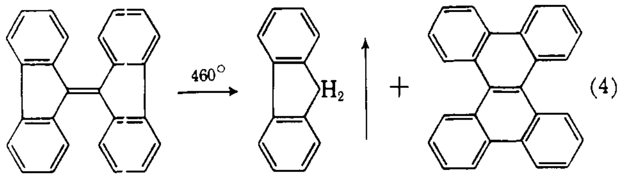
TABLE IV

SUMMARY OF PROPERTIES OF RESIDUES FROM INTERRUPTED D.T.A. RUNS FOR ACENAPHTHYLENE AND 9,9'-BIFLUORENYLIDINE

	Starting material	Temp., °C.	Nature of residue	M.p., °C.[a]	% Residue	Molecular weight	Free radicals
1.	Acenaphthylene	25	Yellow solid	92	. .	152	No
2.	Acenaphthylene	300	Orange crystalline solid	315	92	1890	No
3.	Acenaphthylene	360	Red crystalline solid	325–350	90	950	Yes
4.	Acenaphthylene	410	Brown amorphous solid	210, 340	42	1360	Yes
5.	Acenaphthylene	440	Brown amorphous solid	215, 325	37	2025[b]	Yes
6.	Acenaphthylene	750	Black carbonaceous solid	Infusible	21	. .	Yes
7.	9,9'-Bifluorenylidene	25	Red solid	188	. .	328	No
8.	9,9'-Bifluorenylidene	382	Red solid	110–115	94	396	Slight
9.	9,9'-Bifluorenylidene	400	Red solid	100, 170–184	88	565	Yes
10.	9,9'-Bifluorenylidene	450	Brown-red solid	115, 210–230	72	604	Yes
11.	9,9'-Bifluorenylidene	750	Black carbonaceous solid	Infusible	31	. .	Yes

[a] In several residues, two melting points are reported as the material was heterogeneous. [b] Determined for benzene-soluble portion only.



(4)

9,9'-Bifluorenylidene Fluorene Tetrabenzonaphthalene + reactive condensed aromatic hydrocarbons and radicals

tory aromatic radicals formed by thermal dissociations of hydrogens at reactive ring sites, by cleavage of substituent groups, or by rearrangement. The formation of such stable radicals as well as the internal rearrangements of hydrogens appears to be intrinsic to the thermal condensation or carbonization process for many of the "reactive" aromatic hydrocarbons.

In summary, the thermal reactivities of the aromatic hydrocarbons in our system show a marked dependence on structure. Employing the spectral p-band measurement and the empirically derived ionization potential as a qualitative criterion of reactivity, it is evident that the aromatic hydrocarbons of high ionization potential are thermally "unreactive" whereas those of low ionization potential are thermally "reactive." Molecular size and concomittant physical stability criteria are seen to influence borderline cases in both categories. Additionally, hydrocarbons capable of undergoing vinyl-type polymerizations can produce thermal polymers which represent more reactive molecular entities capable of carbonizing.

Consistent patterns of hydrogen transfer and concurrent condensation to more reactive aromatic hydrocarbon molecules and radicals are found for many of the thermally "reactive" aromatics.

Acknowledgment.—This research was sponsored in part by the Air Research and Development Command and the Air Material Command, U. S. Air Force.

Hydrogen Peroxide–Vanadium Pentoxide Oxidation of Cyclohexenes[1a]

E. J. EISENBRAUN,[1b] A. R. BADER, J. W. POLACHECK, AND E. REIF[1c]

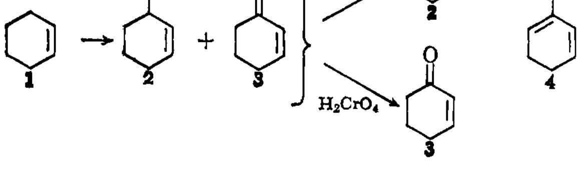
Research Laboratories of the Aldrich Chemical Company, Milwaukee 10, Wisconsin, and the Heidenheimer Chemisches Laboratorium, Heidenheim an der Brenz, Germany

Received January 14, 1963

A re-examination of the oxidation of cyclohexene (**1**) with hydrogen peroxide–vanadium pentoxide (HP–VP, peroxyvanadic acid) revealed 2-cyclohexen-1-ol (**2**) to be a major reaction product. This contradicts an earlier report[2] claiming exclusive formation of 2-cyclohexen-1-one (**3**) as the volatile product. Similar oxidative experiments with the isomeric methylcyclohexenes (**7**, **13**, and **17**) demonstrate the reaction to be essentially nonselective as to site of oxidation and that both alcohols and ketones appear in the volatile products, these being a mixture of direct oxidation products and products derived from allylic shifts.

Treibs[2] and co-workers claimed 2-cyclohexen-1-ol (**2**) to be absent from the products of the oxidation of cyclohexene (**1**) with HP–VP and 2-cyclohexen-1-one (**3**) was reported to be the exclusive low boiling product (40% yield). *trans*-1,2-Cyclohexanediol (**6**) and adipic acid were reported as higher boiling products (9% yield for both). These authors considered 2-cyclohexen-1-one (**3**) to be present in part as the enol **4** to account for the formation of a borate ester.

We have demonstrated that 2-cyclohexen-1-ol (**2**)



---

(1)(a) Presented before the Organic Division at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.; (b) Department of Chemistry, Oklahoma State University, Stillwater, Okla.; (c) Heidenheimer Chemisches Laboratorium, Heidenheim an der Brenz, Germany.

(2) W. Treibs, G. Franke, G. Leichsenring, and H. Roder, *Ber.*, **86**, 616 (1953).

is a major product of the oxidation of cyclohexene with HP–VP, and that it actually exceeds 2-cyclohexen-1-one (**3**) in the product mixture by a ratio of 2.3:1. The oxidation was repreated several times according to the published procedure,[2] and each experiment gave essentially the same product boiling at 61–63° (14 mm.) in reasonable agreement with the reported value. However, gas chromatographic studies show the presence of two sharply defined and completely separated peaks. The mixture of volatile products shows a maximum $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (ϵ 3905) while the reported[3] maximum for **3** is 225 mμ (ϵ 11,270). Strong hydroxyl group absorption was noted in the infrared spectrum of the mixture. These data suggested the mixture to be **2** and **3**. Attempts to separate the mixture by fractional distillation through a spiral column and by preferential reaction with semicarbazide hydrochloride were ineffective. Accordingly, the products were directly interconverted and the identity of the components established through isolation of the individual pure compounds by oxidation to **3** and reduction to **2**.

A Jones' oxidation[4] with chromic acid in acetone solution readily converted the entire mixture to **3**. The course of the reaction was followed conveniently with gas chromatographic analyses at regular intervals. The peak of the gas chromatogram of the reaction product at termination of the oxidation coincides exactly with the smaller and second peak of the chromatogram of the original mixture. The oxidation product was identified as **3** through its ultraviolet spectrum, in agreement with Woodward's rules,[5] its ininfrared spectrum, and the melting point of its red 2,4-dinitrophenylhydrazone.[6] Other syntheses of **3**, each by a different procedure, have been reported.[7]

Reduction of the original volatile oxidation mixture with lithium aluminum hydride in ether solution gave a single product. This product shows no carbonyl band in its infrared spectrum but shows strong absorption in the hydroxyl and double bond regions. These data and the melting point of the phenylurethane derivative,[6] 107–109°, established the identity of the product as 2-cyclohexen-1-ol (**2**).

A reconstituted mixture (70% **2** and 30% **3**) prepared from pure **2** and **3** gives essentially identical spectra (ultraviolet and infrared) and gas chromatographic curve as those from the original mixture obtained by oxidizing cyclohexene with HP–VP.

Pure 2-cyclohexen-1-ol (**2**) was oxidized with HP–VP under the same conditions used for the oxidation of cyclohexene. The steam volatile products from this reaction were shown through gas chromatographic analyses to be a mixture of **2** and **3** in a ratio of 7.3:1. This experiment suggests **2** to be one of the precursors of **3**.

Several routes may exist for the formation of the various products obtained from the oxidation of cyclohexene with HP–VP. 2-Cyclohexen-1-ol (**2**) and 2-cyclohexen-1-one (**3**) may be rationalized as being formed from cyclohexene hydroperoxide by the indicated routes in Fig. 1. *trans*-1,2-Cyclohexanediol (**6**) may arise from cleavage of cyclohexene oxide which has been reported along with **2** as a product of the bimolecular epoxidation of cyclohexene by cyclohexene hydroperoxide.[8,9]

cis-1,2-Cyclohexanediol (**5**) and adipic acid are formed by direct oxidation of the double bond of cyclohexene. We suggest that peroxyvanadic acid, $H_3[V(O_2)O_3]$,[10] attacks the double bond of cyclohexene to form a cyclic ester of peroxyvanadic acid in a reaction reminiscent of the osmic ester formation of olefins.[11,12] The cyclic ester may then be hydrolyzed to *cis*-1,2-cyclohexanediol (**5**) or undergo cleavage to adipic aldehyde in the manner of periodate oxidation of 1,2-glycols.[13] The aldehyde is oxidized in turn to adipic acid. This rationalization suggested the possible presence of some *cis*-1,2-cyclohexanediol (**5**) in the reaction products. The diol **5** is not formed as a major product but we were able to establish its presence through gas chromatographic studies by enrichment of the crude reaction product with authentic *cis*-diol **5**. The diols **5** and **6** are present in the crude reaction product in the ratio of 1:15. The presence of the *trans*-diol **6** was established readily through gas chromatographic studies and direct isolation from the reaction products. Distillation and recrystallization afforded a pure sample of the diol **6** which shows no depression in melting point on admixture with authentic *trans*-1,2-cyclohexanediol (**6**). The proposed routes permit accumulation of *trans*-diol **6** with simultaneous formation of adipic acid.

Milas[14] reported that the HP–VP oxidation of cyclohexene in *t*-butyl alcohol gives a small amount of *cis*-1,2-cyclohexanediol (**5**), an unidentified aldehyde, and considerable quantities of adipic acid. This suggests that it may be possible to control selectively direct attack on the double bond over allylic attack by altering the reaction conditions.

An interesting parallel to the HP–VP oxidation of cyclohexene is provided by the work of Farmer and Moore.[15] These investigators demonstrated that both 2-cyclohexen-1-ol (**2**) and 2-cyclohexen-1-one (**3**) are formed (ratio 6:1) when cyclohexene (**1**) is oxidized with *t*-butyl hydroperoxide at 140°. These authors also demonstrated that oxidation of 1-methyl-1-cyclohexene (**7**) with *t*-butyl hydroperoxide yielded both ketones and alcohols among the products and that all possible allylic positions except on the methyl group were attacked. This is to be expected for a nonselective oxidation process and was rationalized through a free radical mechanism with a hydroperoxide and an olefin radical as intermediates.

The effect of change in concentration of hydrogen peroxide on the composition of the products from the oxidation of cyclohexene was studied with gas chromatography. We found an increase of hydrogen peroxide

---

[3] H. Born, R. Pappo, and J. Szmuszkovicz, *J. Chem. Soc.*, 1779 (1953).

[4] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2548 (1953).

[5] R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941).

[6] F. C. Whitmore and G. W. Pedlow, Jr., *ibid.*, **63**, 758 (1941).

[7] For a reference list of other preparations of 2-cyclohexen-1-one, see K. I. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

[8] R. Criegee, H. Pilz, and H. Flygare, *Ber.*, **72**, 1799 (1939).

[9] E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 121 (1942).

[10] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1950, p. 810.

[11] R. Criegee, *Ann.*, **522**, 75 (1936).

[12] N. A. Milas and S. Sussmann, *J. Am. Chem. Soc.*, **58**, 1302 (1936).

[13] E. L. Jackson, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

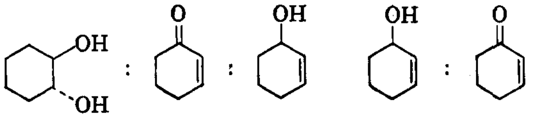
[14] N. A. Milas, *J. Am. Chem. Soc.*, **59**, 2342 (1937).

[15] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 149 (1951).

concentration from $^1/_6$ to $^1/_3$ and $^1/_2$ mole caused an increase in yield of **2** and **3**. However, additional increase of hydrogen peroxide failed to increase the yield, and not all the peroxide was consumed during the reaction. The results of these studies on $^1/_6$, $^1/_3$, and $^1/_2$ mole of hydrogen peroxide per mole of cyclohexene are presented in Table I. Thus, the maximum yields of the mixture of **2** and **3** may be obtained with the $^1/_2$ mole ratio.

TABLE I[a]

SUMMARY OF CYCLOHEXENE OXIDATIONS WITH HYDROGEN PEROXIDE



Moles of hydrogen peroxide per mole cyclohexene	Ratio of peak areas			Ratio
1/6	1	1.9	3.2	1.7
1/3	1	2.8	5.0	1.8
1/2	1	3.0	4.1	1.3

[a] These data are the average of two analyses.

To account for formation of a borate ester Treibs,[2] *et al.*, stated that 2-cyclohexen-1-one (**3**) exists in part as the enol **4**. In our hands, pure 2-cyclohexen-1-one (**3**) failed to give significant yields of borate ester since major portions of unchanged boric acid and 2-cyclohexen-1-one (**3**) were recovered (84 and 67%, respectively). We were, however, able to isolate a low yield (3.2%) of 2-cyclohexen-1-one (**3**) by steam distilling the pot residue after unchanged **3** had been distilled at 25–35° (0.05 mm.). To isolate **3** from the pot residue suggests that some **3** may have reacted with boric acid through the enol **4**. However, under identical conditions, 2-cyclohexene-1-ol reacted completely with boric acid, and a 78% yield of borate ester was isolated.

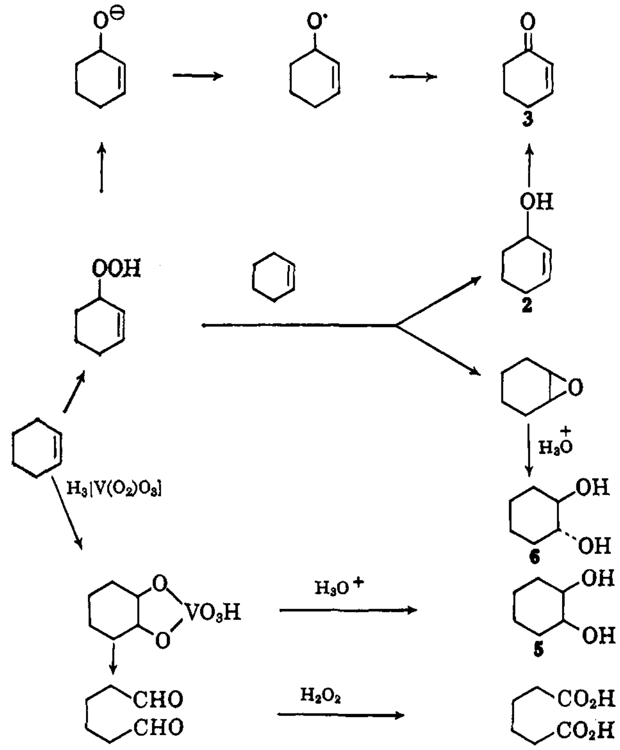
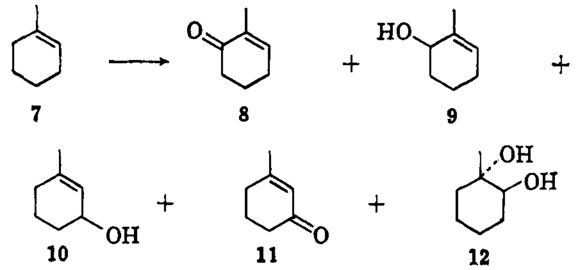


Figure 1

The HP–VP oxidations of each of the methylcyclohexenes (**7**, **13**, and **17**) in acetone were studied to determine whether the methyl substituent has any steric effect or directive influence on the site of the oxidation and, hence, the isomer composition. The gas chromatogram of the reaction products from 1-methyl-1-cyclohexene (**7**) showed seven *major* components of which five have been identified by successive enrichment with authentic products. The identified products from the oxidation of 1-methyl-1-cyclohexene (**7**) are **8–12** (see Table II).



Reduction of the reaction mixture containing **8**, **9**, **10**, **11**, and **12** with lithium aluminum hydride caused

TABLE II

GAS CHROMATOGRAPHIC ANALYSES OF HP–VP–METHYLCYCLOHEXENE OXIDATION PRODUCTS

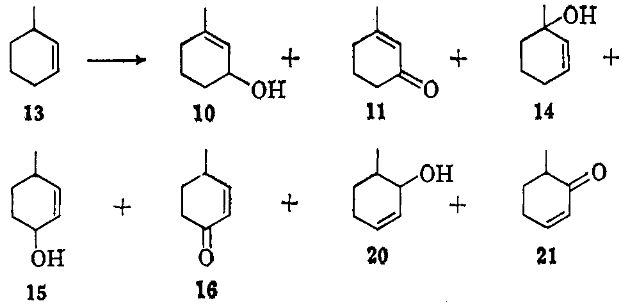
Starting material	Moles of hydrogen peroxide per mole of methylcyclohexene	Column	Oxidation products (time of emergence in min.; relative area)							
7	1/6	Carbowax[a]	Unknown alc.	Unknown ketone (2.8; 1.6)	**8** (5.9; 1)	**9** (8; 3.2)	**10** (8.8; shoulder)	**11** (12; 1.6)	**12** (22.2; 6.6)	
7	1/6	PDEAS[b]	Unknown (2.1; 1.2)	**10** (3.2; 1)	**9** (4.5; 3.3)	**8** (5.4; 1.2)	**11** (12.2; 1.4)	**12** (24.8; 10.7)		
13	1/6	PDEAS[c]	Unknown alc. (1.0; 1.3)	**14** (2.1; 3.3)	**20** (3.2; 5.7)	**15** (5.0; 3.2)	**10** (6.2; 6.3)	**21** (6.5; shoulder)	**16** (8.0; 1.0)	**11** (15; 2.1)
17	1/6	PDEAS[d]	Unknown (5.5; 1.4)	**20** (6.1; 5.3)	Unknown (6.7; shoulder)	**18** (7.0; 2.9)	**10** and **21**[e] (8.5; 1)	**19** (10.0; 2.8)		
17	1/3	PDEAS[d]	Unknown (5.5; 0.7)	**20** (6.1; 2.8)	Unknown (6.7; shoulder)	**18** (7.0; 1.2)	**10** and **21**[e] (8.5; 1)	**19** (10.0; 4.0)		
17	1/2	PDEAS[d]	Unknown (5.5; 0.5)	**20** (6.1; 3.6)	Unknown (6.7; shoulder)	**18** (7.0; 1.5)	**10** and **21**[e] (8.5; 1)	**19** (10.0; 4.2)		

[a] 10% Carbowax 20M on alkaline firebrick; $^1/_4$ in. × 5 ft.; temperature programmed from 130–200°; helium flow, 80 ml./min. [b] 15% PDEAS on acid-washed firebrick; $^1/_4$ in. × 5 ft.; 140°; [c] Same as *b*, except 135°. [d] 15% PDEAS on acid-washed firebrick; $^1/_4$ in. × 4 m.; 160°; helium flow, 65 ml./min. [e] From PDEAS the alcohol **10** emerges with the ketone **21**; these can, however, be separated on Carbowax at 115°. A quantitative estimation is, however, difficult because **21** polymerizes on the alkaline support.

disappearance of **8** and **11**, and an increase of **9** and **10**; this latter compound is present as a minor component in the crude oxidation product. Oxidation of the mixture containing **8**, **9**, **10**, and **11** with Jones' reagent in acetone solution[4] caused disappearance of **9** and **10** with simultaneous increase of **8** and **11**.

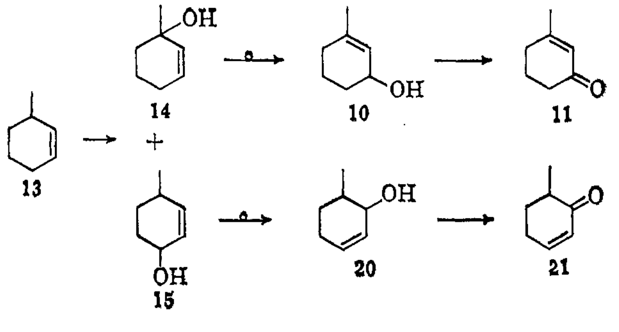
1-Methyl-1-cyclohexene (**7**) was oxidized with chromium trioxide in acetic acid, according to the method of Whitmore and Pedlow,[6] to determine whether this closely related reaction gives the reported mixture of 2-methyl-2-cyclohexen-1-one (**8**) and 3-methyl-2-cyclohexen-1-one (**11**) in the ratio of 1:9.6. We obtained a ratio of 1:7.8. Gas chromatographic analyses also showed the presence of five additional, minor products.

3-Methyl-1-cyclohexene (**13**) was oxidized with the HP-VP oxidant, and the crude product steam distilled to minimize high boiling products (presumed to be diols). These were observed as six minor peaks appearing late in the gas chromatogram. The gas chromatogram of the steam-distilled mixture showed eight peaks, of which seven have been identified (see Table II). The presence of the expected oxidation products **14**, **15**, and **16** from **13** was established by gas chromatographic studies of samples successively enriched with authentic materials.

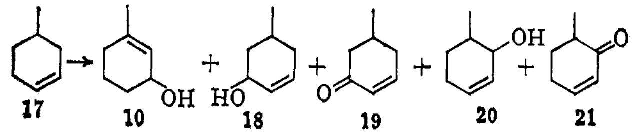


The identities of the remaining peaks were established in a circuitous manner. The total mixture was oxidized with Jones' reagent to a mixture of three ketones with gas chromatography peaks in the ratio 1.0:1.7:3.0. These peaks were shown to be due to ketones **21**, **16**, and **11** in this order, by collecting the ketones in a 2,4-dinitrophenylhydrazine solution as they emerged from the column. The 2,4-dinitrophenylhydrazones were recrystallized and melted at 147–151°, 164–165°, and 176–178°, respectively. An admixture with authentic 2,4-dinitrophenylhydrazones showed no depression in melting point. The presence of the alcohols **10** and **20** was then shown in the HP-VP oxidation mixture by enrichment with authentic materials.

The presence of the abnormal oxidation products **10**, **11**, **20**, and **21** among the expected allylic oxidation products suggested that allylic rearrangement takes place during the HP-VP oxidation of 3-methyl-1-cyclohexene (**13**). The products **10**, **11**, **20**, and **21** are presumed to form as shown (bottom, col. 1).



4-Methyl-1-cyclohexene (**17**) was oxidized similarly and five of the seven major steam-volatile products were identified by enrichment of the product mixture with authentic materials (see Table II). The presence of the unexpected alcohol **10** was confirmed by oxidizing the mixture with Jones' reagent, and showing the presence of **11** in the product by enrichment with authentic **11** in gas chromatographic studies, and by isolating the 2,4-dinitrophenylhydrazone of **11** as it emerged from the column.



While **13** yields both the normal oxidation products, **15** and **16**, and the products of the allylic shift, **20** and **21**, we were unable to detect **15** and **16**, the corresponding products produced by allylic shift accompanying **18** and **19** in the oxidation of **17**.

Experimental

Starting Materials.—The cyclohexene (**1**) used for the HP-VP oxidation was homogenous by gas chromatography (Ucon Polar column at 40°). 1-Methyl-1-cyclohexene (**7**), b.p. 110.3°, showed a single gas chromatographic peak (Ucon Polar column at 50°). 3-Methyl-1-cyclohexene (**13**), b.p. 102.5°, was obtained by fractional distillation from a mixture of 1-methyl-1-cyclohexene (**7**) and 3-methyl-1-cyclohexene (**13**). The gas chromatographic curve (200-ft. squalane capillary column at 26°, hydrogen flame detector) of the fractionated 3-methyl-1-cyclohexene showed 3-methyl-1-cyclohexene (**13**) to be 99% pure. Under these conditions 3-methyl-1-cyclohexene (**13**) and 4-methyl-1-cyclohexene (**17**) showed separation. 4-Methyl-1-cyclohexene (**17**), b.p. 102.7°, was shown to be 99% pure through the same gas chromatographic procedure as described for 3-methyl-1-cyclohexene.

Oxidations with HP-VP.[3] (a) **Cyclohexene, $^1/_6$ Mole Hydrogen Peroxide.**—To an 8-l. vessel equipped with stirrer, condenser, and dropping funnel were added 500 g. (6.1 moles) of cyclohexene (**1**) and 5.0 l. of acetone. To the well stirred mixture was added the catalyst prepared by mixing 20 ml. of 30% hydrogen peroxide and 2.0 g. of vanadium pentoxide at 5–10° and diluting with 200 ml. of precooled (–10°) acetone. The catalyst mixture was filtered as rapidly as possible so that the temperature did not rise above –2° during preparation. The flask was cooled in a water bath and 100 ml. (*ca.* 1 mole total) of 30% hydrogen peroxide was added to the agitated mixture over about 30 min. The reaction was maintained at 30°. After about 10 ml. of hydrogen peroxide was added, the color changed from orange to green. If the color change did not take place, an additional 5.0 ml. of hydrogen peroxide was added. The mixture was stirred an additional hour and then allowed to stand overnight. The reaction mixture was then held at reflux for 1 hr. with stirring and checked for hydrogen peroxide with titanium sulfate solution (if hydrogen peroxide was present, more cyclohexene was added and the reaction held at reflux for an additional hour). If peroxide was absent, acetone and excess cyclohexene were distilled (4 to 4.5 l.), the distillate diluted with water, and about 100 g. of cyclohexene was recovered from the water-insoluble layer. The residue was dried over anhydrous sodium sulfate, filtered, and distilled at 61–63° (14 mm.) to give 42–45 g. of a mixture of 2-cyclohexen-ol (**2**) and 2-cyclohexen-1-one (**3**). Gas chromatographic studies on 15% phenyldiethanolamine succinate (PDEAS) substrate supported on a column of 60–80-mesh acid-washed firebrick ($^1/_4$ in. × 5 ft.) showed the presence of two sharply defined, completely separated peaks (2 min. at 140°; 80 ml. helium/min.; Wilkens Model A-90P, thermal conductivity detector). A cleaner product containing less impurities in the gas chromatogram was obtained if the crude product was steam distilled before final distillation. The distilled product gave λ_{max}^{EtOH} 225 mμ (ϵ 3905)[16]; $\lambda_{max}^{CS_2}$ 3.0 and 5.95 μ.

(b) **Cyclohexene, $^1/_3$ Mole Hydrogen Peroxide and** (c) **Cyclohexene, $^1/_2$ Mole Hydrogen Peroxide.**—These oxidations were carried out essentially as described for part a. The yield of product boiling at 61–64° (14 mm.) was 63–65 g. for $^1/_3$ mole and 78–80 g. for $^1/_2$ mole. Gas chromatographic data on parts a, b, and c are summarized in Table I and described as part of the Jones' oxidation procedure.

(d) **1-Methyl-1-cyclohexene (7).**—The oxidation of **7** was similar to part a and was carried out in a 2-l., three-necked flask containing 1 l. of acetone and 96 g. (1 mole) of **7**. The catalyst was prepared from 0.4 g. of vanadium pentoxide and 2 ml. of cold 30% hydrogen peroxide and diluted with 30 ml. of acetone after 2–3 min.; see Table II for gas chromatographic data of the steam-distilled product mixture. 1-Methyl-*trans*-1,2-cyclohexanediol (**12**) crystallized directly from the reaction mixture and was also isolated as a high boiling fraction, b.p. 100° (12 mm.), m.p. 84–86°.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.53; H, 10.83. Found: C, 64.51; H, 10.59.

(e) **3-Methyl-1-cyclohexene (13) and** (f) **4-Methyl-1-cyclohexene (17).**—These olefins were oxidized in the same manner as described in part d, and the results are tabulated in Table II.

Oxidation of 1-Methyl-1-cyclohexene (7) with Chromic Acid.—1-Methyl-1-cyclohexene (**7**) (96 g. 1.0 mole), was oxidized according to the precedure of Whitmore and Pedlow[6] except that the reaction mixture was steam distilled rather than extracted. The steam distillate was saturated with salt, extracted with ether, the ether dried over anhydrous magnesium sulfate, filtered, and distilled. The distillation residue was directly injected onto a $^1/_4$ in. × 5 ft. gas chromatographic column containing 15% PDEAS on 60–80-mesh acid-washed firebrick. Flow rate was 80 ml. helium/min. and column temperature was 140°. Two major peaks in the ratio of 1:7.8 were observed. These were established as 2-methyl-2-cyclohexen-1-one (**8**) and 3-methyl-2-cyclohexene-1-one (**11**) by successively enriching the reaction product with authentic ketones **8** and **11** and analyzing by gas chromatography.

Jones' Oxidations[4] of the Reaction Products from HP–VP Oxidations. (a) **Crude Mixture of 2-Cyclohexen-1-ol (2) and 3-Cyclohexen-1-one (3).**—The crude reaction product from the oxidation of cyclohexene with HP–VP[2] was steam distilled, the steam distillate saturated with salt, extracted with ether, the ether layer dried over anhydrous magnesium sulfate, filtered, and the ether distilled slowly under water aspirator vacuum. The concentrate (424 g.) was dissolved in 5 l. of redistilled acetone and oxidized by dropwise addition of Jones' reagent[4] to the well stirred solution. The reagent is a mixture of 267 g. of chromium trioxide and 230 ml. of sulfuric acid (Spectro Grade 1.84) made up to 1.0 l. with distilled water.[4] The temperature of the reaction was maintained at 20–30° by cooling in a water bath. Progress of the oxidation (2 hr.) was followed by occasionally withdrawing a 1-ml. sample to which was added about 25 mg. of sodium bicarbonate and the pH checked to ensure neutrality. The sample was shaken; the solution decanted and dried over anhydrous magnesium sulfate. The supernatent liquid was directly injected onto the PDEAS column at 140°. Two peaks were observed before oxidation was begun. As the oxidation proceeded, the second peak grew at the expense of the first peak until at termination only the second peak remained. The orange-yellow end point was maintained for about 10 min. This end point is demonstrated easily with a drop of Jones' reagent in a few mililiters of acetone. A few drops of isopropyl alcohol will consume the excess reagent. The reaction product was decanted and the suspension of green salts rinsed with a few milliliters of acetone. Sodium bicarbonate (50 g.) was added to reaction mixture, suspension filtered, anhydrous magnesium sulfate (500 g.) added, the suspension filtered once more, and the acetone distilled through a Vigreux column. On occasion it was necessary once more to dry the product with anhydrous magnesium sulfate before final distillation. Distillation at 61° (14 mm.) gave 371 g. of 2-cyclohexen-1-one (**3**); λ_{max}^{EtOH} 224 mμ (ϵ 11,716) and $\lambda_{max}^{CS_2}$ 5.95 μ.[16] The red 2,4-dinitrophenylhydrazone was recrystallized from isopropyl alcohol and melts at 166–167°.[3,6]

(b) **Products from 1-Methyl-1-cyclohexene (7).**—The crude reaction product obtained from the HP–VP oxidation of 1-methyl-1-cyclohexene (**7**) was steam distilled, the steam distillate saturated with salt, extracted with ether, the ether separated and concentrated by distillation. The concentrate was oxidized with Jones' reagent in a manner similar to part a but on a smaller scale. The oxidation product was isolated by steam distillation, extracted with ether, and the dried ether concentrate injected onto an alkaline Carbowax 20M gas chromatographic column, temperature programmed from 30–200°.

The peaks represented by 2-methyl-2-cyclohexen-1-one (**8**) and 3-methyl-2-cyclohexen-1-one (**11**) were identified by enriching the reaction product sample with authentic materials. The peaks due to the alcohols **9** and **10** were not present in the gas chromatogram.

(c) **Products from 3-Methyl-1-cyclohexene (13).**—The Jones' oxidation of the products from HP–VP oxidation of **13** was conducted in the same manner as for part b. The gas chromatogram (PDEAS column at 135°) showed three peaks in the ratio of 1.0:1.7:3.0. The ketones were collected from the PDEAS column in a 2,4-dinitrophenylhydrazine solution. The resulting red 2,4-dinitrophenylhydrazone derivatives were collected, recrystallized, and found to melt at 147–151°, 164–165°, and 176–178°. Admixtures of these red 2,4-dinitrophenylhydrazones with 2,4-dinitrophenylhydrazones derivatives of authentic 6-methyl-2-cyclohexen-1-one (**21**), 4-methyl-2-cyclohexen-1-one (**16**), and 3-methyl-2-cyclohexene-1-one (**11**), respectively, show no depression in melting point. The ketones from the individual peaks were collected in ether as they emerged from the column and used to identify peaks in the chromatogram of the crude reaction product and as a source for lithium aluminum hydride reduction to obtain the respective alcohols.

(d) **Products from 4-Methyl-1-cyclohexene (17).**—The Jones' oxidation of **17** was carried out as in part b. The presence of **11**, which emerged last on the PDEAS column, was shown by enrichment with authentic **11** and by the isolation of its red 2,4-dinitrophenylhydrazone derivative, m.p. 176–178°, which does not depress the melting point of the 2,4-dinitrophenylhydrazone of authentic 3-methyl-2-cyclohexen-1-one (**11**).

Lithium Aluminum Hydride Reductions. (a) **Mixture of 2-Cyclohexen-1-ol (2) and 2-Cyclohexen-1-one (3).**—To a 5-l., three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel with pressure equalizing side arm, containing 42 g. lithium aluminum hydride dissolved in 3 l. of anhydrous ether, was added a 300-g. sample of a mixture comprised of 37% 2-cyclohexen-1-one (**3**) and 63% 2-cyclohexen-1-ol (**2**) at a rate to maintain gentle reflux. Two hours were required for addition. The reaction mixture was stirred an additional 4 hr. at reflux temperature and water was added dropwise until evolution of gases ceased. The suspension was allowed to settle; the ether solution was decanted and tested with water to ensure complete destruction of lithium aluminum hydride. The suspended salts were rinsed twice with 200-ml. portions of ether and the combined ether solution dried over anhydrous magnesium sulfate, filtered, and ether distilled. The concentrate was distilled at 64–65° (10.5 mm.) to give 240 g. of 2-cyclohexen-1-ol (**2**) whose infrared spectrum showed $\lambda_{max}^{CS_2}$ 3.0 and 6.08 μ. The gas chromatogram (PDEAS at 115°) showed a single major peak and no peak corresponding to 2-cyclohexen-1-one (**3**). The phenyl urethane melts at 107–109°.[6]

(b) **Crude Products from 1-Methyl-1-cyclohexene (7).**—The crude HP–VP products of 1-methyl-1-cyclohexene (**7**) were reduced with lithium aluminum hydride as described under part a. The products were isolated by steam distillation. The steam distillate was saturated with salt and extracted with ether; the ether layer was separated and washed with small portions of water, dried over anhydrous magnesium sulfate, filtered, and distilled. The concentrate was analyzed with gas chromatography (PDEAS column at 130°). The peaks corresponding to the ketones **8** and **11** were completely absent. The peaks corresponding to the alcohols **9** and **10** were found to have increased.

Borate Ester Preparation. (a) **From 2-Cyclohexen-1-ol (2).**—A mixture of 49.0 g. (0.5 mole) of 2-cyclohexene-1-ol (**2**), 8.4 g. (0.136 mole) boric acid, and 100 ml. of dry benzene was heated at reflux temperature for approximately 2 hr. until water–benzene azeotrope (7.0 ml. total) no longer collected in the Dean–Stark separator. The boric acid completely dissolved within a few minutes after reflux was attained. Most of the benzene (75 ml.) was distilled at atmospheric pressure and the product distilled through a short-path Vigreux column at 30–115° (0.04 mm.). The benzene forerun was discarded and the product fractionated

---

[16] D. Dusterhoft of Lakeside Laboratories kindly carried out these determinations.

through a spiral column to give 15.8 g. recovered **2** and 32.0 g. (0.133 mole, 78% yield based on boric acid) of colorless boric acid ester, b.p. 133–145° (0.2 mm.). A center cut, b.p. 142–145° (0.2 mm.), was used for analyses and infrared spectrum; $\lambda_{\max}^{\text{neat}}$ 2.95, 6.08, 7.05, 7.24, 7.60, 8.00, 9.60, 9.40, 9.56, 10.42, 10.76, 11.11, and 13.80 μ.

Anal. Calcd. for $C_{18}H_{27}BO_3$: B, 3.57. Found: B, 3.73.

A 14.9-g. (0.049 mole) sample of the borate ester of **2** was steam distilled, the distillate extracted with ether, the ether extract dried over anhydrous magnesium sulfate, filtered, and the ether distilled to give 12.3 g. (85% recovery) of regenerated 2-cyclohexen-1-ol (**2**). The infrared spectrum and gas chromatogram (PDEAS at 140°) were identical with those of original **2**. The contents of the steam distillation reaction flask were colorless.

(b) **From 2-Cyclohexen-1-one** (**3**).—Under conditions similar to part a, 2-cyclohexen-1-one (**3**) (0.5 mole) and boric acid (0.136 mole) in 100 ml. of benzene gave 2 ml. of water–benzene azeotrope. The dark-colored reaction product was filtered to yield 7.1 g. (84% recovery) of unchanged boric acid. The filtrate was distilled at 25–35° (0.05 mm.) to give 32.1 g. (66% recovery) of 2-cyclohexene-1-one whose gas chromatogram (PDEAS at 125°) and infrared spectrum were identical with those of original ketone **3**.

The dark-colored, viscous pot residue was steam distilled to give 1.6 g. (0.016 mole, 3.2%) of regenerated 2-cyclohexen-1-one (**3**) whose infrared spectrum, gas chromatogram (PDEAS at 125°) and gas chromatogram of an admixture with **3** were identical with 2-cyclohexene-1-one (**3**). A dark-colored tar remained in the steam distillation flask.

Preparation of Comparison Compounds. (a) ***cis*-1,2-Cyclohexanediol** (**5**).—A sample of a mixture of *cis*-1,2-cyclohexanediol (**5**) and *trans*-1,2-cyclohexanediol (**6**) was separated by gas chromatography on PDEAS at 162° and collected in ethyl acetate. The retention times were 11.5 and 12.4 min., respectively.

(b) **2-Methyl-2-cyclohexen-1-one** (**8**).—2-Methyl-2-cyclohexen-1-one (**8**) was obtained by dehydrohalogenation[17] of 2-chloro-2-methylcyclohexanone[18] with lithium bromide and lithium carbonate in dimethylformamide. The ketone **8**, $n^{23}\text{D}$ 1.4852, $\lambda_{\max}^{\text{neat}}$ 6.05 μ, gives a single peak on the PDEAS gas chromatographic column at 145°. Its red 2,4-dinitrophenylhydrazone crystallized from isopropyl alcohol melts at 207–209°.[19]

(c) **2-Methyl-2-cyclohexen-1-ol** (**9**).—The alcohol **9** was obtained from the ketone **8** *via* lithium aluminum hydride reduction in ether solution followed by steam distillation. The product shows a single gas chromatographic peak on the PDEAS column at 145°.

(d) **3-Methyl-2-cyclohexen-1-ol** (**10**).—A sample of 3-methyl-2-cyclohexen-1-one (**11**) was reduced with lithium aluminum hydride in ether to give 3-methyl-2-cyclohexen-1-ol (**10**), $n^{23}\text{D}$ 1.4835, b.p. 82–84° (15 mm.,) and $\lambda_{\max}^{\text{neat}}$ 3.07 and 6.08 μ. Gas chromatographic analysis on PDEAS at 140° shows a single peak.

(e) **3-Methyl-2-cyclohexen-1-one** (**11**).—A 182-g. (1.0 mole) sample of 4-carbethoxy-3-methyl-2-cyclohexen-1-one,[20] $n^{23}\text{D}$ 1.4842, was hydrolyzed by steam distilling from 1 l. of 15% sulfuric acid. The steam distillate was saturated with salt and extracted with ether; the ether layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and distilled to give 87 g. (0.79 mole, 79% yield) of 3-methyl-2-cyclohexene-1-one (**11**), b.p. 80–95° (9 mm.,) $n^{25}\text{D}$ 1.4910, and $\lambda_{\max}^{\text{neat}}$ 6.05 and 6.2 μ. The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate melts at 176–178°.

(f) **1-Methyl-2-cyclohexen-1-ol** (**14**).—A 24-g. sample (0.25 mole) of 2-cyclohexen-1-one was added to 2 equivalents of methylmagnesium iodide contained in a 1-l., three-necked flask equipped with stirrer, condenser protected with a calcium chloride tube, and dropping funnel. The 2-cyclohexene-1-one was added to the chilled (−5°) reaction flask over a 2-hr. period. The reaction mixture was allowed to come to room temperature and then heated at reflux temperature for 0.5 hr. The reaction mixture was then poured onto 500 g. of ice, and the product was directly steam distilled without addition of ammonium chloride or acid. [It was intentional that acid was avoided to minimize isomerization of 1-methyl-2-cyclohexen-1-ol (**14**) to 3-methyl-2-cyclohexen-1-ol (**10**).] The steam distillate (1 l.) was saturated with salt, extracted with 200 cc. of ether, and washed with two small portions of water; the ether layer separated, dried over anhydrous magnesium sulfate, filtered, and the ether distilled. The concentrate was analyzed with gas chromatography (PDEAS column at 100°) and found to be a mixture of 36% 1-methyl-2-cyclohexen-1-ol (**14**),[6] 58% 3-methylcyclohexanone,[6] and 6% 3-methyl-2-cyclohexen-1-ol (**10**).[6] The 3-methylcyclohexanone and the alcohol **10** were identified by enriching the total reaction product with authentic materials and analyzing by gas chromatography. A pure sample of the alcohol **14** was obtained by collection from the PDEAS column at 125°.

(g) **4-Methyl-2-cyclohexen-1-ol** (**15**).—The ketone **16** was reduced with lithium aluminum hydride in ether to give 4-methyl-2-cyclohexen-1-ol (**15**) which shows essentially a single gas chromatographic peak; the yield of **15** was 71%.

(h) **4-Methyl-2-cyclohexen-1-one** (**16**).—A procedure similar to j was employed in the preparation of 4-methyl-2-cyclohexen-1-one (**16**) from 4-methylcyclohexanone. The ketone **16** gave a red 2,4-dinitrophenylhydrazone which melts at 168–169° on recrystallization from isopropyl alcohol.

(i) **5-Methyl-2-cyclohexen-1-ol** (**18**).—A sample of 5-methyl-2-cyclohexen-1-one (**19**) was purified by gas chromatography on PDEAS, reduced by lithium aluminum hydride, and the product isolated by steam distillation. The product, 5-methyl-2-cyclohexen-1-ol (**18**), shows a single peak on the PDEAS gas chromatographic column.

(j) **5-Methyl-2-cyclohexen-1-one** (**19**).—A 112-g. sample of *dl*-3-methylcyclohexanone was chlorinated with sulfuryl chloride in carbon tetrachloride solution.[19] The chlorocyclohexanone was distilled at 35–87° (0.1 mm.) and shown by gas chromatography on PDEAS at 170° to contain 3-methylcyclohexanone in the initial cut. Center cuts, b.p. 50–80° (0.1 mm.), were free of 3-methylcyclohexanone but appeared to be a mixture of 2-chloro-3-methylcyclohexanone and 2-chloro-5-methylcyclohexanone since double peaks were observed in the gas chromatogram on PDEAS at 170° column temperature.

Dehydrohalogenation[17] in the presence of lithium bromide and lithium carbonate in dimethylformamide solvent was carried out on a 50-g. sample of the mixture of chloro ketones. The product was isolated by steam distillation and extraction of the steam distillate with ether. Dimethylformamide was removed from the ether extract by washing with water. The product, b.p. 34–54° (0.1 mm.), was shown by gas chromatography on PDEAS at 170° to be a mixture containing the desired product, 5-methyl-2-cyclohexen-1-one (**19**) (3.5 min. retention time), as well as 3-methyl-2-cyclohexen-1-one (**11**) and 3-methylphenol (6.2 and 14 min., respectively). The latter compounds were identified by enriching the mixture with authentic materials. A pure sample of 5-methyl-2-cyclohexen-1-one (**19**) was obtained by collecting the ketone as it emerged from the column. An orange 2,4-dinitrophenylhydrazone was prepared from the collected sample and found to melt at 148–149°[21] after recrystallization from methanol.

(k) **6-Methyl-2-cyclohexen-1-ol** (**20**).—A sample of 6-methyl-2-cyclohexen-1-one (**21**) was purified through gas chromatography (PDEAS column at 150°) by collecting in ether solution. The ether solution was added dropwise to a stirred solution of lithium aluminum hydride in ether. The reaction was heated at reflux temperature for approximately 0.5 hr., cooled, and the excess lithium aluminum hydride cautiously destroyed by the dropwise addition of water. Additional water was added and the reaction product steam distilled. The alcohol **20** was isolated from the steam distillate by extraction with ether, the ether solution dried, concentrated, and analyzed by gas chromatography (PDEAS column at 120°) which showed essentially a single peak with a slight trailing shoulder. This shoulder was assumed to be due to the presence of *cis* isomer. The yield of **20** was 72%. The alcohol **20** was added to a sample of the HP–VP oxidation product of 4-methyl-1-cyclohexene (**17**) and this enrichment established the presence of **20** in the reaction mixture.

(l) **6-Methyl-2-cyclohexen-1-one** (**21**) was generously donated by D. R. Coulson and E. J. Warawa of Columbia University. Reduction with lithium aluminum hydride gave 6-methyl-2-cyclohexen-1-ol (**20**).

---

(17) R. Joly, J. Warnaut, G. Nomine, and D. Bertin, *Bull. soc. chim. France*, 360 (1958).

(18) Generously donated by J. Levy and H. L. Goering of the University of Wisconsin.

(19) E. W. Warnhoff and W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 494 (1953).

(20) C. Th. L. Hagemann, *Ber.*, **26**, 876 (1893).

(21) H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **73**, 5863 (1951).