This variation in reactivity of the different secondary amines with *n*-butyl bromide is probably due, as is their variation in rate of addition to acrylic ester, to steric factors associated with their structure and is in harmony with the suggestion that the rate-controlling factor in the replacement reaction is the ability of the amine to approach the carbon atom carrying the halogen.

In general, similar conclusions may be drawn from the results, listed in Table II, obtained with tertiary amines. In the reactions with ethyl β-propionate the extent of the reaction is definitely related to the basicity of the amine (*cf.* amount of tertiary amine salt produced with pyridine and the N-substituted piperidines after the 5.5 hours reaction period). However, within a group of related amines of approximately the same basicity there appears to be some steric factor involved in this elimination reaction, for piperidine (Table I) and the N-substituted piperidines (Table II) show widely different percentages of reaction with the bromo ester after a fifteen-minute reaction period. In this group the reactivity decreases as the size of the group attached to the piperidine nitrogen atom increases.

It was surprising to find that both pyridine and dimethylaniline give considerable amounts of the quaternary salt with the bromo ester. This reaction is not related to the elimination reaction[5] and its occurrence in these cases greatly complicates the interpretation of the results.

The extent of formation of the quaternary salts between butyl bromide and each of the three tertiary amines studied (Table II) is obviously independent of the basicity of the amine. These results parallel those obtained from the reaction of the secondary amines with butyl bromide (Table I) and it is not unlikely that the variations are due to the same causes.

Summary

A study of the rate and course of reaction of ethyl β-bromopropionate and *n*-butyl bromide with a number of secondary and tertiary amines of different basicities has been made. The results obtained lend support to previously suggested mechanisms for the elimination of hydrogen bromide and for the replacement of a bromine atom in an organic molecule by a secondary amino residue.

MADISON, WIS. RECEIVED JUNE 13, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rearrangement During Pyrolysis of the Butenes

BY CHARLES D. HURD AND A. R. GOLDSBY

1-Butene and 2-butene are the simplest olefins to possess the possibility of rearrangement. Therefore, the study of their pyrolysis is particularly significant. It was anticipated that other products would accompany the rearrangement products for the generalization has been established that olefins pyrolyze bidirectionally into simpler compounds and into more complex ones. With isomerization included, this would establish a tridirectional mechanism. Wheeler and Wood,[1] in the only prior work on 1- and 2-butene, have shown 2-butene to be somewhat the more stable isomer at 600°, but no difference in stability was noticed at 650–900° where extensive decomposition took place. Their attention was directed especially to the reaction liquids, which were chiefly cycloalkenes and cycloalkadienes. They gave no consideration to the study of rearrangement. Because of their work on the liquids we omitted them in our study.

To study the problem of rearrangement it was necessary to start with butenes of very high purity and it was even more essential to possess an analytical procedure capable of detecting the several C_4-hydrocarbons in the presence of each other. The absorption method[2] fails because 1-butene, 2-butene, butadiene and propylene all dissolve in the same reagent (83% sulfuric acid). The usual type of Podbielniak fractional distillation serves to separate the C_1, C_2, C_3 and C_4 hydrocarbons into these four groups but it lacks the precision necessary to separate the C_4 compounds individually. The boiling points of these gases are (°C.): 1-butene −6.7, methylpropene (isobutylene) −6.6, butadiene −2.6, butane 0.0, *cis*-2-butene +0.3, *trans*-2-butene[3] +3.0.

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[1] Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930).

[2] Hurd and Spence, THIS JOURNAL, **51**, 3357 (1929).

[3] Schmitt and Boord, *ibid.*, **54**, 756 (1932), show that among olefin isomers with similar skeletons the one with the double bond most deeply buried in the molecule has the highest boiling point. They suggest, therefore, that the *trans*-2-butene should be higher boiling than the *cis*-.

A distillation column similar to the Podbielniak column but of narrower bore (2.5 mm. rather than 5 mm.) was designed by Frey and Hepp[4] for the precision work necessary in analyzing butane–butene mixtures. Since the column appeared to possess the necessary precision it was investigated and found very satisfactory for the purpose.

Results with 1-Butene.—With contact times of 8–12 seconds, 1-butene decomposed to the extent of 2, 12, 60 and 90% at temperatures, respectively, of 500, 600, 650 and 700°. Rearrangement into 2-butene was proved definitely. It seems to start between 600 and 650°. The 2-butene content of the recovered butene fraction was 21% at 650° and 16% at 700°. Analysis showed that the percentage composition of the 2-butene was 63% *cis*: 37% *trans* (*cis* being the low boiling isomer).

In the gaseous products, twice as much propylene was formed as ethylene. Methane was the chief paraffin in the gas although some ethane was identified. No more than a trace of butadiene was isolable at 600°.

Results with 2-Butene.—The synthetic 2-butene was 62% *cis*:38% *trans*. After pyrolysis the recovered 2-butene was the composition of 61% *cis*:39% *trans* for experiments at 650° or 700°. Evidently, therefore, both the *cis* and *trans* isomers shared equally in whatever changes occurred. It is significant also that this is approximately the same ratio as that found in the 2-butene produced from 1-butene. 2-Butene is a more stable hydrocarbon than 1-butene. At 650° and thirteen seconds its extent of decomposition was but 45%. The quantity of 1-butene actually found points to a rearrangement at 650° of 16% and at 700° of 30%. It seems reasonable that even greater isomerization to 1-butene occurred because of the comparative instability of the latter. Furthermore, it is convenient to postulate 1-butene as the precursor of the ethylene from 2-butene. This seems reasonable since so much more ethylene comes from 1-butene than from 2-butene and since the ethylene yield from 2-butene increases so markedly with the temperature, an effect not noticed with 1-butene. Otherwise, the gases from 2-butene resembled those from 1-butene. Methane and propylene predominated.

Non-formation of Isobutylene.—Careful search was made for isobutylene in the gases from both 1- and 2-butenes. Not even traces of it were detectable, which proves that no rearrangement of the butenes occurs involving the rupture of C–C bonds.

Experimental Part

Preparation of 1-Butene.—Two 2-mole runs and one 4-mole run of methylmagnesium bromide plus allyl bromide were performed as proposed by Lucas and Dillon.[5] In the purification process the use of 30% methanol and 37% perchloric acid was recommended to scrub out ether. The use of a Davis fractionating column makes this unnecessary. With this modification, the yield of 1-butene in the 4-mole run was 128 g. (67%), b. p. −7.2 to −6.2°, practically all of which was collected at −6.7°. The yields of the 2-mole runs were 55 and 60%.

Isobutylene was shown to be absent in this material by the Denigès reaction (see below). The absence of 2-butene was demonstrated by distillation in a Frey–Hepp column. For this purpose, ethylene oxide was admixed with the butene. The distillation curve rose abruptly from −6.7 to +11° with no indication of a distillation plateau at 0–3° for 2-butene. This experiment also shows that 1-butene and ethylene oxide form no constant boiling mixture. 1-Butene was entirely absorbed by 83% sulfuric acid in the gas analysis apparatus.

Preparation of 2-Butene.—This was prepared by the dehydration of 2-butanol, b. p. 99–100°, with 60% sulfuric acid.[6] The average yield of 2-butene of boiling point 0 to 3° (Davis column) from three 1-mole runs was 72% and in one 3-mole run was 82%. For further purification, the liquid was fractionated through the Podbielniak column. The first 10–15% of distillate was discarded, thereby removing any traces of 1-butene. The remainder was collected for use. Analysis on the Frey–Hepp column showed 1-butene absent (Fig. 1) and it revealed the ratio of *cis* to *trans* isomers as 62 : 38. This distillation analysis agrees closely with the reported analysis[7] obtained on similarly prepared material by the reaction rates of the dibromides; namely, low boiling 2-butene 58%, high boiling 2-butene 43%, 1-butene −1.1%.

Frey–Hepp Column.—Mention should be made of three significant differences in this column from the familiar Podbielniak type of column which it resembles. (1) The capacity is less. About 500–1000 cc. of gas is taken for an analysis. (2) The bore of the column (containing spiral wire packing) is 2.5 mm. rather than 5 mm. This greatly increases the sensitivity but necessitates a much slower rate of distillation. Usually about twenty-five hours are required to distil one liter of gas, but the distillation may be interrupted without ill effects. (3) The distillation operates at approximately constant temperature which is measured accurately by a 3-junction copper–constantan thermocouple connected to a calibrated Weston millivoltmeter. The Dewar type head of the column is enclosed, thus permitting circulation of ice water through it. Therefore, only liquids distilling in the range of −10° to +10° may be analyzed with this set-up. Pressure changes, read from a manometer attached to the column,

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[4] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 444 (1933).

[5] Lucas and Dillon, THIS JOURNAL, **50**, 1460 (1928).

[6] Young and Lucas, *ibid.*, **52**, 1967 (1930).

[7] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); Young and Lucas, *ibid.*, p. 1966.

indicate the progress of the distillation. The receiver for the distillate is a partially evacuated receiver, the pressure of which is determined on another manometer. The volume of any fraction is calculated by the gas laws.

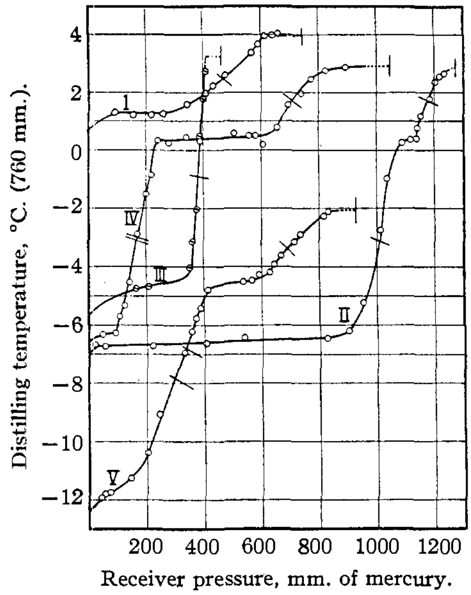

Fig. 1.—Distillation curves of C_4-hydrocarbons. Corrections for ordinates: I, −1°; III, −2°; II and IV, 0°; V, + 5°. I. Synthetic 2-butene, from 2-butanol and 60% sulfuric acid. II. C_4-fraction from pyrolysis of 1-butene at 650°, 10.9 seconds. III. C_4-fraction from 1-butene at 700°, 11.8 seconds. IV. C_4-fraction from 2-butene at 650°, 13.0 seconds. V. C_4-fraction from 2-butene at 700°, 11.8 seconds.

Solubility of Butadiene in Sulfuric Acid.—To determine whether butadiene is absorbed in 63% sulfuric acid (along with isobutylene) or in 83% acid (along with 1-butene, 2-butene and propylene), synthetic mixtures of butadiene and air (8–33% C_4H_6) were studied in the manner outlined by Hurd and Spence.[2] Although it was found that butadiene reacted more rapidly than propylene, the difference was not significant for analytical purposes. Both are absorbed completely in 83% sulfuric acid. After five 2-minute passes into 73% acid, about 40% of the butadiene was removed as contrasted with 21% for propylene. With 63% acid, 5–8% of the butadiene was still soluble whereas the absorption of propylene was less than 1%.

Analysis of butadiene in work below was by treatment of the butene–butadiene fraction at −80° with bromine, then with sodium bisulfite solution, then with 95% alcohol to extract the dibromides from the insoluble butadiene tetrabromide.

Apparatus and Procedure.—The butene was passed from a small steel storage tank into a calibrated 8-liter bottle from which it was forced into the system at a uniform speed by displacement with salt water. The gas was dried with calcium chloride and dehydrite before entering the top of the vertical Pyrex reaction tube (21 mm. inside diameter). The effective hot volume of the tube was 100 cc. The electric furnace was 32 cm. long. Temperature measurements and furnace control were made in the usual way.[8] The effluent gases passed through a trap at 0° and then into a gas receiver (also a calibrated 8-liter bottle). The data of selected experiments are collected in Table I. The gas analysis data are presented in three ways: (1) the total gas, (2) the gas on a total butene-free basis, (3) the gas on a partial butene-free basis, to include the rearranged isomer.

The distillation curves (Frey–Hepp column) of Fig. 1 show the method of analyzing the C_4 members. Data taken from the curves are listed in Table II. In experiments wherein butadiene was estimated as the bromide its quantity was marked on the curve. Too little butadiene was present for a definite break in the distillation curve.

TABLE I

PYROLYSIS OF 1-BUTENE AND 2-BUTENE

	1-Butene				2-Butene	
Temp., °C.	500	600	650	700	650	700
Contact time, sec.	12.1	8.8	10.9	11.8	13.0	11.8
Decn., %	2	10	57	87	44	80
Duration, min.	37	30	39	35	48	97
Gas taken, cc.	6470	6220	5672	3959	6357	11664
Exit gas, cc.	6462[a]	6150	6214	5240	5830	13600
Change in vol., %	−0.8	−1.1	9.5	32.4	−8.4	16.6
Analysis of exit gas, per cent. by volume						
Propylene	98.5	3.5	16.8	20.5	8.9	20.5
1-Butene		90.9	39.6	9.6	11.7	7.5
2-Butene		0.0	10.5	1.8	61.2	16.6
Ethylene	0.3	1.6	8.3	16.7	1.8	8.6
Hydrogen	.0	0.2	1.9	6.9	2.6	8.7
Methane	1.2	2.3	18.3	39.4	8.8	32.6
Ethane		1.5	4.4	4.4	4.6	4.6
Butadiene	..	trace	[b]	[b]	0.4	1.0
Exit gas, exclusive of butenes, per cent. by volume						
Propylene	..	38.4	33.7	23.1	32.8	27.0
Ethylene	..	17.6	16.6	18.9	6.7	11.3
Hydrogen	..	2.2	3.8	7.8	9.6	11.4
Paraffins	..	41.8	45.9	49.5	49.5	49.0
Butadiene	..	trace	..	..	1.5	1.3
Exit gas, exclusive of original butene, per cent. by volume						
Propylene	..	38.4	27.8	22.8	22.9	24.6
1-Butene	..	..	..	..	30.2	9.0
2-Butene	..	0.0	17.4	2.0	..	..
Ethylene	..	17.6	13.7	18.6	4.7	10.3
Hydrogen	..	2.2	3.2	7.7	6.7	10.4
Paraffins	..	41.8	37.9	48.9	34.6	44.5
Butadiene	..	trace	..	..	1.0	1.2

[a] This value may be 1–5% high since the Podbielniak fractionation was omitted. [b] Undetermined.

TABLE II

ANALYSIS OF THE C_4 FRACTIONS

Curve	I	II	III	IV	V
Total gas distd., cc.	965	1665	300	1375	1217
Final receiver, press., mm.	753	1272	231	1046	929
1-Butene	0.0	79	84	16	30
Butadiene (via $C_4H_6Br_4$)	0.0	..	...	0.4	4
cis-2-Butene	62	13	16	51	40
trans-2-Butene	38	8		33	26

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(8) Meinert and Hurd, THIS JOURNAL, **52**, 4543 (1930).

Denigès' Reagent[9] for Isobutylene

The usual reagent for isobutylene is 63–68% sulfuric acid but this is of value only when considerable quantities of isobutylene are present. It is unreliable for the detection of traces. Denigès' reagent, essentially acidified mercuric nitrate, is not only sensitive but selective. To prepare the reagent, 20 g. of mercuric oxide was mixed with 100 cc. of water and then heated with 40 cc. of concd. nitric acid. When dissolved, the solution was diluted with 400 cc. of water.

When passed into this reagent, isobutylene gives a yellowish turbidity, the turbidity increasing with the temperature. On boiling, a heavy orange precipitate settles. We found that 1- and 2-butenes also dissolve readily in the reagent but without the formation of yellow turbidity or precipitate. Trimethylethylene does not give the test.

In a quantitative run it was found that 52 cc. (0.13 g.) of pure isobutylene produced 2.90 g. of the precipitate. For this purpose, the gas was passed into 200 cc. of reagent which, after heating, was poured into a liter of hot water. The precipitate coagulated rapidly. It was collected on a filter, washed with hot water and dried over phosphorus pentoxide. If Denigès' formula of $HgNO_3 \cdot C_4H_8 \cdot Hg_2NO_3$ were correct, only 1.81 g. of precipitate should have formed. The 2.90 g. corresponds to 4.48% by weight of isobutylene. In a similar run 0.115 g. (46 cc.) of isobutylene gave rise to 2.52 g. of precipitate, or 4.56% of C_4H_8. Whether or not this method might be extended to a quantitative determination of isobutylene cannot be stated without further data.

Non-Formation of Isobutylene.—Four hundred cc. of the butene fraction from the 600° (8.8 sec.) experiment with 1-butene was divided into equal parts, A and B. A was passed into 200 cc. of cold Denigès' reagent. No turbidity appeared in thirty minutes and none occurred after heating. Into B was admixed 0.2 cc. of pure isobutylene before performing a similar test. A slight turbidity appeared in thirty minutes. Then the solution was warmed. It assumed an opaque yellow color. On boiling, the solution cleared up with the formation of an almost imperceptible precipitate. Thus it may be concluded that no isobutylene was formed from 1-butene by pyrolysis.

Summary

The gaseous decomposition products of 1-butene and 2-butene at 500–700° were studied. 2-Butene was the more stable isomer. In both cases, especially at 650°, extensive rearrangement occurred into the other isomer. No isobutylene was produced. The ratio of low-boiling (*cis*) to high-boiling (*trans*) 2-butene (62–38) was practically unchanged during pyrolysis. More *cis* than *trans* isomer was found in the 2-butene produced from 1-butene.

Experiments are included which deal with the identification of isobutylene and butadiene. The utility of the Frey–Hepp column in the analysis of mixtures of C_4-hydrocarbons is pointed out.

EVANSTON, ILLINOIS RECEIVED JUNE 14, 1934

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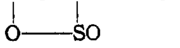
[9] Denigès, *Compt. rend.*, **126**, 1043 (1898).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. Cyclohexene

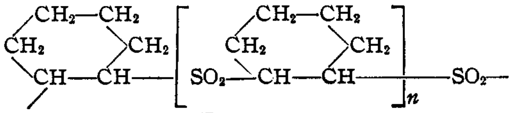
BY D. S. FREDERICK, H. D. COGAN AND C. S. MARVEL

The possibility of preparing long chain molecules by the addition of sulfur dioxide to olefins has apparently been largely overlooked by organic chemists since it was first observed by Solonina[1] in a study of certain allyl ethers and related compounds. Matthews and Elder[2] obtained a patent covering resinous products prepared by the addition of sulfur dioxide to simple olefins such as ethylene, propylene and butylene. Recently Seyer and King[3] have observed that sulfur dioxide combines with cyclohexene if oxygen is present in the reaction mixture. In each of these reports the addition compounds were described as amorphous products whose empirical formulas indicated that the respective olefins had combined with sulfur dioxide in a one to one ratio. Solonina wrote a monomeric, cyclic formula (I) for his products. Matthews and Elder recognized that their products were polymeric, but did not attempt to write structural formulas for them.



I

Seyer and King suggested a polysulfone structure (II) for the addition product of cyclohexene and sulfur dioxide. However, they described no



II

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[1] Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898); *Chem. Zentr.*, [I] 248 (1899).

[2] Matthews and Elder, British Patent 11,635 (1914); *C. A.*, **9**, 2971 (1915).

[3] Seyer and King, THIS JOURNAL, **55**, 3140 (1933).