acid and by comparison of individual spectra, vpc retention times, and semicarbazone derivatives (mp 176–177°).[3]

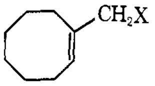
The pseudo-first-order rate data and activation parameters for **2**–Cl ($k_{30.1°} = 1.44 \times 10^{-5}$, $k_{40.0°} = 4.24 \times 10^{-5}$, $k_{49.9°} = 1.26 \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 20.7$ kcal/mol; $\Delta S^{\ddagger} = -12.5$ eu) and Δ^1-cyclooctenylmethyl chloride (**4**–Cl; $k_{30.1°} = 7.20 \times 10^{-5}$, $k_{40.0°} = 2.16 \times 10^{-4}$, $k_{49.9°} = 6.60 \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 22.1$ kcal/mol; $\Delta S^{\ddagger} = -7.8$ eu) reveal that the reactivity of **4**–Cl is enhanced over that of **2**–Cl by a factor of 5.



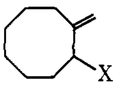
2, R = H
6, R = D



3, R = CH_3
7, R = CD_2H



4



5

Chloride **4**–Cl was obtained admixed with **5**–Cl (from which it could readily be separated using vpc techniques) by reaction of **4**-OH[4] with thionyl chloride and pyridine. When hydrolyzed as above, **4**–Cl was converted into a mixture of **4**–OH (27%), **5**–OH (22%), **4**–OCH_2CH_3 (33%), and **5**–OCH_2CH_3 (19%).[3] These results, although consisting of competitive processes in the case of **2**–Cl (see below), demonstrate the inability of the COT ring to provide meaningful anchimeric assistance.

As regards the origin of the methyl group in **3**, it became clear that hydrogen incorporation from the solvent system was not operative since hydrolysis of **2**–Cl in D_2O–C_2H_5OD gave no deuterium incorporation. Also, **3** does not arise from further rearrangement of **2**–OH or **2**–OCH_2CH_3 since these are stable to the reaction conditions. When hydrolyzed in the predescribed manner, dideuteriochloride **6**–Cl gave **6**–OH (75%), **6**–OCH_2CH_3 (10%), and **7** (15%; $\delta_{TMS}^{CDCl_3}$ 9.62 (t, $J = 2$ Hz, 1), 7.12 (m, 4), 3.62 (d, $J = 2$ Hz, 2), and 2.20 (br s, 1, $-CD_2H$); calcd m/e 136.0857, found 136.0859).

The greatly increased yield of unrearranged alcohol, when coupled with the decreased amount of aldehyde, serves to rule out a common mechanistic pathway to these two products. Direct S_N2 displacement by solvent on **2**–Cl and **6**–Cl logically accounts for the formation of **2**–OH, **6**–OH, and presumably also the derived ethers. In contrast, since the diminished proportion of **7** in the product mixture arising from **6**–Cl is directly related to the secondary kinetic deuterium isotope effect expected for rate-determining ionization of the latter chloride,[5] it would appear that ionization of the cyclooctatetraenylcarbinyl chlorides is rate limiting only for aldehyde formation.

These experiments establish that ionization of **2**–Cl leads to a cationic intermediate which reacts with water to give a covalent species, ready conversion of which to benzenoid product results in ortho placement of the methyl and acetaldehyde substituents. These requirements are met in homocyclopropenium cations **11** and **13**. Invocation of one or the other of these precursor ions, precedent for which has been obtained during earlier studies of the halocyclooctatetraene to *trans*-β-halostyrene rearrangement,[6] uniquely provides in plausible terms for the observed substitution pattern. Thus nucleophilic attack by water on **11** or **13** (presumably chiefly from the exo direction[6a]) affords alcohols **12** and **14**, respectively, conrotatory opening of which generates aromatic character and leads *via* **15** to **3**.

A priori reasoning suggested that the generation of a carbonium ion from **2**–Cl could result either from exclusive operation of one of three distinctively different mechanisms or from an indiscriminate merging of these pathways as a consequence of compression of the energy scale for the various possibilities into a narrow, simultaneously accessible region (Scheme I). In the first of these, cation **11** could arise by valence isomerization of preformed **8** and subsequent 1,3-hydride shift, generation of **9** without recourse to **8** by kinetically controlled ionization of the structurally related valence isomeric chloride,[7] or a process involving 1,3-hydride shift concomitant with halide ion departure from this bicyclic chloride to produce **11** directly.[8] Alternatively, access to **11** might be gained by internal return of chloride ion to **8** to give the allylic isomer, 1,3-hydrogen shift to provide 1-Cl-2-MeCOT, and ultimate valence isomerization and ionization of this halide according to the Huisgen mechanism.[6a] Lastly, **2**–Cl could undergo ionization from that valence tautomer which gives rise to **10**, the resultant p orbital in which can align itself conveniently for operation of a 1,4-hydride shift[9] to afford **13**.

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(1) L. A. Paquette and K. A. Henzel, *J. Amer. Chem. Soc.*, **95**, 2726 (1973).

(2) This alcohol was prepared by $LiAlH_4$ reduction of carbomethoxycyclooctatetraene.

(3) Satisfactory (±0.3%) elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds.

(4) A. C. Cope and P. E. Burton, *J. Amer. Chem. Soc.*, **82**, 5439 (1960).

(5) An excellent review of this subject has recently made its appearance: V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., ACS Monograph 167, Van Nostrand-Reinhold, New York, N. Y., 1970, Chapter 2.

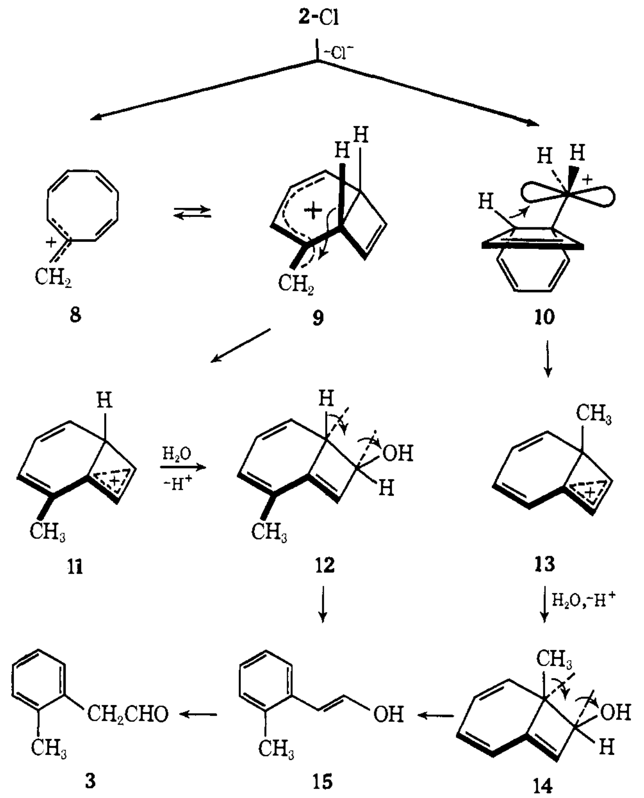
(6) These reactions involve a formal 1,3 migration of halogen: (a) R. Huisgen and W. E. Konz, *J. Amer. Chem. Soc.*, **92**, 4102 (1970); (b) R. Criegee, C. Schweickhardt, and H. Knoche, *Chem. Ber.*, **103**, 960 (1970).

(7) Compare, for example, the preequilibria which accompany the solvolysis of 7-cycloheptatrienylcarbinyl derivatives: (a) G. D. Sargent, N. Lowry, and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 5985 (1967); (b) L. A. Paquette and G. L. Thompson, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, paper ORGN 132; (c) L. A. Paquette and G. L. Thompson, *J. Amer. Chem. Soc.*, **95**, 2364 (1973).

(8) Related 1,2-hydride shifts are now recognized to obtain during solvolysis of cyclohexyl tosylates: (a) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972); (b) J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972).

(9) M. Saunders and J. J. Stofko, Jr. [*J. Amer. Chem. Soc.*, **94**, 252 (1972)] have recently demonstrated that 1,3-hydride shifts in acyclic

Scheme I



We note, however, that the valence isomerization of cyclooctatetraene to bicyclo[4.2.0]octatriene must overcome $\Delta H^{\ddagger} = 27$ kcal/mol, a barrier height which depends little on ring substitution.[6a,10] The low activation enthalpy for hydrolysis of **2**-Cl (20.7 kcal/mol) seemingly excludes the incursion of those pathways initiated by valence isomerization. Before final acceptance of **8** as the sole intermediate of mechanistic consequence, however, supportive data in the form of isotopic labeling studies and results realized from independent generation of **8** are, of course, needed. Work along these lines is currently in progress.

Notwithstanding, the driving force underlying the generation of cation **11** undoubtedly stems from the highly stabilized nature of homocyclopropenium cations.[11] The absence of overt anchimeric assistance in **2**-Cl can be traced to the folded nature of the π system in **8** which is adequate to misalign the p orbitals sufficiently to generate a measurable level of inductive rate retardation.[12]

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carbonium ions occur with an activation energy of 8.5 kcal/mol, while 1,4-hydride shifts are only slightly more demanding (12–13 kcal/mol).

(10) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, 76, 432 (1964); *Angew. Chem., Int. Ed. Engl.*, 3, 442 (1964); R. Huisgen and F. Mietzsch, *Angew. Chem.*, 76, 36 (1964); *Angew. Chem., Int. Ed. Engl.*, 3, 83 (1964).

(11) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).

(12) J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **92**, 1660 (1970); V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

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[8]Annulene as a Neighboring Group. II. Response of the Cyclooctatetraene Ring to Homoallylic Electron Deficiency[1]

Sir:

An interesting contrast in reactivity is found in the susceptibility of cyclooctatetraene (COT) and benzene to electrophilic attack. Owing to the lack of significant resonance stabilization in COT and its conversion under such conditions to stabilized homotropylium cations, its ease of protonation far exceeds that of benzene which is transformed to the benzenonium cation. Despite the energy disadvantage associated with the latter process, β-phenethyl derivatives do solvolyze by way of σ-bridged phenonium ions. However, the latent potential of COT to function as a like neighboring group, perhaps with formation of related homotropylium ions, has not been examined. We now describe a novel series of rearrangements which operates upon ionization of β-COT ethyl derivatives.

Lithiation of BrCOT followed by reaction with ethylene oxide gave **1**-OH (OPNB, mp 79–81°; ODNB, mp 69–70°;[2] OBs, mp 41–42°).[3] The solvolytic reactivity of **1**-OBs in buffered acetic acid, the data for which are summarized in Table I, clearly is allied more closely to the behavior of the fully saturated **2**-OBs than to that of **3**-OBs. Good first-order kinetic behavior was noted in all three cases. When solvolyzed for ten half-lives at 85°, **2**-OBs afforded only **2**-OAc. Acetolysis (50°) of **3**-OBs under highly buffered conditions (tenfold molar excess of NaOAc) led to the formation of **3**-OAc (34%), **4** (55%), and **5** (10%);[4] the structures of these products were confirmed by independent synthesis. Reduction in the amount of buffer and increased temperatures favored enhanced conversion to **3**-OAc as well as to small amounts of unidentified elimination products.[5]

Table I. Buffered (NaOAc) Acetolysis Rate Data

Brosylate	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate, 65°
1-OBs	55.00 ± 0.02	1.91×10^{-6}	25.3	−7.9	5
	65.00 ± 0.03	6.58×10^{-6}			
	75.00 ± 0.03	1.87×10^{-5}			
2-OBs	65.0	1.43×10^{-6} [a]	24.9	−11.8	1
	75.00 ± 0.03	4.69×10^{-6}			
	85.00 ± 0.03	1.16×10^{-5}			
	95.00 ± 0.03	3.25×10^{-5}			
3-OBs	45.00 ± 0.02	3.43×10^{-5}	24.9	−0.78	260
	55.00 ± 0.03	1.25×10^{-4}			
	65.00 ± 0.03	3.74×10^{-4}			

[a] Extrapolated value based on activation parameters.

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(1) Part I: L. A. Paquette and K. A. Henzel, *J. Amer. Chem. Soc.*, **95**, 2724 (1973).

(2) A. C. Cope and D. F. Rugen, *J. Amer. Chem. Soc.*, **75**, 3215 (1953).

(3) Satisfactory (±0.3%) elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds reported herein.

(4) Roughly comparable results have been realized previously from deamination of 3-NH_2 and hydrolysis of 3-OTs: M. Hanack, H. Schneider-Berlohr, H.-J. Schneider, R. Huttinger, and G. Wentrup, *Justus Liebigs Ann. Chem.*, 717, 41 (1968).

(5) As might be expected, 3-OAc was stable to the reaction conditions. In contrast, 4 underwent partial conversion to 3-OAc and 5 (4:1), while 5 isomerized exclusively to 3-OAc. One of the elimination products has been identified as 2-ethyl-1,3-cyclooctadiene.