Stereochemistry of the Addition of *t*-Butyl Hydroperoxide to Cyclopentadiene

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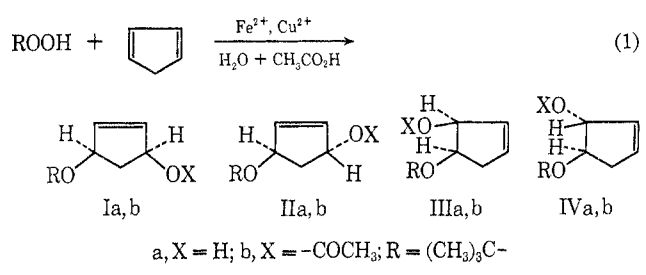
The isomeric addition products of the reaction of *t*-butyl hydroperoxide to cyclopentadiene are reported. The major isomeric adducts were isolated by preparative gas chromatography. Characterization of the adducts was accomplished by the use of nmr and ir spectroscopy, and the major products were shown to be the *cis*- and *trans*-1,4 adducts, with little of the corresponding 1,2 adducts detected. An analysis of the nmr spectra and stereochemical assignments is given and the reaction is discussed.

Addition reactions of cyclic conjugated dienes, other than Diels–Alder reactions, have not been extensively studied.[1] Structural analyses of product geometries are necessary as a first step in understanding the mechanisms of these reactions. Bromination studies of cyclopentadiene in petroleum ether and in chloroform were reported some years ago,[2] and it was shown that *cis*-3,5-dibromocyclopentene (*cis*-1,4 adduct) was an important direct product of these reactions. The *trans*-1,4 adduct was also obtained, but in impure form. Electrophilic addition of *t*-butyl hypochlorite to cyclopentadiene in reactive hydroxylic solvents has been reported to give mainly the *trans*-1,4 adducts, although isomeric mixtures were obtained.[3]

As part of a study of addition reactions to cyclic dienes, the reaction of *t*-butyl hydroperoxide to cyclopentadiene in aqueous acetic acid in the presence of ferrous sulfate and cupric acetate was carried out. The stereochemical course of this addition reaction is reported in this paper. Adduct structures which could be expected to be formed in this reaction are shown in eq 1. A complex mixture of eight components including both alcohol and acetate adducts is possible. It was therefore desirable to simplify such mixtures by converting acetate groups to alcohols without affecting the stereochemical configurations of the adducts.



(1) For a discussion, see A. Liberles, "Introduction to Theoretical Organic Chemistry," Macmillan, New York, N. Y., 1968, pp 413–415.

(2) W. G. Young, H. K. Hall, Jr., and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 4338 (1956).

(3) R. Riemschneider and R. Nehring, *Justus Liebigs Ann. Chem.*, **660**, 41 (1962); R. Riemschneider and R. Nehring, *Monatsh. Chem.*, **92**, 744 (1961).

Results and Discussion

Cyclopentadiene was allowed to react with *t*-butyl hydroperoxide in aqueous acetic acid in the presence of ferrous sulfate and cupric acetate. The temperature was kept below 15°. Details of the reaction are given in the Experimental Section. An infrared spectrum of the crude product clearly indicated the presence of both alcohol and acetate adducts. In order to simplify analysis of the mixture, it was reduced with lithium aluminum hydride, thus converting the acetate to alcohol adducts and lowering the number of potential isomers to four. This reduction has an additional advantage since the alcohols should be less prone to rearrangement during subsequent separation procedures than the corresponding acetates. The yield of crude adducts based on the hydroperoxide used and on the amount of adduct obtained after reduction was about 65%.

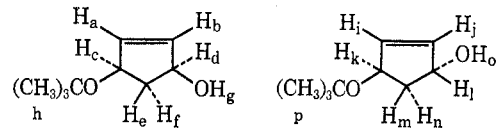
Distillation of the reduced adduct mixture followed by gas chromatographic analysis revealed the presence of four components, two present in major amounts and two in only minor amounts. The major components were isolated in pure form by preparative gas chromatography and shown to be the *cis*- and *trans*-1,4 adducts, Ia and IIa, respectively. The *cis*-1,4 adduct Ia represented 33% and the *trans*-1,4 adduct IIa, 53% of the total mixture (normalized to 100%). Thus the predominant product of the reaction was that corresponding to 1,4 addition to the diene.

Structural assignments of the *cis*- and *trans*-1,4 adducts, Ia and IIa, were made from their 100-MHz nmr spectra. Spectral parameters for isomer Ia, based on a first-order analysis, are listed in Table I.

In the nmr spectrum of isomer Ia, protons H_e and H_f are a pair of double triplets reflecting the large geminal and the two equivalent *cis* (or *trans*) vicinal coupling constants. The higher field proton H_e was assigned to that proton *cis* to the two ring substituents on the basis of the large diamagnetic shift it experiences due to the anisotropy of the two eclipsed C–O bonds and by its smaller *trans* vicinal coupling with the methine protons H_c and H_d. Conversely, the downfield methylene proton H_f experiences a paramagnetic shift and exhibits the larger *cis* vicinal coupling with the adjacent methine

TABLE I

NMR SPECTRAL PARAMETERS FOR ISOMERS Ia AND IIa



Ia IIa

	δ, ppm (J^a)					
Isomer	$H_{a,b}$	$H_{c,d}$	H_e	H_f	H_g	H_h
Ia	5.78[b]	4.44 m[c]	1.44 dt	2.60 dt	4.15 s	1.19 s

	δ, ppm (J^d)				
Isomer	$H_{i,j}$	$H_{k,l}$	$H_{m,n}$	H_o	H_p
IIa	5.78[e]	4.79	1.88	4.44 s	1.17 s

[a] $J_{a,b} = 5.8$ Hz; $J_{e,f} = 13.5$; $J_{c,f} = J_{d,f} = 7.2$; $J_{c,e} = J_{d,e} = 5.0$. [b] Center of multiplet, ($|\delta_{H_a} - \delta_{H_b}| = 0.15$ ppm). [c] Center of multiplet. [d] $|J_{m,l} + J_{m,k}| = |J_{n,l} + J_{n,k}| = 10.0$ Hz. [e] Center of multiplet, ($|\delta_{H_i} - \delta_{H_j}| = 0.04$ ppm).

protons.[4] These stereochemical assignments based on chemical shifts of the methylene protons are in accord with data on *cis*- and *trans*-cyclopentene-3,5-diols and dibenzoates.[5] This data showed that the methylene proton *cis* to a C–O bond is at higher field relative to the *trans* proton. In the *trans*-diol or dibenzoate, the methylene proton signal appears at an intermediate position since the protons are both *cis* and *trans* to C–O bonds. Further supporting data for these assignments may be found in a comparison of chemical shifts in the nmr spectra of acenaphthalene and its hydroxy and acetoxy derivatives.[6]

The methine protons H_c and H_d have essentially the same chemical shift and show a symmetrical pattern of four broadened peaks centered at 4.44 ppm. The olefinic protons H_a and H_b are not equivalent and appear as a typical AB pattern with, however, each AB peak further split owing to weak coupling with the methine protons H_c and H_d. No appreciable coupling of the olefinic protons occurs with H_e and H_f, as is evident from the sharpness of the latter signals.

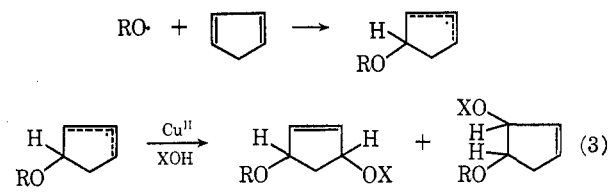
In the *trans* isomer IIa, the methylene protons H_m and H_n are accidentally chemically equivalent as are the methine protons H_k and H_l. These protons appear as a deceptively simple AA′XX′ pattern[7] and the chemical shifts and sum of the *cis* and *trans* coupling constants are listed in Table I. In contrast to the *cis* isomer Ia the olefinic protons H_i and H_j show no appreciable coupling with the other ring protons. This difference is probably due to conformational effects in the two isomers. The methylene protons H_m and H_n have chemical shifts intermediate between those observed for the methylene protons of isomer Ia, since each methylene proton is both *cis* and *trans* to a C–O bond.[5,6]

One of the minor components was isolated by preparative gas chromatography. Further gas chromatographic analysis of this component indicated that it was about 95% pure and contained 5% of the second minor component. This latter component, which constituted 7% of the total adduct mixture could not be separated. The minor component isolated constituted about 6% of the total mixture. Analysis by nmr suggested that it was a 1,2 adduct but its exact isomeric composition was not determined. The infrared spectrum was very similar to those of the major adducts, providing further evidence for its isomeric nature.

In the presence of ferrous ion, *t*-butyl hydroperoxide decomposes to *t*-butoxy radicals[8] (eq 2) which add to

$$(CH_3)_3C{-}OOH + Fe^{II} \longrightarrow (CH_3)_3C{-}O\cdot + Fe^{III}OH \quad (2)$$

the diene[9] to give intermediate allylic radicals. The intermediate radicals are oxidized by cupric ion[10,11] and in the presence of a reactive hydroxylic solvent the latter is incorporated in the adduct (eq 3).



(3)

cis + *trans*

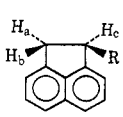
R = $(CH_3)_3C$–; X = H or CH_3CO–

Cupric ion oxidation of the allylic radicals may involve formation of an allylic carbonium ion which is then attacked by solvent, or may involve a transition state with considerable cationic character (electron transfer).[10,11] Contrary to additions of *t*-butyl hydroperoxide to acyclic dienes[10] in which the predominant adduct formed corresponds to 1,2 addition, with cyclopentadiene the 1,4 adducts are by far the predominant products. No thermal isomerization during distillation or gas chromatographic analysis occurred since the separated *t*-butoxy adducts were subjected to further gas chromatographic analysis without rearrangement. Since the reaction was carried out under mild conditions similar to those used in acyclic systems[10] where the thermodynamically less stable adducts were formed, it seems likely that kinetic control was in effect. Further work will be carried out in order to more fully define the mechanism of this addition reaction. The absence of appreciable amounts of the 1,2 adducts may be due to steric hindrance to solvation of the cation by the *t*-butoxy group in the transition state leading to 1,2 adduct.

(4) In cyclopentene systems *cis* vicinal coupling is generally regarded as larger than *trans*. For instance, J_{cis} is 7.4 Hz while J_{trans} is 4.6 Hz in cyclopentene, which is known to be puckered. See G. W. Ratjens, Jr., *J. Chem. Phys.*, **36**, 3401 (1962). The difference in coupling constants is magnified in the more planar *cis*-3,5-dibromocyclopentene, $J_{cis} = 6.9$ Hz and $J_{trans} = 1.5$ Hz. See H. J. Jakobsen, *Tetrahedron Lett.*, No. 21, 1991 (1967).

(5) H. Z. Sable, W. M. Ritchey, and J. E. Nordlander, *Carbohyd. Res.*, **1**, 10 (1965).

(6) In the acenaphthalene derivatives V_a and V_b, a proton *cis* to the C–O bond experiences an upfield shift while the *trans* proton is shifted considerably downfield relative to V: C. K. Fay, S. Sternhell, and P. W. Westerman, unpublished work; L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, p 233.



	R	δH_a	δH_b
V	H	3.36	3.36
V_a	OH	3.70	3.14
V_b	$OCOCH_3$	3.72	3.26

(7) See, for example, E. D. Becker, *J. Chem. Educ.*, **42**, 591 (1965).

(8) A. Tobolsky and R. Mesrobian, "Organic Peroxides," Interscience, New York, N. Y., 1954, p 95.

(9) M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).

(10) J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 2785 (1962).

(11) For reviews of Kochi's work, see also J. K. Kochi, *Rec. Chem. Progr.*, **27**, No. 4, 207 (1966); J. K. Kochi, *Science*, **155**, 415 (1967).

This explanation is tentative at this stage. The observation of predominant 1,4 addition is in accord with the electrophilic addition of *t*-butyl hypochlorite to cyclopentadiene, a reaction which also involves a cationic intermediate.[3]

Experimental Section

t-Butyl hydroperoxide (Monomer–Polymer Laboratories) was distilled (helix-packed column), and the fraction, bp 38–39° (20 mm), was used. Gas chromatographic analyses were carried out with a Hewlett–Packard 5750 instrument using a 10-ft 10% Carbowax 20M column at 165°. Gas chromatographic separations were carried out with a Hewlett–Packard 5798A preparative attachment unit. The nmr spectra were run in carbon tetrachloride solution on a Varian HA-100 instrument. Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Reaction of *t*-Butyl Hydroperoxide with Cyclopentadiene.—A solution of ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 0.25 mol) in 125 ml of distilled water was added dropwise over 90 min to a well-stirred mixture of cupric acetate (monohydrate, 0.25 mol), *t*-butyl hydroperoxide (22.5 g, 0.25 mol), freshly distilled cyclopentadiene (20 g, 0.30 mol), and 275 ml of glacial acetic acid. The temperature of the reaction mixture was kept below 15° during this addition. The reaction mixture was stirred for 30 min with continued ice-bath cooling, then poured into 1 l. of ice water. The product was extracted with methylene chloride, and the extract was washed with sodium bicarbonate and water and dried over anhydrous magnesium sulfate. The product was a clear yellow liquid, 35.3 g. An ir spectrum was consistent with an alcohol and acetate adduct mixture showing O—H str, also acetate C=O str (1742 cm^{-1}) and C—O str (1250 cm^{-1}), as well as strong ether absorption (1075 cm^{-1}).

Reduction of *t*-Butyl Hydroperoxide Adduct Mixture.—The crude adduct mixture (30.0 g) was reduced with lithium aluminum hydride (3 g) in diethyl ether. The reaction mixture was hydrolyzed under alkaline conditions[12] giving 21.3 g of product. The crude reduction product (20.1 g) was distilled at reduced pressure (0.7 mm) through an annular Teflon spinning-band column and the following fractions collected: (1) bp 53–64°, 2.2 g; (2) bp 56–66°, 8.1 g; (3) bp 66–66.5°, 5.3 g; (4) bp 48–56° (0.1 mm), 0.3 g; residue 2.4 g. Fractions 1 and 2 had ir spectra consistent with the expected adducts but showed weak carbonyl absorption (C=O str, 1730 cm^{-1}) indicating the presence of some unreduced acetate adduct. An ir of fraction 3 was consistent with the expected alcohol adduct (O—H str, 3390 cm^{-1}, ether C—O str, 1053 cm^{-1}, both very strong). Fraction 4 was identical with 3. Analysis of each fraction was done by gc. Fraction 3 was an isomeric adduct mixture, and this was further verified by elemental analysis.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found (fraction 3): C, 69.44; H, 10.61.

Pure isomers shown to be *cis*- and *trans*-1,4 adducts Ia and IIa were separated from fraction 3 by preparative gc and these were shown by further analytical gc to be homogeneous and to correspond exactly to the two peaks present in the gc of fraction 3. The structure of each of these adducts was confirmed by nmr as discussed (*vide supra*). The ir spectra of the separated 1,4 adducts Ia and IIa were very similar and consistent with the expected adduct structures. *trans* adduct IIa showed O—H str at 3390 cm^{-1}, ether C—O 1053 cm^{-1}, =CH str 3067 cm^{-1}. Similar bands were present in the spectrum of Ia.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found (*trans* adduct): C, 69.19; H, 10.49.

There was insufficient *cis* adduct for C, H analysis. Further gc analysis of a weighed mixture of Ia and IIa showed that the area per cent calculated by the peak height width at half-height method agreed with the weight per cent as expected for similar isomers.

Registry No.—*t*-Butyl hydroperoxide, 75-91-2; 1,3-cyclopentadiene, 542-92-7; Ia, 25594-22-3; IIa, 25594-23-4.

Acknowledgment.—The authors would like to thank Professor L. M. Jackman of Pennsylvania State University for his constructive suggestions. A portion of the work was done under a City University Doctoral Faculty Research Grant (H. H.).

(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 584.

Oxidative Cleavage of Cyclopropanes. VII. Kinetics of the Cleavage of Some Bicyclo[*n*.1.0]alkanes and Spiro[*n*.2]alkanes by Thallium Triacetate[1,2]

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The rates of cyclopropane ring cleavage of spiro[5.2]octane, spiro[4.2]heptane, and fluorene-9-spirocyclopropane by thallium triacetate in acetic acid at 17.95° have been determined. Bicyclo[5.1.0]octane, bicyclo[4.1.0]heptane, and bicyclo[3.1.0]hexane cyclopropane ring cleavages were studied at 29.30 and 50.05°. The kinetics of the cleavage reactions were overall second order, first order in each reactant. Stability of the incipient carbonium ion is the rate-controlling feature in the case of the spiroalkanes. However, steric features of each molecule are noted in the spiroalkanes and the steric factor becomes preeminent in the case of the bicycloalkanes.

The rates of cyclopropane ring cleavage by mercury(II) acetate,[3] thallium(III) acetate,[4] and lead(IV) acetate[5] have been determined in acetic acid using arylcyclopropanes as reference substrates. In addition to establishing an order of reactivity of $Tl(OAc)_3 > Hg(OAc)_2 > Pb(OAc)_4$ these studies have yielded information concerning the selectivity of the metal acetates as reflected by the magnitude of ρ^+. The ρ^+ values for $Tl(OAc)_3$, $Hg(OAc)_2$, and $Pb(OAc)_4$ are -4.3, -3.2, and -1.7, respectively. Therefore not only is $Tl(OAc)_3$ the most reactive of the metal acetates studied, it also is the most selective. While the mechanistic interpretation of these data has only been partially successful it is clear that from an experimental viewpoint $Tl(OAc)_3$ is a reagent that should be studied further in a variety of oxidation reactions of organic molecules.

Our kinetic studies of the oxidative cleavage of cyclo-

(1) Paper VI: A. South, Jr., and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7064 (1968).

(2) This research was supported by Grant GP6778 from the National Science Foundation.

(3) R. J. Ouellette, R. D. Robins, and A. South, Jr., *ibid.*, **90**, 1619 (1968).

(4) Paper VI.[1]

(5) R. J. Ouellette, D. Miller, A. South, Jr., and R. D. Robins, *ibid.*, **91**, 971 (1969).