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Racemization of Phenylalkanes in Presence of Lewis Acids

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Optically active 2-phenylbutane racemizes rapidly and completely in the presence of aluminum chloride at 0°C. at which temperature there is little disproportionation to *m*- and *p*-di-*sec*-butylbenzene. Racemization appears to be due to formation of the 2-phenyl-2-butylcarbonium ion followed by transfer of a hydride ion from a 2-phenylbutane molecule in a chain reaction, since in the presence of α,β-dideuterocumene, substantial amounts of deuterium are transferred to the 2-phenylbutane. Optically active α-deuteroethylbenzene is not completely racemized under much more drastic conditions.

Burwell and Shields[2] have recently reported on the racemization of 2-phenylpentane in the presence of aluminum chloride. In the course of an investigation which was nearly complete when we learned of the prior work of Burwell and Shields we have confirmed and extended certain observations of these authors using 2-phenylbutane and α-deuteroethylbenzene as substrates.

When active 2-phenylbutane was heated with aluminum chloride at 100°, it was extensively disproportionated to benzene and a dialkylbenzene fraction which proved to be a mixture of the *meta* and *para* isomers. The recovered starting material was completely racemized. *A priori*, two mechanisms might be suggested for the racemization; one (a) in which the alkyl group comes off as a carbonium ion and then returns and another (b) involving a hydride transfer chain from an alkylbenzene to an aralkyl carbonium ion:[3a]

$$\begin{aligned}&d\text{-}C_6H_5CH(CH_3)C_2H_5 + AlCl_3 + HCl \longrightarrow \\ &\qquad C_6H_6 + dl\text{-}CH_3C^+HC_2H_5 + AlCl_4^- \longrightarrow \\ &\qquad\qquad dl\text{-}C_6H_5CH(CH_3)C_2H_5 + AlCl_3 + HCl \quad \text{(a)}\end{aligned}$$

$$\begin{aligned}&d\text{-}C_6H_5CH(CH_3)C_2H_5 + AlCl_3 + HCl \longrightarrow \\ &\qquad dl\text{-}C_6H_5C^+(CH_3)C_2H_5 + AlCl_4^- + H_2 \\ &dl\text{-}C_6H_5C^+(CH_3)C_2H_5 + d\text{-}C_6H_5CH(CH_3)C_2H_5 \longrightarrow \\ &\qquad dl\text{-}C_6H_5CH(CH_3)C_6H_5 + dl\text{-}C_6H_5C^+(CH_3)C_2H_5 \quad \text{(b)}\end{aligned}$$

Burwell and Shields[2] have already pointed out (for the case of 2-phenylpentane) that mechanism (b) is more likely since racemization takes place under conditions where transalkylation (which may involve the 2-pentylcarbonium ion[3b]) is almost inoperative. In the case of 2-phenylbutane, complete racemization occurs with aluminum chloride in 12 hr. at room temperature and even in 2 hr. at ice-bath temperature, though in the latter case the yield of transalkylation product is reduced to 9%.

A more compelling argument for mechanism (b) was obtained from a treatment of equimolar amounts of 2-phenylbutane and α,β-dideuterocumene with aluminum chloride at ice-bath temperature. The recovered 2-phenylbutane contained 0.28 atom of deuterium per molecule as indicated by mass spectrometry. Statistical distribution of the α-deuterium and α-hydrogen atoms among the cumene and 2-phenylbutane molecules should have given 2-phenylbutane containing 0.50 atom of

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[1] Peter C. Reilly Fellow, 1952–53; Socony Vacuum Fellow, 1953–54. This work is taken in part from the Ph.D. dissertation of P. H. W. and was presented before the Organic Division of the American Chemical Society at Minneapolis, Minnesota, on September 14, 1955.

[2] R. L. Burwell, Jr., and A. D. Shields, *J. Am. Chem. Soc.*, **77**, 2766 (1955).

[3] (a) The initiation step in mechanism (b) is not definitive; several reasonable alternatives exist. The inclusion of HCl in the initiation steps requires comment: no hydrochloric acid was added to the reaction mixture, but the formation of traces of this reagent due to adventitious moisture is quite likely. (b) This point is arguable in the case of a secondary alkyl group; *cf.* D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **75**, 2411 (1953); H. C. Brown and C. R. Smoot, *Ibid.*, **78**, 2176 (1956); H. C. Brown and H. Jungk, *Ibid.*, **78**, 2182 (1956). However, even if the transalkylation is an S_N2 reaction, a version of mechanism (a) can be written which will lead to racemization: $2d\text{-}C_6H_5R^* \rightarrow meso\text{-}C_6H_4R_2^* + C_6H_6 \rightleftarrows 2dl\text{-}C_6H_5R^*$ where R* is an asymmetric alkyl group such as 2-butyl.

deuterium; the discrepancy is undoubtedly due to the fact, evident from mass spectrum and elementary deuterium analysis, that the α,β-dideuterocumene used in this investigation was not isotopically pure.

When optically active α-deuteroethylbenzene[4] was heated with aluminum chloride at 65–70° for several hours, the recovered starting material still retained one third of its original activity.[5] This fact is consistent with mechanism (b) [though it does not exclude (a)], since a hydride transfer reaction involving the secondary α-phenethyl carbonium ion:

$$dl\text{-}C_6H_5C^+DCH_3 + d\text{-}C_6H_5CHDCH_3 \longrightarrow dl\text{-}C_6H_5CHDCH_3 + dl\text{-}C_6H_5C^+DCH_3 \quad \text{(c)}$$

should involve higher activation energy than the corresponding reaction [Equation (b)] involving the tertiary 2-phenylbutyl carbonium ion.[6]

One of our experiments involving racemization of 2-phenylbutane was carried out under conditions identical with those used[7] in the alkylation of benzene with optically active butanol-2 in the presence of aluminum chloride. The fact that 2-phenylbutane racemizes totally under these conditions while it does not racemize extensively in the presence of boron trifluoride[8] may explain why Price and Lund obtained slightly active material in the alkylation of benzene with active butanol-2 in the presence of boron trifluoride but not with aluminum chloride which yielded totally racemized product.[7]

It is of interest that although 2-phenylbutane is racemized rapidly by aluminum chloride, we have found that it can be acetylated to give an optically active product with acetyl chloride in the presence of aluminum chloride. The same is true of 2-phenylpentane[9] and of α-deuteroethylbenzene.[4] Probably the acetyl chloride as well as the ketone formed in the acylation complexes with the catalyst in such a way as to make it ineffective for the promotion of reaction sequence (b).

A few improvements were made in the synthesis of active 2-phenylbutyric acid required as an intermediate for active 2-phenylbutane. The reaction sequence employed was the following:

$$PhCH_2CH_3 \longrightarrow PhCHBrCH_3 \longrightarrow PhCH(CH_3)CH(CO_2Et)_2 \longrightarrow PhCH(CH_3)CH(CO_2H)_2 \longrightarrow PhCH(CH_3)CH_2CO_2H$$

Ethylbenzene was brominated photochemically in 81% yield employing carbon tetrachloride as a solvent. Alkylation of malonic ester with the bromide was effected in 82% yield by using sodium hydride as the base and a mixture of benzene and dimethylformamide as solvent.[10] Decarboxylation of the malonic acid was effected conveniently in boiling 2,6-lutidine. In the resolution of β-phenylbutyric acid (best effected by means of α-phenethylamine) it was found convenient to let the racemate crystallize from a petroleum ether solution of the partly resolved material. This increased the optical purity of the acid from 56 to 76%.

EXPERIMENTAL[11]

α-Phenethylmalonic ester. A suspension of 26 g. (1.13 g. atom) of sodium hydride in 800 ml. of sodium-dried benzene and 300 ml. of pure dimethylformamide (technical material was azeotropically distilled with benzene, b.p. 150–150.5°) in a three-necked flask equipped with stirrer, reflux condenser and dropping funnels, was cooled to 5–10° under a slow stream of nitrogen. Ethyl malonate (180 ml., 190 g., 1.19 mole) diluted with its own volume of benzene, was added at such a rate that hydrogen was evolved gently. After the solution had become homogeneous, 201 g. (1.08 mole) of α-phenethyl bromide[12] was added and the temperature gradually raised to 75–80° and maintained there for 2 hr. by the application of a hot water bath. The mixture was then cooled, washed with water in a separatory funnel, and the water layer twice extracted with benzene. The combined benzene layers were washed twice with dilute hydrochloric acid, once with water, once with 10% aqueous sodium carbonate, and again with water, dried over sodium sulfate, concentrated, and the residue distilled at reduced pressure. The product boiling at 131–133°/0.8 mm. (lit.[13] 138°/1.5 mm.) weighed 234.1 g. (82%).

β-Phenylbutyric acid. The above ester (132 g., 0.5 mole) was boiled under reflux for 1 hr. with a solution of 118 g. (2 moles) of potassium hydroxide in one liter of 95% ethanol. The alcohol was then distilled on a steam bath and replaced by water, 250 ml. of water being added each time 250 ml. of distillate had been collected until the total distillate amounted to almost one liter. The aqueous solution was then poured into an excess (4–5 moles) of concentrated hydrochloric acid[14] and the α-phenethylmalonic acid which precipitated was collected and dried, m.p. 142–143° (lit.[13] 142–143°); yields as high as 92% were obtained.

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[4] E. L. Eliel, *J. Am. Chem. Soc.*, **71**, 3970 (1949).

[5] The diethylbenzene fraction isolated from this experiment was inactive. We are continuing the study of the optical course of the Friedel-Crafts transalkylation as well as the rearrangement reaction.

[6] Only hydride transfer is shown in equation (c) for the sake of clarity. A lesser amount of deuteride transfer is, of course, an alternative possibility and would also lead to racemization. The formation of light ethylbenzene and ethylbenzene-α,α-d_2 in the disproportionation is to be expected.

[7] C. C. Price and M. Lund, *J. Am. Chem. Soc.*, **62**, 3105 (1940).

[8] R. L. Burwell, Jr., L. M. Elkin, and A. D. Shields, *J. Am. Chem. Soc.*, **74**, 4570 (1952).

[9] D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2152 (1952). Complete absence of racemization in the acetylation step was demonstrated in this case.

[10] This excellent technique was first described by A. W. Burgstahler, Ph.D. dissertation, Harvard University, 1953.

[11] All melting and boiling points are uncorrected. Mass spectrometric analyses were carried out by Mr. George Young on a Consolidated 21-103A Analytical Mass Spectrometer, employing an ionization potential of 70 volts. Infrared spectra were recorded by Anthony Verbiscar and Rolland Ro on a Baird double-beam instrument.

[12] Prepared in 81% yield by brominating ethylbenzene (159 g.) in 300 ml. carbon tetrachloride by the addition of 240 g. bromine in 150 ml. carbon tetrachloride under illumination with a 1000-watt unfrosted tungsten projector lamp.

[13] E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937).

[14] Addition of the acid to the aqueous solution may lead to precipitation of the monopotassium salt.

The malonic acid (170 g.) was boiled with 250 ml. of 2,6-lutidine[15] for 2 hr., the solution was cooled and poured into an excess of 20% hydrochloric acid, and the aqueous emulsion was extracted four times with ether. The combined ether layers were extracted four times with dilute hydrochloric acid, then with water, dried over sodium sulfate, and concentrated. 3-Phenylbutyric acid boiled at 118–119°/0.8 mm. (lit.[13] 140–141°/2 mm.); n_D^{25} 1.5140 and crystallized to a solid melting at 35–36° (lit.[16] 39–40°). The yield in several preparations varied from 87 to 91%. With thermal decarboxylation[13] the yield was only 71%.

Partial resolution of β-phenylbutyric acid. To a solution of 141.6 g. (0.86 mole) of β-phenylbutyric acid in 385 ml. of ethanol and 412 ml. of water was added 104.1 g. (0.86 mole) of (+)-α-phenethylamine.[17] An exothermic reaction ensued and within 5 min. needle-shaped crystals began to separate. Crystallization was allowed to proceed undisturbed and the amine salt (114.7 g.) was collected; m.p. 138–141°. No attempt was made to purify the salt, since optically pure materials were not needed in the present work. The mother liquor from this salt became cloudy during filtration and was heated to produce a clear solution which deposited crystals (40.0 g., m.p. 127–129.5°) on standing in the refrigerator. The crystals were removed and the resulting solution was evaporated almost to dryness and cooled, whereupon a third crop of crystals separated and was collected, weight 97.5 g., m.p. 119–121°.

The various crops of amine salts were separately dissolved in warm methanol and the solution was poured into an excess of dilute hydrochloric acid. The free β-phenylbutyric acid separated as an oil and was extracted with three portions of ether which were then combined and washed once with dilute hydrochloric acid and once with water, dried over sodium sulfate, and concentrated and distilled at reduced pressure. The following fractions of resolved acid were thus obtained:

From Fraction	Wt. (G.)	%	B.P./0.8 Mm.	n_D^{25}	α_D^{25} (l = 1 Dm., Neat)
I	50	35	115–117°	1.5140	−32.42°
II	17.3	12.2	115–117°	1.5135	+ 1.31°
III	46.2	33	115–117°	1.5140	+35.38°

Since the rotation of the pure acid is 56.5°,[20] fraction I was 57% optically pure and fraction III was 62.5% optically pure. The optical purity could be increased as follows: Ten g. of acid, α_D^{25} −32.42° was dissolved in 20 ml. of Skellysolve B. The solution was chilled to 0° and seeded with a crystal of the *dl* acid. After 24 hr., the bottom of the flask was covered with crystals. The solution was decanted and concentrated. The residue had α_D^{25} −43.06° (l = 1 dm., neat) corresponding to 76% optical purity.

Addition of base to the acidic aqueous layer obtained in the decomposition of the diasteroisomeric salt led to recovery of most of the α-phenethylamine used in the resolution.

Active 2-phenylbutane. The active β-phenylbutyric acid was reduced to 3-phenylbutanol in 80% yield by means of lithium aluminum hydride.[20] The alcohol had b.p. 132.5–135°/18–19 mm., n_D^{25} 1.5184; lit.[20] b.p. 138–140°/33 mm., n_D^{25} 1.5186. Conversion of this alcohol to the bromide by means of phosphorus tribromide[21] was effected in 80–84% yield and the product boiled at 134–135°/26 mm., n_D^{25} 1.5350; lit.[20] n_D^{25} 1.5350.

The reduction of 21.1 g. (0.1 mole) of the bromide by means of 0.5 g. (0.013 mole) of lithium aluminum hydride and 1.2 g. (0.15 mole) of lithium hydride in 50 ml. of tetrahydrofuran was effected in the usual way,[22] reflux time 4 hr. The reaction mixture was worked up in the usual way with the inclusion of a phosphoric acid wash to remove any residual tetrahydrofuran[4] and the product was obtained in 86–89% yield, b.p. 168–170°, n_D^{25} 1.4870 (lit.[23] n_D^{25} 1.4863–1.4880; b.p. 172.5°). The infrared spectrum of the material so obtained was identical with that reported in the literature.[24]

In this series of transformations, β-phenylbutyric acid of α_D^{25} +25.28° (l = 1 dm., neat) gave 2-phenylbutane of α_D^{25} +21.83° (l = 2 dm., neat). The ratio of the observed rotation of product (corrected to a 1-dm. tube) to that of starting material is 0.43, exactly the same as that reported in the literature[20] for very slightly different temperatures.

p-sec. Butylacetophenone. This was prepared in 90% yield by the Perrier modification of the Friedel-Crafts Reaction[25] and boiled at 142–143°/17 mm., n_D^{20} 1.5195, n_D^{25} 1.5178; lit.[26] b.p. 134–135°/11 mm., n_D^{20} 1.5195. The 2,4-dinitrophenylhydrazone melted at 145.5–147°; lit.[27] 146–147°. Optically active 2-phenylbutane of α_D^{25} +21.83° (l = 2 dm., neat) gave ketone having α_D^{25} −15.73° (l = 1 dm., neat).

Cumene-α,β-d₂. The catalytic reduction of α-methylstyrene with deuterium was carried out in a low-pressure apparatus made by the Parr Instrument Co. of Moline, Ill. The tank was flushed thoroughly with nitrogen before the admission of deuterium gas.

A solution of 23.6 g. (0.200 mole) of freshly distilled α-methylstyrene, b.p. 62.6–62.9° (19 mm.), in 150 ml. of absolute ethanol was first reduced in the presence of 0.40 g. of platinum oxide catalyst at 24.4° and an initial deuterium pressure of 26.9 lb. The calculated amount of deuterium was absorbed within 10 min.

A second portion of 35.5 g. (0.300 mole) of the same unsaturated compound in 150 ml. of ethanol was then reduced in the presence of 0.50 g. of catalyst at 25.0° and an initial deuterium pressure of 34.8 lb. The absorption took 17 min.

The reduction mixtures were filtered in the usual manner. The combined ethanolic filtrates were poured into 1.5 l. of water and the aqueous mixture was extracted twice with pentane. The pentane solution was washed with water and 20% calcium chloride solution, dried over anhydrous calcium chloride, and then fractionated through a 20-cm. glass helices-packed column to give 51.7 g. (84.6%) of cumene-α,β-d_2, b.p. 150.0–151.5° (747 mm.), n_D^{20} 1.4902. (Pure cumene has b.p. 152.4/760 mm. and n_D^{20} 1.4915.[23])

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[15] We are indebted to Dr. Frank Cislak of the Reilly Tar and Chemical Corp. for a generous gift of 2,6-lutidine.

[16] H. Rupe, *Ann.*, **369**, 323 (1909).

[17] The amine was resolved by means of pyroglutamic acid[18] which, in turn, was prepared by pyrolysis of commercial glutamic acid.[19] Since this work was completed, a very convenient method for the resolution of α-phenethylamine with D-tartaric acid has been published: W. Theilacker and H. G. Winkler, *Ber.*, **87**, 690 (1954).

[18] R. J. Dearborn and J. A. Stekol, U. S. Patent **2,528,267** (1950); *C. A.*, **45**, 2984d (1951).

[19] G. Braun, U. S. Patent **2,112,329** (1938); *C. A.*, **32**, 3773 (1938).

[20] D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952).

[21] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **108**, 413 (1935).

[22] J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 3664 (1948).

[23] G. Egloff, *Physical Constants of Hydrocarbons*, Vol. III, Reinhold, New York, N. Y., 1946.

[24] N.R.L. Report No. C-3274 of the Navy Research Laboratory, Washington, D. C., pp. 84–85.

[25] D. T. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

[26] G. F. Hennion and S. F. de C. McLeese, *J. Am. Chem. Soc.*, **64**, 2421 (1942).

[27] D. V. Nightingale, H. B. Hucker, and O. L. Wright, *J. Org. Chem.*, **18**, 244 (1953).

Anal. C_9H_{12}, 24.3, 24.1%; $C_9H_{11}D$, 39.4, 40.0%; $C_9H_{10}D_2$, 24.8, 25.1%; $C_9H_9D_3$, 6.9, 6.8%; $C_9H_8D_4$, 2.8, 2.7%; $C_9H_7D_5$, 1.2, 1.0%; $C_9H_6D_6$, 0.5, 0.2%; $C_9H_5D_7$, 0.0, 0.1%. This composition, determined by mass spectrometry at reduced ionizing voltage,[28] corresponds to a deuterium content of 10.8 (first analysis) or 10.7 (second analysis) atom %; found 10.6%.[29]

Treatment of active 2-phenylbutane with aluminum chloride. 2-Phenylbutane (40.5 g.), α_D^{25} +1.53° (l = 1 dm., neat) was placed in a 125-ml. three-necked flask equipped with a sealed stirrer and an outlet protected by a drying tube and cooled in an ice bath for 30 min. Eight g. of aluminum chloride was then added and the suspension stirred for 2 hr. at ice bath temperature. The mixture was then poured onto 100 g. of ice and 20 ml. of concentrated hydrochloric acid and the organic layer was separated, dried over calcium chloride and fractionated. There was recovered 28.8 g. (71%) of 2-phenylbutane, b.p. 55–57°/11 mm., n_D^{25} 1.4870. The material was collected in two fractions which had the same refractive index. The rotation of the first fraction was found to be 0.00°. Higher boiling material (b.p. 105–108°/11 mm., n_D^{25} 1.4848) weighed 2.6 g. (9% calculated as *di-sec.* butylbenzene).

When the reaction was carried out at ice bath temperature as above, followed by standing at room temperature for 12 hr., inactive material was again obtained. Recovered starting material, b.p. 54–56°/11 mm., n_D^{25} 1.4870 weighed 19.0 g. (47%). There was also obtained 7.9 g. (28%) of material boiling at 102–108°/11 mm., n_D^{25} 1.4842. The infrared spectrum of the lower-boiling fraction was identical with that of the starting material.

In a reaction of 80 g. (0.6 mole) of 2-phenylbutane, α_D^{25} +2.16° (l = 1 dm., neat) with 16 g. of aluminum chloride at 100° for 3 hr. there was obtained 10.6 g. (23%) of benzene, b.p. 78–81°, n_D^{25} 1.4925 (lit. b.p. 80°, n_D^{25} 1.4981), 29.7 g. (37%) of recovered 2-phenylbutane, b.p. 53–60°/11 mm., n_D^{25} 1.4862–1.4866, α_D^{25} (of various fractions) 0.00–0.02° (l = 1 dm., neat) and 16.8 g. (30% calculated as di-*sec.* butylbenzene) of fractions boiling from 102–114°/11 mm., n_D^{25} 1.4840–1.4848, n_D^{25} 0.00–0.02°.

The low-boiling fraction was identified as benzene by the preparation of *m*-dinitrobenzene, m.p. 90–91° (lit. 90°). The intermediate fractions had infrared spectra almost identical to that of 2-phenylbutane but showing slight contamination which manifested itself especially in a strong band at 13.6 μ. The high-boiling fractions were probably mixtures of *m*- and *p-di-sec.*butylbenzene as evidenced by the infrared spectrum (band at 12.1 μ due to *p*-isomer, bands at 12.7 and 14.2 μ due to *m*-isomer[30]) and the fact that permanganate oxidation followed by esterification with diazomethane gave a mixture of esters from which dimethyl terephthalate, m.p. 138–141° (lit. 140°) undepressed by admixture of an authentic specimen, was isolated.

Treatment of an equimolar mixture of 2-phenylbutane and cumene-α,β-d₂ with aluminum chloride.[31] A mixture of 20.13 g. (0.15 mole) of *dl*-2-phenylbutane and 18.33 g. (0.15 mole) of cumene-α,β-d_2 was stirred with 5.00 g. of anhydrous aluminum chloride at ice-bath temperature for 2 hr. and then poured onto ice and hydrochloric acid. The aqueous acidic mixture was extracted three times with pentane. The combined pentane extracts were washed with water, dried over calcium chloride, freed of solvent, and then distilled through a 20-cm. glass helices-packed column. A fraction boiling at 170.0–172.6 (746 mm.) n_D^{20} 1.4894 was considered as recovered 2-phenylbutane and analyzed by mass spectrometry at reduced ionizing voltage.[28]

Anal: $C_{10}H_{14}$, 73.0, 73.3%; $C_{10}H_{13}D$, 25.2, 25.2%; $C_{10}H_{12}D_2$, 1.8, 1.5%.[32]

Disproportionation of (+)-ethylbenzene-α-d with aluminum chloride. A mixture of 7.7 g. (0.072 mole) of (+)-ethylbenzene-α-d,[4] α_D^{25} +0.49 ± 0.01°, and 1.8 g. of anhydrous aluminum chloride (Baker and Adamson, reagent grade) was stirred at room temperature for 15 min. and then heated up to and maintained at 65–70° while a reduced pressure of 100 mm. was applied to the system. The benzene thus distilled out and collected in a cold trap weighed 0.83 g. (0.0106 mole). The dark brown reaction mixture was allowed to cool at the end of 1 hr. and then poured onto crushed ice. The aqueous mixture was extracted with one 50-ml. and two 25-ml. portions of ether. The combined ethereal extract was washed with water, dried over sodium sulfate, freed of the solvent, and then fractionated to give 1.23 g. (0.0115 mole) of ethylbenzene-α-d, b.p. 59–60° (50 mm.), and 1.79 g. (0.0131 mole) of deuterated diethylbenzenes, b.p. 96–97° (50 mm.). The mixture of diethylbenzenes was optically inactive, α_D = 0.00 ± 0.02°, whereas a solution of one volume of the recovered ethylbenzene in two volumes of pentane had a rotation of α_D = +0.05 ± 0.01° (1-dm. tube). A similar solution of the original ethylbenzene-α-d in pentane had α_D = +0.16 ± 0.01°.

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(28) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

(29) Hydrogen-deuterium exchange with the solvent as well as with the cumene and α-methylstyrene presumably accounts for the undeuterated, monodeuterated, and polydeuterated material; *cf.* E. L. McDaniel and H. A. Smith, *Advances in Catalysis*, Vol. IX, Academic Press, New York, N. Y., in press and R. L. Burwell, Jr., and A. B. Littlewood, *J. Am. Chem. Soc.*, **78**, 4170 (1956).

(30) *cf.* G. F. Hennion, A. J. Driesch, and P. L. Dee, *J. Org. Chem.*, **17**, 1102 (1952).

(31) We thank Professor C. C. Price for suggesting this experiment.

(32) The value for the di-deuterated material, though small, appears to be real and suggests a small amount of exchange at a position other than the *alpha*-position in the side-chain—probably in the aromatic ring.