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

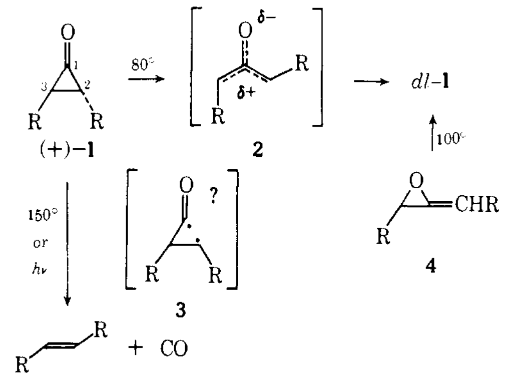
[a] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Chapter 2.6.

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

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[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).

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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

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

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

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[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).