fitted with a thermometer, a reflux condenser, and an agitator for vigorous agitation. The amalgam was then added, followed by 30 g. of the compound to be reduced, added through the condenser. Vigorous agitation was maintained at reflux temperature. Samples were taken at timed intervals by stopping the agitator, allowing the layers to separate, drawing off some of the top layer, and washing it well with water to remove all acid. Each sample was then analyzed by gas chromatography as described here.

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Pyrolysis of 2-Butyl Acetate

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In conjunction with the study of the stereoselective dehydration of butanols over alumina catalysts[1,2] the pyrolytic decomposition of 2-butyl acetate was reinvestigated. It was reported in the literature[3,4] that the pyrolysis of acetates gives exclusively the least substituted olefins following the Hoffmann rule. Contrary to the above reported findings and in accordance with recently published results on the pyrolytic decomposition of 2-heptyl acetate,[5] it was found that the pyrolysis of 2-butyl acetate yields a mixture composed of 1- and 2-butenes. The concentration of 1-butene in the reaction product varied from 55 to 69%, depending upon the experimental conditions used. The remainder of the product was composed of *cis*-2- and *trans*-2-butene in an approximate ratio of *cis*/*trans* = 0.5. The percentage of 1-butene produced approximates that expected from statistical elimination of the neighboring hydrogen atoms.

TABLE I

PYROLYSIS OF 2-BUTYL ACETATE

Temp., °C.	Flow Rate, Ml./hr.	Nitrogen Added	Packing Kind	Conversion, %	Butenes 1-	*cis*-2-	*trans*-2	*cis*/*trans*
410	5	–	Glass	12	61.5	25.9	12.6	0.49
450	5	–	Glass	100	57.8	27.4	14.8	0.54
450	10	–	Glass	54	62.0	24.2	13.8	0.57
450	50	–	Glass	9	69.1	20.7	10.2	0.49
450	5	+	Glass	47	55.4	28.4	16.2	0.57
490	14	+	Quartz	82	55.4	28.6	16.0	0.56
510	5	–	Glass	81	58.3	27.0	14.7	0.54
510	20	–	Glass	69	58.2	27.1	14.7	0.54
510	40	–	Glass	65	61.6	25.2	13.2	0.52
525	12	+	Quartz	71	57.5	26.7	15.8	0.58

The experimental results are summarized in Table I. The flow rate of 2-butyl acetate in the experiments carried out at 450° and 510° was varied and in the case of 450° experiments the composition of the butenes produced was plotted against the percentage of 2-butyl acetate which underwent pyrolysis. By extrapolating the plot to zero conversion, the composition of the primary products of the pyrolysis could be established. They were composed of 71% 1-butene, 9% *cis*-2- and 20% *trans*-2-butene (Fig. 1). The ratios of *cis*- to *trans*-2-butene approximate the thermodynamic equilibrium mixture.[6] Butenes *per se* do not undergo isomerization under the experimental conditions used for the pyrolysis of the acetate. The reason therefore for the change of the composition of the butenes with change in the extending of 2-butyl acetate decomposition is not immediately apparent

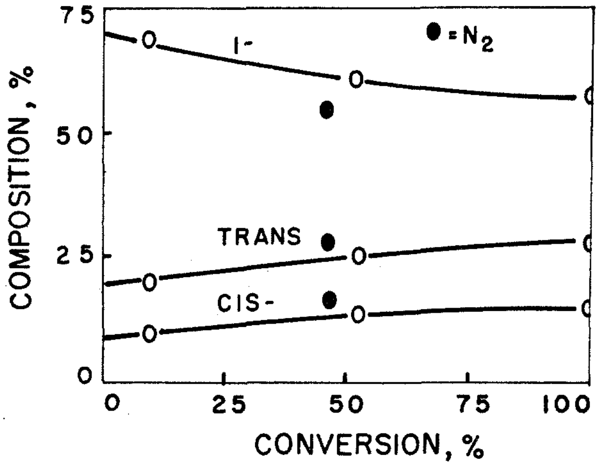

Fig. 1. Pyrolysis of 2-butyl acetate at 450°. Primary products: 71%. 1-butene, 20% *trans*-2-, 9%, *cis*-2-

n-Butyl acetate on pyrolysis formed only 1-butene.

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(1) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(2) H. Pines and W. O. Haag, Paper presented before the Division of Colloid Chemistry, American Chemical Society, April 13–18, 1958, San Francisco, Calif.

(3) W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(4) W. J. Bailey, J. J. Hewitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

(5) E. E. Royals, *J. Org. Chem.*, **23**, 1822 (1958).

(6) J. E Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Stand.*, **36**, 554 (1946).

The apparatus used for the pyrolysis of the acetates consisted of a Pyrex reaction tube having a reaction zone of 1.5 cm. outside diameter and packed with 15 ml. of about $^1/_8$ inch quartz chips or $^1/_8$ inch glass beads. The tube was heated by a thermostatically controlled vertical furnace. The acetates were introduced by means of a motor driven syringe.

The butenes were analyzed by vapor phase chromatography using a column described previously.[1]

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Preparation of Pyrrole

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The requirement for relatively large quantities of pyrrole in this laboratory prompted an investigation for a rapid inexpensive synthesis of this material. Of the methods reported in the literature, the dehydrogenation of pyrrolidine using a flow system offered the greatest promise.

Catalysts which have been used in the dehydrogenation of cyclic amines include platinum or palladium on asbestos,[1] oxides of magnesium, calcium or zinc or mixtures of these,[2] and nickel-nickel chromite.[3] Although the catalysts most frequently employed in the dehydrogenation of pyrrolidine or substituted pyrrolidines have been platinum or palladium on asbestos, the effectiveness of rhodium on alumina in reducing nitrogen heterocyclic systems,[4] suggested that it might be a superior dehydrogenation catalyst for cyclic amines. Accordingly, this was the catalyst investigated in these experiments.

The optimum conditions for the dehydrogenation of pyrrolidine using rhodium on alumina were 650° with an HLSV[5] of 8–10. Shorter contract times resulted in lower yields of pyrrole while longer contact times produced more decomposition. It is interesting to note that the dehydrogenation using platinum or palladium on asbestos is reported to occur at 300°.[1]

Two other potential catalysts were investigated: Berl saddles were ineffective; activated alumina pellets were about half as effective as rhodium on alumina at optimum conditions.

In addition to pyrrole and unreacted pyrrolidine in the dehydrogenated product, there was obtained some of the 2-(2-pyrrolidyl)pyrrole reported by Fuhlhage and Vander Werf.[6] It appears that 1-pyrroline is an intermediate in dehydrogenation reactions in which rhodium on alumina is the catalyst.

The slightly better yield of pyrrole obtained in the distillation procedure is probably due to the dissociation of the 2-(2-pyrrolidyl)pyrrole present in the crude dehydrogenation mixture.

Bell[7] reports that diethylamine can be converted into pyrrole when introduced into a hot tube. Using the optimum conditions of the pyrrolidine experiments and a rhodium on alumina catalyst, pyrrole was produced in less than 1% yield.

EXPERIMENTAL[8]

Materials. The pyrrolidine used in these experiments was the practical grade supplied by the Matheson, Coleman and Bell Co. The rhodium catalyst, 0.5% rhodium on $^1/_8''$ activated alumina pellets, was obtained from Baker and Co., Inc. and the Puralox catalyst, $^1/_8''$ activated alumina pellets, from the Harshaw Scientific Co.

Apparatus. The apparatus consisted of a vertically arranged vycor reactor tube (2.5 × 30 cm.) in a continuous flow system. The reactor contained 30 ml. of the catalyst and an upper layer (30 ml.) of Berl saddles. A vycor preheater tube containing 30-ml. Berl saddles was used to volatilize the sample which was introduced into the preheater from a buret and flushed through the system by a stream of dry nitrogen.

Preparation of pyrrole. Eighty-five grams of pyrrolidine was introduced into the flow type apparatus at an HLSV of 8–10 and nitrogen flow rate of 440 ml./min. The temperature of the reactor, containing 30 ml. of 0.5% rhodium on alumina was maintained at 650° and the preheater temperature was maintained at 300°. The weight of the condensed pyrolysis product was 70 g. The crude product was added to 200 ml. of water, saturated with Dry Ice and then separated from the carbonic acid solution. After a second treatment, the combined aqueous portions were extracted with three 100-ml. portions of ether, the ether extract combined with the carbonic acid insoluble layer and dried over sodium sulfate. Distillation of the residue after removal of the drying agent and the ether yielded 35.6 g. (45%) of pyrrole, b.p. 127–129°, n_D^{20} 1.5040. Analysis by gas chromatography indicated the pyrrole to be 99.5% pure. In addition to the pyrrole, a tarry residue (5.1 g.) was obtained.

The crude product could also be purified by distillation in a Podbielniak High-Temperature Fractional Distillation Apparatus to give pyrrole in 50% yield. Columns of lesser efficiency were ineffective.

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(1) N. D. Zelinsky and Y. K. Yur'ev, *Ber.*, **62**, 2589 (1929).

(2) I. G. Farben Ind., Brit. Patent **515,865**, Dec. 15, 1939.

(3) H. Adkins and L. G. Lundsted, *J. Am. Chem. Soc.*, **71**, 2964 (1949).

(4) Brochure, *The Role of Platinum Group Metal as Catalysts*, Baker and Co., Newark, N. J.

(5) Hourly liquid space velocity = volume of reactant/volume of catalyst/hour.

(6) D. W. Fuhlhage and C. A. Vander Werf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

(7) C. A. Bell, *Ber.*, **10**, 1868 (1877).

(8) Melting points were taken on a Fisher-Johns melting point apparatus and are corrected. Boiling points are uncorrected. Microanalyses were by Weiler and Strauss, Oxford, England.