crystallized from aqueous methanol to give colorless prisms (62 mg.), m.p. 240–241°, identical in all respects with mauiensine.

Thin Layer Chromatography.—The R_f values were found to be dependent on concentration, the thickness of the alumina on the plates, and other variables in the system which reduced their reproducibility. These values are relative, and the difference between any two may vary as greatly as 0.1 units in a given chromatogram. The system of 2% ethanol in benzene afforded a better separation of the components of a mixture than did 4% ethanol in benzene. The chromatograms were developed by spraying with the modified Dragendorff's reagent.[13]

	Ethanol in benzene	
	2%	4%
Ajmaline		0.9
Mauiensine	0.56	
Dihydromauiensine	0.40	
Tetraphyllicine		0.66

Acknowledgment.—The authors wish to express their gratitude to Dr. W. I. Taylor for helpful discussion and to the U. S. Public Health Service, Division of General Medical Sciences, for generous financial support (GM 05095).

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A Study of 1,2-Benzyl and 1,3-Phenyl Radical Migrations

LYNN H. SLAUGH, EUGENE F. MAGOON, AND VINCENT P. GUINN

The Shell Development Company, Emeryville, California

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The 2,2-dibenzylethyl radical, generated in solution either by the decarbonylation of 3,3-dibenzylpropanal or by the "Kharasch reaction" of 1,1-dibenzyl-2-chloroethane, does not rearrange *via* a 1,2-benzyl shift. Evidence suggests that for free radicals the migratory aptitude is in the order phenyl > benzyl. These results are compared with those reported for carbanions. The 3-phenylpropyl-1-C^{14} radical similarly generated does not rearrange to the 1-phenylpropyl-1-C^{14} radical *via* a 1,3-phenyl shift.

Very few examples have been reported of authentic radical 1,2-alkyl migrations. In fact, several workers have established firmly that such rearrangements do not occur within certain selected radicals. These have been generated either in solution, *via* radical additions to olefins, decarbonylation of aldehydes and decomposition of azo compounds,[1] or in the gas phase by the reaction of iodine and other free radical sources with hydrocarbons at elevated temperatures[2] (400–600°).

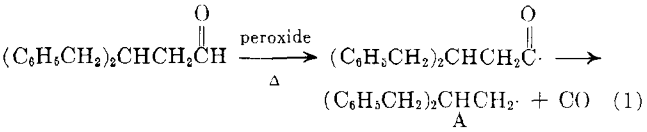
Reports of certain reactions thought to give products of radical rearrangement have been shown to be incorrect[3,4] or to involve cleavage–recyclization[5] rather than a true 1,2-alkyl shift.

Noteworthy is the work of Cvetanović who has presented some evidence that alkyl migrations occur within diradicals formed by the addition of oxygen atoms (obtained by the mercury sensitized photolysis of nitrous oxide) to olefins.[6] However, these migrations may be only partly internal. Other reports of saturated alkyl shifts have been made, but further work is needed to establish the mechanisms.[7]

A recent molecular orbital treatment of the chemistry of 1,2-shifts has indicated that carbanions should be even less prone to rearrangement, *via* 1,2-alkyl group migrations, than are free radicals.[8] For this reason, the observation of Grovenstein and Williams that the benzyl group does undergo a 1,2-shift within carbanions even more readily than the phenyl group[9] is very interesting. One might therefore expect that the migratory aptitude of the benzyl group would be greater than that of an alkyl group or even an aryl group in a radical system. In an attempt to establish this point, we have sought to bring about a 1,2-benzyl migration. Incidental to this study, a test was also made for a 1,3-phenyl migration within the 3-phenylpropyl-1-C^{14} radical.

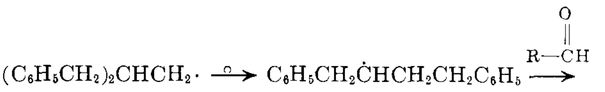
Results and Discussion

As a test for a 1,2-benzyl shift, the peroxide-induced decarbonylation of 3,3-dibenzylpropanal (equation 1) was studied. The intermediate radical A propagates



$$(C_6H_5CH_2)_2CHCH_2\overset{\overset{\displaystyle O}{\|}}{C}H \xrightarrow[\Delta]{\text{peroxide}} (C_6H_5CH_2)_2CHCH_2\overset{\overset{\displaystyle O}{\|}}{C}\cdot \longrightarrow \underset{\text{A}}{(C_6H_5CH_2)_2CHCH_2\cdot} + CO \quad (1)$$

the chain reaction by abstracting a hydrogen from the reactant aldehyde to give 1,1-dibenzylethane. Should radical A rearrange *via* a 1,2-benzyl shift prior to abstracting a hydrogen, 1,4-diphenylbutane would be the product (equation 2). Very dilute *o*-dichlorobenzene



$$(C_6H_5CH_2)_2CHCH_2\cdot \xrightarrow{?} C_6H_5CH_2\dot{C}HCH_2CH_2C_6H_5 \xrightarrow{R-\overset{\overset{\displaystyle O}{\|}}{C}H} C_6H_5CH_2CH_2CH_2CH_2C_6H_5 \quad (2)$$

solutions of the aldehyde (0.075–1.0 molar) and rather high decarbonylation temperatures (~160°) were used to encourage possible rearrangements. Both conditions have been shown to be beneficial to radical rearrangements.[10,11] Approximately 78% decarbonylation was obtained when a one molar solution of the aldehyde was

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[2] (a) L. H. Slaugh and J. H. Raley, *ibid.*, **82**, 1259 (1959); **84**, 2640 (1962); (b) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *ibid.*, in press.

[3] M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, **19**, 1150 (1954); **20**, 680 (1955).

[4] J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959).

[5] J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960); **84**, 3337 (1962).

[6] R. J. Cvetanović, *Can. J. Chem.*, **36**, 623 (1958).

[7] (a) F. F. Rust, and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954); (b) J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962).

[8] H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

[9] E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 2537 (1961).

[10] Ref. 1e.

[11] L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

used. After hydrogenation to saturate any olefins present, the product contained 1,1-dibenzylethane (75% yield based on the carbon monoxide evolved) but no 1,4-diphenylbutane, indicating that rearrangement had not occurred. Rearrangement could not be induced by decarbonylating an even more dilute (0.075 molar) solution of the aldehyde wherein the average radical life time should be greater. The extent of decarbonylation in the latter case was 42% and the yield of 1,1-dibenzylethane was ~98% of the carbon monoxide evolved.

Another attempt to induce rearrangement in this system was made by treating an ether solution of 1,1-dibenzyl-2-chloroethane and cobaltous bromide with the Grignard reagent prepared from ethyl bromide (Kharasch reaction).[12,13] This reaction is believed to generate radicals by halogen atom abstraction from the organic halide.[15] Gas chromatographic analysis of the product, after hydrogenation to convert olefins to saturated hydrocarbons, indicated an ~70% yield of 1,1-dibenzylethane. Apparently little or no rearrangement ($\leq 0.5\%$) occurred as indicated by the relative yields of 1,1-dibenzylethane and 1,4-diphenylbutane.

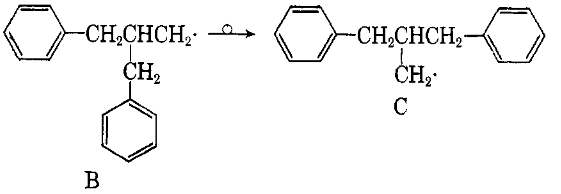
No attempt was made to isolate and determine the structure of the $C_{32}H_{34}$ hydrocarbons which might have resulted from dimerization of radicals produced during either of these reactions. Since the monomer yields were good, they should be an adequate indicator of any possible rearrangement.[16]

It is of interest to compare the migratory aptitudes of the benzyl and phenyl groups. Under conditions comparable to those of the present study, the 2-phenylethyl-1-C[14] radical undergoes rearrangement, *via* 1,2-phenyl shift (equation 3), to the extent of 5–20%.[11,16]

$$C_6H_5CH_2C^{14}H_2\cdot \xrightarrow{\text{rearrangement}} C_6H_5C^{14}H_2CH_2\cdot \qquad (3)$$

This rearrangement does not produce a more stable radical nor does it alleviate steric compression. On the other hand, a 1,2-benzyl shift (equation 2) of the 2,2-dibenzylethyl radical does not occur even though it should have a greater driving force to do so. That is, a more stable secondary radical would have been formed from the initially prepared primary radical and the rearrangement possibly would have brought about a slight alleviation of steric compression. Therefore, it is concluded that the migratory aptitude for 1,2-shifts within free radicals is larger for the phenyl group than for the benzyl group. Since the migratory aptitude for carbanions is the opposite, benzyl > phenyl,[9] a basis is thereby provided for distinguishing between the two types of intermediates in reaction mechanism studies. The prediction and use of this principle was made recently by Grovenstein and Williams.[9]

Since a 1,3-phenyl shift is possible in the 2,2-dibenzylethyl radical, it must also be considered. However, if it had occurred, a radical identical to the original would have been obtained (equation 4) and the rearrangement would not have been detected (B≡C). To determine the likelihood of a 1,3-phenyl shift, the rearrangement of the 3-phenylpropyl-1-C[14] radical was studied (equation 5). The two rearrangements (equations 4 and 5) are similar since the radicals formed are all primary, and steric compression as a driving force, while not necessarily equal, should be slight.



(4)

$$C_6H_5CH_2CH_2C^{14}H_2\cdot \xrightarrow{\text{rearrangement}} C_6H_5C^{14}H_2CH_2CH_2\cdot \qquad (5)$$

The 3-phenylpropyl-1-C[14] radical was generated, in the same manner as the 2,2-dibenzylethyl radical, by the peroxide-induced decarbonylation of 4-phenylbutanal-2-C[14] and the Kharasch reaction on 3-phenyl-1-chloropropane-1-C[14]. In both instances, conditions were chosen to facilitate rearrangement. The degree of rearrangement from both reactions was found by determining the relative amounts of 3-phenylpropane-1-C[14] and 1-phenylpropane-1-C[14] in the product. This was accomplished simply by comparing the total C[14] activity of the product *n*-propylbenzene-C[14] and the benzoic acid obtained upon oxidation of the product.

In both reactions, no detectable 1,3-phenyl migration occurred. These results suggest that a 1,3-phenyl migration within the 2,2-dibenzylethyl radical (equation 4) probably did not occur. Apparently, 1,3-phenyl shifts do not occur as readily as 1,2-phenyl shifts since under similar conditions the 2-phenylethyl-1-C[14] radical rearranged to the extent of 5–20%.[11,16] Phenyl migrations other than 1,2-shifts are possible since Winstein, Heck, Lapport, and Baird[17] established a 1,4-phenyl migration within a free radical. However, unlike the 3-phenylpropyl-1-C[14] radical, the rearrangement they observed involved the conversion of a primary to a tertiary radical and, consequently, should have had a greater driving force.

Experimental[18]

Radioactivity Measurements.—The C[14]-activities were determined by the liquid scintillation method[19] employing toluene as the organic solvent. In general, counting efficiencies were about 75% for all compounds. All net counting rates were converted to disintegrations per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated C[14] solutions.

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(12) The 1,1-dibenzyl-2-chloroethane was not added to excess Grignard reagent containing cobaltous bromide as is usually practiced[13] because this leads to considerable interchange between the Grignard reagent and the organic chloride.[14] The net result would be a decreased yield of 2,2-dibenzylethyl radicals.

(13) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944).

(14) L. H. Slaugh, *ibid.*, **83**, 2734 (1961).

(15) (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions on Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 126; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 588, 589.

(16) It is interesting that less rearrangement occurred during the decarbonylation[11] of 3-phenylpropanal-2-C[14] than during the Kharasch reaction of 2-phenyl-1-chloroethane-1-C[14] [W. B. Smith and J. B. Anderson, *J. Am. Chem. Soc.*, **82**, 656 (1960)]. In the present study, it is questionable whether or not the Kharasch reaction would have provided a better test for rearrangement than the decarbonylation reaction. The present Kharasch reaction was carried out somewhat differently from the method employed by Smith and Anderson who treated organic bromides with magnesium and an equivalent of cobaltous bromide. Attempts to use their technique on 1,1-dibenzyl-2-chloroethane were not successful. The latter is unreactive and forms a Grignard reagent slowly.

(17) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(18) Melting points and boiling points were not corrected.

(19) See V. P. Guinn in C. G. Bell, Jr., and F. N. Hayes, "Liquid Scintillation Counting," Pergamon Press, New York, N. Y., 1958, pp. 166–182.

1,1-Dibenzyl-2-chloroethane.—An ether solution of 400 g. (1.66 moles) of α-benzylhydrocinnamic acid (Eastman Kodak, White Label) was reduced with 100 g. (2.64 moles) of freshly powdered lithium aluminum hydride according to the procedure of Nystrom and Brown.[20] After the ether was removed, *in vacuo*, the pale yellow residue was dissolved in 500 ml. of benzene and added to a solution of 214 g. (1.8 moles) of thionyl chloride and 40 ml. of pyridine in 500 ml. of benzene. The solution was refluxed for 2 hr., cooled, and poured into 1000 ml. of ice-water. The benzene layer was washed with a dilute potassium bicarbonate solution and dried over anhydrous potassium bicarbonate. The benzene was removed *in vacuo* using a rotating evaporator. The residue was distilled at reduced pressure through an 18-in. spinning-band column to give 268 g. (1.1 moles) or a 66% yield, based on the starting α-benzylhydrocinnamic acid, of a colorless oil, b.p. 142° (2.6 mm.); $d^{20}{}_4$ 1.0821.

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.52; H, 7.00; Cl, 14.5; mol. wt., 244. Found: C, 78.58; H, 7.01; Cl, 14.4 (neutron activation); mol. wt., 251 ± 7 (ebullioscopic, benzene).

1,1-Dibenzylethane.—A solution of 4.9 g. (0.02 mole) of 1,1-dibenzyl-2-chloroethane, 0.76 g. (0.02 mole) of lithium aluminum hydride, and 0.16 g. (0.02 mole) of lithium hydride in 20 ml. of freshly dried and distilled tetrahydrofuran, was refluxed for 12 hr. After hydrolysis with 50% aqueous tetrahydrofuran and subsequent addition of dilute sulfuric acid, the mixture was extracted with *n*-pentane. The *n*-pentane solution was washed twice with water and dried over anhydrous potassium carbonate. The solvent was removed *in vacuo* to give 3.85 g. (98% yield) of 1,1-dibenzylethane which was essentially free of impurities as determined by g.l.c. The material was further purified by vacuum distillation through an 18-in. spinning-band column, b.p. 131–132° (5.2 mm.). Mass spectrometric analysis confirmed the calculated molecular weight. This material was used for g.l.c. comparison as subsequently shown.

A second reduction *via* hydrolysis of a Grignard prepared from 1,1-dibenzyl-2-chloroethane and triply sublimed magnesium was carried out to give a 68% yield of 1,1-dibenzylethane.

Neither sample of 1,1-dibenzylethane contained 1,4-diphenylbutane, the end product of rearrangement of the 2,2-dibenzylethyl radical.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.2; H, 8.6.

1,4-Diphenylbutane.—Eastman Kodak White Label 1,4-diphenyl-1,3-butadiene was washed with ethanol and then recrystallized from benzene; m.p. 150–151°. This purified material was dissolved in benzene and hydrogenated at 20° and 1 atm. of hydrogen, using as a catalyst 10% palladium on carbon. After filtering to remove the catalyst, the clear solution was evaporated to give a white solid in 93% yield. After recrystallization from ethanol (m.p. 52–53°, lit.[21] m.p. 52°), mass spectrometric analysis of this compound confirmed the calculated molecular weight and showed that olefins were not present.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.0; H, 8.7.

A g.l.c. comparison of 1,4-diphenylbutane with 1,1-dibenzylethane showed the two compounds to have different retention times. Using a 0.25 in. × 25 ft. column (20% Dow Corning 710 silicone oil on 40–60-mesh firebrick) at 265°, the 1,1-dibenzylethane emerged at 27 min. and the 1,4-diphenylbutane emerged at 36 min.

3,3-Dibenzylpropanenitrile.—1,1-Dibenzyl-2-chloroethane (244 g., 1.0 mole) was converted to 3,3-dibenzylpropanenitrile by following the general procedures of Smiley and Arnold[22] and Friedman and Schechter.[22] The dimethyl sulfoxide solution of sodium cyanide and 1,1-dibenzyl-2-chloroethane was heated at 140° for 1.0 hr. before cooling and diluting with water to obtain the crude nitrile which was not purified further.

3,3-Dibenzylpropanoic Acid.—The crude 3,3-dibenzylpropanenitrile was added to a mixture of concentrated sulfuric acid (570 ml.), glacial acetic acid (570 ml.), and water (570 ml.) and refluxed with stirring for 4 hr. After cooling, the acid mixture was poured onto crushed ice and extracted with ether. After washing the combined ether solutions several times with water, the 3,3-dibenzylpropanoic acid was extracted from the ether with dilute sodium hydroxide. The crude acid obtained by acidifying this basic solution with hydrochloric acid was recrystallized from aqueous methanol to give a 91% yield, based on the chloride, of pure 3,3-dibenzylpropanoic acid, m.p. 83.5–84.4°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; neut. equiv., 254. Found: C, 80.29; H, 7.16; neut. equiv., 256.

The anilide of this acid was prepared from the corresponding acid chloride (see the following preparation) and recrystallized from methanol, m.p. 125–125.8°.

Anal. Calcd. for $C_{23}H_{23}ON$: C, 83.85; H, 7.03; N, 4.25. Found: C, 83.91; H, 7.14; N, 4.14.

3,3-Dibenzylpropanoyl Chloride.—3,3-Dibenzylpropanoic acid (216 g., 0.85 mole) in 500 ml. of anhydrous benzene was brought to reflux and 202 g. (1.7 moles) of thionyl chloride in 300 ml. of benzene slowly added. After the addition was complete, the solution was refluxed for 2 hr. The solvent and excess thionyl chloride were removed under vacuum in a rotating evaporator with further additions of 200-ml. portions of benzene to aid in the thionyl chloride removal. The amber colored oil (229.5 g., theoretical, 232.5 g.) was not further purified. The conversion of an aliquot of the acid chloride into the amide, m.p. 78–78.5°, from *n*-hexane, indicated a 95% yield of the acid chloride from 3,3-dibenzylpropanoic acid.

Anal. Calcd. for amide, $C_{17}H_{19}NO$: C, 80.59; H, 7.56. Found: C, 80.8; H, 7.5.

3,3-Dibenzylpropanal.—A portion of the crude 3,3-dibenzylpropanoyl chloride (102 g., 0.374 mole) was reduced with 100 g. (~0.4 mole) of lithium aluminum tritertiary butoxy hydride (Metal Hydrides, Inc.) in 500 ml. of anhydrous tetrahydrofuran by following the procedure of Brown and Subba Rao.[23] An aliquot of the crude aldehyde was converted to its 2,4-dinitrophenylhydrazone (m.p. 103–104°, from ethanol). From the weight of the derivative, the yield of aldehyde, from the acid chloride, was estimated to be 68.4%.

Upon distillation through an 18-in. spinning-band column, pure 3,3-dibenzylpropanal was obtained; b.p., 125–126° (0.3 mm.); $n^{20}{}_D$ 1.56236. The infrared spectra had a strong carbonyl absorption at 1715 cm.$^{-1}$ and indicated the absence of acids, alcohols, or olefins.

Anal. Calcd. for aldehyde $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.7; H, 7.6.

Anal. Calcd. for the 2,4-dinitrophenylhydrazone $C_{23}H_{21}N_4O_4$: C, 66.17; H, 5.07; N, 13.42. Found: C, 66.4; H, 5.3; N, 13.3.

Impure samples of this aldehyde also were prepared in low yields by the reaction of triethyl orthoformate with the Grignard reagent prepared from 1,1-dibenzyl-2-chloroethane. That these aldehydes were the same was indicated by the elemental analyses and mixture melting point (103–104°) of their 2,4-dinitrophenylhydrazone derivatives.

Decarbonylation of 3,3-Dibenzylpropanal.—Fifty mmoles of freshly distilled 3,3-dibenzylpropanal in 38 ml. of *o*-dichlorobenzene (1.0 *M* in aldehyde) was heated at 160 ± 2° for 2.5 hr. Fifteen mmoles of di-*t*-butyl peroxide were added in eleven equal portions over the first 2 hr. The collected gases contained 39.0 mmoles of carbon monoxide, indicating 78.1% decarbonylation of the aldehyde. The liquid product was washed repeatedly with ferrous sulfate solution and finally with water. After drying, the solution was hydrogenated over 10% palladium on charcoal at 20° and at atmospheric pressure until no more hydrogen was absorbed. As a test for catalyst activity, extraneous olefins added to the solution were readily hydrogenated. The hydrogenated liquid solution contained 29.2 mmoles, 74.8% of the carbon monoxide collected, of 1,1-dibenzylethane and no 1,4-diphenylbutane, the product of rearrangement.

In a second experiment, 14.6 mmoles of the 3,3-dibenzylpropanol in 187 ml. of *o*-dichlorobenzene (0.075 molar in aldehyde) was heated to 160 ± 2° for 2.5 hr. Six mmoles of di-*t*-butylperoxide was added in several portions over the first 2 hr. The collected gases contained 6.1 mmoles of carbon monoxide (42% decarbonylation). The liquid product contained 6.0 mmoles of 1,1-dibenzylethane (an ~98% yield based on the carbon monoxide collected) and no rearranged product, 1,4-diphenylbutane (g.l.c. analyses).

The product, 1,1-dibenzylethane, was trapped as it emerged from the g.l.c. and analyzed on the mass spectrometer. The molecular weight and cracking pattern of the material were iden-

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[20] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

[21] P. Sabatier and J. B. Senderens, *Compt. rend.* **135**, 89 (1902); R. Kahn and A. Winterstein, *Helv. Chim. Acta*, **11**, 137 (1928).

[22] (a) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960); (b) I. Friedman and H. Schechter, *ibid.*, **25**, 877 (1960).

[23] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

tical to those of authentic 1,1-dibenzylethane. The absence of 1,4-diphenylbutane in these products was easily shown since its emergence time from a g.l.c. column was greatly different from that of 1,1-dibenzylethane described previously.

Kharasch Reaction on 1,1-Dibenzyl-2-chloroethane.—To a blue-green solution made from 2.4 g. (10 mmoles) of 1,1-dibenzyl-2-chloroethane, 0.05 g. of cobaltous bromide and 20 ml. of anhydrous ether, was slowly (1 hr.) added, with stirring at room temperature, 15 mmoles of ethylmagnesium bromide in 25 ml. of ether. Further portions of cobaltous bromide (total, 0.2 g.) were added during the Grignard addition. The solution was refluxed for 30 min., cooled, hydrolyzed, and the ether solution dried over anhydrous potassium carbonate after washing with water. The solution was concentrated, dissolved in benzene, and hydrogenated as in the previous manner to saturate olefins which may have been formed by disproportionation reactions. From the amount of hydrogen consumed, the material was estimated to contain 20–30% monoolefin. Analyses of the final solution by g.l.c. indicated a yield of ~70% 1,1-dibenzylethane. A compound having the same retention time as authenic 1,4-diphenylbutane accounted for $\leqq 0.5\%$ of the $C_{16}H_{18}$ material recovered. Approximately 10% of the starting chloride was recovered as shown by g.l.c.

3-Phenylpropanoic-1-C^{14} Acid.—In a suitable flask were placed 100 g. (0.712 mole) of 2-phenyl-1-chloroethane 46.6 g. (0.950 mole) of sodium cyanide, 0.05 mc. of $KC^{14}N$, 100 ml. of ethanol, and 55 ml. of water. After refluxing 38 hr., 400 ml. of benzene and 400 ml. of water were added and the layers separated. The water layer was extracted with additional benzene and the total benzene extracts combined. The latter was washed with water and dried over calcium chloride. The benzene was removed by distillation and the crude 3-phenylpropanenitrile-1-C^{14} refluxed with a solution of 125 ml. of concentrated sulfuric acid, 125 ml. of glacial acetic acid, and 125 ml. of water for 2.5 hr. The mixture was cooled and poured into 250 ml. of ice–water. The oily layer was diluted with ether and the 3-phenylpropanoic-1-C^{14} acid extracted from the ether with dilute sodium hydroxide solution. The acid was recovered by precipitation with dilute hydrochloric acid.

3-Phenyl-1-chloropropane-1-C^{14}.—The 3-phenylpropanoic-1-C^{14} acid was converted to the chloride in a manner similar to that used in the preparation of 1,1-dibenzyl-2-chloroethane. After distillation, 3-phenyl-1-chloropropane-1-C^{14}, b.p. 89.6–90.0° (9.5 mm.), was obtained in an over-all yield, based on 2-phenyl-1-chloroethane, of 21.4%.

4-Phenylbutanal-2-C^{14}.—This aldehyde was prepared in a manner similar to that used by Cohen[24] for the preparation of 3-phenylpropanal. The Grignard reagent prepared from 1.0 mole of 3-phenyl-1-chloropropane-1-C^{14} was converted to the acetal by treatment with triethyl orthoformate. After hydrolysis, the aldehyde was recovered as the bisulfite adduct. The 4-phenylbutanal-2-C^{14}, obtained by steam distillation of a sodium carbonate solution of the bisulfite adduct, was further purified by distillation, b.p. ~159° (10 mm.), to give a 21.3% yield. A 2,4-dinitrophenylhydrazone derivative of the aldehyde was made, m.p. 111.5–112.5°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.52; H, 4.91; N, 17.07. Found: C, 59.0; H, 4.9; N, 16.9.

A small sample of this aldehyde was oxidized *via* a basic potassium permanganate solution to benzoic acid in 32.5% yield. After recrystallization from *n*-pentane–methylene chloride, the acid, m.p. 120–120.5°, was shown to be devoid of any C^{14}; thereby demonstrating that rearrangement had not occurred during the synthesis.

Decarbonylation of 4-Phenylbutanal-2-C^{14}.—Approximately 54 mmoles of the aldehyde in 50 ml. of *o*-dichlorobenzene containing 18 mmoles of di-*t*-butyl peroxide was decarbonylated at 149°. After gas evolution was completed, 35 mmoles of carbon monoxide (64.3%) was recovered. The *n*-propylbenzene-C^{14}, resulting from the decarbonylation, was diluted with 20 g. of *n*-propylbenzene and separated from the *o*-dichlorobenzene solution by distillation to give 16.7 g., b.p. 159.1–159.3°. The *n*-propylbenzene was shown to be 99.2% pure by g.l.c. analysis.

The degree of rearrangement from this reaction was found by determining the relative amounts of 3-phenylpropane-1-C^{14} and 1-phenylpropane-1-C^{14} in the product. This was accomplished by comparing the total C^{14} activity of the *n*-propylbenzene-C^{14} and that of its oxidation product, benzoic acid.

C^{14}-activities measured: product *n*-propylbenzene-C^{14}, 1,274 d.p.m./mmole; benzoic acid from oxidation of the *n*-propylbenzene-C^{14}, $\leqq 2$ d.p.m./mmole. Therefore, the extent of rearrangement was $\leqq 0.16\%$.

Kharasch Reaction of 3-Phenyl-1-chloropropane-1-C^{14}.—The reaction of this chloride was carried out in a manner similar to that for 1,1-dibenzyl-2-chloroethane, using 17.5 g. (0.113 mole) of 3-phenyl-1-chloropropane-1-C^{14}, a total of 1.4 g. (0.01 mole) of cobaltous bromide, and 0.15 mole of ethylmagnesium bromide. After refluxing for 2 hr., 20 ml. of *n*-propylbenzene was added to dilute the *n*-propylbenzene-C^{14} product. The yield of β-methylstyrene and *n*-propylbenzene was estimated to be 23%. The amount of rearrangement was determined as previously mentioned for the decarbonylation reaction.

C^{14}-Activities measured: product *n*-propylbenzene-C^{14}, 1,760 d.p.m./mmole; benzoic acid, ~0 d.p.m./mmole. No detectable rearrangement occurred during the reaction.

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(24) H. Cohen, *J. Chem. Soc.*, 432 (1935).

The Chemistry of Xylylenes. XX. The Gas Phase Oxidation of *p*-Methylbenzyl Radicals and *p*-Xylylene

L. A. ERREDE AND W. D. ENGLISH

Contribution No. 236 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota[1]

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p-Methylbenzyl radicals generated *via* fast flow pyrolysis of *p*-xylene are converted to *p*-xylylene as the gas stream travels away from the furnace. The *p*-methylbenzyl radicals and *p*-xylylene produced in this way are oxidized to *p*-toluic acid and terephthalic acid, respectively, when the hydrocarbon stream is quenched with pyrolyzed nitric acid or nitrogen dioxide. *p*-Toluic acid is isolated exclusively when the two streams are mixed at or near the pyrolysis zone, whereas terephthalic acid is isolated exclusively when the two streams are mixed at a considerable distance away from the pyrolysis zone. Aldehydes are obtained instead of acids when the hydrocarbon stream is mixed with a limited amount of pyrolyzed nitric acid. The yield of oxidized products is about equal to the per cent conversion of *p*-xylene to *p*-methylbenzyl radicals in the pyrolysis zone of the reactor. In contrast, only nitroxylene, dinitroxylenes, and *p*-methylbenzyl nitrate are obtained when pyrolyzed *p*-xylene is quenched with nonpyrolyzed nitric acid.

It was reported in a previous publication[2] that the mechanism for formation of *p*-xylylene *via* fast flow pyrolysis of *p*-xylene at low pressure involves thermal rupture of the C—H bond to give hydrogen and *p*-methylbenzyl radicals[3] (equations 1 and 2), and subse-

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(1) This work was done in the laboratories of the M. W. Kellogg Company. The data were acquired by the Minnesota Mining and Mfg. Company with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Company in March, 1957.

(2) L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 73 (1963).

(3) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).