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Hydrogen Migration Studies during the Catalytic Reduction of 3-Phenyl-1-butene with Deuterium

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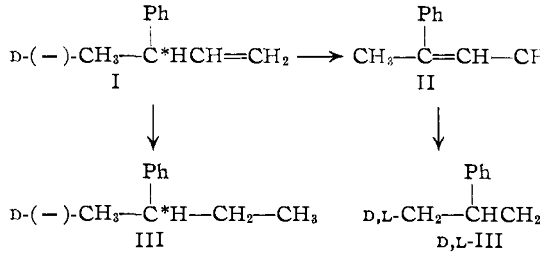
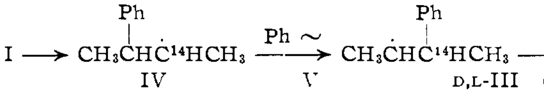
Since neither double bond migration[2,3] nor phenyl migration[4] appeared to be an adequate explanation for the partial racemization observed[2] during catalytic reduction of 3-phenyl-1-butene to 2-phenylbutane, an alternative racemization path has been investigated. This postulated path involves the partial hydrogenation of the olefin precursor to a 3-phenyl-2-butyl radical, which undergoes hydrogen migration to a 2-phenyl-2-butyl radical, which is subsequently reduced non-stereospecifically to racemic 2-phenylbutane. In order to test this hypothesis 3-phenyl-1-butene was reduced in a deuterium atmosphere with a variety of catalysts, and the deuterated 2-phenylbutane products were examined for their side-chain deuterium distribution by means of nuclear magnetic resonance spectrometry. With most catalysts, evidence for fairly extensive aliphatic as well as aromatic H–D exchange *during*, but not subsequent or (except at Cl in the olefin precursor) prior to reduction was noted, a fact which has precluded our quantitative estimation of the importance of hydrogen migration as a mechanism for racemization during the catalytic reduction of 3-phenyl-1-butene.

The partial racemization (1–11%) of D-(−)-3-phenyl-1-butene (I) during its hydrogenation with a variety of catalysts was reported[2] by Cram in 1952. Since the reduction product, D-(−)-2-phenylbutane (III), was itself unracemized under the reaction conditions, Cram concluded that the small amount of racemic product (D,L-III) formed must have been produced *during* and not *after* hydrogenation, and suggested that the prior rearrangement of I to the conjugated intermediate II prior to its reduction might be a reasonable mechanistic interpretation of his observations. Huntsman and Schlesinger have more recently cast some doubt upon the adequacy of this interpretation in that they have found[3] that double bond migration (I→II) was much slower than racemization in the reduction in question. They thus concluded that racemization must proceed by some alternate, unspecified mechanism. In 1958, we investigated[4] one plausible alternative mechanism, namely, the partial hydrogenation of I to a 3-phenyl-2-butyl radical IV which, undergoing non-stereospecific phenyl migration to an equivalent rearranged radical V, would ultimately yield partially racemic product. The non-intervention of a mechanism such as 2, however, was demonstrated by our finding[4] that the catalytic hydrogenation of 3-phenyl-1-butene-2-C^{14} under a variety of conditions yielded primarily unrearranged 2-phenylbutane-3-C^{14}, and less than 1% of rearranged 2-phenylbutane-2-C^{14}. Since mechanism 2 was thus obviously not responsible for the racemization of optically active 3-phenyl-1-butene on hydrogenation, an alternative hypothesis (3) is now postulated. In this postulate, olefin I is partially hydrogenated to a 3-phenyl-2-butyl radical (IV), which rearranges to a 2-phenyl-2-butyl radical (VI) by hydrogen migration prior to subsequent reduction to 2-phenylbutane.



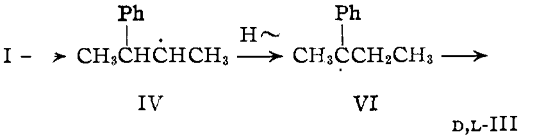
$$\begin{array}{ccc} \text{D-}(-)\text{-}CH_3-\overset{\displaystyle Ph}{\overset{|}{C}}{}^*HCH=CH_2 & \longrightarrow & CH_3-\overset{\displaystyle Ph}{\overset{|}{C}}=CH-CH_3 \\ \text{I} & & \text{II} \\ \downarrow & & \downarrow \\ \text{D-}(-)\text{-}CH_3-\overset{\displaystyle Ph}{\overset{|}{C}}{}^*H-CH_2-CH_3 & & \text{D,L-}CH_2-\overset{\displaystyle Ph}{\overset{|}{C}}HCH_2CH_3 \\ \text{III} & & \text{D,L-III} \end{array}$$

(1)



$$\text{I} \longrightarrow \underset{\text{IV}}{CH_3\overset{\displaystyle Ph}{\overset{|}{C}}H\dot{C}^{14}HCH_3} \xrightarrow[\text{V}]{Ph\sim} CH_3\dot{C}H\overset{\displaystyle Ph}{\overset{|}{C}}{}^{14}HCH_3 \longrightarrow \text{D,L-III}$$

(2)



$$\text{I} \dashrightarrow \underset{\text{IV}}{CH_3\overset{\displaystyle Ph}{\overset{|}{C}}H\dot{C}HCH_3} \xrightarrow{H\sim} \underset{\text{VI}}{CH_3\overset{\displaystyle Ph}{\overset{|}{\underset{\cdot}{C}}}CH_2CH_3} \longrightarrow \text{D,L-III}$$

(3)

To the extent that the hydrogen migration in 3 might be non-stereospecific and that the rearranged radical VI might be incapable of maintaining its asymmetry in the neighborhood of the catalyst surface, a process such as 3 should yield racemic 2-phenylbutane. Mechanism 3 is perhaps more attractive than 2 on energetic grounds, since it involves the rearrangement of a secondary aliphatic radical to a more stable tertiary benzyl radical, and should thus be energetically quite feasible.

Although a heterogeneous catalytic process, mechanism 3 has certain precedents, at least, in several previously observed instances of hydrogen migration during reactions believed to proceed *via* free radical intermediates. Thus Boyer and Straw have found[5] that during the free-radical pyrolysis of a number of α-azidoketones to produce α-iminoketones, nitrogen was lost with a concomitant group migration which, without exception, followed the pattern $H > C_6H_5 > CH_3$. Glazebrook and Pearson have proposed[6] a hydrogen migration during photochemical decompositions of isopropyl ketone. In the alkaline degradation of 2-*p*-toluylbenzenediazonium salts in the presence of carbon tetrachloride, Detar and Relyea have rationalized[7] the simultaneous production of 2-

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[1] The authors are indebted to the National Science Foundation for its generous support of a portion of this investigation.

[2] D. J. Cram, This Journal, **74**, 5518 (1952).

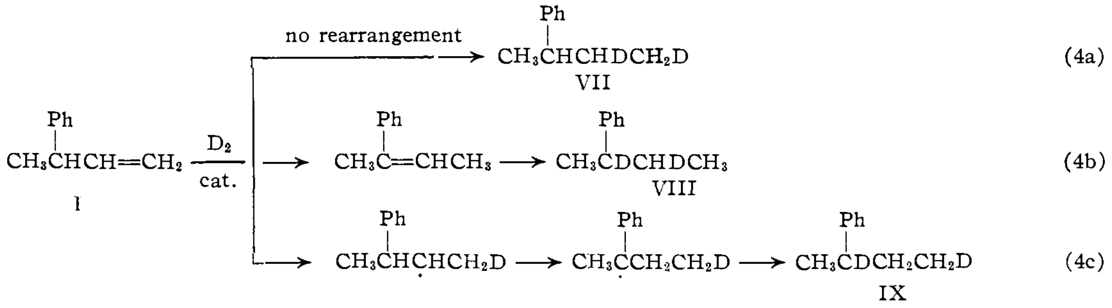
[3] W. D. Huntsman and S. I. Schlesinger, Abstract in' A Report on Research under Sponsorship of the Petroleum Research Fund Administered by the American Chemical Society," 1954–1956, p. 18.

[4] W. A. Bonner, C. E. Stehr and J. R. do Amaral, This Journal, **80**, 4732 (1958).

[5] J. H. Boyer and D. Straw, *ibid.*, **75**, 1642 (1953).

[6] H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 1777 (1936).

[7] D. F. DeTar and D. I. Relyea, This Journal, **78**, 4302 (1956).



$$\underset{\text{I}}{CH_3\overset{Ph}{C}HCH{=}CH_2} \xrightarrow[\text{cat.}]{D_2} \begin{cases} \xrightarrow{\text{no rearrangement}} \underset{\text{VII}}{CH_3\overset{Ph}{C}HCHDCH_2D} & \text{(4a)} \\ \longrightarrow CH_3\overset{Ph}{C}{=}CHCH_3 \longrightarrow \underset{\text{VIII}}{CH_3\overset{Ph}{C}DCHDCH_3} & \text{(4b)} \\ \longrightarrow CH_3\overset{Ph}{C}H\dot{C}HCH_2D \longrightarrow CH_3\overset{Ph}{\dot{C}}CH_2CH_2D \longrightarrow \underset{\text{IX}}{CH_3\overset{Ph}{C}DCH_2CH_2D} & \text{(4c)} \end{cases}$$

chloro-4-methylbenzophenone along with the anticipated 2-chloro-4′-methylbenzophenone in terms of a hydrogen migration from the *o*-position of one aromatic nucleus to that of the second. Kharasch and co-workers have postulated[8] hydrogen migration, followed by disproportionation, to explain the production of 1-phenyl-1-propene along with *n*-propylbenzene when 3-phenyl-1-propyl chloride reacts with *n*-butylmagnesium iodide in the presence of cobaltous chloride. Similarly the possible intervention of hydrogen migration during the free radical decarbonylations of β-*p*-anisyl-β-phenylpropionaldehyde[9] as well as cyclopentylacetaldehyde[10] has been suggested. An experimental test of the possible free-radical hydrogen migration hypothesis suggested in 3 is the subject of the present paper.

If 3-phenyl-1-butene is catalytically reduced with deuterium instead of hydrogen, the distribution of deuterium along the 2-butyl side chain of the product should give an indication of the relative importance of the possible alternative paths of hydrogenation in 4. Thus to the extent that no rearrangement of any sort occurs during reduction (4a), 2-phenylbutane-3,4-$H_2{}^2$ (VII) should be produced. Prior double bond migration to a conjugated olefin (4b) (Cram's hypothesis[2]) should lead to the formation of 2-phenylbutane-2,3-$H_2{}^2$ (VIII). If the presently postulated hydrogen-migration mechanism 3 intervenes (4c), the final product should contain 2-phenylbutane-2,4-$H_2{}^2$ (IX). It was hoped that by the catalytic reduction of 3-phenyl-1-butene with deuterium followed by a nuclear magnetic resonance (n.m.r.) spectral evaluation of the distribution of deuterium in the deuterated 2-phenylbutane reduction product, a quantitative estimate of the relative importance of reduction paths 4a, 4b and 4c could be made.

3-Phenyl-1-butene was subjected to catalytic reduction with deuterium using the catalysts indicated in Table I. The deuterated 2-phenylbutane products were isolated and purified by vapor–liquid partition chromatography, then examined for deuterium content and deuterium distribution by means of n.m.r. spectral experiments. The results of these studies are summarized in Table I.

In order to test for the possibility of hydrogen–deuterium exchange both prior to the reduction of 3-phenyl-1-butene and subsequent to its conversion of 2-phenylbutane, the following additional experiments were conducted. Authentic 2-phenylbutane and Pd–C catalyst were stirred in a deuterium atmosphere for 4.5 hours, duplicating the reduction conditions employed. The product was isolated and purified by vapor–liquid partition chromatography, then its n.m.r. spectrum was examined. No deuterium was found along the 2-butyl side chain in the product, but evidence of H–D exchange in the aromatic nucleus was noted in its infrared spectrum. Thus no aliphatic H–D exchange occurred in 2-phenylbutane under hydrogenation conditions, an observation which is in accord with Cram's failure to observe racemization of optically active 2-phenylbutane under similar conditions.[2] Similarly, 3-phenyl-1-butene was reduced to 50% completion using deuterium and Pd–C catalyst. The product was isolated and the unreacted olefin was recovered using vapor–liquid partition chromatography; n.m.r. spectral examination of the unreacted olefin indicated that H–D exchange had occurred at C1 of the olefin (corresponding to C4 in 2-phenylbutane). No detectible amount of H–D exchange was evident at any of the other aliphatic carbons in the side chain of the unreacted olefin.

TABLE I

DEUTERIUM CONTENT AND DISTRIBUTION IN 2-PHENYLBUTANE SAMPLES OBTAINED ON CATALYTIC REDUCTION OF 3-PHENYL-1-BUTENE WITH DEUTERIUM

		Total	Number of D-atoms per molecule located at				
Run	Catalyst	D-atoms per molecule	C1	C2	C3	C4	Phenyl nucleus
1	Pd–C	2.21	0.18	0.23	0.58	1.17	0.05
			(6.0)[a]	(23.0)	(29.0)	(39.0)	(1.0)
2	Pd–$CaCO_3$	2.19	0.21	0.07	0.55	1.36	0.00
			(7.0)	(7.0)	(27.5)	(45.3)	(0.0)
3	PtO_2	1.56	0.04	0.10	0.59	0.62	0.21
			(1.3)	(10.0)	(29.5)	(20.7)	(4.2)
4	Raney Ni	1.88	0.02	0.06	0.86	0.80	0.14
			(0.7)	(6.0)	(43.0)	(26.7)	(2.8)
5	Pd–C	2.15	0.14	0.18	0.54	1.22	0.07
			(4.7)	(18.0)	(27.0)	(40.7)	(1.4)

[a] The numbers in parentheses represent percentage of total possible deuterium located at each position; thus the first figure is $0.18/3 = 6.0\%$

It is obvious from examination of Table I that an important process during the catalytic reduction of 3-phenyl-1-butene with deuterium is H–D exchange at several sites along the aliphatic side chain. Such exchange has precluded our estimation, *via* appropriate simultaneous equations, of the relative importance of the simple reduction paths 4a, 4b and 4c postulated above.

The presence of deuterium at C1 in the deuterated 2-phenylbutane product (corresponding to C4 in

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[8] M. S. Kharasch, F. L. Lambert and W. H. Urry, *J. Org. Chem.*, **10**, 298 (1945).

[9] D. Y. Curtin and M. J. Hurwitz, THIS JOURNAL, **74**, 5381 (1952).

[10] F. J. Seubold, Jr., *ibid.*, **76**, 3732 (1954).

its olefinic precursor) indicates that H-D exchange occurs at this carbon either directly or by some alternative process other than those postulated in eq. 4, such exchange or hydrogen migration occurring *during* and not prior or subsequent to reduction. The presence of significant quantities of deuterium at the benzylic C2 position in the reduction product (C3 in the olefin precursor) is noteworthy in view of the absence of deuterium at this position in the "control" 2-phenylbutane and 3-phenyl-1-butene experiments described above. The occurrence of deuterium at C2 in the 2-phenylbutane product must accordingly arise *via* double-bond migration (4b), hydrogen migration (4c) or direct H-D exchange at the benzylic center *during* the reduction process. Our data do not permit a distinction between these alternatives. It should be emphasized that any of these alternatives could lead to racemization at this position in the case of optically active 3-phenyl-1-butene. The excessive quantities of deuterium noted in runs 1, 2 and 5 at C4 in the 2-phenylbutane product (C1 in the olefin precursor) are noteworthy. It is obvious that the combined paths in eq. 4 alone could never yield more than one D-atom per molecule at C4 of the product. The excess deuterium at C4 noted in runs 1,2,5 is probably best explained in terms of the apparent direct exchange of hydrogen and deuterium at C1 in unreacted 3-phenyl-1-butene, as observed in the "control" experiment with this olefin described above. The fact that H-D exchange has occurred in the aromatic nucleus in all of the 2-phenylbutane products (except no. 2) is perhaps in accord with the observations[11] that aromatic H-D exchange occurs more readily than aliphatic H-D exchange. Application of this generalization to the present reductions would suggest that the (comparable) occurrence of deuterium at C1 in the 2-phenylbutane products has arisen by some means other than direct exchange, possibly by hydrogen migration.

In the experiments (no. 3,4) employing PtO_2 and Raney nickel catalysts, significantly less than the theoretical two deuterium atoms per molecule were found in the 2-butyl side chain of the reduction products. The source of the "superfluous" hydrogen in the side chain of these products is unknown. It appears possible that hydrogen might have entered into the picture from the ethanol solvent *via* the reaction

$$CH_3CH_2OH \xrightarrow{\text{catalyst}} CH_3CH{=}O + H_2, \qquad (5)$$

a process which, in the case of Raney nickel at least,[12] has been well documented. Experiments to test this hypothesis, employing as solvent CH_3CD_2OD, are currently contemplated.

It is noteworthy that the Pd-C catalyst (runs 1 and 5) which yielded the maximum deuterium content at the benzylic C2 position in the 2-phenylbutane product also showed the greatest racemization ability[2,3] during hydrogenation of optically active 3-phenyl-1-butene.

Experimental

3-Phenyl-1-butanol.—4-Methyl-4-phenyl-1,3-dioxane was prepared by the sulfuric acid-catalyzed condensation of formaldehyde with α-methylstyrene after the procedure of Shortridge.[13] The distilled product (44 g.), b.p. 90-96° (1 mm.), $n^{25}\mathrm{D}$ 1.5244, m.p. 34.5-36°,[14] was heated with ethanol (50 ml.) and copper-chromium oxide catalyst[15] (3.4 g.) and the mixture was hydrogenated at 225° and 1250-1700 p.s.i. for 72 hours after the method of Emerson.[14a] The crude product, 36 g. (98%), was distilled yielding 33.2 g. of 3-phenyl-1-butanol having b.p. 66-69° (1 mm.) and $n^{26}\mathrm{D}$ 1.5145.[16]

3-Phenyl-1-butene.—The above 3-phenyl-1-butanol was converted to 3-phenyl-1-butyl bromide by the action of phosphorus tribromide, after the method of Rupe and van Walraven.[17] The distilled bromide, b.p. 65-70° (0.8 mm.), $n^{20}\mathrm{D}$ 1.5329,[4] was converted to dimethyl-(3-phenyl-1-butyl)-amine, and the latter to its N-oxide by the procedure of Cram.[16] The general method of Cram[16] was utilized for the pyrolytic conversion of the above dimethyl-(3-phenyl-1-butyl)-amine oxide into 3-phenyl-1-butene. The pyrolysis was conducted in a Claisen flask under 5 mm. nitrogen atmosphere, heating the flask gradually from 90 to 140° and collecting the crude olefin product in a Dry Ice trap. The condensate was extracted into pentane and the extract was washed with dilute hydrochloric acid, then dilute sodium hydroxide solution and water. The pentane extract was dried, stripped of solvent and the residue was distilled, collecting the fraction of b.p. 65-67° (17 mm.), $n^{26}\mathrm{D}$ 1.5050.[16] The infrared spectrum of the distilled 3-phenyl-1-butene product was identical with that recorded in the literature,[16] and analysis by vapor-liquid partition chromatography showed only a single component.

Catalytic Hydrogenation of 3-Phenyl-1-butene.—Typical reduction conditions and product isolation are illustrated in the following example. 3-Phenyl-1-butene (1.00 g.), Raney nickel catalyst (*ca.* 0.5 g.) and absolute ethanol (15 ml.) were placed in a magnetically-stirred buret hydrogenator, which was then purged 4 times with helium and filled with hydrogen. Stirring was started, and 99.2% of the theoretical hydrogen uptake was noted in 2.5 hours. The catalyst was filtered and washed twice with ethanol and the filtrates were added to water (75 ml.). The mixture was extracted 4 times with 20-ml. portions of pentane and the extracts were dried over sodium sulfate, filtered and stripped of solvent. The crude residual 2-phenylbutane weighed 0.92 g. (90.5%) and had $n^{26}\mathrm{D}$ 1.4821. It was purified by successive injections onto a 0.375 × 60 inch stainless steel vapor-liquid partition chromatographic column filled with Ucon Polar packing[18] and operated at 171° with helium at 3 p.s.i. as carrier gas. When pure 2-phenylbutane, prepared by the method of Huston and Kaye,[19] was injected onto the column under identical conditions, a single product peak was noted at 7.6 minutes. When the above hydrogenation product was similarly treated an initial small peak was observed at 5.8 minutes, followed by the major peak at 7.6 minutes. The product corresponding to the latter peak was collected by chilling the exit helium stream from the column in a Dry Ice trap. Successive injections of the crude hydrogenation product onto the column afforded sufficient purified 2-phenylbutane for the n.m.r. studies below. Its infrared spectrum was identical with that of the above authentic sample.

Catalytic Reduction of 3-Phenyl-1-butene with Deuterium.—Five reduction experiments were conducted using four different catalyst samples, employing 99.5% deuterium in place of hydrogen. In all runs 1.00 g. of the above 3-phenyl-1-butene was reduced, the reaction was allowed to proceed until a constant uptake volume prevailed in the system and the product was isolated and purified by vapor-liquid partition chromatography as described above. Yield data for these experiments are given in Table II. The infra-

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[11] T. I. Taylor, P. H. Emmett "Catalysis," Reinhold Publishing Corp., New York, N. Y., 1957, p. 267.

[12] W. A. Bonner, THIS JOURNAL, **74**, 1033 (1952); W. Reeves and H. Adkins, *ibid.*, **62**, 2874 (1940); E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

[13] R. W. Shortridge, THIS JOURNAL, **70**, 873 (1948).

[14] (a) W. S. Emerson, R. L. Heider, R. I. Longley, Jr., and T. C. Shafer, *ibid.*, **72**, 5314 (1950); (b) C. C. Price, F. L. Benton and C. J. Schmidle, *ibid.*, **71**, 2860 (1949).

[15] T. W. Riener, *ibid.*, **71**, 1130 (1949).

[16] D. J. Cram, *ibid.*, **74**, 2137 (1952).

[17] H. Rupe and F. van Walravren, *Helv. Chim. Acta*, **13**, 369 (1930).

[18] Wilkens Instrument and Research Corp.

[19] R. C. Huston and I. A. Kaye, THIS JOURNAL, **64**, 1576 (1942).

TABLE II

YIELDS DURING CATALYTIC REDUCTION OF 3-PHENYL-1-BUTENE WITH DEUTERIUM

Run	Catalyst (g.)	Reaction time, hr.	Deuterium uptake, %	Crude product G.	yield %
1	Pd-C (0.70)	6.5	99	0.81	78.6
2	Pd-$CaCO_3$ (1.00)	5.0	98	.83	80.5
3	PtO_2 (0.025)	4.5	99	.94	91.3
4	Raney Ni (0.5)	5.5	98	1.02	99.0
5	Pd-C (0.93)	4.5	98	0.94	91.3

red spectra of the purified deuterated 2-phenylbutane products from the reductions in Table II were similar to that of authentic 2-phenylbutane, except for additional absorption bands at 4.6 and 8.2 μ for aliphatic and aromatic C–D bonds.

Hydrogen–Deuterium Exchange in 3-Phenyl-1-butene.—To investigate the possibility of H–D exchange in 3-phenyl-1-butene *prior* to its reduction in the experiments in Table II, the following experiment was conducted. A mixture of 1.00 g. of 3-phenyl-1-butene, 1.0 g. of Pd–C catalyst and 15 ml. of absolute ethanol was catalytically reduced as described above up to the point of approximately 50% of the theoretical deuterium uptake. The catalyst was filtered and the partially reduced product was isolated as described above.

Into a 0.25 × 180-inch vapor–liquid partition chromatographic column packed with crushed firebrick (9 parts) impregnated with isosorbide dipelargonate (1 part) and operated at 125° with helium at 15 p.s.i. as carrier gas was injected 0.05 ml. of a 60–40% mixture, respectively, of authentic samples of 3-phenyl-1-butene and 2-phenylbutane. After 40.0 minutes a smaller peak corresponding to 2-phenylbutane appeared, and after 45.6 minutes the well-resolved, larger peak due to 3-phenyl-1-butene was noted. Successive portions of the above partially deuterated 3-phenyl-1-butene were next injected onto the column under identical conditions, when the reduction product appeared at 40.8 minutes and the unreduced olefin at 45.5 minutes. The latter product was collected by chilling the exit helium stream until sufficient unreacted olefin was available for n.m.r. studies.

Hydrogen–Deuterium Exchange in 2-Phenylbutane.—In order to investigate possible H–D exchange in the deuterated 2-phenylbutane produced on reduction of 3-phenyl-1-butene, the following experiment was undertaken. Authentic 2-phenylbutane (1.00 g.), Pd–C catalyst (1.00 g.) and ethanol (15 ml.) were mixed and stirred under a deuterium atmosphere in the buret hydrogenator. After 4.5 hours, stirring was stopped and the product was isolated as previously described, then purified as before on the Ucon Polar vapor–liquid partition chromatographic column. The purified 2-phenylbutane was investigated by n.m.r. as described below.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra of the samples from the above experiments, leading ultimately to an estimate of the number of deuterium atoms at each of the chain-carbons and in the aromatic ring of the deuterated 2-phenylbutane products, were measured on an n.m.r. spectrometer at Varian Associates of Palo Alto, Calif., using a Hewlett-Packard integrating voltmeter to measure the area under each n.m.r. proton peak.[20] From the latter integrated voltages it was readily possible to determine separately the number of hydrogen and (by difference) deuterium atoms in the phenyl ring and the aliphatic chain of each deuterated 2-phenylbutane sample. The average deviation in the integrated voltages observed during successive measurements in individual homogeneous samples, and hence the hydrogen and deuterium contents calculated therefrom, was in the neighborhood of ±0.5% or less. The numbers of hydrogen and deuterium atoms in various portions of the molecule in each deuterated sample are given in Table III. The number legend is the same as that of Tables I and II.

TABLE III

HYDROGEN AND DEUTERIUM CONTENT IN VARIOUS PORTIONS OF THE MOLECULE IN DEUTERATED 2-PHENYLBUTANE SAMPLES

Run	Number of hydrogen atoms Total	Nucleus	Chain	Number of deuterium atoms Total	Nucleus	Chain
1	11.79	4.95	6.84	2.21	0.05	2.16
2	11.81	5.00	6.81	2.19	.00	2.19
3	12.44	4.79	7.65	1.56	.21	1.35
4	12.12	4.86	7.26	1.88	.14	1.74
5	11.85	4.93	6.92	2.15	.07	2.08

TABLE IV

HYDROGEN ATOMS AT VARIOUS ALIPHATIC CHAIN CARBONS IN DEUTERATED 2-PHENYLBUTANE SAMPLES

Run	No. of H atoms, total in chain	C1	No. of H atoms at C2	C3	C4
1	6.84	2.82	0.77	1.42	1.84
2	6.81	2.79	.93	1.45	1.64
3	7.65	2.96	.90	1.41	2.38
4	7.26	2.98	.94	1.14	2.20
5	6.92	2.86	.82	1.46	1.78

In another set of n.m.r. experiments the spectra of the products in Table II were measured in carbon tetrachloride solution. Here the integrated areas under each of the proton peaks for the various types of chain protons was measured from the integration curve using calipers. Knowing the total number of protons in the aliphatic side chain of each sample (Table III), the number of protons at each individual carbon atom could then be calculated by a simple proportion. The number of protons at each chain carbon atom for the samples in Table III are shown in Table IV. The deuterium values at each chain carbon in the various products (Table I) are obtained from the data in Table IV by difference.

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[20] We are particularly indebted to Drs. James Shoolery, Larry Piette and L. F. Johnson for their invaluable aid in measuring and helping to interpret our n.m.r. spectra.