characteristic region of the benzimidazole spectrum. All substituted benzimidazoles have bands in this region which vary in position and intensity with the nature and position of the substituent. The spectra of most substituted benzimidazoles only have two bands, one around 1620 cm.$^{-1}$ and the other around 1590 cm.$^{-1}$. The band around 1590 cm.$^{-1}$ is in general fairly intense because of the conjugation between the benzene and imidazole rings. In the infrared spectrum of 4,7-dimethoxybenzimidazole and its 2-(1-hydroxyethyl) analog this band is absent. The frequencies of these bands also vary with the electronegativity of the substituent. The 2-substituted benzimidazoles show the least variation in frequency for these two bands since groups in this position are less apt to influence the vibrations of the benzene ring. Substitution in the 2-position is accompanied by the appearance of a rather intense band around 1550 cm.$^{-1}$. This band has been reported to be characteristic of 2-substitution.[7] Our data appears to support this although the band is absent in the infrared spectrum of 2-acetylbenzimidazole.

All benzimidazoles show strong bands in the 1500–1400-cm.$^{-1}$ region which could be attributed to skeletal in-plane vibrations. 5(6)- and 4(7)-substituted benzimidazoles show intense and sometimes broad bands around 1480, 1450, and 1420 cm.$^{-1}$. Similar bands are observed for the 2-substituted compounds. In the 1400–1300-cm.$^{-1}$ region, 5(6)-substituted benzimidazoles usually show two bands around 1370 and 1350 cm.$^{-1}$. The spectra of the 2-substituted benzimidazoles have a strong band around 1320 cm.$^{-1}$, and a medium to strong band around 1380 cm.$^{-1}$. In the case of the nitro substituted benzimidazoles, it is difficult to distinguish the bands in the 1570–1500- and 1370–1300-cm.$^{-1}$ regions from the nitro group absorptions.

Heterocyclic compounds also show a series of characteristic bands in the 1250–1000-cm.$^{-1}$ region which may be assigned to in-plane CH deformations and ring-breathing modes. The position of these bands is reported to be similar for compounds with the same number of hydrogen atoms in the same orientation. Similarly, substituted benzimidazoles also show a number of bands in this region which are similarly located. The C–O vibrations of aralkyl ethers are reported to cause strong absorption around 1250 and 1150 cm.$^{-1}$. Strong bands in these regions are noted when alkoxy groups are present.

Bands which appear regularly in the spectra of the simple benzimidazoles near 1000 and 960 cm.$^{-1}$ may be associated with benzenoid ring-breathing modes, and bands near 760 and 880 cm.$^{-1}$ with the heterocyclic ring-breathing modes.[7] Out-of-plane CH deformations and in-plane ring deformations cause absorption in the 1000–650-cm.$^{-1}$ region. The out-of-plane CH bending frequencies of substituted benzenes also fall in this region. The spectra of all 5(6)- and 4(7)-substituted compounds have an intense band around 950 cm.$^{-1}$ which is the strongest band in the region. The pattern found in the spectra of 2-substituted benzimidazoles is less constant although a band of medium intensity is sometimes present around 960 cm.$^{-1}$.

The out-of-plane CH bending frequencies of some substituted benzimidazoles have been assigned[8] as follows: 735 cm.$^{-1}$ for 2-methylbenzimidazole; 870, 812, and 800 cm.$^{-1}$ for 5(6)-methylbenzimidazole; 900, 830, and 820 cm.$^{-1}$ for 5(6)-nitrobenzimidazole. These values were derived by considering the 2-position as that of an *o*-disubstituted benzene (770–735 cm.$^{-1}$) and the 5(6)-position as having one isolated pair of hydrogens and one isolated hydrogen (850–800 cm.$^{-1}$, 900–830 cm.$^{-1}$). All bands were strong, although there were medium bands of doubtful identity.[8]

The spectra of 5(6)-substituted benzimidazoles show broad strong bands in the 900–800-cm.$^{-1}$ region and it is hard to make specific assignments. The spectra of 2-substituted benzimidazoles show a fairly constant band around 850 cm.$^{-1}$ of variable intensity. The spectra of all 2-substituted benzimidazoles have a very intense band between 747–733 cm.$^{-1}$. This band is the most intense in this region and one of the most intense in the spectra. It may be ascribed to the out-of-plane CH bending frequency. A medium to weak band is also present around 760 cm.$^{-1}$. The spectra of the 5(6)-substituted compounds show two intense bands around 790 and 740 cm.$^{-1}$. The out-of-plane CH bending frequencies of 4(7)-substituted benzimidazoles should cause absorption in the 800–700- and 720–685-cm.$^{-1}$ regions. The infrared spectrum of the 4(7)-nitrobenzimidazole shows two intense bands at 798 and 728 cm.$^{-1}$ which could be ascribed to the out-of-plane bending frequencies of a 4(7)-substituted benzimidazole.

In addition to vibrations typical of the benzimidazole ring, the vibrations typical of the groups attached to the ring must be considered. In general, substituents show the same characteristic bands regardless of whether they are attached to a benzene or benzimidazole ring. However, some of these vibrations may be modified by the heterocyclic nucleus if a strong electronic interaction occurs between the ring and the substituent. For instance, in the case of 2-acetylbenzimidazole, conjugation of the keto group with the heterocyclic ring is evidenced by its absorption at 1664 cm.$^{-1}$, typical of α,β-unsaturated ketones.

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Reactions of Free Radicals with Olefins. Thermal Decomposition of *t*-Butyl Peracetate in the Presence of 4-Vinylcyclohexene

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To obtain additional information on free radicals and their reactions with specific olefins, a study was undertaken complementing work previously published from this laboratory.[1,2] These earlier studies involved

(1) J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, **26**, 2185 (1961).
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reactions of *t*-butoxy and *t*-butylperoxy radicals with 4-vinylcyclohexene, conducted in the presence of cobalt or cupric ions. In a reaction of 4-vinylcyclohexene with *t*-butyl hydroperoxide in the presence of cobalt ions, the olefin was peroxidated mainly in the 6-position and to a minor extent in position 3, with only traces of product attributed to reaction at the tertiary C–H in the 4-position. It was further concluded that this distribution of isomers is probably due to steric factors.

To determine the generality of these reactions as well as the preference of radicals toward substitution *vs.* addition, research was extended to methyl and acetoxy free radicals. These radicals were generated by thermal decomposition of *t*-butyl peracetate.

$$CH_3CO_2OC(CH_3)_3 \xrightarrow{130^\circ} CH_3CO_2\cdot + \cdot OC(CH_3)_3$$

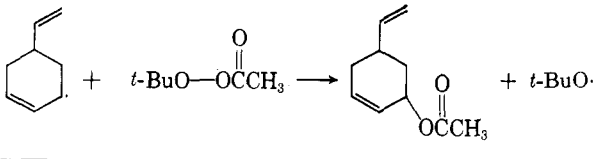
$$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2$$

It was shown by Bartlett and Hiatt[3] that the thermal decomposition of *t*-butyl peracetate involves the rupture of the O–O bond in the primary step, followed by loss of carbon dioxide. Thus, *t*-butoxy, acetoxy, and methyl radicals were made available.

Some possible products which might be formed by thermal decomposition of *t*-butyl peracetate in the presence of 4-vinylcyclohexene are given in Chart I. After removal of excess 4-vinylcyclohexene, the reaction mixture was hydrogenated and then reduced with lithium aluminum hydride in order to simplify the analysis. V.p.c. and infrared analysis of the reaction mixture showed that compounds **1**, **2**, **3**, **4**, **7**, and **10** were absent. Compound **8** was found to be present in 2.6% and compound **6** in 1.3%. V.p.c. further indicated that 2-ethylcyclohexanol was present (<0.4%); however, this was not substantiated unequivocally by infrared. It was shown that *n*-propylcyclohexane (compound **9**) was a product. A large amount of dehydro dimer of 4-vinylcyclohexene also was isolated. Although *t*-butyl alcohol and methane were found in large amounts, neither acetic acid nor ethane could be detected.

The formation of *t*-butyl alcohol and methane supports the supposition that *t*-butoxy radicals and methyl radicals remove an allylic hydrogen from 4-vinylcyclohexene to yield 4-vinylcyclohexenyl radicals A, B, C (Chart I). These radicals can then combine to form dehydro dimer, and/or couple with $CH_3\cdot$ or $CH_3CO_2\cdot$ to give substitution products.

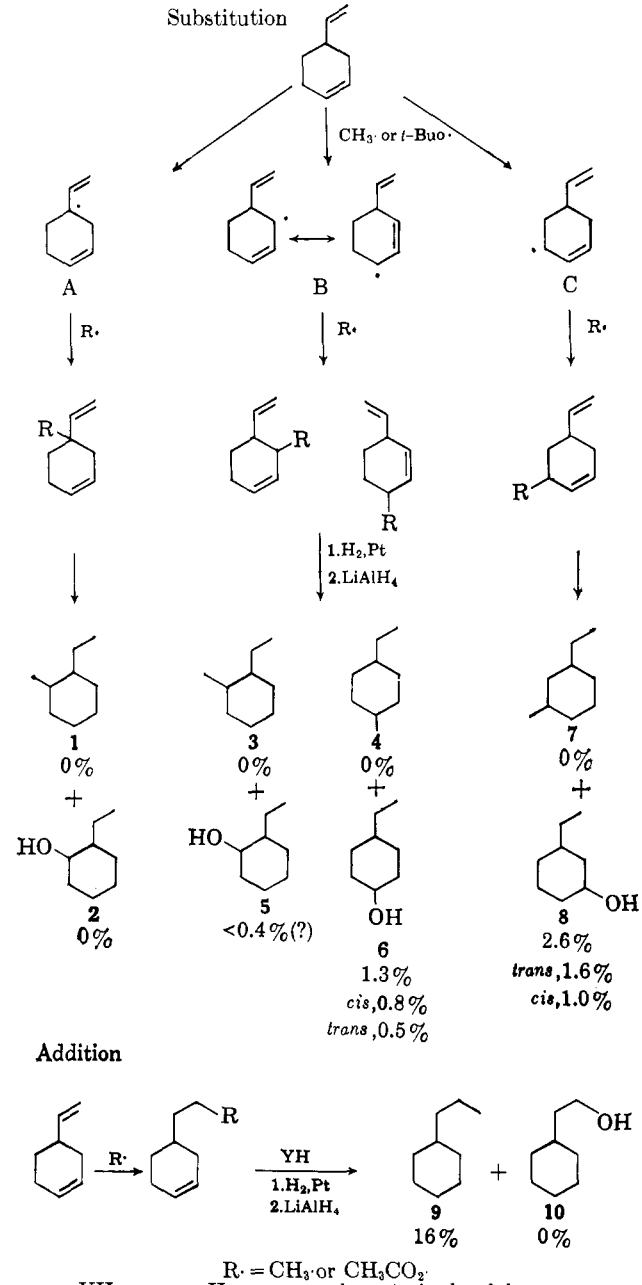
Alternatively, in view of the instability of acetoxy radicals, the radicals derived from 4-vinylcyclohexene might attack the perester directly to form the observed products. While peresters are not so subject to radical-induced decomposition as diacyl and diaroyl peroxides, the relatively small amount of acetate esters obtained (approximately 5% based on perester) could result from reactions of the following type.



(3) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

CHART I

SOME POSSIBLE PRODUCTS OF THE THERMAL DECOMPOSITION OF *t*-BUTYL PERACETATE IN 4-VINYLCYCLOHEXENE



Addition

R· = $CH_3\cdot$ or $CH_3CO_2\cdot$
YH = some H source, such as 4-vinylcyclohexene

The isomer distribution indicates that the less sterically hindered position 6 is the preferred one for hydrogen absrtaction leading to products derived from radical C. This is in keeping with previous findings.[1] The formation of the 4 isomer (compound **6**) probably arises from attack of $CH_3\cdot$ and/or *t*-BuO· on 4-vinylcyclohexene in the 2-position to form B which, being resonance stabilized, yields the sterically favored compound. Supporting this contention is the fact that a small amount of the 2 isomer (compound **5**) seems to be present. If compounds **6** and **8** resulted from addition of acetate radicals to the internal double bond with subsequent removal of hydrogen, equal amounts would be expected, and, as seen from Chart I, such was not the case. Furthermore, if addition of acetoxy radicals occurred, it should have taken place preferentially at

the vinyl double bond.[4] However, addition of CH_3· evidently did occur; and (see Chart I), after hydrogenation of the product, *n*-propylcyclohexane was identified.

The major product was the relatively nonvolatile dehydro dimer, formed probably by self-coupling and combination of radicals B and C. Since a large excess of 4-vinylcyclohexene was used and considerable amounts of methane and *t*-butyl alcohol were found, the concentration of the 4-vinylcyclohexenyl radicals must have been sufficient to produce these dimers.

Infrared analysis of the residue gave a spectrum which showed both vinyl and internal unsaturation and resembled the dehydro dimer with the exception that additional bands characteristic of acetate were present. Thin layer chromatography resulted in two poorly resolved spots which were not further analyzed or identified. It seems reasonable, however, to assume that the residue contained rather low molecular weight telomers (probably dimeric and trimeric) terminated by acetoxy and/or 4-vinylcyclohexenyl radicals.

The relative amounts of the various products of the reaction of radicals derived from *t*-butyl peracetate with 4-vinylcyclohexene are compared in Table I.

TABLE I

RELATIVE AMOUNTS OF PRODUCTS

Original perester	21.0 g.	0.159 mole	
t-Butyl alcohol	9.2	0.124	78% based on weight of perester
n-Propylcyclohexane	3.2	0.029	
Cyclo esters	1.3	0.008	
Dehydro dimer	14.5	0.068	
		0.105	66%
Residue	18.5		

These reactions in 4-vinylcyclohexene demonstrated that abstraction of allylic hydrogen is the preferred path with a combination of methyl and oxy radicals derived from *t*-butyl peracetate leading to formation of dehydro dimer and substitution products. Addition of methyl radical to the vinyl double bond also occurred, as evidenced by the addition product (compound **9**) and the formation of what appeared to be telomers of 4-vinylcyclohexene.

Experimental

Reagents.—The 4-vinylcyclohexene[5] was purified by pouring the required amount through a column of activated alumina immediately before reaction, $n^{24}D$ 1.4613, lit.[6] $n^{20}D$ 1.4624. The *t*-butyl peracetate (Lupersol No. 7) was supplied[7] as a 75% solution in benzene which was washed once with dilute sodium carbonate solution and dried over magnesium sulfate. Slow distillation removed all the benzene; the ester distilled at b.p. 27–28° (0.9 mm.), lit.[8] b.p. 23–24° (0.5 mm.).

Reaction of *t*-Butyl Peracetate with 4-Vinylcyclohexene.—In a typical reaction 172 g. (1.59 moles) of 4-vinylcyclohexene was placed in a round-bottomed flask with 21.0 g. (0.159 mole) of *t*-butyl peracetate under nitrogen at atmospheric pressure and heated at reflux temperature with magnetic stirring. The evolution of carbon dioxide was checked from time to time by bubbling the effluent gas through a freshly prepared barium hydroxide solution. Analysis of the evolved gas through a 24-ft. column (silicone grease on Chromosorb) at Dry Ice temperature gave evidence for carbon dioxide and methane. No ethane was detected. After approximately 12–14 hr. (24 to 28 half-lives), the carbon dioxide evolution had stopped and the reaction was terminated.

The clear but faintly yellow reaction mixture was very slowly distilled under nitrogen through a 10-in. column packed with glass helices. Fractions collected were (1) b.p. 79–83°, 9.2 g.; (2) b.p. 118–128°, 133.4 g.; (3) b.p. 57–65° (30 mm.), 3.7 g.; (4) b.p. 92–97° (12 mm.), 1.3 g.; and residue, 33 g.

Analysis of the Reaction Products.—By means of infrared and v.p.c. analysis of the fraction, cut 1 was shown to be essentially pure *t*-butyl alcohol. The infrared spectrum was in agreement with the literature.[9a] A 3,5-dinitrobenzoate derivative melted at 141.8°, lit.[10] 142°. Cut 2 consisted of unchanged 4-vinylcyclohexene. Cut 3 was essentially a hydrocarbon mixture. Cut 4 showed strong acetate absorption.

Identification of the Hydrocarbon.—V.p.c. analysis of cut 3 showed that it was composed of essentially two components. Hydrogenation of this material over Adams' catalyst in acetic acid produced the saturated hydrocarbon which was a mixture of 13% ethylcyclohexane[9b] and 84% *n*-propylcyclohexane.[9c] A trace impurity which had been detected in 4-vinylcyclohexene prior to its use in the reaction had concentrated during the fractionation so that several extraneous infrared bands were found in the mixture. After hydrogenation this impurity is converted to cyclooctane which was identified by means of an authentic sample and the literature infrared spectrum.[11]

A specific search was made for 2-methyl-1-ethylcyclohexane, 3-methyl-1-ethylcyclohexane, and 4-methyl-1-ethylcyclohexane with negative results.

Identification of Ester—Fraction 4 gave a positive ester test.[10] Infrared of this material gave evidence of acetate ester (1250–1230 cm.$^{-1}$), vinyl (3080, 1640, 997, 910 cm.$^{-1}$), and internal unsaturation (3030 cm.$^{-1}$). To ease the analysis of this material, this fraction was hydrogenated over Adams' catalyst in acetic acid. Following the usual work-up procedure, the reduced material was treated subsequently with 0.5 g. of lithium aluminum hydride in 75 ml. of ether. The reaction mixture, after stirring for several hours was treated with approximately 10 ml. of sodium carbonate solution, and extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated to give a residue of 0.4 ml. Examination of this material by v.p.c. (Carbowax on Chromosorb column, at 100° and 50 ml./min. He flow) produced a chromatogram with six bands having retention times of 12, 16, 18, 20.5, 23.5, and 26.5 min., respectively. A comparison of the retention times and infrared spectra with the isomeric ethylcyclohexanols gave evidence for the following compounds (see Table II).

For the *cis,trans*-3-ethylcyclohexanol and the *cis*-4-ethylcyclohexanol, the absorbance–concentration plots were linear at 840, 815, and 990 cm.$^{-1}$, respectively. Considerable difficulty was encountered with the *trans*-4-ethylcyclohexanol since the 1090 cm.$^{-1}$ band is the only one that is free from interference; unfortunately, this band is very small.

The absence of 1-ethylcyclohexanol and 2-cyclohexylethanol was established by a comparison with reported infrared spectra.[1,12]

The v.p.c. bands (Table II) 3 and 4 corresponded to a mixture of *cis*- and *trans*-2-ethylcyclohexanol, but the presence of these compounds in the final product could not be established unequivocally by infrared.

Although routine infrared spectra were obtained on a Perkin-Elmer 237B spectrophotometer, the infrared spectra used in the identification of the ethylcyclohexanols were obtained on Beckman IR-7 and IR-8 spectrometer. The per cent composition of this mixture was obtained by selecting the characteristic peaks that showed least interference with those of other isomers and applying the base line technique.[13]

Comparison Compounds.—The following compounds were prepared so that their v.p.c. and infrared spectra could be compared with the products of the reaction: *cis,trans*-3-ethylcyclo-

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TABLE II

VAPOR PHASE CHROMATOGRAPHY RETENTION TIMES AND INFRARED SPECTRA FOR ETHYLCYCLOHEXANOLS

V.p.c. band	Retention time, min.	%	Compound	Characteristic absorption bands, cm.$^{-1}$
1	12	3		
2	16	4		
3	18	1	2-Ethylcyclohexanol (*cis*- and *trans*-)	880, 845, 820
4	20.5	7		
5	23.5	44	*trans*-3-Ethylcyclohexanol	1036, 1014, 968, 857, 815
			cis-4-Ethylcyclohexanol	1144, 990, 952, 897
6	26.5	41	*trans*-4-Ethylcyclohexanol	1090, 1052, 965, 897
			cis-3-Ethylcyclohexanol	1111, 1049, 957, 839

hexanol, *cis,trans*-4-ethylcyclohexanol, *cis,trans*-2-ethylcyclohexanol, 2-methyl-1-ethylcyclohexane, 3-methyl-1-ethylcyclohexane, 4-methyl-1-ethylcyclohexane, and ethylcyclohexane. Each was obtained by a method reported in the literature. The physical properties were in agreement with the reported values.

Analysis of the Residue.—Approximately 25 g. of the residue was placed in the bulb of a small modified retort and heated in a 60° oil bath for 24 hr. under vacuum (0.5 mm.). The volatile material (5.6 g.) was trapped in a second bulb contained in a Dry Ice–acetone bath. When the volatile material was chromatographed it gave two peaks with only minor impurities (less than 3%). This material was identified by means of infrared as the dehydro dimer.[2]

The remaining viscous residue was chromatographed using the thin layer technique (t.l.c.). The adsorbant was silica gel g and the eluent benzene (or petroleum ether, b.p. 30–60°). Two spots were observed when the plate was treated with iodine. One of these had an R_f value identical with that of the dehydro dimer. By v.p.c. it was shown that this viscous residue still contained 5.3 g. of dehydro dimer. The original 33 g. of residue, therefore, was composed of 14.5 g. (0.068 mole based on perester) of dehydro dimer and 18.5 g. of higher molecular weight material. Infrared of the entire residue showed it to be very much like the dehydro dimer but contaminated with acetate esters.

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The Isomerization of 1,2-Di-*n*-octylcyclopropene with Alumina

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The fatty acids that contain a cyclopropene ring, sterculic acid and malvalic acid, are formed as triglycerides in *Sterculia foetida* oil and in cottonseed oil and are remarkable both for their unique chemical structure and for the physiological effects that have been observed when they are included in poultry diets.[1-4] Because destruction of the cyclopropene ring by hydrogenation,[2] rearrangement,[5] or reaction with gaseous hydrogen chloride or sulfur dioxide[6] eliminates the biological effects, we have been interested in the structures of the products that are formed by these procedures.

This paper concerns the nature of the products formed when the cyclopropene ring is destroyed by rearrangement with alumina. The simplicity of sterculene (I, 1,2-di-*n*-octylcyclopropene) together with its ready availability[7a] led to its choice as a model compound for the isomerization.

Sterculene was stirred at room temperature under nitrogen with an equal weight of activated alumina in ten volumes of petroleum ether (b.p. 30–60°). During the reaction its characteristic cyclopropene infrared bands at 5.38 and 9.92 μ[7b] gradually diminished in size and were replaced by bands at 6.13 and 11.15 μ (unsymmetrical disubstituted olefin) and 10.37 μ (*trans* double bond).

After 35 hr. the cyclopropene infrared bands had disappeared and the reaction mixture no longer gave the Halphen test,[8] an empirical test for sterculic and malvalic acid derivatives. The solution was filtered and distilled to give a 72% yield of a clear colorless oil having the same boiling point as I; redistillation showed the same boiling point and did not yield any residue.

A portion (12%) of the product polymerized during the isomerization, and the remainder (16%) could not be extracted from the alumina with petroleum ether.

The isomerized material smoothly consumed 1.7 moles of hydrogen per $C_{19}H_{36}$, which suggested that it is a mixture of compounds, 30% of the material containing one double bond and 70% containing two double bonds. Under the same conditions, I consumed 0.95 mole of hydrogen per $C_{19}H_{36}$.

The ultraviolet spectrum of the isomerized material showed an absorption peak with a maximum at 232 mμ. By assuming a molar extinction coefficient of 22,000[9] the material was calculated to contain 64% of compounds having conjugated double bonds.

The isomerized material reacted with maleic anhydride in refluxing xylene. After removal of solvent and saponification, 36% of the starting material was ex-

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