is described by Cartwright, *et al.*,[2] and will not be discussed here.

To obtain an adequate quantity of *gamma*-resorcylic acid[2a] for further clinical evaluation a synthesis has been developed utilizing 2-methylresorcinol which is available commercially.[3] The conversion of 2-methylresorcinol to 2,6-dimethoxytoluene was carried out in a methanol-dimethyl sulfate solution using sodium methoxide and gave a 75% yield.

The oxidation of 2,6-dimethoxytoluene was carried out using aqueous pyridine and potassium permanganate and gave a pure product in 55% yield. Neither step can be considered conventional or straightforward.

Cartwright, *et al.*,[2] discuss briefly a similar approach in which the reactions are carried out in aqueous media. These conditions are not adequate. For example, a repetition of their aqueous methylation step gave no better than a 20% conversion to 2,6-dimethoxytoluene. The difficulty of completely methylating 2-methylresorcinol is shown by the fact that even in methanol with the theoretical quantity of dimethyl sulfate (1 mole:2 moles) a maximum yield of only 38% was obtained. A large excess of dimethyl sulfate is required.

A repetition of the Cartwright, *et al.*,[2] procedure for the aqueous potassium permanganate oxidation of 2,6-dimethoxytoluene gave at best a 14% conversion to 2,6-dimethoxybenzoic acid. The use of pyridine is necessary to obtain good yields in this oxidation.

Acknowledgment. The author would like to express his appreciation to Dr. Robert E. Mosher of Providence Hospital, Detroit, Michigan for his helpful suggestions. This work was supported in part by the Michigan Heart Association.

EXPERIMENTAL[4]

2,6-Dimethoxytoluene. A solution of 74.4 g. (0.6 mole) of 2-methylresorcinol (m.p. 115–120°, as received; m.p. 119–120°),[5] 302.4 g. (2.4 moles) of dimethyl sulfate, and 200 ml. of methanol was treated dropwise over a period of two hours with a solution of 129.6 g. (2.4 moles) of sodium methoxide in 600 ml. of methanol, keeping the temperature at 25–30°.

The mixture was refluxed for 30 minutes and 650 ml. of solvent was removed by distillation. The cooled residue was treated with 600 ml. of water. The oily product was collected by filtration, washed with 500 ml. of water, dried and distilled; yield 79.7 g. (87.4%), b.p. 219–220°/731 mm., m.p. 37.5–40° (Previous b.p. 220–222°, m.p. 35°;[6] m.p. 39°.[7] The crystals had a slight oily quality which was removed by recrystallization from 7.5:1 methanol-water; yield 68.4 g. (75%), m.p. 39–40.5°.

The distillate can be used in the oxidation without recrystallization. In the example below the purified material was used.

2,6-Dimethoxybenzoic acid. A vigorously stirred mixture of 50.6 g. (0.33 mole) of 2,6-dimethoxytoluene, 125 ml. (1.55 moles) of pyridine, and 400 ml. of water was treated with 158 g. (1 mole) of potassium permanganate in small portions over a period of one hour while keeping the mixture at 45–50°. Stirring was continued for an additional two hours at the same temperature. The mixture was allowed to stand overnight, filtered, and the manganese dioxide was washed with 150 ml. of water. The combined filtrate was distilled under reduced pressure until a total of 300 g. of solvent had been removed.

The cooled, aqueous residue was extracted twice with 100 ml. of ether. The ether was added to the manganese dioxide. The aqueous portion was treated with 100 g. of 40% sulfuric acid (by wt.). The colorless product was collected, washed with 100 ml. of water, and dried at 60°; yield 35.8 g. (65.5%), m.p. 183–186.5°. The product was recrystallized from ethylene dichloride; yield 30.5 g. (55.8%), m.p. 187.5–188.5°; Literature m.p. 186–187°.[2]

A total of 4.5 g. of 2,6-dimethoxytoluene was recovered from the manganese dioxide by ether extraction. The yield of acid is based on the starting material actually consumed.

Anal. Calc'd for $C_9H_{10}O_4$: Neut. equiv., 182.2. Found: 183.4.

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(2) Cartwright, Jones, and Marmion, *J. Chem. Soc.*, 3499 (1952).

(2a) While reading proof, it came to our attention that γ-resorcylic acid was now available in this country (Aldrich Chemical Co., Milwaukee, Wis.)

(3) Sold by Coalite and Chemical Products, Ltd., Bolsover, near Chesterfield, England.

(4) Melting points and boiling points are uncorrected.

(5) Bauer-Benedikt and Punzengruber, *Monatsh.*, **81**, 772 (1950).

(6) Mitter and Biswas, *J. Indian Chem. Soc.*, **7**, 839 (1930).

(7) Shibata, *J. Pharm. Soc. Japan*, **59**, 111 (1939).

Chain Scission in the Oxidation of Hevea. III. Effect of Temperature[1]

E. M. BEVILACQUA

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When molecular oxygen reacts with raw hevea rubber in latex at 90°, two molecules of carbon dioxide and two of "volatile acid" (one each of acetic and formic) are produced for each apparent scission of the hydrocarbon chain, estimated from solution viscosity changes. This corresponds to the complete destruction of one isoprene unit, and if the severed hydrocarbon end-groups are oxidized, requires a minimum of six molecules of oxygen per scission.[2] Estimates of oxygen requirements for scission during accelerated oxidation of vulcanized hevea much lower than this have been made.[3] It has been suggested the apparent high efficiency of scission in vulcanized rubber is the result of the predominance of scission at crosslinks over random cutting of the hydrocarbon chain.[4,2] To investigate the less likely

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(1) Contribution No. 150 from this Laboratory.

(2) Bevilacqua, *J. Am. Chem. Soc.*, **77**, 5396 (1955).

(3) Tobolsky, Metz, and Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950); *cf.* also Baxter, Potts, and Vodden, *Ind. Eng. Chem.*, **47**, 1481 (1955).

(4) Bueche, *J. Chem. Physics*, **21**, 614 (1953); Berry and Watson, *J. Polymer Sci.*, **18**, 201 (1955).

possibility that the mechanism of the reactions leading to scission changes sharply with the rate of oxidation, the earlier estimates[2] of yields of scissions and of "volatile acids" during oxidation of hevea latex at 90° have been supplemented by measurements at 70° and 110°.

RESULTS

Results of the determinations of scission efficiency and of volatile acid yield are summarized in Table I.

TABLE I

YIELDS OF ACIDS AND OF SCISSIONS

Temperature, °C	70	90	110
Oxidation rate (mmoles/100 g.-hr.)	0.7	2.0	6.0
Per mole of oxygen:			
scissions (mole)	0.037	0.054	0.062
volatile acids (eq.)	0.071	0.095	0.118
Eq. acids/mole scissions	1.9	1.8	1.9

Carbon dioxide was not determined in these experiments, but was shown to vary directly with volatile acid by titration of the latexes after oxidation.

The results given in Table I show that, in latex, there is no important change in the mechanism of scission within the temperature range of this investigation. Although scission efficiency increases with temperature, the ratio of acid produced to scissions remains constant.

EXPERIMENTAL

The latex used was similar to that used previously. Experimental procedures were as described before[2] except for oxidations at 110°. These were carried out in sealed twelve-ounce bottles fitted with Nylon gaskets and perforated caps, filled initially with oxygen at room temperature and a pressure of one atmosphere. Oxygen consumed was estimated by weighing the water required to restore the pressure to atmospheric, after cooling the bottles containing the samples to room temperature.

Data for oxidations at 90° are taken from reference 2.

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Conversion of Dihydrocodeinone to Dihydrothebaine

A. H. HOMEYER

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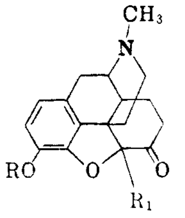
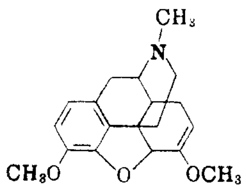
Some time ago, in connection with a study of methyldihydromorphinone [Metopon (I)] an attempt was made to introduce the nuclear methyl group directly into dihydrocodeinone (II) by the action of methyl sulfate in the presence of a sodium alkoxide.



I $R = H, R_1 = CH_3$

II $R = CH_3, R_1 = H$



III

Instead of the desired methyldihydrocodeinone there was obtained a good yield of Δ^6-dihydrothebaine (III), the enol ether of dihydrocodeinone.[1]

EXPERIMENTAL

Sodium (1.25 g.) was dissolved with gentle warming in a mixture of dry *tert*-butyl alcohol (100 ml.) and dry methanol (2 ml.). An additional quantity of *tert*-butyl alcohol (80 ml.) was added to dissolve the crystals which formed upon cooling to room temperature. Dihydrocodeinone (15 g.) was readily soluble in the solution although the alkaloid is sparingly soluble in the alcohol alone. Methyl sulfate (6.3 g.) dissolved in *tert*-butyl alcohol (20 ml.) was added slowly. A slight turbidity and an orange coloration developed. After standing at room temperature for one hour the mixture was refluxed for one hour on the steam-bath. Most of the solvent then was distilled off and to the residue there was added water (500 ml.) containing a little ammonia. An oil which soon crystallized was produced. The solid (10 g.) was filtered off and dried. It was recrystallized once from alcohol (m.p. 158–161°) and once from ethyl acetate (m.p. 162–163). The mixture melting point with an authentic sample of dihydrothebaine, prepared by reduction of thebaine showed no depression.

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[1] This finding was communicated to Dr. Lyndon F. Small who mentioned it in one of his publications [Sargent and Small, *J. Org. Chem.*, 16, 1031 (1951) footnote 2].

The Reaction of 1,2-Dichloro-1,1,3,3,3-Pentafluoropropane with Ethanolic Alkali

E. T. MCBEE AND ROBERT FILLER[1]

Received November 22, 1955

It has been reported[2] that 1,2-dichloro-1,1,3,3,3-pentafluoropropane (I) reacts with aqueous sodium hydroxide to give 2-chloro-1,1,3,3,3-pentafluoropropene (II). We have found, however, that I reacts with potassium hydroxide in absolute ethanol to form ethyl 2-chloro-3,3,3-trifluoropropionate, CF_3-

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[1] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois.

[2] Truchan, Ph.D. Thesis, Purdue University (1950).