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.

GENERAL LABORATORIES
UNITED STATES RUBBER CO.
PASSAIC, NEW JERSEY

Conversion of Dihydrocodeinone to Dihydrothebaine

A. H. HOMEYER

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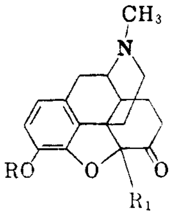
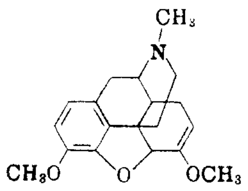
Some time ago, in connection with a study of methyldihydromorphinone [Metopon (I)] an attempt was made to introduce the nuclear methyl group directly into dihydrocodeinone (II) by the action of methyl sulfate in the presence of a sodium alkoxide.



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).

$CHClCO_2C_2H_5$ (III) as the principal product (64% yield).

The structure assigned to III is supported by elemental analysis and by its infrared spectrum. The compound exhibited a strong carbonyl absorption at 1760 cm^{-1} (liquid film), a shift from the frequency range (1750–1735 cm^{-1})[3] for the carbonyl group of normal saturated esters, but typical of esters having an electron-withdrawing group α to the C=O.[4-6] Further evidence for structure III is found in the work of Sweeney,[7] who obtained this compound by the sodium ethoxide-catalyzed reaction of II with ethanol and further characterized the ester by conversion to the anilide. The physical properties of our compound are in excellent agreement with those given by Sweeney.

The formation of III could be postulated as follows:

$$\underset{\text{I}}{CF_3CHClCClF_2} \xrightarrow{KOH} \underset{\text{II}}{(CF_3CCl{=}CF_2)} \xrightarrow{C_2H_5OH}$$

$$\underset{\text{IV}}{(CF_3CHClCF_2OC_2H_5)} \xrightarrow{OC_2H_5^-} \underset{\text{III}}{CF_3CHClCO_2C_2H_5}$$

It has been demonstrated[8] that conversions of the type I→IV proceed *via* an olefin intermediate rather than by a displacement (Williamson) reaction. Further reaction of a saturated α-difluoro ether with an alcohol in a basic medium often produces an ortho ester,[9] which, in turn, may be hydrolyzed to the ester with concentrated sulfuric acid.[10] The ether may be converted directly to the ester with this reagent.[10,11] Tarrant and Brown[9] observed, however, that when $CF_2{=}CCl_2$ was refluxed with ethanol and potassium hydroxide, ethyl dichloroacetate was obtained. We were unable to detect any saturated ether or ortho ester. It was also found that II, prepared from I, using aqueous alkali,[2] could be converted to III using Sweeney's procedure[7] (sodium ethoxide in absolute ethanol); the yield, however, was only 35%.

EXPERIMENTAL

Reaction of 1,2-dichloro-1,1,3,3,3-pentafluoropropane with potassium hydroxide in ethanol. In a 200-ml., round-bottomed flask, fitted with a reflux condenser to which a Dry Ice trap was attached, was placed 50 g. (0.246 mole) of 1,2-dichloro-1,1,3,3,3-pentafluoropropane and a solution of 14 g. (0.25 mole) of potassium hydroxide in 100 ml. of absolute ethanol. The mixture was heated under reflux for 6 hrs. No material was found in the trap. The reaction mixture was washed with water, dried over Drierite, and distilled. Thirty grams (64%) of ethyl 2-chloro-3,3,3-trifluoropropionate, b.p. 128–129°, n_D^{20} 1.3635, d_4^{20} 1.322, were obtained. Sweeney[7] reported, b.p. 118° (630 mm.), n_D^{20} 1.3636, d_4^{20} 1.322. The compound possessed a strong absorption band at 1760 cm^{-1} (C=O).

Anal. Calc'd for $C_5H_6ClF_3O_2$: C, 31.51; H, 3.17. Found: C, 31.47; H, 3.42.

Reaction of 2-chloro-1,1,3,3,3-pentafluoropropene with sodium ethoxide in ethanol. A 500-ml., 3-necked, round-bottomed flask was equipped with a stirrer, a condenser cooled with a Dry Ice-trichloroethylene mixture, and an addition tube. In the flask was placed a solution containing 4.6 g. (0.2 g.-atom) of sodium in 200 ml. of absolute ethanol. Then (50 g., 0.3 mole) of redistilled 2-chloro-1,1,3,3,3-pentafluoropropene (b.p. 7°),[2] was placed in an ampule which was attached to the addition tube. The olefin was allowed to boil into the reaction mixture, which was kept at room temperature and stirred continuously. The addition proceeded during 3 hours. Stirring was continued for an additional 2 hours. Starting material (20 g.) was recovered in a trap, cooled with Dry Ice-trichloroethylene, which was attached to a Friedrichs' condenser after the addition was complete. The reaction mixture was washed with water, dried over Drierite, and distilled. There was obtained 12 g. (35%) of ethyl ester, b.p. 128.5–129°, n_D^{20} 1.3630. An unidentified higher-boiling residue (b.p. *ca.* 160–170°), was also obtained in a 6-g. amount.

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PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

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[3] Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N.Y. 1954, p. 153.

[4] Rasmussen and Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

[5] Rappaport, Hauptschein, O'Brein, and Filler, *J. Am. Chem. Soc.*, **75**, 2695 (1953).

[6] Hampton and Newell, *Anal. Chem.*, **21**, 914 (1949).

[7] Sweeney, Ph.D. Thesis, University of Colorado (1952).

[9] Tarrant and Brown, *J. Am. Chem. Soc.*, **73**, 1781 (1951).

[8] Tarrant and Young, *J. Am. Chem. Soc.*, **75**, 932 (1953).

[10] Young and Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).

[11] Young and Tarrant, *J. Am. Chem. Soc.*, **72**, 1860 (1950).

Preparation of 1-Phenoxyethyl Acetate

B. B. CORSON, H. E. TIEFENTHAL,[1] AND W. J. HEINTZELMAN

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1-Phenoxyethyl acetate was first prepared by Gershtein and Shostakovskii[2] in 49% yield by heating vinyl phenyl ether with acetic acid for 8–10 hours at 200–210° in an autoclave; later by Adelman[3] in 44% yield by the reaction of phenol with vinyl acetate at 25° in the presence of copper resinate, mercuric acetate, and sulfuric acid.

We obtained 1-phenoxyethyl acetate in 85% yield by refluxing a mixture of vinyl phenyl ether, acetic acid or acetic anhydride, and dimethylaniline.

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[1] Present address: Verona Research Center, Koppers Co., Inc., Verona, Pa.

[2] Gershtein and Shostakovskii, *Zhur. Obshchei Khim.*, **18**, 1989 (1948); *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 19 (1952): *Chem. Abstr.*, **43**, 3786 (1949); *Chem. Abstr.*, **48**, 580 (1954).

[3] Adelman, U. S. Patent 2,579,411 (1951); *Chem. Abstr.*, **46**, 11226 (1952).