proximately 5 g. of calcium carbonate was added to the silver solution before the reaction was initiated. The addition of potassium carbonate after termination of the reaction was omitted.

Control Experiments.—A number of control experiments (ten) were performed in order to determine the efficiency of the techniques employed and the extent of solvolysis not attributable to reaction with silver ion. Since the experiments were relatively straightforward, detailed descriptions of all of them will not be presented. One example will be given.

In order to determine whether any appreciable amount of solvolysis of the butenyl nitrates occurred during the workup procedure, and, furthermore, to estimate the efficiency of the ether extraction technique employed, a mixture of the following composition (given in weight per cent.) was prepared: 19.29% *n*-decane, 31.32% *trans*-crotyl alcohol, 27.84% α-methallyl alcohol, 12.09% crotyl nitrate, 9.46% α-methallyl nitrate. The mixture was added to the heterogeneous system normally employed, containing sodium chloride, silver chloride and potassium carbonate. The mixture was shaken and subsequently worked up and analyzed by the standard technique. The results of the analysis were: 20.59% *n*-decane, 31.00% *trans*-crotyl alcohol, 27.56% α-methallyl alcohol, 11.93% crotyl nitrate, 8.91% α-methallyl nitrate. These data indicate that no measurable amount of solvolysis occurred during the workup procedure and that the ether extraction was essentially 100% efficient.

Vapor Phase Chromatography.—The instrument employed in this work was a Perkin–Elmer model 154B vapor fractometer. The two columns used were 2 meters in length and were filled with Perkin–Elmer packing "A" and "B," respectively. Helium was employed as the carrier gas.

Two separate analyses were performed on each of the ether solutions resulting from the partial solvolysis experiments. Analysis of a 20-microliter sample at 65° (gas pressure, 12 p.s.i.; flow meter reading 4.85) using column A provided data on the percentage composition of the mixture with respect to α-methallyl alcohol, α-methylallyl chloride and crotyl chloride. Under these conditions, *cis*- and *trans*-crotyl alcohols could not be resolved satisfactorily, nor could the area of the peak produced by crotyl nitrate be measured quantitatively. Accurate measurement of the relative percentages of the *primary* and *secondary* nitrate esters, *cis*- and *trans*-crotyl alcohols, and α-methallyl alcohol was possible when columns A and B were employed in series at 120° (gas pressure, 30 p.s.i.; flow meter reading, 4.72). At this temperature, however, a considerable amount of rearrangement of the butenyl chlorides was observed. Consequently, a combination of the data obtained from analyses at both temperatures was necessary for the calculation of the relative percentages of all compounds present. Under no conditions could *cis*- and *trans*-crotyl chlorides be resolved. No evidence of a separation of the two crotyl nitrates was observed.

Peak areas were calculated by evaluation of the product of the carefully measured values of the peak height and the width of each peak at half the altitude. Control experiments indicated that this method is very accurate. Since recorder response, and consequently peak area, cannot be correlated directly either with weight or mole per cent., a correction factor, *R*, was required. This factor was determined empirically by injecting samples of known composition into the instrument, measuring the peak areas, and calculating the factor by which the measured area of a peak need be multiplied in order to give a number representative of the weight per cent. of the corresponding compound present in the mixture. The following table gives the factor *R* for each of the eight compounds studied.

Compound	*R*
α-Methallyl alcohol	1.000
Crotyl alcohol (*cis*- and *trans*-)	1.009
α-Methallyl chloride	1.122
Crotyl chloride	1.045
α-Methallyl nitrate	1.242
Crotyl nitrate	1.239
n-Decane	0.961

Control experiments performed with mixtures of known composition and measurements of the reproducibility of analyses have shown that, unless otherwise stated, the percentage composition figures are accurate to ± 1.6% (absolute). In some cases, as noted in tables and the text, the accuracy is considerably greater.

Hydrolysis with Dilute Aqueous Sodium Hydroxide.—The method of Young and Andrews[3] was employed for reactions with 0.8 *N* aqueous sodium hydroxide. Analysis was by v.p.c. using columns A and B as described above.

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Deuterium Isotope Effects During the Raney Nickel Catalyzed C1–C2 Cleavage of 2-Phenylethanol[1]

BY WILLIAM A. BONNER

RECEIVED JULY 27, 1959

In order to gain information as to the rate determining step in the Raney nickel catalyzed C1–C2 cleavage of 2-phenylethanol into toluene, this reaction has been studied from the viewpoint of its deuterium isotope effects, analyzing the mole ratios of cleavage product (toluene) to dehydroxylation product (ethylbenzene) by vapor liquid partition chromatography. When 1,1-dideuterio-2-phenylethanol reacted with ordinary Raney nickel in refluxing ethanol the toluene/ethylbenzene ratio was identical with that of a control using stock 2-phenylethanol. However when 2-phenylethanol reacted with deuterated Raney nickel in *O*-deuterioethanol solvent the toluene/ethylbenzene ratio decreased markedly, indicating a normal deuterium isotope effect of about 2.1 for the cleavage reaction. Mechanistically these observations are most reasonably interpreted as indicating that the attack on the substrate molecule by hydrogen adsorbed on the catalyst surface is the rate determining step in such heterogeneous C1–C2 hydrogenolyses.

In 1957 we reported the observation that the action of excess Raney nickel in refluxing ethanol on a variety of 2-substituted 2-aryl-ethanols resulted both in simple C1 dehydroxylation producing alkylaromatic hydrocarbons as well as C1–C2 carbon bond cleavage yielding alkylaromatics one homolog lower.[2] Since that time we have studied this hydrogenolytic cleavage reaction extensively with the aid of stereochemical as well as deuterium and radioactive carbon tracer techniques, with the additional findings (a) that the single carbon fragment produced in such C1–C2 cleavages consists of carbon monoxide strongly adsorbed on the nickel catalyst surface,[3] (b) that in neither dehydroxylation nor C1–C2 fission are intermediates produced which in their catalytic environment show an

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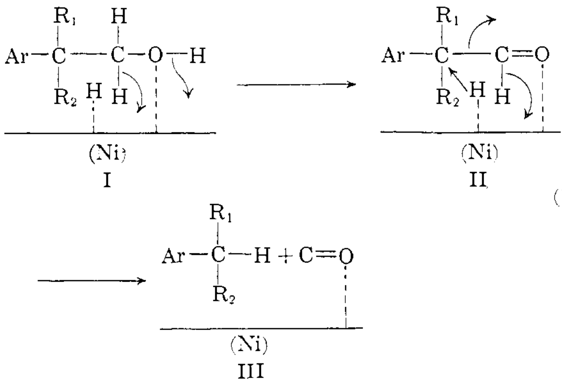
[1] This constitutes communication XIV in the series "The Stereochemistry of Raney Nickel Action"; for XIII see ref. 6.

[2] J. A. Zderic, W. A. Bonner and T. W. Greenlee, THIS JOURNAL, **79**, 1696 (1957).

[3] W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 2122 (1959).

appreciable tendency to undergo molecular rearrangement,[3,4] (c) that extensive hydrogen exchange occurs between the catalyst and substrate molecule undergoing cleavage, such exchange being most rapid at C2 and occurring there with predominant retention of configuration,[5] (d) that the cleavage/dehydroxylation ratio is increased by the presence of alkyl or aryl substituents at C2, but is not markedly affected by *ortho, para or meta*-directing groups in the *para*-position of the nucleus of the 2-arylethanol undergoing cleavage[6] and (e) that the C1-C2 cleavage process occurs with substantial retention of optical activity and predominant *retention* of configuration at C2.[5] (In our earlier publication[5] we erroneously concluded from our optical and chemical data that the cleavage of (−)-2-methyl-2-phenyl-1-butanol to (+)-2-phenylbutane proceeded with inversion rather than retention of configuration. We wish herewith to correct this misinterpretation and to express our gratitude to Prof. D. J. Cram for calling this oversight to our attention.)

These observations now may be tentatively rationalized[2,3,5] by a mechanism such as (1), which is in qualitative accord with both the chemical and stereochemical aspects of such cleavage reactions. Examination of equation 1 discloses that several bond-breaking processes are involved in the over-all mechanism, namely, those of C–H at C1 and O–H in I, those of C–H at C1 and C–C at C1–C2 in II and lastly that of Ni—H as adsorbed hydrogen leaves the catalyst surface during its attack upon II. In order to find out which of the bond-breaking processes in (1) might be involved in a rate-determining step, we have now undertaken to examine the Raney nickel catalyzed cleavage of 2-phenylethanol for possible hydrogen-deuterium isotope effects under varying sets of conditions.



(1)

When Raney nickel in refluxing ethanol acts upon 2-phenylethanol two products result,[2] ethylbenzene from simple dehydroxylation at C1 and toluene from cleavage between C1 and C2. We have examined this system for deuterium isotope effects by determining the cleavage/dehydroxylation (*i.e.*, toluene/ethylbenzene) ratio by means of quantitative vapor liquid partition chromatographic (v.l.p.c.) analysis in cleavage experiments where both the Raney nickel catalyst surface was deuterated and the two hydrogens at C1 were replaced by deuterium (*i.e.*, with 1,1-dideuterio-2-phenylethanol). The results of these experiments are summarized in Table I.

TABLE I

THE CLEAVAGE OF 2-PHENYLETHANOL IN DEUTERIUM LABELED SYSTEMS

No.	Catalyst	Substrate	Toluene, mole %	Ethylbenzene, mole %	Mole % toluene/ Mole % ethylbenzene
1	Ni(H)	Ph-CH_2-CH_2-OH	52.5	47.5	1.105
2	Ni(D)	Ph-CH_2-CH_2-OD	36.9	63.1	0.585
3	Ni(H)	Ph-CH_2-CH_2-OH	54.9	45.1	1.217
4	Ni(H)	Ph-CH_2-CD_2-OH	47.3	52.7	0.898
5	Ni(H)	Ph-CH_2-CH_2-OH	46.6	53.4	0.872

No. 1 in Table I shows the toluene/ethylbenzene ratio for the cleavage of stock 2-phenylethanol with fresh Raney nickel catalyst. No. 2 shows this ratio for the cleavage of stock 2-phenylethanol using deuterated Raney nickel catalyst in refluxing *O*-deuterioethanol, while No. 3 represents the results of identically conducted control experiments run simultaneously. No. 4 summarizes the cleavage results using ordinary Raney nickel in ethanol with 1,1-dideuterio-2-phenylethanol, while No. 5 gives the data for control experiments conducted concurrently with the experiments in No. 4. Ideally, the toluene/ethylbenzene ratios in Nos. 1, 3 and 5 would be constant. The fact that they are not emphasizes (*cf.* Experimental) the importance on the cleavage–dehydroxylation ratio of such unknown factors affecting the catalyst surface as the technique of catalyst preparation and the age of catalyst. Thus the data in No. 2 should be compared only with those in the control No. 3, and those in No. 4 only with its control in No. 5. Comparison of Nos. 4 and 5, where the analytical data are identical within experimental error, indicates that no deuterium isotope effect results in the cleavage of 2-phenylethanol under these conditions when the two hydrogens at C1 are replaced by deuterium. Comparison of Nos. 2 and 3, however, shows that a substantial isotope effect favoring dehydroxylation over cleavage occurs when either (a) the adsorbed hydrogen on the catalyst surface is replaced by deuterium and/or (b) the hydroxylic hydrogen of 2-phenylethanol is replaced by deuterium (assuming rapid and complete OH → OD exchange under the reaction conditions employing *O*-deuterioethanol).

The absence of a deuterium isotope effect in the cleavage reaction of 1,1-dideuterioethanol argues either that C–H bond rupture at C1 in 2-phenylethanol is not rate determining, or that the rate of H–D exchange between C1 and the catalyst surface is fast compared to the rate of C1–C2 cleavage, yielding, for practical purposes, non-deuterated substrate. We have at present no basis for a choice between these alternatives. The occurrence of an isotope effect decreasing the cleavage/dehydroxylation ratio when the catalyst surface is deuterated and the 2-phenylethanol substrate is *O*-deuterated suggests, on the other hand, three possible rate-determining alternatives: (a) O–H bond breaking in I of equation 1, (b) rapid pre-

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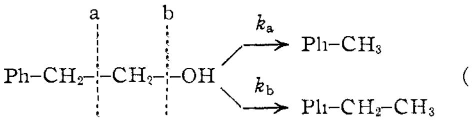
[4] W. A. Bonner, THIS JOURNAL, **81**, 1181 (1959).

[5] W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 3336 (1959).

[6] T. W. Greenlee and W. A. Bonner, *ibid.* **81**, 4303 (1959).

liminary H → D exchange at C1 in I of equation (1), followed by rate-determining C–D fission at C1 or (c) Ni—H rupture in II of equation 1. The first alternative appears improbable because of the known lability of the O–H bond in a hydroxyl environment, while the second appears somewhat unlikely because of the known ease with which alcohols are dehydrogenated in the presence of Raney nickel.[7] The third alternative, that H-desorption from the catalyst surface is rate determining in the above C1–C2 cleavage, finds some support in our previously observed difficulty in desorbing hydrogen from a Raney nickel surface, a process which requires baking the dried catalyst *in vacuo*.[3] This tentative conclusion that the rate determining step in the cleavage reaction is the desorption of hydrogen from the catalyst surface during attack on the aldehyde intermediate (II in equation 1) is in accord with other observations regarding isotope effects during heterogeneous catalytic processes. Thus the hydrogenation of ethylene in the presence of various metal catalysts including nickel has been found to be generally slower with deuterium than with hydrogen.[8] Similarly, since normal isotope effects have been observed in the adsorption of hydrogen on metal surfaces,[9,10] it is reasonable to assume that such isotope effects should also prevail in desorption processes. Any preliminary H–D exchange reactions at C2[11] in No. 2, Table I, would yield a deuterated substrate whose C1–C2 cleavage would presumably be subject to only a smaller second order isotope effect.

From the data in Table I it is possible to get some idea of the magnitude of the present deuterium isotope effect. The reaction under consideration consists of two competing processes, a and b in equation 2. If one assumes that both the cleavage (a) and dehydroxylation (b)



$$\text{Ph–CH}_2\text{–}\overset{a}{\vdots}\text{–CH}_2\text{–}\overset{b}{\vdots}\text{–OH}\left\langle\begin{array}{l}\xrightarrow{k_a}\text{Ph–CH}_3\\[6pt]\xrightarrow{k_b}\text{Ph–CH}_2\text{–CH}_3\end{array}\right.\qquad(2)$$

paths are kinetically of the same order (presumably pseudo first order in 2-phenylethanol), then it follows that the observed toluene/ethylbenzene ratios in Table I are also the ratios of the corresponding rate constants, *i.e.*

$$\frac{k_{a-H}}{k_{b-H}} = 1.217 \text{ and } \frac{k_{a-D}}{k_{b-D}} = 0.585$$

Furthermore if the dehydroxylation path (b) in equation 2, being mechanistically different[12,13] from cleavage, is *not* subject to a normal deuterium isotope effect, *i.e.*, if $k_{b-H} = k_{b-D}$, then the isotope effect in the cleavage process is given by $k_{a-H}/k_{a-D} = 1.217/0.585 = 2.08$. If, on the other hand, path b in (2) is subject to a normal isotope effect of unknown magnitude, such that $k_{b-H} = nk_{b-D}$, then it follows that the isotope effect in the cleavage path a is expressible as $k_{a-H}/k_{a-D} = n \times 2.08$. Thus while the value 2.08 for the isotope effect in the cleavage reaction is a reasonable one in the light of other deuterium isotope effect studies,[7] it must be looked upon as a *minimum* value, since we currently have no experimental data on the presence or absence of isotope effects in Raney nickel catalyzed dehydroxylation reactions. This latter question is currently under investigation.

Experimental

Raney Nickel.—This was prepared in the usual fashion,[14] then stored under water until used. Immediately prior to use the catalyst slurry was rapidly filtered damp-dry on a sintered glass funnel and quickly transferred to a tared watch glass. The desired weight of damp catalyst was immediately treated with the requisite quantity of solvent (ethanol or *O*-deuterioethanol) for each cleavage experiment. The same catalyst batch was used within a one-month period for all of the experiments described below.

Deuterated Raney Nickel.—The deuterated catalyst was prepared by equilibrating the requisite weight of the above damp-dry catalyst with 99% deuterium oxide as previously described.[15] Four 24-hour equilibrations with fresh deuterium oxide were employed, filtering the catalyst damp-dry between each rinse. Deuterated catalyst samples were prepared in duplicate, along with duplicate samples of catalyst "equilibrated" by an identical procedure with ordinary water as control, for simultaneous use in one of the cleavage experiments described below.

O-Deuterioethanol was prepared by the action of 99% deuterium oxide on a suspension of sodium ethylate in anhydrous ether as described earlier.[15] Examination of the twice-distilled product, b.p. 77.5–78.8°, by v.l.p.c. techniques indicated it to be better than 96% chemically homogeneous. It was accordingly used as solvent in one of the cleavage experiments below with no additional purification.

1,1-Dideuterio-2-phenylethanol was prepared by the reduction of phenylacetic acid with lithium aluminum deuteride in ether solution. The crude product, which had been freed of unreacted acid by washing with sodium hydroxide solution, was purified by distillation, b.p. 125–127° (50 mm.); v.l.p.c. analysis of the distillate showed the presence of only a single component. Mass spectrometric analysis (kindly performed by the California Research Corporation) of the distillate indicated it to contain above 95% of the desired product.

Vapor Liquid Partition Chromatographic Analyses.—The percentages of toluene, ethylbenzene and residual solvent in the crude cleavage reaction products described below were determined by v.l.p.c. analysis. A 1.2 × 120 cm. v.l.p.c column packed with a 2:1 Celite–silicone packing was employed. Operating conditions entailed a column temperature of 153° and a helium flow rate of 76 ml./min. The output signal from the platinum thermal conductivity detector in the column assembly was recorded on a Varian G-10 recorder, and the bridge circuit and sample size injected into the column were selected to give nearly full scale recorder deflection as components left the column. Under these conditions solvent, toluene and ethylbenzene were completely resolved, the latter two components emerging from the column about two minutes apart.

Analytical data were obtained from the v.l.p.c. traces by measuring the area under the curve for each component using the product of peak height times half-peak width. The former parameter was measured with dividers and the latter with the aid of a traveling microscope. A series of known mixtures of toluene and ethylbenzene was prepared and analyzed as above to establish the precision of the method and to provide a series of standards which could later be analyzed alongside product mixtures of unknown concentration for control purposes. Table II indicates the results of these preliminary duplicate analyses (except for sample 11,

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[7] W. A. Bonner, THIS JOURNAL, **74**, 1033 (1952); W. Reeves and H. Adkins, *ibid.*, **62**, 2874 (1940); M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944); E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948); R. Paul, *Bull. soc. chim.*, **8**, 507 (1941); *Compt. rend.*, **208**, 1319 (1939); L. Palfray and S. Sabetay, *ibid.*, **208**, 109 (1939).

[8] K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[9] R. M. Barrer, *Trans. Faraday Soc.*, **32**, 481 (1936).

[10] E. B. Maxted and C. H. Moon, *J. Chem. Soc.*, 1542 (1936).

[11] W. A. Bonner, THIS JOURNAL, **76**, 6350 (1954); W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 4369 (1956).

[12] W. A. Bonner, J. A. Zderic and G. A. Casaletto, *ibid.*, **74**, 5086 (1952).

[13] W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 3218 (1956).

[14] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[15] W. A. Bonner, THIS JOURNAL, **76**, 6350 (1954).

which represents six analyses) of known mixtures. It is seen that the area % for each component is reproducible over-all to about 0.5% absolute, and that the area % accords with the known mole % for each component approximately within experimental error.

TABLE II

VAPOR LIQUID PARTITION CHROMATOGRAPHY ANALYSIS OF TOLUENE–ETHYLBENZENE MIXTURES

Sample	I	II Component	III	IV
		Toluene		
Vol., ml.	1.00	2.00	3.00	4.00
Moles	0.00941	0.0188	0.0282	0.0377
Mole %	22.3	43.4	63.3	82.2
Area, %	21.9 ± 0.3	43.3 ± 0.6	63.0 ± 0.8	83.1 ± 0.2
		Ethylbenzene		
Vol., ml.	4.00	3.00	2.00	1.00
Moles	0.0327	0.0245	0.0164	0.00817
Mole, %	77.7	56.6	36.7	17.8
Area, %	78.1 ± 0.2	56.7 ± 0.6	37.0 ± 0.8	16.9 ± 0.2

Recovery of Toluene and Ethylbenzene by Isolation Procedure.—In order to establish the adequacy of the procedure for isolating toluene and ethylbenzene from the cleavage reactions below, the following control experiment was performed. Raney nickel slurry (1 teaspoonful), water (75 ml.), ethanol (12 ml.), toluene (0.50 g., 0.00543 mole) and ethylbenzene (1.03 g., 0.00971 mole) were mixed. The mixture was extracted with 40 ml. of pentane, then three times with 20-ml. portions of pentane. The combined extracts were passed through a 2 × 15 cm. column of alumina, rinsing with 50 ml. of pentane. The pentane was removed from the column effluent by slow distillation through a 24-inch glass helix packed column (unheated jacket) until distillation ceased. The column was allowed to drain back into the still pot and the residue (1.52 g.) was analyzed directly as above on the v.l.p.c. column. It contained 79.4% toluene and ethylbenzene and 20.6% pentane, corresponding to a 78.9% recovery of toluene and ethylbenzene. In triplicate analyses the area % for the toluene fraction was 32.2 ± 0.6 and that for the ethylbenzene 67.8 ± 0.6, compared with starting mole % of 35.9 for toluene and 64.1 for ethylbenzene. In view of these results arbitrary correction factors of + 3.7 % for toluene and −3.7% for ethylbenzene have been added to the respective area % in the v.l.p.c. analyses below to convert these into the mole per cent. figures given in Table I.

Reaction of 2-Phenylethanol with Raney Nickel.—A mixture of the above damp-dry catalyst (10.3 g.), 2-phenylethanol (1.23 g.) and absolute ethanol (12 ml.) was heated under reflux with occasional swirling for a period of 4 hours, then cooled and added to water (75 ml.). The aqueous mixture was extracted with pentane and the crude products were isolated from the extracts exactly as described in the recovery experiment above. Triplicate v.l.p.c. analysis of the crude residue showed a 53% yield of toluene and ethylbenzene and area percentages of 48.8 ± 0.2 for toluene and 51.2 ± 0.2 for ethylbenzene. The above experiment was repeated two additional times within a 4-day period (triplicate analyses in each case) in order to estimate the over-all reproducibility of the data. Product yields varied from 53 to 67% and over-all average area % were 48.8 ± 0.5 and 51.2 ± 0.5 for toluene and ethylbenzene, respectively, indicating a substantial reproducibility of the data.

2-Phenylethanol with Deuterated Raney Nickel.—A mixture of the above damp-dry deuterated Raney nickel (11.4 g.), the above *O*-deuterioethanol (12.0 ml.) and phenylethanol (1.23 g.) was heated under reflux for 4 hours. A duplicate reaction mixture containing proportional quantities of the same components was refluxed at the same time. Simultaneously, two similar control experiments were conducted in absolute ethanol using non-deuterated catalyst which had been "equilibrated" with ordinary water as described above. The products from each of the four concurrently run experiments were isolated as before and subjected to triplicate v.l.p.c. analysis. Hydrocarbon yields varied from 69 to 76%. The over-all averages of area % in the deuterated catalyst experiments were: toluene, 33.2 ± 0.5%; ethylbenzene, 66.8 ± 0.5%. The area % in the non-deuterated catalyst controls were: toluene, 51.2 ± 1.3%; ethylbenzene, 48.8 ± 1.3%.

1,1-Dideuterio-2-phenylethanol and Raney Nickel.—Duplicate cleavage experiments similar to those described above were conducted simultaneously using the above 1,1-dideuterio-2-phenylethanol and ordinary Raney nickel catalyst in absolute ethanol solvent. At the same time duplicate control experiments were conducted employing ordinary Raney nickel and stock 2-phenylethanol in absolute ethanol. Customary product isolation and triplicate v.l.p.c. analyses in each case gave these over-all averages for area % of each component: from 1,1-dideuterio-2-phenylethanol, toluene, 43.6 ± 0.5%; ethylbenzene, 56.4 ± 0.5%; from stock 2-phenylethanol, toluene, 42.9 ± 0.4%; ethylbenzene, 57.1 ± 0.4%. The results of the experiment and its control were thus identical within experimental error, indicating the absence of an isotope effect.

It should be noted that in both the present and the preceding experiment the percentages of toluene and ethylbenzene in the products from the control runs are not in accord with those recorded earlier above for cleavage reactions employing ordinary Raney nickel and stock 2-phenylethanol, even though reaction conditions were identical. There are possible explanations for each of these discrepancies. In the previous experiment the catalyst in the control runs was "equilibrated" with ordinary water in a manner simulating the equilibration of the deuterated catalyst with heavy water, an additional series of steps which may have changed its surface characteristics. In the present experiment the catalyst used in the control runs was about 3 weeks older than in the earlier experiments, such that unknown changes on aging may explain the discordant results. In any case the control runs in the last two experiments gave consistent results which are, we believe, validly comparable with the results of each respective deuterium analog experiment in question.

During the v.l.p.c. analysis of the crude products from each of the above cleavage reaction experiments, one of the known mixtures in Table II was analyzed simultaneously to provide a check on the constancy of the analytical method. In no case was the control analysis significantly beyond the experimental error of the corresponding analysis in Table II.

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