Thermal Reactions of a Cyclopropanone. Racemization and Decarbonylation of *trans*-2,3-Di-*tert*-butylcyclopropanone[1]

Sir:

We wish to report experiments on the resolution and racemization of *trans*-2,3-di-*tert*-butylcyclopropanone (**1**), of relevance to the problem of thermal reorganization reactions of small-ring systems[2] and of interest to the question of the role of oxyallyl species (*e.g.*, **2**) in reactions of cyclopropanones.[3]

Partial resolution of *trans*-2,3-di-*tert*-butylcyclopropanone was effected by asymmetric destruction with *d*-amphetamine. Trap-to-trap distillation at reduced pressure afforded (+)-cyclopropanone, $[\alpha]^{25}{}_{436}$ +76° (*c* 0.5, CCl_4), displaying a positive Cotton effect with a peak at 370 nm [λ_{max} in the uv is at 354 nm (ϵ 33)].

Upon heating, neat or in solution, the compound racemizes. The rate of racemization is first order in **1**, shows a small increase with increasing polarity of the solvent (Table I), is weakly accelerated by benzoic acid,[4] and is not affected by light. Racemization in *tert*-butyl alcohol-*O*-*d* does not lead to deuterium incorporation in recovered cyclopropanone, excluding enolization for the mechanism of the racemization. We have previously described the isolation of one of the isomers of 1,3-di-*tert*-butylallene oxide (**4**).[5] The isomer in hand, of unknown stereochemistry,[6] isomerizes to the *trans*-cyclopropanone **1** but at a rate slower than that of racemization of (+)-**1**.

Table I. Racemization of (+)-*trans*-2,3-Di-*tert*-butylcyclopropanone at 79.6°

Solvent	$k \times 10^4$, sec^{-1}	$E_T{}^a$
Acetonitrile	3.35	46.0
Pyridine	1.78	40.2
Benzene	0.86	34.5
Tetrahydrofuran	0.80	37.4
Isooctane	0.27	30.9

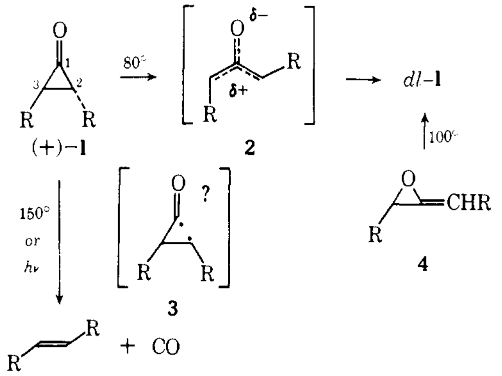
[a] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Chapter 2.6.

Other possibilities for the racemization are: (a) ring opening of the 1,2 bond to diradical **3**, rotation around the 2,3 bond, closure to *cis*-cyclopropanone, and reversal of the sequence to *dl*-*trans*-**1**; (b) ring opening to the oxyallyl species **2**. Efforts to trap species such as **2** or **3** have been unsuccessful.

At higher temperatures (150°) the cyclopropanone decomposes to *trans*-di-*tert*-butylethylene and carbon monoxide. This change may also be effected by the photolysis of **1**. Upon irradiation (sun lamp) at 0° the rate of loss of optical activity equals the rate of disappearance of the cyclopropanone and no allene oxide is observed.

In summary, decarbonylation proceeds both thermally and photochemically; racemization proceeds only thermally. The most attractive possibility for the racemization is disrotatory ring opening to the oxyallyl species **2**.[7] The results and interpretation are summarized in Chart I. The evidence is suggestive of the novel situation in which addition of thermal energy to a compound (a cyclopropanone) results first in the reversible cleavage of one type of bond (the 2,3 bond) and, as the temperature is increased, in cleavage of *different* bonds (the 1,2 and 1,3 bonds); in the overall process the 2,3 bond is not only retained, but is strengthened.

Chart I



R = *tert*-butyl

---

(1) Financial support from the National Science Foundation is gratefully acknowledged.

(2) See the following and references cited therein: (a) H. Quast and E. Schmitt, *Angew. Chem.*, **82**, 395 (1970); *Chem. Ber.*, **103**, 1234 (1970); (b) F. D. Greene and J. F. Pazos, *J. Org. Chem.*, **34**, 2269 (1969).

(3) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969); S. S. Edelson and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2770 (1970).

(4) Benzoic acid increases the rate of racemization and also converts the cyclopropanone, in part, to the benzoyloxy hemiketal of the cyclopropanone (rapidly and reversibly) and to α-benzoyloxydineopentyl ketone (slowly and irreversibly); k_{racem} (0.47 *M* acid)/k_{racem} (no acid) $\simeq$ 2.

(5) R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 7349 (1968).

(6) Probably with the alkyl groups at C-4 and C-5 cis to each other.

(7) See R. Hoffman, *J. Amer. Chem. Soc.*, **90**, 1475 (1968), and references cited therein. For a MINDO/2 calculation on cyclopropanone and oxyallyl, see N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

* Address correspondence to this author.

David B. Sclove, José F. Pazos
Ronald L. Camp, Frederick D. Greene*
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 26, 1970

The Active Species in Cation-Radical Reactions with Nucleophiles: Cation Radical or Dication?

Sir:

Second-order kinetics and inhibition by unoxidized substrate led to the recent suggestion[1] that the dication of thianthrene is the reactive species during hydroxylation of the cation radical in acetonitrile containing water. The following mechanism was proposed to account for the facts (eq 1 and 2). It was also suggested that equilibrium 1 must be considered for reactions of anodically generated cation radicals. Results of a rotating disk electrode study of anodic pyridination of anthracenes have recently been presented as unequivocal evidence of the ECE mechanism[2] and a cyclic voltametric study was presented to show the

$$Th\cdot^{+} + Th\cdot^{+} \rightleftharpoons Th^{2+} + Th \qquad (1)$$

$$Th^{2+} + H_2O \longrightarrow ThO + 2H^{+} \qquad (2)$$

---

(1) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 1872 (1969); Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

(2) G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, **91**, 4584 (1969).

steric requirements of the nucleophile during reaction with anodically generated cation radicals.[3] If equilibrium 1 is important during reactions of cation radicals at the anode, results of the voltametric studies[2,3] do not necessarily reflect reactivities of cation radicals and reactions that have been proposed to be ECE may instead be ECC (eq 3–5).

$$\mathrm{R} \xrightarrow[\mathrm{E}]{} \mathrm{R}\cdot^{+} + \mathrm{e} \tag{3}$$

$$2\mathrm{R}\cdot^{+} \underset{\mathrm{C}}{\rightleftarrows} \mathrm{R}^{2+} + \mathrm{R} \tag{4}$$

$$\mathrm{R}^{2+} + \mathrm{Nu} \xrightarrow[\mathrm{C}]{} \mathrm{R}^{+}\mathrm{Nu}^{+} \tag{5}$$

Another mechanism, analogous to that suggested for the conversion of phenoxathiin cation radical to the oxide,[4] may also fit the data. In the first step, the cation radical reacts with water to give the radical and a proton (eq 6). The cation radical then acts as

$$\mathrm{Th}\cdot^{+} + \mathrm{H_2O} \rightleftarrows (\mathrm{ThOH})\cdot + \mathrm{H}^{+} \tag{6}$$

oxidizing agent to produce substrate and protonated product (eq 7). There is precedent for the oxidation

$$(\mathrm{ThOH})\cdot + \mathrm{Th}\cdot^{+} \rightleftarrows (\mathrm{ThOH})^{+} + \mathrm{Th} \tag{7}$$

step, since neutral organic molecules have been oxidized

$$(\mathrm{ThOH})^{+} \rightleftarrows \mathrm{ThO} + \mathrm{H}^{+} \tag{8}$$

by cation radicals in homogeneous reactions[5] and slow electron transfers have been observed.[6] If the latter step, the electron-transfer reaction, is rate determining, approximate second-order kinetics as well as inhibition by substrate would be predicted. It is difficult to distinguish between the two mechanisms from the kinetic data.

For purpose of discussion, suppose that the anodic hydroxylation of thianthrene follows the ECC pathway (eq 3–5). Increasing the thianthrene concentration during the homogeneous reaction[1] was found to reduce the rate, and the mechanism predicts that increasing the dication concentration would have the opposite effect. By assuming reversible behavior, one can readily estimate the concentration of Th^{2+} from the fact that the potential separation (ΔE) for oxidation of thianthrene to the cation radical and oxidation of the cation radical to the dication is equal to about 350 mV.[7]

Approximate concentration ratios ($\mathrm{Th}^{2+}/\mathrm{Th}\cdot^{+}$), calculated from the Nernst equation, are given in Table I. Since Th^{2+} concentration increases rapidly with increasing potential, the rate of the pseudo-first-order reaction of Th^{2+} with water would increase markedly with increasing anode potential.

Table I. Extent of Hydroxylation of Thianthrene as a Function of Anode Potential

		Per cent[c] substrate consumed at $[\mathrm{H_2O}]$, m*M*				
E, mV	$(\mathrm{Th}^{2+})/(\mathrm{Th}\cdot^{+})$[b]	10	65	120	175	230
E_1[a]	1.15×10^{-6}					
$E_2 - 300$	8.13×10^{-6}	29	43	59	78	87
$E_2 - 250$	5.75×10^{-5}	29	44	58	78	86
$E_2 - 200$	4.07×10^{-4}	30	45	59	78	87
$E_2 - 150$	2.88×10^{-3}	33	50	62	80	87
$E_2 - 100$	2.00×10^{-2}	43	59	69	86	91
$E_2 - 50$	1.41×10^{-1}	69	79	86	90	99
E_2[a]	1.00	87	92	87	95	100

[a] E_1 is the peak potential for the oxidation of thianthrene in acetonitrile measured at a voltage sweep rate of 10 V/min and was equal to 1.25 *V vs.* the aqueous saturated calomel electrode, while E_2 is the peak potential for oxidation of $\mathrm{Th}\cdot^{+}$ to Th^{2+}. [b] Calculated from the Nernst equation assuming that E_2 is equal to $E°$ for the reaction: $\mathrm{Th}\cdot^{+} \xrightarrow{-e} \mathrm{Th}^{2+}$. The true value of $E_2°$ is not known and our assumption is not correct, but we are only interested in showing the relative effect of electrode potential on $(\mathrm{Th}^{2+})/(\mathrm{Th}\cdot^{+})$ which is independent of the true value of $E_2°$. [c] Data obtained by measurement of the cation-radical reduction current after holding the potential at *E* for 30 sec.

The importance of equilibrium 1 or 4 and thus the ECC mechanism (eq 3–5) in the anodic hydroxylation of thianthrene can be shown to be small by a potentiostatic technique. If the potential of a solid anode under quiet conditions is held more anodic than the peak potential for oxidation of a substrate until the $it^{1/2}$ decay is virtually constant, the concentration of oxidized substrate for some distance out from the electrode is equal to that of the substrate in the bulk of the solution, providing that the oxidized species is stable during the time of measurement.[8] If the holding time is followed by a cathodic scan, a peak due to reduction of oxidized substrate, equal in height to the oxidation peak, will be observed. On the other hand, if a reaction occurs which consumes the oxidized species, the ratio of cathodic to anodic currents will be less than unity, the magnitude of the difference being a measure of the extent of the reaction. Applying this technique to the thianthrene problem, we note that the relative concentrations of Th^{2+} and $\mathrm{Th}\cdot^{+}$ at the anode can be varied by changing the anode potential (see Table I for calculated concentrations). Thus at holding potential E_1 we generate a ratio of reactants $(\mathrm{Th}^{2+}/\mathrm{Th}\cdot^{+})_1$ while at potential E_2 a different ratio $(\mathrm{Th}^{2+}/\mathrm{Th}\cdot^{+})_2$ is generated. Measurement of $\mathrm{Th}\cdot^{+}$ reduction peak currents as a function of holding potential then gives an estimate of the extent of reaction as a function of the reactant ratio.

A series of such potentiostatic experiments (Table I) was conducted on the oxidation of thianthrene (1.0 m*M*) in acetonitrile containing $\mathrm{Bu_4NBF_4}$ (0.1 *M*) and varying amounts of water.[9] The results are illustrated by Figure 1. The striking feature of these results is that at a given water concentration, the extent of reaction is essentially independent of the anode potential up to

---

(3) V. D. Parker and L. Eberson, *Tetrahedron Lett.*, 2839 (1969).

(4) C. Barry, G. Cauquis, and M. Maurey, *Bull. Chim. Soc. Fr.*, 2510 (1966).

(5) C. E. H. Bawn, F. A. Bell, and A. Ledwith, *Chem. Commun.*, 599 (1968).

(6) G. A. Russell and A. G. Bemis, *J. Amer. Chem. Soc.*, **88**, 5491 (1966); R. G. Wilkinson, Ph.D. Thesis, Liverpool, 1970.

(7) Referee II pointed out that the position of equilibrium 1 is only dictated by the electrode potential at the surface of the electrode, and at any distance away from the electrode equilibrium 1 is upset due to the fact that Th^{2+} diffusing away from the electrode reacts with Th giving $\mathrm{Th}\cdot^{+}$. However, if we make the reasonable assumption that the diffusion coefficients of Th^{2+} and $\mathrm{Th}\cdot^{+}$ are nearly equal, this effect would be counteracted by the diffusion of $\mathrm{Th}\cdot^{+}$ to the electrode; thus, equilibrium conditions would be approached in the absence of other reactions. However, we must emphasize that equilibrium conditions are never reached because of the reactions of Th^{2+} and $\mathrm{Th}\cdot^{+}$ with water.

(8) The potential holding technique was developed as a means of establishing a base line for measurement of the reverse current in order to evaluate peak current ratios during cyclic voltammetry (R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, pp 156–158).

(9) The working electrode was a Beckman platinum button (39273). The holding potential was set at the desired value and the current was turned on and allowed to decay for 30 sec before initiating the cathodic sweep. Other electrolytes were used with comparable results.

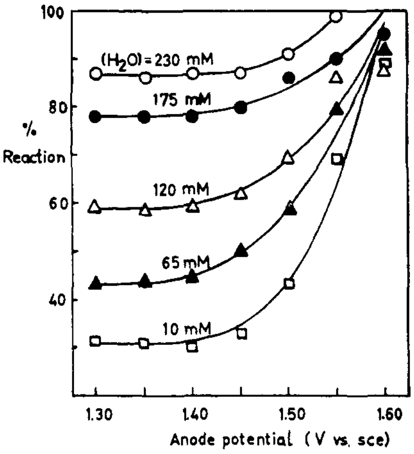


Figure 1. Extent of hydroxylation of thianthrene as a function of anode potential and water concentration.

about 200 mV beyond the peak potential for the oxidation of substrate. In this potential interval, the dication concentration increased by approximately 3000. At potentials greater than (E_1 + 200 mV), the extent of reaction (and hence the reaction rate) increased markedly with increasing potential and at E_1 + 350 mV (E_2) the reaction went to completion at all water concentrations. From these results we can conclusively say that the cation radical is the kinetically active species during hydroxylations at potentials less than (E_1 + 200 mV). We can also estimate that the dication is about 10^3 times as reactive as the cation radical. However, since the cation-radical concentration is about 10^6 times that of the dication in solutions of $Th\cdot^+$ in acetonitrile, Th^{2+} would have to be 10^8 times as reactive as the cation radical in order that 99% of the hydroxylation reaction follow the dication mechanism.

Similar conclusions may be drawn from a rotating disk electrode study of the anodic hydroxylation of thianthrene. Likewise, the results from the anodic pyridination of anthracenes[2] are not consistent with the dication mechanism.

Although our results only apply directly to the anodic reactions of cation radicals, there is no evidence that the homogeneous reactions should differ markedly. A mechanism similar to the ECE process (eq 6–8) may also account for the data previously presented[1] and should thus be considered for the reaction of thianthrene cation radical with water.

Disproportionation of cation radicals to dications has been postulated in other systems, for example during the anodic hydroxylation of phenothiazines.[10]

Further studies on these and other systems will be reported soon.

(10) F. H. Merkle and C. A. Discher, *Anal. Chem.*, **36**, 1639 (1964).

* Address correspondence to this author.

Vernon D. Parker, Lennart Eberson*
Division of Organic Chemistry, Chemical Center
University of Lund, Lund, Sweden
Received April 21, 1970

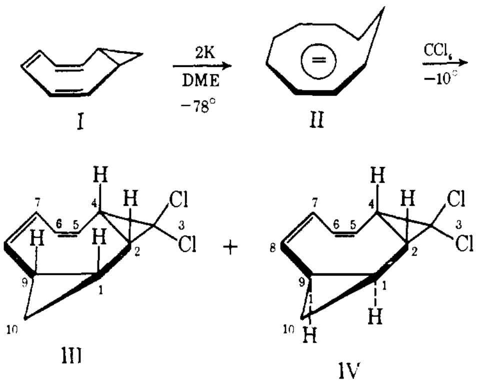
Reaction of the Monohomocyclooctatetraene Dianion

Sir:

Reaction of the recently reported 10π-electron monohomocyclooctatetraene dianion (II)[1] as a nucleophile[2] has proved to be interesting and useful. We now describe additional information on the chemical behavior of II, specifically its behavior upon reaction with carbon tetrachloride. The results obtained from this reaction are also useful in discussing the mechanism of the reaction of the alkali metal cyclooctatetraenides with gem dihalides, and the stereochemistry of the products formed.[3]

Generation of the potassium salt of I was accomplished initially[1] by allowing a solution of *ca.* 25 mg of bicyclo[6.1.0]nona-2,4,6-triene (monohomocyclooctatetraene (I)) in *ca.* 1.5 ml of 1,2-dimethoxyethane (DME) to stand under high vacuum at −80° over a mirror of excess K. Although this procedure produces the dianion, it was cumbersome, requiring the use of a vacuum line, and only small amounts of I could be reduced at one time. Recently, however, we have been able to reduce larger quantities, *ca.* 1–15 g, of the starting material with K under argon at low temperatures. This procedure produces the dianion in amounts much more suitable for synthetic use. The technique employed for this large-scale reduction requires the use of a high-speed stirrer and a Morton flask (indented sides), so that the starting material can be completely reduced within a short time, before the initially produced dianion begins to decompose.

Addition of a DME solution of the dianion II, prepared by the above procedure, to carbon tetrachloride at −10° produced an immediate color change from dark brown to light yellow with no further change as the solution was allowed to come to room temperature. Work-up of the reaction mixture and vacuum distillation produced a colorless liquid which was shown to be a mixture of two products by vpc. Separation and collection by preparative vpc afforded two of the four products possible from this reaction, the 3,3-dichloro-*cis*- and -*trans*-tricyclo[7.1.0.0^{2,4}]deca-5,7-dienes (III and IV) in 60 and 30% yields, respectively;[4] 3,3-dichloro-*cis*-tricyclo[7.1.0.0^{2,4}]deca-5,7-diene (III): nmr (CCl_4) τ 4.10 (m, 2, inner vinyl $H_{6,7}$), 4.65 (m, 2, outer vinyl $H_{5,8}$), 8.10–8.85 (m centered at 8.52, 2, allylic $H_{4,9}$), 8.87–9.63 (m centered at 9.21, 3, nonallylic tertiary $H_{1,2}$ and anti methylene H at C_{10}), 9.85 (m, 1, syn methylene H at C_{10}); 3,3-dichloro-*trans*-tricyclo[7.1.0.0^{2,4}]deca-5,7-diene (IV): nmr (CCl_4)



---

(1) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4731 (1966).

(2) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967).

(3) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963); *ibid.*, **86**, 4876, 5194 (1964).

(4) All compounds prepared gave satisfactory carbon, hydrogen, and chlorine analyses.