Isotopic Rearrangement of 2-Phenyl-2-^{14}C-butane. Relationship to Other Lewis Acid Catalyzed Reactions of *sec*-Alkylbenzenes[1]

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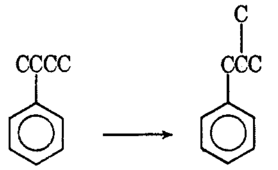
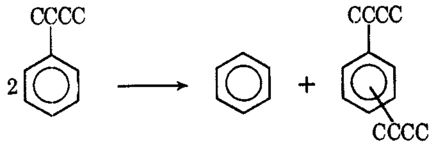
The surprising rearrangement of *sec*-butylbenzene to isobutylbenzene, induced by heating with aluminum chloride at 80 to 100°, was reported in 1959.[2] Disproportionation (transalkylation) of *sec*-butylbenzene takes place at lower temperatures (*e.g.*, 25°, $AlCl_3$[2a] or $HF + BF_3$ catalyst[3]) without side-chain rearrangement.

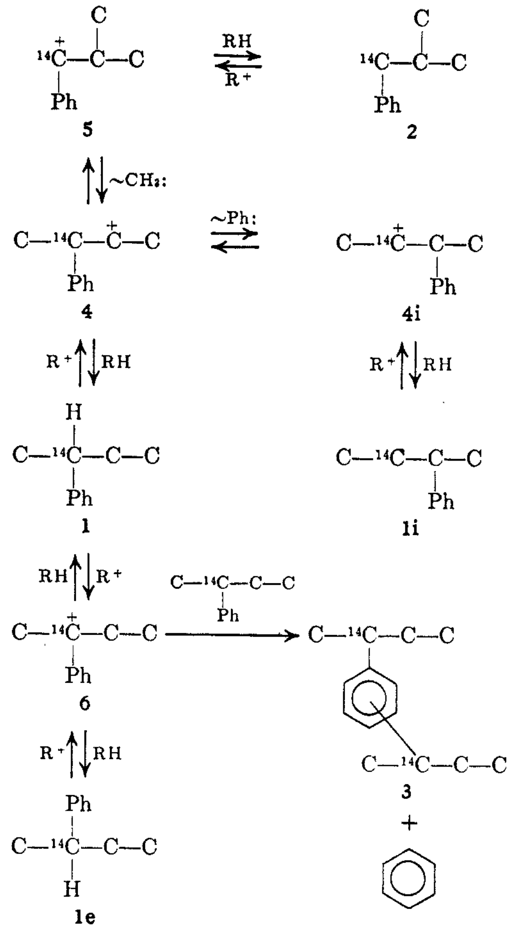




Another kind of rearrangement of *sec*-butylbenzene might be expected on the basis of the behavior of higher *sec*-alkylbenzenes. 2- and 3-phenylpentanes are interconverted by aluminum chloride at 25°,[4,5] and 2-phenyldodecane is isomerized to an equilibrium mixture of 2-, 3-, 4-, 5-, and 6-phenyldodecanes at 50°.[6] An investigation of the analogous rearrangement of *sec*-butylbenzene, which can only be observed in the case of an isotopically labeled molecule such as 2-phenyl-2-^{14}C-butane (**1**, Scheme I), is the subject of this paper.

This system has several interesting features. (1) It is the simplest one in which a shift of a phenyl group between secondary carbon atoms can occur. (2) The end result of rearrangement is a 1:1 distribution of the isotopic isomers, **1** and **1i** (neglecting a small isotope effect). (3) The expected phenyl shift can be detected with precision by radiochemical analysis in molecules which can be shown by spectroscopic and chromatographic analysis to have undergone no other kind of rearrangement.

SCHEME I



The results of six experiments in which 2-phenyl-2-^{14}C-butane (**1**) was treated with aluminum halide catalysts are presented in Table I. With water-activated aluminum chloride at 25°, rearrangement to 2-phenyl-3-^{14}C-butane (**1i**) occurred, producing the equilibrium mixture (1:1) of the isotopic isomers in 1 hr, but, at −14 to −17° with the same catalyst or with anhydrous aluminum bromide, no rearrangement occurred in 15 min. After 1 hr at 0° with $AlCl_3 + H_2O$, 21% rearrangement had occurred. Disproportionation to benzene and di-*sec*-butylbenzene [mainly *meta* and *para* isomers (**3**)] occurred in all experiments,

TABLE I
REARRANGEMENT OF 2-PHENYL-2-^{14}C-BUTANE TO 2-PHENYL-3-^{14}C-BUTANE

Temp, °C	Time, min	Catalyst[a]	2-Phenyl-2-^{14}C-butane remaining, %
25	60	$AlCl_3 + H_2O$[b]	50[c]
0	60	$AlCl_3 + H_2O$[b]	79[d]
−14	15	$AlCl_3 + H_2O$[b]	100[d]
−14	15	$AlBr_3$	100[e]
−17	15	$AlBr_3$	100[f]

[a] 2-Phenyl-2-^{14}C-butane:AlX_3 mole ratio = 3:1. [b] $AlCl_3$:H_2O mole ratio = 1:1. [c] Two experiments. Starting materials: 10 g of 2-phenyl-2-^{14}C-butane in each, (1) 0.607 μCi/mmol and (2) 0.293 μCi/mmol. [d] Starting material: 10 g of 2-phenyl-2-^{14}C-butane, 0.607 μCi/mmol. [e] Starting material: 8.0 g of 2-phenyl-2-^{14}C-butane. [f] Starting material: 7.9 g of 2-phenyl-2-^{14}C-butane, 0.293 μCi/mmol.

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[1] (a) Part XVIII of the series "New Friedel-Crafts Chemistry." Part XVII, A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 926 (1966). (b) Supported by the Robert A. Welch Foundation.

[2] (a) R. M. Roberts, Y. W. Han, C. H. Schmid, D. A. Davis, *J. Amer. Chem. Soc.*, **81**, 640 (1959); (b) C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959).

[3] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, **75**, 2411 (1953). The catalyst was $HF \cdot BF_3$.

[4] R. L. Burwell, Jr., and A. D. Shields, *ibid.*, **77**, 2766 (1955).

[5] R. M. Roberts, J. R. Baker, and S. E. McGuire, unpublished results.

[6] A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

but no rearrangement to isobutylbenzene (**2**) (or other isomers[7,8]).

It is interesting to consider the reaction pathways by which 2-phenyl-2-^{14}C-butane (**1**) may be converted into four different kinds of products (**1i**, **1e**, **2**, and **3**, Scheme I). Isomerization to 2-phenyl-3-^{14}C-butane (**1i**) and to isobutylbenzene (**2**) may both involve the intermediate secondary carbonium ion **4**. On the basis of stability of the carbonium ions produced, competition between the phenyl and methyl shifts would be expected to be in favor of the latter, since the charge on **5** may be delocalized by the benzene ring. The experimental observation that the isotopic isomerization ($\mathbf{1} \rightleftarrows \mathbf{1i}$) reaches equilibrium under conditions that produce no *sec*-butylbenzene–isobutylbenzene isomerization ($\mathbf{1} \rightleftarrows \mathbf{2}$) seems to indicate that participation of the phenyl group in the 1,2 shift is a more important factor than the stabilization of the ion **5**.

The fact that the production of **3** and benzene by disproportion is an even more facile reaction than the isotopic isomerization may be rationalized, however, on the basis that the tertiary benzylic carbonium ion **6** is formed much more readily than the aliphatic secondary ion **4**,[9] and the disproportionation proceeds by the Pines–Streitwieser alkylation–dealkylation mechanism.[10] This explanation is consistent also with the observation[4] that racemization of optically active 2-phenylpentane by aluminum chloride is much more rapid than isomerization to 3-phenylpentane. Although our 2-phenyl-2-^{14}C-butane was not optically active, racemization of asymmetric molecules would undoubtedly follow the pathway $\mathbf{1} \rightleftarrows \mathbf{6} \rightleftarrows \mathbf{1e}$, which involves the same intermediate (**6**) required for the disproportionation.[11]

Experimental Section

Synthesis of 2-Phenyl-2-^{14}C-butane (**1**).—The radioactive title compound was synthesized by methods described previously. $C_6H_5{}^{14}COCH_3$ was prepared from $CH_3{}^{14}CO_2Na$, benzene, and $AlCl_3$;[8a] treatment of $C_6H_5{}^{14}COCH_3$ with ethylmagnesium bromide was followed by catalytic reduction of the crude product to give **1**.[8b,c] This product (and the 2-phenylbutane recovered after reaction with $AlCl_3$) was converted into *p*-nitrobenzoic acid by reaction with concentrated nitric acid (reflux, 24 hr). The crude *p*-nitrobenzoic acid was purified by dissolving it in aqueous NaOH solution, extracting nonacidic organic impurities into ether, and reprecipitating the *p*-nitrobenzoic acid by the addtion of concentrated HCl. It was recrystallized from aqueous ethanol and sublimed under reduced pressure; radioassay was carried out by wet combustion to CO_2, which was counted on a vibrating-reed electrometer.[8a]

Reaction of 2-Phenyl-2-^{14}C-butane with Aluminum Halides.—Details of six experiments are given in Table I. The reaction mixtures were stirred with Teflon-covered magnetic stirring bars, decomposed with crushed ice and HCl, and worked up by addition of ether and extraction in the usual way.[8] *sec*-Butylbenzene (2-phenylbutane) was recovered by fractional distillation; vpc showed it to be free of *n*-butyl- and *t*-butylbenzene isomers; and it indicated the absence of isobutylbenzene.[12] Disproportionation to benzene and di-*sec*-butylbenzene in even the lowest temperature reactions was demonstrated, both by vpc and by the fractional distillations of the reaction mixtures. The amount of *sec*-butylbenzene recovered ranged from 30% at 25° to 60% at −14°.

Registry No.—**1**, 17398-79-7.

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[7] Skeletal rearrangements to isobutyl-, *t*-butyl-, or *n*-butylbenzene would have been detected by vpc or ir analysis.[8] Rearrangement to 2-phenyl-1- or -4-^{14}C-butane is unlikely on the basis of requiring primary carbonium ion intermediates and also because a loss of more than 50% of the ^{14}C from the 2 position would probably have been observed in the 25° experiments.

[8] (a) R. M. Roberts and J. E. Douglass, *J. Org. Chem.*, **28**, 1225 (1963); (b) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955); (c) R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957).

[9] The intermediate ion **4** may not only be produced directly from **1** by intermolecular hydride abstraction as shown in Scheme I, but also from **6** by intramolecular hydride shift. It is probably impossible to distinguish experimentally between these alternatives, and actually it is likely that **4** is produced in both ways. The rationalization of the relative ease of formation of products **1i**, **1e**, **2**, and **3** on the basis of the stability of the intermediates **4** and **6** has the same relevance whether **4** is formed directly from **1** or indirectly *via* **6**.

[10] (a) H. Pines and J. T. Arrigo, *J. Amer. Chem. Soc.*, **80**, 4369 (1958); (b) A. Streitwieser, Jr., and L. Reif, *ibid.*, **86**, 1988 (1964).

[11] By analogy with the behavior of 2-phenylpentane,[4] racemization of optically active 2-phenylbutane would be expected to be still faster than disproportionation.

[12] Analysis of the butylbenzenes by vpc and ir is described by R. M. Roberts and D. Shiengthong, *J. Amer. Chem. Soc.*, **82**, 732 (1960).

The Solvent Isotope Effect in the Acid-Catalyzed Isomerization of *cis*-Stilbenes[1,2]

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It has been pointed out several times in recent years that deuterium isotope effects should vary with structure in a rational manner, reaching a maximum in situations where the hydrogen isotope is symmetrically disposed in the transition state. Westheimer has presented these concepts in more quantitative terms.[5] He assumes that A–H and B react to form A and B–H by way of a linear transition state A–H–B, and finds that the isotope effect is at a maximum when k_1 is equal to k_2, where k_1 and k_2 represent the stretching force constants of the A–H and H–B bonds in the transition state.

Bell and Goodall,[6] in a particularly careful study have observed that the deuterium isotope effect is at a maximum for the ionization of deuterated nitroparaffins when the proton transfer is between two acid–base systems of approximately equal p*K*. The recent study by Goodall and Long[7] has likewise shown that a very similar result obtains in the reverse reaction involving deuterated acids in deuterated medium.

In recent studies from these laboratories we have examined in some detail the mechanism of the acid-catalyzed isomerization of a group of substituted *cis*-stilbenes.[8] As the rate-limiting step was shown to be the initial proton transfer from the acidic medium to the organic substrate, this series of compounds represents a useful group in which to examine the variation of the solvent isotope effect as a function of structure.

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[2] A portion of this work has been reported in a preliminary communication: D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **86**, 3584 (1964).

[3] Shell Fellow in Chemistry, 1963–1964.

[4] National Science Foundation Cooperative Fellow, 1962–1964.

[5] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[6] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

[7] D. M. Goodall and F. A. Long, *J. Amer. Chem. Soc.*, **90**, 239 (1968).

[8] D. S. Noyce, D. R. Hartter, and F. B. Miles, *ibid.*, **90**, 4633 (1968).