

possibility that the mechanism of the reactions leading to scission changes sharply with the rate of oxidation, the earlier estimates<sup>2</sup> 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<sup>2</sup> 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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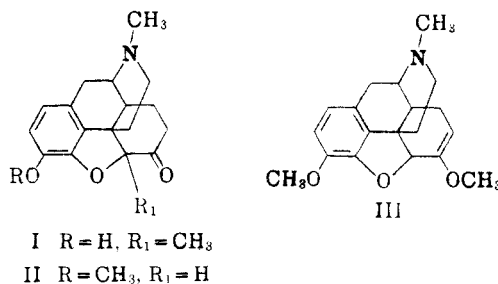
## Conversion of Dihydrocodeinone to Dihydrothebaine

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Some time ago, in connection with a study of methyl dihydromorphinone [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.



Instead of the desired methyl dihydrocodeinone there was obtained a good yield of  $\Delta^6$ -dihydrothebaine (III), the enol ether of dihydrocodeinone.<sup>1</sup>

### 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

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It has been reported<sup>2</sup> 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-pentafluoropropane (II). We have found, however, that I reacts with potassium hydroxide in absolute ethanol to form ethyl 2-chloro-3,3,3-trifluoropropionate, CF<sub>3</sub>-

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