after recrystallization from ethanol, 180°; yield 1.7 g. X gave no ferric chloride reaction and on treatment, in alcoholic solution, with magnesium and hydrochloric acid gave an orange-red color at room temperature.[7]

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 74.0; H, 4.1. Found: C, 73.6; H, 4.1.

6-Formyl-7-hydroxy-5-methoxyflavone (XI).—To 1 g. of X dissolved in a warm (50°) mixture of glacial acetic acid (10 ml.) and 25% sulfuric acid (20 ml.) was added 6.7 ml. of a 30% sodium dichromate solution. The reaction, which started at once, proceeded with elevation of temperature and evolution of carbon dioxide; after a few minutes, colorless XI began to separate out. The mixture then was left to cool at room temperature and was diluted to 100 ml. with water and filtered. After recrystallization from ethanol, the colorless needles of XI had m.p. 207°, yield 0.8 g. XI dissolved in dilute sodium hydroxide solution with a yellow color and gave a red ferric chloride reaction. An orange color was obtained when an alcoholic solution of *p*-phenylenediamine was mixed with a concentrated alcoholic solution of XI. The test with magnesium and hydrochloric acid, carried out as for X, gave a yellow color.

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.9; H, 4.0. Found: C, 68.6; H, 4.3.

Oxime of XI.—To 200 mg. of XI in 5 ml. of a 5% sodium hydroxide solution was added a solution of 200 mg. of hydroxylamine hydrochloride in 5 ml. of water. The solution was left to stand for 6 hr. It was then acidified with acetic acid and the precipitated oxime was filtered off and crystallized from a mixture of methanol and acetone as colorless needles, m.p. 266°.

Anal. Calcd. for $C_{17}H_{13}O_5N$: C, 65.6; H, 4.2; N, 4.5. Found: C, 65.7; H, 4.3; N, 4.6.

6,7-Dihydroxy-5-methoxyflavone (XII).—To a solution of XI (0.5 g.) in 5 ml. of 4% sodium hydroxide solution cooled to 0° was added 1.25 ml. of a 30% hydrogen peroxide solution and the reaction mixture was kept in the refrigerator overnight. It was then acidified and the precipitate thus obtained was collected and crystallized from dilute ethanol as yellowish needles, m.p. 223–224° (darkens), yield 300 mg.; XII was soluble in dilute sodium hydroxide solution with a yellow-orange color and had an intense green-black ferric chloride reaction turning red-brown on addition of dilute sodium bicarbonate solution. With a drop of lead acetate solution in alcohol, XII gave a yellow color or precipitate. The test with magnesium and hydrochloric acid carried out as for X gave a deep red color.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.6; H, 4.2. Found: C, 67.3; H, 4.3.

Demethylation of XII to 5,6,7-Trihydroxyflavone (XIII) (Baicalein).—One-half gram of XII was refluxed for 3 hr. with 100 ml. of 18% hydrochloric acid. The original substance dissolved in a few minutes and, after a half-hour, yellow XIII began to separate out. After the reaction was over, the precipitate was collected by filtration and recrystallized from dilute acetic acid, m.p. 263–264° undepressed by an authentic sample of baicalein, yield 300 mg. The yellow prisms of XIII were soluble in 4% sodium hydroxide solution with a green color and gave a greenish-brown ferric chloride reaction.

Anal. Calcd. for $C_{15}H_{10}O_5$: C, 66.7; H, 3.7. Found: C, 66.5; H, 4.0.

The trimethyl ether of XIII which was prepared by the procedure described for the methylation of II, crystallized from alcohol as colorless needles, m.p. 165–167° (reported m.p. 165–166°[5]) giving a yellow color with concentrated sulfuric acid. The trimethyl ether of XIII also was obtained by the methylation of XII under similar conditions (m.p. and mixed m.p.).

Physiological Tests.—Although bergapten (I) is known to be photodynamically active, all the coumarins II–VI synthesized from this substance were found to be inactive when tested under the conditions described by Musajo, Rodighiero and Caporale.[8]

Acknowledgment.—We are indebted to Professor T. R. Seshadri for carrying out the mixed m.p. determination of XIII with an authentic sample of baicalein.

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[7] For references to the reactions of flavones with magnesium and hydrochloric acid, see T. A. Geissman and R. O. Clinton, THIS JOURNAL, **68**, 700 (1946).

[8] L. Musajo, G. Rodighiero and G. Caporale, *Bull. soc. chim. biol.*, **36**, 1213 (1954).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. XIV.[1] Isomerization of Methyl-C^{14}-cyclohexane in the Presence of Aluminum Bromide

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Although no isomerization takes place when methylcyclohexane is treated with aluminum halide in a batch reaction, a new species of methylcyclohexane was formed when methyl-C^{14}-cyclohexane is treated with aluminum bromide, hydrogen bromide and small amounts of *sec*-butyl bromide. About 31% of the radioactive carbon appears in the cyclohexyl ring. In the absence of *sec*-butyl bromide, only 2% of the radioactive carbon is found in the ring. A chain mechanism for the isomerization is discussed. The synthesis of methyl-C^{14}-cyclohexane and methods of analysis are described.

It has been reported previously that little if any apparent reaction occurred when methylcyclohexane was treated with aluminum bromide or aluminum chloride, or even aluminum chloride and hydrogen chloride at elevated temperatures.[3]

The apparent lack of isomerization of methylcyclohexane might be due to the unfavorable equilibrium constants. The calculated values of equilibrium constants for isomerization of methylcyclohexane to alkylcyclopentanes, as calculated from the free energy data,[4] are given in Table I.

Definite evidence for the isomerization of methylcyclohexane to dimethylcyclopentanes was accomplished recently[5] by refluxing methylcyclohexane with aluminum chloride in the presence of wa-

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[1] For paper XIII of this series see H. Pines, R. W. Myerholtz, Jr., and H. M. Neumann, THIS JOURNAL, **77**, 3399 (1955).

[2] Universal Oil Products Co. Predoctoral Fellow, 1951–1954.

[3] (a) N. D. Zelinsky and M. B. Turova-Pollak, *Ber.*, **62B**, 1658 (1929); (b) R. Stratford, *Ann. Combustibiles Liquides*, **4**, 83, 317 (1929); (c) C. D. Nenitzescu, E. Cioranescu and I. P. Cantuniari, *Ber.*, **70B**, 277 (1937); (d) M. B. Turova-Pollak and Z. Makaeva, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 1279 (1939); (e) G. C. A. Schuit, H. Hoog and J. Verheus, *Rec. trav. chim.*, **59**, 793 (1940); (f) N. D. Zelinsky, M. B. Turova-Pollak, N. F. Tsvetkova and E. G. Treschova, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **21**, 2156 (1951).

[4] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

[5] R. Van Volkenburgh, K. W. Greenlee and C. E. Boord, Abstracts of Papers, 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3–9, 1950, p. 36-N.

TABLE I

EQUILIBRIUM CONSTANTS FOR ISOMERIZATION OF METHYLCYCLOHEXANE TO

Isomer, cyclopentane	*K*
Ethyl-	1.20×10^{-3}
1,1-Dimethyl-	5.37×10^{-3}
cis-1,2-Dimethyl-	5.75×10^{-4}
trans-1,2-Dimethyl-	8.32×10^{-3}
cis-1,3-Dimethyl-	2.40×10^{-3}
trans-1,3-Dimethyl-	5.75×10^{-3}

ter and by removing the lower boiling alkylcyclopentanes by constantly distilling them away from the reaction zone.

Although there seemed to be no isomerization when methylcyclohexane was treated with aluminum bromide or aluminum chloride in a batch reaction, isomerization to a new species of methylcyclohexane normally indistinguishable from the starting material was not excluded.

It seemed of interest, therefore, to reinvestigate this reaction using methyl-C^{14}-cyclohexane.

Accordingly, methyl-C^{14}-cyclohexane was synthesized and treated at room temperature with aluminum bromide and hydrogen bromide in the presence of *sec*-butyl bromide to serve as a chain initiator. An experiment also was made without *sec*-butyl bromide to determine the effect of this reagent on the course of the reaction.

Methyl-C^{14}-cyclohexane was obtained by the catalytic hydrogenolysis of benzyl alcohol-hydroxymethyl-C^{14}.

The extent of isomerization was determined by degradation. This involved the dehydrogenation of methylcyclohexane to toluene followed by oxidation to benzoic acid and decarboxylation to benzene and carbon dioxide. The activities of barium carbonate obtained from the decarboxylation reaction and that from combustion of benzene are summarized in Table II.

TABLE II

ACTIVITIES OF BARIUM CARBONATES

The isomerization reactions were carried out at room temperature for 21 hr.

	Activities in c.p.m.[a]			
Expt.	Methyl-cyclohexane[b]	CO_2[c]	Benzene	Isom., %
I[d]	318	1624	122	31[e,f]
II[g]	1163	. . .	25	2[h]

[a] Counts per minute, average of four determinations, corrected for background and coincidence. [b] Starting methyl-C^{14}-cyclohexane. [c] From the decarboxylation. [d] Molar ratio of reagents used: $C_7H_{14}/AlBr_3/HBr/s\text{-}C_4H_9Br = 100/4/2/0.2$. [e] $(122)(6)(100)/(1624) + (122)(6) = 31\%$. [f] Radiochemical balance: $(1624/7) + (122 \times 6/7) = 336$. [g] Molar ratio of reagents used: $C_7H_{14}/AlBr_3/HBr = 100/4/2$. [h] $(25)(6)(100)/(7)(1163) = 2\%$.

On the basis of the results obtained it was calculated that 31% of the total activity of the recovered methylcyclohexane was in the ring. This shows that the methylcyclohexane recovered after treatment with aluminum bromide and hydrogen bromide in the presence of *sec*-butyl bromide is indeed a different species from the starting material.

In the absence of a chain initiator, such as 2-butyl bromide, the isomerization of methyl-C^{14}-cyclohexane occurs only to the extent of 2%. This result is not surprising since it was previously shown that a promoter is necessary to serve as a chain initiator for isomerization of this type.[6,7] The small amount of isomerization which was observed might have been due to traces of peroxides or other impurities present in the methyl-C^{14}-cyclohexane used.[7b]

The results obtained can be interpreted by a carbonium ion chain reaction similar to the one proposed previously.[6-8] This reaction involves the formation of a methylcyclohexylcarbonium ion which by a ring contraction can form dimethylcyclopentylcarbonium ion. The latter through a ring expansion in which the methyl-C^{14} participates is converted to methylcyclohexylcarbonium ion having the C^{14} in the ring.

Experimental Part

Synthesis of Methyl-C^{14}-cyclohexane. A. Benzoic Acid-carboxyl-C^{14}.—Benzoic acid-carboxyl-C^{14} was prepared from 40 mmoles of phenylmagnesium bromide and 30.2 mmoles of radioactive barium carbonate, according to the published procedure[9]; yield 3.05 g., 83%.

B. Benzyl Alcohol-hydroxymethyl-C^{14}.—The benzoic acid obtained above and 2.80 g. of inactive benzoic acid were dissolved in 75 ml. of dry ether and reduced with 3.3 g. of lithium aluminum hydride suspended in 75 ml. of ether, according to the usual procedure; b.p. 90.0–90.5° at 11 mm., $n^{20}D$ 1.5398, yield 3.9 g. (76%).

C. Methyl-C^{14}-cyclohexane.—The benzyl alcohol obtained in the preceding step was added to 14.4 g. of inactive benzyl alcohol and hydrogenated in a rotating autoclave in the presence of 3 g. of nickel–kieselguhr catalyst at an initial pressure of 110 atmospheres. The temperature was maintained at 110–120° for two hours and then at 140–150° until the pressure remained constant. The hydrogen uptake corresponded to the theoretical value; b.p. 97–100°, $n^{20}D$ 1.4230, yield 9.85 g. (65%).

A portion of this product was diluted with appropriate amounts of inactive methylcyclohexane and a portion was burned and the resulting barium carbonate assayed. Samples of methylcyclohexane were prepared with respective activities of 318 and 1163 c.p.m.

Isomerization Experiments.—Using a high vacuum technique,[6] 5.1×10^{-2} mole of labeled methylcyclohexane with an activity of 318 c.p.m., 2.08×10^{-3} mole of aluminum bromide, 1.1×10^{-3} mole of hydrogen bromide and 1.26×10^{-4} mole of *sec*-butyl bromide were introduced into a reaction tube (mole ratio: 100/4/2/0.2).

After pumping to 10^{-6} mm. pressure, the reaction tube was sealed off from the line and the promoter ampoule broken. Agitation was begun and continued for 21 hours at room temperature. The reaction tube then was attached to the vacuum line and the contents distilled out. A small amount of yellow sludge remained behind and probably was polymeric material. The hydrocarbon was washed three times with 10% potassium carbonate and three times with distilled water, then dried over calcium chloride.

In the experiment where *sec*-butyl bromide was omitted the technique was the same, and all reactants were used in the same molar amounts. The activity of methylcyclohexane used was 1163 c.p.m.

(a) **Dehydrogenation.**—The hydrocarbon obtained from the isomerization reaction was passed four times over 18 ml. of platinized alumina catalyst at 284–288° until no more hydrogen evolved.[10] The dehydrogenated product, 3.0 g., with a refractive index of 1.4880 contained about 90% toluene.

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(6) H. Pines, B. M. Abraham and V. N. Ipatieff, THIS JOURNAL, **70**, 1742 (1948).

(7) (a) H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951); (b) **74**, 5544 (1952).

(8) H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).

(9) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 178–180.

(10) H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **70**, 533 (1948).

The product then was chromatographed[11] on a 30-inch column of 60–200 mesh silica gel. Absolute ethanol was used as eluent. Collection of the aromatic fraction was begun when the effluent reached $n^{20}\mathrm{D}$ 1.4752; collected 2.2 g.

(b) **Oxidation.**—The product of the preceding step was oxidized by refluxing for 20 hours with 15 g. of potassium permanganate dissolved in 230 ml. of water. Five ml. of methyl alcohol was then added to remove the last traces of permanganate. The reaction mixture was filtered hot and the cake of manganese dioxide washed with 200 ml. of hot distilled water. The solution was evaporated to *ca.* 50 ml. and the hot solution acidified with concentrated hydrochloric acid and cooled in an ice-bath. The precipitate was filtered on a sintered glass funnel, washed with ice-water, air-dried, and then transferred to a desiccator; m.p. 121–121.5° (cor.).

The yield was not determined on the active run since some ethanol was mixed with the toluene after chromatographing. Exploratory experiments using 3.0 g. of toluene gave 60% yield.

(c) **Decarboxylation.**—Decarboxylation of the benzoic acid obtained in the preceding step was carried out according to the procedure outlined by Calvin, *et al.*,[12] using 0.8 g. of copper chromite catalyst and 10 ml. of redistilled quinoline. A nitrogen sweep carried the benzene into a Dry Ice trap and the carbon dioxide evolved was collected in sodium hydroxide, precipitated as barium carbonate, and assayed. The benzene recovered had $n^{20}\mathrm{D}$ −1.5011, yield 75–80%.

A portion of the benzene was burned and the carbon dioxide converted to infinitely thick barium carbonate samples, which were then assayed. It was found that 31% of the radioactive carbon was in the benzene ring and 69% on the methyl group.

In the experiment where *sec*-butyl bromide was a chain initiator only 2% of the radioactive carbon was present in the ring.

Acknowledgment.—The authors are indebted to Dr. H. M. Neumann for his assistance in developing many of the techniques for handling and measuring the radioactive carbon.

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[11] B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

[12] Reference 9, page 229.

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[CONTRIBUTION NO. 147 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Scission in the Oxidation of Hevea. I

BY E. M. BEVILACQUA

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The efficiency of chain scission of raw hevea by molecular oxygen increases rapidly with increase in temperature, to a limiting value of about 6.2 molecules of oxygen per bond broken. This value is close to the theoretical for destruction of one isoprene unit per bond broken, which leads to the inference that the higher efficiencies which have been reported for oxidation of vulcanized rubber may be the result of scission at the points of cross-linking.

Introduction

The essential role of oxygen in the reduction of viscosity of unvulcanized rubber during mastication is well known in a qualitative way, but there is little quantitative information about the efficiency with which it is used in this process. A recent study of the low temperature breakdown of hevea by Pike and Watson[1] clearly suggests that the efficiency (measured in terms of scissions of the hydrocarbon chain per mole of oxygen absorbed) is high under conditions where mechanical rupture of carbon to carbon bonds is important. At elevated temperatures (above about 120°) the viscosity of hevea has fallen sufficiently so that mechanical rupture is no longer effective and mastication serves only to mix the rubber and to expose continuously fresh surfaces to air. Measurements of the efficiency of oxidation on films thin enough so that oxygen diffusion does not affect the results should therefore be satisfactory to determine the efficiency of oxidative scission under practical milling conditions.

It is not possible to make such measurements with ordinary forms of rubber without some preliminary degradation of the hydrocarbon, either accompanying solution in a solvent or during milling to produce a thin sheet. The USF rubber process[2] affords a particularly convenient source of undegraded rubber, which has been used in this investigation.

Experimental

USF type rubber was prepared by a slight modification of the published procedure.[2] Normal latex, preserved with 0.4% formaldehyde by weight, was diluted with distilled water to give a calculated ash content in the final rubber equal to that of commercial USF. After adjustment of the *p*H to 3.8 to 4.0 with formic acid, the mixture was allowed to cream for 24 hours. The cream was separated from the clear serum and spread on glass to give a final film of the desired thickness after drying. All the films used were less than 0.01 cm. thick. Films were wrapped in desized glass cloth for oxidation.

Oxidations were carried out at a constant pressure of one atmosphere of oxygen in a simple apparatus consisting of a large test-tube mounted in a circulating air oven. The test-tube was connected by capillary glass tubing to a reference manometer and a manually operated gas buret maintained at 30°. The reference manometers were connected to a reservoir of air at constant temperature to eliminate the effect of variations in atmospheric pressure. Lumps of barium oxide were mounted in the oxidation cells during an experiment to absorb evolved water and acid.

Cells containing the samples were evacuated with a mechanical pump, allowed to reach the oven temperature, then filled with oxygen preheated to the operating temperature. Oxygen consumed was measured with the gas buret by periodic adjustment to the reference pressure. During an experiment samples were removed from the oven after the desired amount of oxygen had been absorbed and cooled rapidly to room temperature. Intrinsic viscosities of the oxidized rubbers were determined in benzene solution.

Molecular weights were calculated from the relationship between intrinsic viscosity and number average molecular weight reported by Carter, Scott and Magat.[3] Use of this relation involves the implicit assumption that the ratio of number average to viscosity average molecular weight does not change materially during oxidation.

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[1] W. F. Watson, *Trans. Inst. Rubber Ind.*, **29**, 32 (1953); M. Pike and W. F. Watson, *J. Polym. Sci.*, **9**, 229 (1952).

[2] J. McGavack, C. E. Linscott and J. W. Haefele, *Ind. Eng. Chem.*, **34**, 1335 (1942).

[3] W. C. Carter, R. L. Scott and M. Magat, THIS JOURNAL, **68**, 1480 (1946).