[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Deuterium Tracers in the Pyrolysis of Butane and Propylene

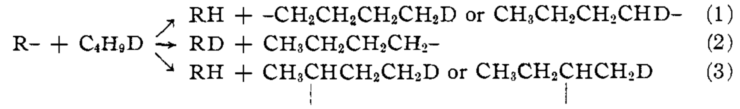
BY CHARLES D. HURD AND JULIAN L. AZORLOSA

The pyrolysis of butane at 600° is known[1] to yield methane, propylene, ethane, ethylene, butylene and hydrogen, and evidence is good that these transformations proceed by way of free radicals. In these experiments the amount of recovered butane serves as a measure of the "extent of decomposition." This term implies that the so-called "undecomposed fraction" has undergone no change. One might imagine, however, that the recovered butane was not exclusively the original material but might include regenerated butane. The present paper deals with this problem by studying butane containing deuterium in the molecule.

The problem with olefins[2] is similar. Propylene is regarded as pyrolyzing by way of radicals, and the question arises whether or not the recovered propylene is or is not exclusively the original propylene.

The butane–butane-*d* fraction recovered after pyrolysis of butane-1-*d* was found to contain less deuterium than the original material. On the other hand, the propene–propene-*d* fraction isolated after pyrolysis of propene-3-*d* was found to possess the same deuterium content as the original material. As will be developed in what follows, it may be concluded that the free radical mechanism explains these observations satisfactorily. In the considerations which follow, it is assumed that a single deuterium in the butane molecule will neither influence the position of carbon–carbon scission at 650–750° nor affect the fate of the radicals in their reactions with hydrocarbons. This assumption probably is not strictly valid but any differences should not be large. The situation seems different from the one involving pyrolysis of hydrocarbons containing carbon isotopes, such as propane-1-C^{13} where it was established[3a] that ordinary C–C bonds rupture 8% more frequently than C^{12}–C^{13} bonds. Also, completely deuterated hydrocarbons would not provide a reliable analogy, but mention should be made of the observation[4] that ethane-d_5 and ethane-*d* were produced during pyrolysis of a mixture of ethane and ethane-d_6.

Butane.—The radical R, formed by initial scission of butane-1-*d*, may react with a butane-1-*d* molecule so as to produce all possible butyl radicals



$$\begin{array}{lll} & \nearrow \mathrm{RH} + \text{-}\mathrm{CH_2CH_2CH_2CH_2D} \text{ or } \mathrm{CH_3CH_2CH_2CHD}\text{-} & (1)\\ \mathrm{R}\text{-} + \mathrm{C_4H_9D} & \rightarrow \mathrm{RD} + \mathrm{CH_3CH_2CH_2CH_2}\text{-} & (2)\\ & \searrow \mathrm{RH} + \mathrm{CH_3}\underset{|}{\mathrm{CH}}\mathrm{CH_2CH_2D} \text{ or } \mathrm{CH_3CH_2}\underset{|}{\mathrm{CH}}\mathrm{CH_2D} & (3) \end{array}$$

Of the three reactions given above, the probability of reaction (1) is 5/18, (2) is 1/18 and (3) 12/18, since there are five primary hydrogens and one primary deuterium each with an assigned reactivity of 1, and four secondary hydrogens each with a reactivity[5] of about 3. These butyl or butyl-*d* radicals have three alternative courses: decomposition into smaller fragments, combination to form larger molecules (octanes), or removal of a hydrogen or deuterium atom from another hydrocarbon molecule so as to regenerate a butane molecule. Only the last of these alternatives is treated in the present work. If x represents the mole fraction of butane formed as a result of the butyl radical selecting a deuterium atom, then $(1 - x)$ is the mole fraction of butane formed as a result of selecting hydrogen.

The exact value of x will depend on the relative concentrations of the several substances present in the reaction mixture from which the butyl radicals can select deuterium and hydrogen, and also upon the relative reactivities of the several types (primary, secondary, allylic) of deuterium or hydrogen present. Although butyl radicals may conceivably react with any of the molecules present, hydrogen, methane, ethane, ethylene, propane, butane, propylene and butylene, reaction with the first five is less likely due to the higher activation energies involved.

Of the last three, only butane in the form of butane-1-*d* is present at first, and it remains in relatively the largest concentration so long as the pyrolysis is less than approximately 70% complete.[6] Consequently, although hydrogen and deuterium may be more reactive in the primary and especially the secondary allylic positions of propylene and butylene than in the primary positions of butane, most of the hydrogen and deuterium acquired by butyl radicals during the major part of the pyrolysis must be donated by butane-1-*d*.

As already explained, the probability that a butyl radical acquires deuterium from butane-1-*d* is 1/18. This, then, should be the approximate value of x at the beginning of the pyrolysis. As the pyrolysis progresses, the value of x may be expected to increase because of the gradual replacement of some butane-1-*d* by 3- and 4-carbon olefins whose ratios for deuterium:hydrogen in the relatively reactive allylic positions exceed the ratio for deuterium:hydrogen in the primary positions of butane-1-*d*.

Of the regenerated butane, x includes $C_4H_8D_2$ formed by processes 1 and 3 and C_4H_9D formed by process 2, and $1 - x$ includes C_4H_9D formed by processes 1 and 3 and C_4H_{10} formed by process 2. Since the C_4H_9D is indistinguishable from the original butane-1-*d*, only the $C_4H_8D_2$ and the C_4H_{10} need be further considered.

If reactions 1, 2 and 3 were equally effective,

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[1] Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

[2] Hurd and Meinert, *ibid.*, **52**, 4978 (1930).

[3] (a) Beeck, Otvos, Stevenson and Wagner, *J. Chem. Phys.*, **16**, 993 (1948); (b) *ibid.*, **17**, 418 (1949).

[4] Wall and Moore, paper presented at the Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

[5] Kossiakoff and Rice, THIS JOURNAL, **65**, 590 (1943).

[6] Egloff, Thomas and Linn, *Ind. Eng. Chem.*, **28**, 1283 (1936).

the $C_4H_8D_2$ from 1 and 3 would be $5x/18$ and $12x/18$, and the C_4H_{10} from 2 would be $(1 - x)/18$. The ratio $C_4H_8D_2:C_4H_{10} = (5x/18 + 12x/18):(1 - x)/18$ would be 17:17 if $x = 1/18$. This result suggests that the final butane fraction would have the same deuterium content as the original, whereas the experimental result was a loss of deuterium. Furthermore, if x is larger than 1/18, the resulting value for the ratio suggests that the final butane fraction would have a gain in deuterium content.

However, evidence[7] is strong that *n*-butyl is more active in butane production than *s*-butyl. Consequently, in the over-all butane production, reaction 3 may be considered negligible in comparison with reactions 1 and 2. If reaction 3 is disregarded, the relative probabilities of reactions 1 and 2 are 5/6 and 1/6, and the ratio $C_4H_8D_2:C_4H_{10} = 5x/6:(1 - x)/6$ becomes 5:17 if $x = 1/18$; furthermore, the ratio does not become 5:5 unless x is increased to so much as 3 times 1/18. This result suggests preponderance of C_4H_{10} in the regenerated butane, in agreement with the experimental finding.

The above rough calculations are helpful in providing a qualitative interpretation of the results. In five representative runs at 650–750° showing "undecomposed butane" in the amount of 28 to 61%, the change in deuterium content was from −2.3 to −5.3% (a still larger negative deviation (−7.5 and −9.8%) was found in two earlier runs). The deviation of −2.3 to −5.3% is well outside the limits of experimental error. The change in deuterium content of final butane as compared to initial butane must mean that much of the butane isolated following thermal treatment is synthetic material and not original butane. Also, the fact that the deuterium content is lower is evidence that the *n*-butyl radical participates more strongly in this synthesis than *s*-butyl.

Propylene.—Insofar as the propylene is concerned which is recovered following its pyrolysis, its history involves these steps. An allyl radical is formed as the result of interaction of an initially formed radical with propylene. The α-hydrogens are so much less reactive than the β-hydrogens that the possible formation of methylvinyl radicals may be disregarded.

With propane-3-*d* two allyl-*d* radicals, $CH_2{=}CHCHD{-}$, will be formed for each allyl radical, $CH_2{=}CHCH_2{-}$. Since there are two allylic hydrogens and one allylic deuterium in propene-3-*d*, the probability of formation of the $CH_2{=}CHCHD{-}$ and $CH_2{=}CHCH_2{-}$ radicals is 2/3 and 1/3, respectively. Each allyl radical possesses a 2/3 chance of changing into propane, C_3H_8, and a 1/3 chance of returning to propene-*d*, C_3H_5D. Each allyl-*d* radical possesses a 2/3 chance of becoming propene-*d* and a 1/3 chance of becoming propene-*d*$_2$, $C_3H_4D_2$. Therefore, the relative amounts of the several propenes would be: C_3H_6, 2/9; $C_3H_4D_2$, 2/9; C_3H_5D, 5/9. Thus, 9/9 of the deuterium appears in the propene fraction. From this it follows that the deuterium content of the recovered propene should be the same as the original.

Actually, in four runs at 700° showing 67–81% of "undecomposed propene," the change in deuterium content from the original propene-3-*d* ranged from 0.07 to 0.68%, the average being 0.36%. This is within the range of experimental error.

Butane-1-*d* was prepared by adding water-*d*$_2$ to a 20% excess of butylmagnesium bromide. Preliminary runs with ordinary water gave yields of about 75%. Combustion of several butane-*d* samples showed mole fractions of deuterium oxide of 0.0995, 0.911, 0.0842 and 0.0812. The expected value was 0.0995.

Hydrolysis of allylmagnesium bromide was not satisfactory for the synthesis of propylene. Yields were less than 50%; hence this method was abandoned. Direct reduction of allyl bromide by means of zinc dust and acetic acid was developed so that yields of 55–75% were obtained. Propene-3-*d* was prepared by this method, using acetic acid-*d* which was made by reaction of acetic anhydride and water-*d*$_2$: $CH_2{=}CHCH_2Br + CH_3COOD + Zn \rightarrow CH_2{=}CHCH_2D + CH_3COOZnBr$. The propene-*d* was converted to the dibromide for storage. It was regenerated by means of zinc dust and alcohol. Analyses of the combustion water from two different samples of propene-3-*d* showed 0.1441 and 0.1494 mole per cent. of deuterium oxide (calcd., 0.1658).

Experimental Part

Butane-1-*d*.—A Grignard reagent was prepared using 24 g. of magnesium, 100 g. of butyl bromide and 400 ml. of butyl ether. To the vigorously stirred solution 11.0 g. of water-*d*$_2$ (99.5% D_2O by weight obtained from Ohio Chemical and Mfg. Co.) was added slowly. The solution was then heated and the liberated butane-*d* was collected in a trap at −78°. Preliminary experiments with water, in place of heavy water, showed that it was necessary to reflux the butyl ether to expel all the butane. Yields were 10–15% lower if stirring was not maintained throughout the boiling-off period.

The collected butane-1-*d* was purified by distillation through a Davis column, using acetone and Dry Ice to chill the still-head reservoir to about −10°, so as to maintain a reflux ratio of about 5 to 1. The material was collected at −0.5 to −0.2° and 750 mm.; yield 27.6 g. or 85.2%. It was sealed off in an ampoule. Butane-1-*d* from three similar runs were used in the pyrolytic work. Analyses for deuterium content are presented in Table III.

1,2-Dibromopropane-3-*d*.—Acetic acid-*d* was prepared by adding 10.06 g. of water-*d*$_2$ (99.5% D_2O by weight) to 56.6 g. of acetic anhydride (b. p. 136–137.5°) in a small flask. The flask was stoppered and warmed slightly until all the acetic anhydride had reacted. This acetic acid-*d*, 400 ml. of dioxane (dried over sodium), and 140 g. of zinc dust were placed in a 3-neck flask equipped with dropping funnel, condenser and mercury-sealed stirrer. Then 115 g. of allyl chloride (b. p. 45–45.3°) was added during two hours. The evolved gas was liquefied at −78° and distilled through a Davis column. The propene-3-*d* fraction boiling at −47 to −46° (atm. pressure) was passed into a large gas holder containing sodium chloride solution. The volume obtained was 19 l. The gas was passed during 6 hours into an excess of bromine in carbon tetrachloride solution at −5°. Excess bromine was removed by shaking the cold solution with crushed ice and sodium bicarbonate. The organic layer was separated, rinsed thrice with sodium carbonate solution, then with water, and dried over calcium chloride. Distillation of this 1,2-dibromopropane-3-*d*-yielded 169.5 g. of product boiling at 66–67° (60 mm.). This yield is 75.5%, based on the water-*d*$_2$.

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(7) Frey and Hepp, THIS JOURNAL, **55**, 3357 (1933).

TABLE I

PYROLYSIS OF BUTANE-1-*d* AND BUTANE

Run		1	2	3	4	5	6	7	1R	2R
Temp., °C.		650	650	700	750	750	700	650	650	650
Time, sec.	Of run	660	600	1080	330	330	2000	2240	480	450
	Contact	9.2	6.3	11.8	2.4	2.7	15.8	16.3	5.4	5.4
Volume, ml.	Initial	2060	2190	1800	2500	1970	2000	3100	2000	1790
	Final	2680	2660	2620	3750	3260	4250	4000	2500	2250
	Butane–butene	1570	1400	720	1160	1000	650	1900	1400	1280
Butenes, %		2.9	4.7	....	8.3	8.1	13.3	....	3.7	....
Oxygen, %		0.8	0.4	....	0.6	0.6	0.5	....	....	....
Undecmpd. butane, %		73	61	40	42	46	28	61	68	72

Propene-3-*d*.—Fourteen grams of 1,2-dibromopropane-3-*d* was dropped slowly into a flask containing 200 ml. of refluxing absolute ethyl alcohol and 14 g. of zinc dust. The flask, in addition to the dropping funnel, was equipped with a mercury-sealed stirrer and condenser. Vigorous stirring was maintained. The evolved propene-3-*d* was conducted through a stopcock into a tube at −78° which was attached to a Davis column, the reflux head of which was also cooled to −78°. When the addition was complete, refluxing was continued for another half hour. Then the stopcock was closed and the cooling bath lowered away from the tube containing the propene-3-*d*. When reflux was established in the column, the olefin was distilled (b. p. −44 to −43°). It was collected and stored over brine in a 5-liter bottle. Atmospheric pressure was maintained throughout the distillation by adjustment of a levelling bottle connected to the gas-holder. The volume obtained was 1200 ml., or 78% of theoretical. Analysis of two such preparations for the deuterium content is given in Table III.

Combustion of Butane-1-*d* and Propene-3-*d*.—Two methods were used in burning these gases. In one, the gas was burned directly in oxygen and the water formed was collected and then passed over copper oxide at about 600° so as to remove any organic matter. The purified water was condensed and sealed until it was analyzed for deuterium.

In the second method the gas, dried by calcium chloride, was passed at a rate of 500 ml. per hour directly from the gas holder into the copper oxide combustion tube at 600°. Comparable results were obtained with butane-1-*d* using both methods. All the propene samples were oxidized by the second method. Being a one-step operation, it was more convenient. The water was collected and stored as in the first method.

Pyrolysis.—An ampoule containing liquid butane-1-*d* was cooled to −78°. Its tip was then broken open and the open end attached to a tube leading to a calibrated bottle filled with saturated sodium chloride solution which was to serve as gas holder. The liquid in the ampoule was then warmed and the butane evaporated into the gas holder, displacing the brine.

A tube from the gas holder led through a stopcock past a flow meter and manometer into a drying tube and then to the top of a vertical quartz reaction tube (hot volume, 80 ml.) surrounded by an electrically heated furnace, the temperature of which was automatically controlled and recorded by a Leeds and Northrup potentiometer type recorder–controller. A single junction chromel–alumel thermocouple, encased in glass, was placed within the quartz tube. The reaction tube delivered into a side-arm test-tube kept in an ice-bath. The escaping gas passed from there through a 3-way stopcock into another brine-filled gas holder. A siphon arrangement carried the brine to another bottle and adjustment of levels between the gas holder and this bottle made it possible to maintain atmospheric pressure (manometer) within the system.

Both gas holders were then shut off by the stopcocks. The system was evacuated and filled with the butane-1-*d* by opening the first stopcock. The furnace was then heated up to the desired temperature within 40 minutes, after which the butane was passed through the furnace by adding brine from a constant head into the first gas holder.

The propene-3-*d* was pyrolyzed similarly, but since it was not ampouled in liquid form, the gas holder containing it was directly attached to the system.

Isolation of the Butane Fraction Following the Pyrolysis.—The off-gas from the pyrolysis of butane-1-*d* was slowly separated by means of an analytical Podbielniak column into a butane–butene fraction (−5 to +3°). It was collected in a 4-l. bottle over saturated sodium chloride solution. A 60-ml. portion of the butane–butene fraction was analyzed in an Orsat apparatus for oxygen and total butene content.

It was necessary to remove the butenes and any trace of propene from the butane. This was accomplished by shaking the butane–butene fraction repeatedly with 83% sulfuric acid until absorption was complete. The undissolved butane was then passed into a gas holder and subsequently burned.

The results of the pyrolyses of butane-1-*d* are given in Table I. Several preliminary runs were conducted with ordinary butane in order to standardize the technique of operation. The results of two of these runs, 1R and 2R, are included in the table. Runs 1–2, 3–6 and 7 were from three different syntheses of butane-1-*d*.

Isolation of the Propene Fraction Following Pyrolysis of Propene-3-*d*.—The off-gas from the pyrolysis of the propene-3-*d* was distilled through an analytical Podbielniak column, using liquid nitrogen to cool the reflux. The propane–propene fraction (−48 to −40°) was collected in the usual type of gas holder. This gas was passed through a cold solution (−5°) of bromine in carbon tetrachloride (1.0 g. of bromine per 2.7 ml.) at the rate of 400 ml. an hour. The excess bromine was removed and the solution washed and dried in the manner described above. The dibromide was then distilled through a 15-cm. Vigreux column with a boiler capacity of 15 ml. The dibromide fraction (b. p. 139–140°) was collected and sealed off in a tube. The residue was very slight, never amounting to more than 0.5 g. Preliminary trials with propene had indicated a 90% yield in converting propene to its dibromide. This method avoided any possible deuterium–hydrogen exchange. The propene was recovered from the dibromide as described above.

The results of the pyrolyses of propene-3-*d* and propene (1R) are given in Table II. Runs 1 and 2 were from the same sample of propene-3-*d*, and Runs 3 and 4 from a different sample.

TABLE II

PYROLYSIS OF PROPENE-3-*d* AND PROPENE

Run		1	2	3	4	1R
Temp., °C.		700	700	700	750	650
Time in sec.	Run	1980	2680	6000	2280	6120
	Contact	19	28	31	11	67
Vol. mol.	Initial	2500	2650	4550	5050	2350
	Final	2530	2680	4700	5000	2240
Vol. propane–propene (ml.)		2000	1800	3300	4100	1550
% Undecomposed propene		80	67	72	81	66

Analysis of Combustion Water Samples for Deuterium.—Each water sample obtained from the combustion of a deuterium sample was thoroughly purified and its density determined by the balanced float method after dilution with about 30 parts of standard water according to the method of Dole and Slobod.[8] The deuterium content is related to the density.

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(8) Dole and Slobod, THIS JOURNAL, **62**, 471 (1940).

TABLE III

ANALYSES FOR DEUTERIUM CONTENT OF BUTANE-1-*d* AND PROPENE-3-*d* SAMPLES

Run	ΔR	W_0, g.	W', g.	D (p. p. m.)	$N'_{D_2O} \times 10^3$	$n°_{D_2O} \times 10^3$	$N°_{D_2O}$
			Butane-1-*d*				
Control (1-2)	0.1412	1.9453	43.913	450.9	4.174	10.65	0.0995
1	.0811	0.8377	30.196	259.0	2.398	4.14	.0897
2	.0955	0.9361	29.253	305.0	2.824	4.74	.0920
Control (3-6)	.1283	1.3105	29.845	409.7	3.793	6.56	.0911
3	.0806	0.9239	33.084	257.4	2.383	4.50	.0885
4	.0946	0.9873	29.209	302.1	2.796	4.69	.0863
5	.1523	1.5704	29.152	475.3	4.400	7.50	.0868
6	.0464	0.4721	30.204	148.2	1.372	2.34	.0890
Control, 7*	.1322	1.4482	29.147	427.2	3.955	6.72	.0842
7*	.0373	0.4243	30.294	120.5	1.116	1.90	.0815
Non-acid treated*	.0910	1.0671	30.473	294.1	2.722	4.77	.0812
Acid treated*	.0983	1.1517	30.383	317.7	2.941	5.15	.0812
			Propene-3-*d*				
Control (1A-1B)*	0.1583	1.0214	29.599	511.5	4.735	8.05	0.1441
1A*	.1223	0.7815	29.739	395.2	3.659	6.20	.1451
1B*	.0942	0.5990	29.634	304.4	2.818	4.73	.1445
Control (IIA-IIB)*	.1745	1.1257	30.570	563.9	5.220	9.20	.1494
IIA*	.1865	1.9201	48.722	602.7	5.579	15.70	.1495
IIB*	.1801	1.8137	47.879	582.0	5.388	14.88	.1500

The temperature was actually measured in terms of the resistance of a platinum thermometer and expressed in ohms. The accuracy of the method can best be shown by mentioning the results for three standard water samples run in succession. The balancing resistances were 22.04241, 22.04248 and 22.04242, where 0.00001 ohm corresponds to 0.4 part per million difference in deuterium content or 0.00004%.

The data obtained are collected in Table III. ΔR represents $R_s - R_0$ wherein R_s represents in ohms the resistance of the platinum thermometer at the balancing temperature of the diluted combustion water sample, and R_0 the resistance for the standard water sample. W_0 is the weight of the undiluted sample of combustion water, and W' the weight of standard water used in diluting it. The term "control" refers to the original butane-1-*d* or propene-3-*d* used in a particular series of runs; *e. g.*, "control (1-2)" refers to the original butane-1-*d* used in runs 1 to 2 inclusive, and "control (IA-IB)" refers to the original propene-3-*d* used in pyrolyses IA and IB. The term "non-acid treated" refers to a sample of butane-1-*d* as originally prepared, whereas the same sample in the "acid treated" run was shaken repeatedly with 83% sulfuric acid as above described for the separation of butenes from butane. The fact that both mole fractions were 0.0812 shows that there was no deuterium-hydrogen exchange on contact of butane-1-*d* with 83% sulfuric acid. This confirms work reported by other workers.[3b]

Calculation of Analytical Results.—The difference in density between the diluted sample and the standard sample, D (expressed in parts per million), was calculated from the equation: $D = 2.51\ \Delta R/0.000786$. The value of 2.54 instead of 2.51 was used in the runs of Table III marked with an asterisk, denoting use of a different float.

The mole fraction of water-d_2 in the diluted sample, N'_{D_2O}, was calculated using Swift's[9] equation $N'_{D_2O} = 9.257 \times 10^{-6}\ D/(1 - 3.3 \times 10^{-8}\ D)$ which was simplified to $N'_{D_2O} = 9.257 \times 10^{-6}\ D$, since the factor $(3.3 \times 10^{-8}\ D)$ in the denominator was not significant in these analyses.

In order to calculate the mole fraction of water-d_2 in the undiluted sample, $N°_{D_2O}$, the following equations were derived. The treatment is not rigorous, but the relative values of $N°_{D_2O}$ which are of interest in this work will not be affected. In the formulations below, $n°_{D_2O}$ and $n°_{H_2O}$ represent the number of moles of water-d_2 and water, respectively, in the undiluted sample, n'_{H_2O} the number of moles of water in the standard water added, W_0 the grams of undiluted sample, and W' the grams of standard water added. Then

$$W_0 = 18.02\ n°_{H_2O} + 20.03\ n°_{D_2O} \tag{1}$$

$$W_0 - 2.01\ n°_{D_2O} = 18.02\ (n°_{H_2O} + n°_{D_2O}) \tag{2}$$

$$N'_{D_2O} = n°_{D_2O}/(n°_{D_2O} + n°_{H_2O} + n'_{H_2O}) \tag{3}$$

$$N°_{D_2O} = n°_{D_2O}/(n°_{D_2O} + n°_{H_2O}) \tag{4}$$

Divide (4) by (3), then substitute (2)

$$N°_{D_2O} = N'_{D_2O}\left[1 + \frac{W'}{W_0 - 2.01\ n°_{D_2O}}\right] \tag{5}$$

The value of 2.01 $n°_{D_2O}$ was of the order of 1-2% of W_0, so its value was calculated only to three significant figures. The calculations are given in Table III.

Acknowledgment.—We are grateful for helpful suggestions from Professor Malcolm Dole in the design of some of the apparatus employed and to Mr. Glenn Jenks for instruction in the analytical procedure.

Summary

Butane-1-*d*, 1,2-dibromopropane-3-*d* and propene-3-*d* have been prepared. Butane-1-*d* does not undergo hydrogen-deuterium exchange with 83% sulfuric acid within the period of time required to absorb butenes. Effective means were found for the separation of butane and propene from other reaction products, following pyrolysis of butane-1-*d* and propene-3-*d*.

The "undecomposed fraction" of butane-1-*d* recovered after pyrolysis contained less deuterium than the original material, whereas the

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(9) Swift, THIS JOURNAL, **61**, 198 (1939).

"undecomposed fraction" of propene-3-*d* was found to have the same deuterium content as the original propene-3-*d*. These results indicated that the parent hydrocarbon which is recovered after pyrolysis is not exclusively the original unchanged material but includes substantial amounts of synthetic material. The free radical mechanism explains these results satisfactorily. The data confirm previous findings that *n*-butyl participates more actively in butane production than *s*-butyl.

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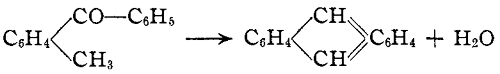
Deuterium Tracers in the Elbs Reaction

BY CHARLES D. HURD AND JULIAN AZORLOSA

Two groups of workers[1] preceded Elbs in studying the thermal decomposition of *o*-methylbenzophenones, but it was Elbs[2] who made the first extensive study, in consequence of which the behavior is known as the Elbs reaction. In the simplest example, *o*-methylbenzophenone changes on refluxing into anthracene and water

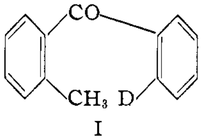


$$C_6H_4\begin{matrix}\diagup CO—C_6H_5\\ \diagdown CH_3\end{matrix} \longrightarrow C_6H_4\begin{matrix}\diagup CH \diagdown\\ \diagdown CH \diagup\end{matrix}C_6H_4 + H_2O$$

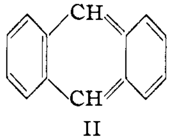
No further important study of this reaction was made for four decades, but between 1929–1935 several investigators made important contributions.

Morgan and Coulson[3] found that the low yields reported by Elbs could be increased considerably by removing the anthracene derivative at intervals from the reaction zone. Many polynuclear hydrocarbons containing the anthracene skeleton have been synthesized[4] by means of the Elbs reaction.

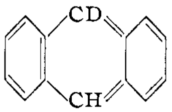
Any mechanism of the Elbs reaction must explain the disappearance of the carbonyl oxygen and the appearance of a hydrogen atom at the 9-position in anthracene. Obviously, the hydrogen must have come either from the ortho nuclear position or from the methyl group, since these were the only locations involving any loss of hydrogen. To gain insight into this question, benzophenones were synthesized in the present investigation which contained deuterium in an ortho nuclear position. 2-Methylbenzophenone-2'*d* (I) would conceivably give rise to anthracene itself (II), anthracene-9*d* (III) or anthracene-1*d* (IV).



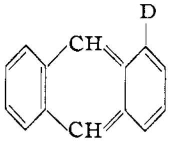
I



II



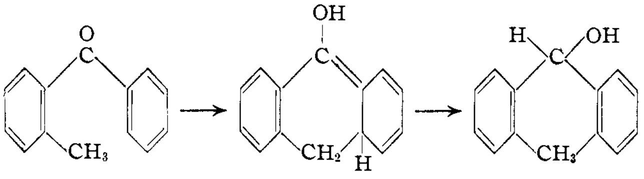
III



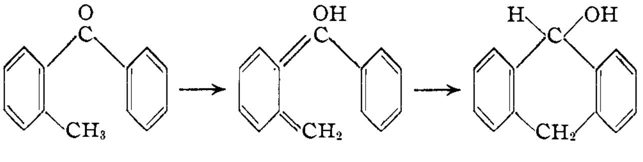
IV

Since heavy water would be formed in the production of II but not of III or IV, analysis of the evolved water for presence or absence of deuterium would provide a clue as to the course of reaction. Only one of the three possible reaction products shows deuterium at position 9. Hence oxidation of the anthracene to anthraquinone would serve as check on the previous observation, since if this operation caused loss of deuterium content in the quinone and formation of heavy water, it would prove that deuterium was at position 9 in the hydrocarbon molecule.

Three courses have been suggested for the route of the Elbs reaction. Fieser's[5] proposal involves an intramolecular 1,4-addition of the aliphatic (methyl) group to the opposite conjugated system of the ketone, thus making the first step one of cyclization. A tautomeric shift gives rise to dihydroanthrol, from which anthracene results by dehydration or anthrone by dehydrogenation.



Cook[6] also proposed dihydroanthrol as intermediate but he favored tautomerism as the initial step followed by 1,4-addition of the aromatic (phenyl) group to the opposite conjugated enolic system.



Use of an ortho deuterium atom in the ketone would not distinguish between these two mechanisms, since the same dihydroanthranol-*d* would arise from either one. Anthracene-9*d* would result by dehydration of this compound.

Morgan[7] made a third proposal to account not

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(1) Behr and Van Dorp, *Ber.*, **6**, 753 (1873); **7**, 16 (1874); Ador and Rilliet, *ibid.*, **11**, 399 (1878).

(2) Elbs and co-workers, *ibid.*, **17**, 2847 (1884); **18**, 1797 (1885); **19**, 408 (1886); *J. prakt. Chem.*, **33**, 180 (1886); **35**, 465 (1887); **41**, 1, 121 (1890).

(3) Morgan and Coulson, *J. Chem. Soc.*, 2203, 2551 (1929).

(4) Clar, *Ber.*, **62**, 350, 1378, 3021 (1929); **63**, 2967 (1930); Cook, *J. Chem. Soc.*, 456 (1932); Fieser and Seligman, THIS JOURNAL, **57**, 228, 942 (1935).

(5) Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

(6) Cook, *J. Chem. Soc.*, 487 (1931).

(7) Morgan and Coulson, *ibid.*, 2328 (1931).