n^{25}_D 1.4599), was prepared by the oxidative chlorination of 2-octanethiol.[10]

l-**2-Octanesulfonyl Chloride.**—The preparation of this compound from *l*-2-octanol[24] of $[\alpha]^{20}_D$ −7.7° (homogeneous) was similar to the preparation of the racemic compound. The product had a b.p. 93–95° (0.3 mm.), n^{26}_D 1.4593, d^{20}_4 1.053, and $[\alpha]^{20}_D$ −0.72° (homogeneous).

d-**2-Octanesulfonyl Chloride.**—*l*-2-Bromoöctane,[25] $[\alpha]^{20}_D$ −29° (homogeneous), was converted to *d*-2-octyl thiocyanate, b.p. 111–111.5° (9 mm.), n^{20}_D 1.4633, $[\alpha]^{20}_D$ +44.8° (homogeneous) (lit.[12] b.p. 98.5–99.0° (4 mm.), n^{20}_D 1.4635), 27 g. (0.16 mole) of which was chlorinated below 25° in a solution of 150 ml. of glacial acetic acid and 20 ml. of cold water until an excess of chlorine was evident. The solution was poured into ice-water, and the organic phase was extracted with benzene, washed with sodium sulfite solution, and dried. Distillation gave a first fraction, b.p. 62–80° (7 mm.), n^{22}_D 1.4356, α^{20}_D −7.47° (homogeneous), which was presumably largely *l*-2-chloroöctane (lit.[26] b.p. 68° (22 mm.), n^{20}_D 1.4267). After an intermediate fraction was removed, the major portion of the material distilled at 119–121° (7 mm.), α_D +3.1° (homogeneous). This was redistilled to give 23 g. (0.113 mole, 71%) of *d*-2-octanesulfonyl chloride, n^{22}_D 1.4582, $[\alpha]^{20}_D$ +0.87° (homogeneous).

In another preparation, *l*-2-bromoöctane, $[\alpha]^{20}_D$ −31.5° (homogeneous), was converted through the isothiouronium salt to *d*-2-octanesulfonyl chloride, b.p. 82° (0.05 mm.), n^{20}_D 1.4621, $[\alpha]^{27}_D$ +1.21° (*c* 2.4, benzene).

The Decomposition of 2-Octanesulfonyl Chloride.—The decompositions were carried out in Claisen flasks fitted with drying tubes, appropriate receivers and gas-bubbling apparatus for observing the decomposition. In some instances the sulfur dioxide and hydrogen chloride were collected as silver sulfite and chloride, which were distinguished by the solubility of the former in nitric acid.

The decompositions were carried out as recorded in Tables I and II. After the evolution of gas ceased, the contents of the flasks were fractionated *in vacuo* to separate the products. From the decompositions carried out in purified[27] N,N-dimethylformamide[28] as a solvent, the products were obtained by dissolving in benzene, washing with water, drying and distilling.

The Racemization of *d*-**2-Chloroöctane.**—A lithium chloride–N,N-dimethylformamide solution (15 ml., mole ratio 1.0:4.5) was added to 3.00 g. of *d*-2-chloroöctane, $[\alpha]^{20}_D$ +30.1° (homogeneous), and the solution was heated to 135°. After one hour at this temperature, 8 ml. was withdrawn, dissolved in ether, washed with water, dried and distilled. Racemic 2-chloroöctane, 0.89 g., b.p. 76–77° (28 mm.), n^{18}_D 1.4250, was obtained.

Irradiation of *l*-2-chloroöctane, $[\alpha]^{20}_D$ −2.61° (homogeneous), with ultraviolet light for 4.5 hr. at 135–140° led to the recovery of *l*-2-chloroöctane of unchanged specific rotation.

TROY, NEW YORK

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[24] J. Kenyon in "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 418.

[25] C. M. Hsueh and C. S. Marvel, THIS JOURNAL, **50**, 855 (1928).

[26] A. J. H. Housa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929)

[27] G. R. Leader and J. F. Gormley, THIS JOURNAL, **73**, 5731 (1951).

[28] We are grateful to the Rohm and Haas Co. for a generous gift of this compound.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Free Radicals with Aromatics. I. The Unimportance of the "Identity Reaction" with Benzylic Radicals[1]

BY ERNEST L. ELIEL, PHIL H. WILKEN,[2] FABIAN T. FANG AND SAMUEL H. WILEN

RECEIVED JANUARY 6, 1958

The decomposition of acetyl peroxide in optically active 2-phenylbutane gives rise to an optically inactive dimer, but the recovered 2-phenylbutane is only slightly racemized, indicating that the "identity reaction" [(i), shown below, R = 2-phenyl-2-butyl, X = H] does not proceed to a major extent. The absence of identity reaction requires that the peroxide-induced hydrogen abstraction from toluene-α-*d* should proceed with a reasonable over-all isotope effect, and that the same should be true, contrary to a previous report, for *p*-xylene-α-*d*. This was verified.

By "identity reaction"[3] is meant the reaction of a molecule R–X with the corresponding radical R· according to the equation

$$R{-}X + R\cdot \longrightarrow R\cdot + R{-}X \qquad \text{(i)}$$

Although the identity reaction does not result in any net chemical change, it may be detected under certain circumstances. Thus if R–X is optically active due to asymmetry of R at its point of attachment to X, the radical R· will be incapable of maintaining optical activity[4] and the identity reaction will lead to racemization of R–X. The identity reaction may also manifest itself in labeled molecules, *e.g.* Brown and Russell[5] have shown that the

$$C_6H_5CH_2D + C_6H_5CHD\cdot \longrightarrow C_6H_5CH_2\cdot + C_6H_5CHD_2 \qquad \text{(ii)}$$

identity reaction does not occur in the free-radical chlorination of several hydrocarbons and, in particular, that reaction ii does not occur in the course of the free-radical chlorination of toluene-α-*d* to benzyl chloride. Wang and Cohen,[6] using a variation of the labeling technique, have recently proved that little or no identity reaction occurs in the course of the dimerization reaction of diphenylmethyl radicals in the presence of diphenylmethane (eq. i, R = $(C_6H_5)_2CH\cdot$, X = H), except in the presence of chain-transfer agents. In contrast, it has been reported[7] that in the reaction of *p*-xylene-α-*d* with benzoyl peroxide, an identity reac-

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[1] Presented in part before the Division of Organic Chemistry of the American Chemical Society at Minneapolis, Minn., September 14, 1955, and before the Petroleum Chemistry Division at Atlantic City, N. J., September 20, 1956.

[2] Part of this work is from the Ph.D. thesis of P.H.W., Peter C. Reilly Fellow, 1952–1953; Socony-Mobil Fellow, 1953–1954.

[3] This type of reaction is described by W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 2nd ed., London, England, 1948, p. 19 but the terminology is our own: Preprints. Division of Petroleum Chemistry, Am. Chem. Soc., **1** (3), 195 (1955).

[4] *Cf.* E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 140–142. A particularly clear-cut demonstration of this point has recently been provided by D. F. DeTar and C. Weiss, THIS JOURNAL, **79**, 3045 (1957).

[5] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952). For a similar demonstration in bromination, see K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

[6] C. H. Wang and S. G. Cohen, *ibid.*, **79**, 1924 (1957).

[7] J. I. Cadogan, V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 561 (1955).

tion involving p-$CH_3C_6H_4CH_2D$ and one of the three possible benzylic radicals derived therefrom proceeds to equilibrium before dimerization of the radicals to a deuterated p,p'-dimethylbibenzyl occurs. This conclusion was reached since the dimer contained the statistically calculated amount of deuterium (corresponding to an isotope effect of unity), even though the primary process of hydrogen abstraction from the p-xylene-α-d must, on theoretical grounds and by analogy with similar cases, have involved a substantial discrimination in favor of hydrogen removal over deuterium removal.[8]

Before the work of Cadogan, Gold and Satchell[7] appeared, we had studied the corresponding hydrogen abstraction–dimerization of optically active 2-phenylbutane, $C_6H_5CH(CH_3)C_2H_5$, by means of methyl radicals obtained from the pyrolysis of acetyl peroxide. Although the dimer (3,4-diphenyl-3,4-dimethylhexane)—apparently a mixture of the *dl*- and *meso*-forms (see Experimental)—was optically inactive as expected,[4] the recovered 2-phenylbutane was racemized only slightly, suggesting that the identity reaction (i, R = 2-phenylbutyl) had occurred to but a very minor extent.[9] The alternative possibility that the hydrogen transfer involved in the identity reaction proceeded more rapidly than racemization of the 2-phenylbutyl radical was disproved when it was shown that 2-phenylbutane recovered from a dimerization reaction with acetyl peroxide in the presence of cumene-α,β-d_2 was only 1–2% deuterated. In this case the reaction (R = 2 phenylbutyl, R′ = 1-deutero-2-phenyl-2-propyl)

$$R\cdot + R'D \longrightarrow R\text{-}D + R'\cdot$$

if it proceeded to equilibrium should have led to the formation of substantial amounts of 2-phenylbutane-2-*d*.

Two differences exist between the reaction of 2-phenylbutane with acetyl peroxide mentioned above and the reaction of xylene-α-d with benzoyl peroxide studied by the previous investigators.[7] One lies in the fact that 2-phenylbutane gives rise to a tertiary radical whereas xylene-α-d gives a primary radical; the other lies in the different peroxides used. To see whether these differences in substrates might account for the diverging experimental results we next investigated the reaction of toluene-α-d with acetyl, benzoyl and di-*t*-butyl peroxide. The results are shown in Table I, entries 1–7. It is evident that in all cases substantial isotope effects are observed, and therefore the identity reaction was again of little importance.

Eventually we decided to reinvestigate the dimerization of p-xylene-α-d[7,10] in order to eliminate the remote possibility that toluene-α-d and p-xylene-α-d might exhibit qualitatively different behavior. The results, shown in Table I, entries 8 and 9, clearly show an isotope effect in the dimerization of p-xylene-α-d which is not very different from that observed in the dimerization of toluene-α-d with the same peroxide. Thus the hypothesis that the identity reaction ii proceeds to any substantial extent[7] is no longer tenable. The discrepancy of our results with those of Cadogan, Gold and Satchell[7] is an experimental one and may well be due to the fact that these investigators worked with material of relatively low isotopic purity (66.7%). Under these circumstances the span in deuterium analysis of the dimer calculated for an isotope effect of unity (6.49%) and for an isotope effect of three (7.01%) is only half as large as in our work, where the isotopic purity of the substrate was high (94.8%) and the calculated difference of deuterium content of the dimer for an isotope effect of unity (8.78%) and for an isotope effect of three (9.81%) is well outside any reasonable error in the analysis.

TABLE I

ISOTOPE EFFECTS IN THE DECOMPOSITION OF PEROXIDES IN ALKYLBENZENES DEUTERATED IN THE α-POSITION IN THE SIDE CHAIN

Entry no.	Substrate	Peroxide	Mole ratio[a]	Temp., °C.	Isotope effect[b]
1	$PhCH_2D$	Ac_2O_2[c]	4	125	7.1
2	$PhCH_2D$	Ac_2O_2[c]	4	112–122	6.8
3	$PhCH_2D$	Ac_2O_2	10.3	109–115	2.5
4	$PhCH_2D$	Ac_2O_2	10.0	109–115	4.4
5	$PhCH_2D$	Ac_2O_2	1.4[d]	Reflux	4.4
6	$PhCH_2D$	Bz_2O_2	10.6	110–116	3.1
7	$PhCH_2D$	DTBP[e]	10.1	107–116	3.8
8	p-$CH_3C_6H_4CH_2D$	Ac_2O_2	6	122–124	8.9
9	p-$CH_3C_6H_4CH_2D$	Bz_2O_2	23.7	80	2.8
10	p-$CH_3C_6H_4CH_2D$	Bz_2O_2	23.7	80	1[f]

[a] Moles substrate/moles peroxide. [b] From deuterium content of dimer. [c] The commercial 25% solution in dimethyl phthalate was used. [d] See footnote 33 and Experimental for details of this run. [e] Di-*t*-butyl peroxide. [f] Reference 7.

While our results show that the identity reaction does not take place to a major extent, they do not prove that it does not occur at all. It was hoped that further evidence on this point might be obtained along lines suggested by equation ii above by showing, mass spectrometrically, whether or not the substrate recovered from a dimerization or $ArCH_2D$ contained any $ArCHD_2$.[11] Unfortunately, the results were inconclusive. In run 8, Table I (dimerization of p-xylene-α-d using acetyl peroxide) the recovered xylene was free of d_2-isomer, within the limits of experimental error. However, because of the low conversions in these dimerizations, the significance of this result is doubtful.[12] In one

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(8) *Cf.* K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955); C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 176.

(9) An alternative source of racemic 2-phenylbutane is disproportionation of the racemic radical: $2\ dl\text{-}C_6H_5\dot{C}(CH_3)C_2H_5 \rightarrow dl\text{-}C_6H_5CH(CH_3)C_2H_5 + C_6H_5\dot{C}(CH_3){=}CHCH_3$. However, as shown in the experimental part, no olefin was found.

(10) This decision was reached in understanding with Dr. Gold with whom we discussed the problem in July, 1955.

(11) A rather sensitive analysis for species such as $ArCH_3$, $ArCH_2D$, $ArCHD_2$ and $ArCD_3$ in the presence of each other is available in the method of mass spectrometry at reduced ionizing voltage: D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950); F. L. Mohler and V. H. Dibeler, L. Williamson and H. Dean, *J. Research Natl. Bur. Standards*, **48**, 188 (1952); F. H. Field and S. H. Hastings, *Anal. Chem.*, **28**, 1248 (1956). See also R. E. Honig, *ibid.*, **22**, 1474 (1950).

(12) For example, we have calculated that the mole per cent. toluene-α,α-d_2 in the recovered toluene-α-d in run 7 would be expected to be only 0.25% assuming that the discrepancy between the apparent isotope effects as determined from the deuterium content of the bibenzyl and that of the methane (see Experimental and footnote 27) were due to an identity reaction. This is close to the limit of what can be detected by mass spectrometry.

run (5, dimerization of toluene-α-*d* using acetyl peroxide) the conversion was intentionally pushed up by using high acetyl peroxide concentrations—a device of doubtful advisability at best. In this run the recovered toluene contained 0.3 ± 0.2 mole % toluene-d_2—not enough to give definitely significant evidence for even a minor occurrence of the identity reaction in this particular system.

Experimental[13]

(+)-2-Phenylbutane and cumene-α,β-d_2 were prepared as described in a previous paper.[14]

Toluene-α-d.—Benzylmagnesium chloride was prepared by the addition of 126.6 g. (1.000 mole) of benzyl chloride in 500 ml. of ether to 24.3 g. (1.00 gram-atom) of magnesium turnings in 100 ml. of ether. The Grignard reagent was heated under reflux with vigorous stirring while 30.0 g. (1.50 moles) of deuterium oxide (Stuart Oxygen Co., 99.5%) was added dropwise over the course of 1.5 hours and the grayish-white mixture was refluxed with stirring for four more hours. The volatile components of the reaction mixture were then distilled out and fractionated. Toluene-α-*d* was collected at 108.6–109.0°(738 mm.), n^{20}_{D} 1.4957, yield 61.8 g. (66.3%). (Pure toluene has b.p. 110.625° (760 mm.) and n^{20}_{D} 1.49693[15]). Mass spectrometric analysis at reduced ionizing voltage[11]; C_7H_8, 1.3 ± 0.2%; C_7H_7D, 98.7 ± 0.2%.

In two subsequent runs, a combined yield of 77.6% was attained by recovering additional toluene-α-*d* from the reaction mixtures by steam distillation and ether extraction of the steam distillate. This isolation procedure did not appear to affect the isotopic purity of the product; mass spectrometric analysis at reduced ionizing voltage[11]: batch A, C_7H_7D, 97.7 ± 0.2%; C_7H_8, 2.3 ± 0.2%; batch B,[16] C_7H_7D, 97.5 ± 0.2%; C_7H_8, 2.5 ± 0.2%.

Anal. Calcd. for C_7H_7D: D, 12.50 atom %. Found: batch A, D, 12.25 ± 0.1 atom %; batch B, D, 12.36 ± 0.1 atom %. This corresponds to 98.0 ± 0.8% labeled material in batch A and 98.7 ± 0.8% labeled material in batch B.

In order to ascertain the extent, if any, of ring deuteration, a 2.0-g. sample of toluene-α-*d* (batch B) was oxidized with potassium permanganate (alkaline conditions).[17] The benzoic acid so obtained was recrystallized from water, dried (m.p. 123.5–124°) and analyzed for deuterium.

Anal. Found: 0.05 atom per cent. D, *i.e.*, after correction for naturally occurring deuterium, 0.03 atom per cent. D. The latter figure corresponds to 0.18% of C_6H_4-DCOOH.[18] Because of the low figure, the analysis is not very accurate.

α-Chloro-*p*-xylene.—A mixture of *p*-xylene[20] (Matheson, Coleman and Bell, 109.8 g., 1.03 moles), carbon tetrachloride (108 g.), sulfuryl chloride (40.5 g., 0.3 mole) and benzoyl peroxide (0.25 g., 0.01 mole) was heated gradually to reflux. Gas evolution and progress of the reaction could be followed by allowing the gases formed to pass first through a cold trap and then through a sulfuric acid bubbler. Liquid which accumulated in the trap was added to the reaction mixture from time to time. Gas evolution ceased after heating 1.5 hours. The mixture was allowed to cool, carbon dioxide gas was passed through the liquid to flush out residual sulfur dioxide and hydrogen chloride, and the mixture was fractionally distilled. After the carbon tetrachloride and unreacted *p*-xylene had come over, there was obtained 34.7 g. (82%) of α-chloro-*p*-xylene, b.p. 93.5–103° (21 mm.). Prior to use, the combined products of several chlorination experiments were redistilled to give material boiling at 90–96° (16 mm.) (lit.[21] 92–94° (20 mm.)), n^{20}_{D} 1.5342 (lit.[22] 1.5380).

p-Xylene-α-d.—*p*-Methylbenzylmagnesium chloride was prepared in the usual fashion by adding 111.7 g. (0.795 mole) of α-chloro-*p*-xylene in 400 ml. of ether to 19.3 g. (0.795 gram-atom) of magnesium turnings covered with 100 ml. of ether. Addition of deuterium oxide (32 g., 1.6 moles) and isolation of the deuterated hydrocarbon were carried out essentially as described in the preparation of toluene-α-*d*. There was obtained 53.0 g. (62%) of *p*-xylene-α-*d*, b.p. 136–137° (746 mm.), n^{20}_{D} 1.4957. (Pure *p*-xylene has b.p. 138.350° (760 mm.) and n^{20}_{D} 1.49581[15]). Mass spectrometric analysis at reduced ionizing voltage[11]: C_8H_9D, 94.8 ± 0.2%,[16] 95.3 ± 0.2%; C_8H_{10}, 5.2 ± 0.2%,[16] 4.7 ± 0.2%.

Anal. Calcd. for C_8H_9D: D, 10.00 atom per cent. Found: D, 9.40 ± 0.1 atom per cent. corresponding to 94 ± 1% isotopic purity.

Decomposition of Acetyl Peroxide in (+)-2-Phenylbutane.—A 25% solution of acetyl peroxide (2.88 g., 0.0244 mole) in dimethyl phthalate was introduced slowly beneath the surface of 15.96 g. (0.119 mole) of freshly distilled (+)-2-phenylbutane, b.p. 170.4–171.4° (738 mm.), $[\alpha]^{25}_{\mathrm{D}}$ +9.94 ± 0.01 (*l* 2 dm., neat), with stirring and heating to maintain the reaction mixture at 125–130°. The addition took 50 minutes and the heating and stirring were continued for 15 minutes. The reaction mixture was then distilled under reduced pressure to recover 11.57 g. of 2-phenylbutane, b.p. 64–67.0° (18 mm.), $[\alpha]^{25}_{\mathrm{D}}$ +9.70°. Redistillation of the recovered material through a 20-cm. glass helices-packed column gave three fractions of essentially identical refractive index (n^{20}_{D} 1.4890–1.4895) and specific rotation ($[\alpha]^{25}_{\mathrm{D}}$ +9.65 to +9.69°).

The remainder of the reaction mixture was heated under reflux for three hours with a solution of 9.3 g. of potassium hydroxide in 60 ml. of methanol and 6 ml. of water, then freed of methanol by steam distillation, and extracted three times with ether. The combined ethereal solution was washed with water, dried over calcium chloride, freed of solvent, and then distilled *in vacuo* to give 0.77 g. of a slightly yellow viscous liquid, b.p. 103–104° (0.04 mm.), which crystallized when triturated with a small amount of ethanol. Three recrystallizations from the same solvent yielded 46.1 mg. of *meso*-3,4-dimethyl-3,4-diphenylhexane as colorless plates, m.p. 98–98.5° (lit.[23] 93°).

In another experiment, 68 g. of starting material having α^{25}_{D} +2.46° (*l* = 1 dm., neat) gave rise to recovered 2-phenylbutane (47.9 g.), b.p. 56° (11 mm.), n^{25}_{D} 1.4869–1.4870, three successive fractions of which had α^{25}_{D} +2.37, +2.35° and +2.34°. There was also obtained 7.5 g. of dimer, b.p. 141–145° (0.9 mm.). One fraction weighing 3.5 g. was dissolved in 14 ml. of ether. The rotation of this solution observed in a 2-dm. tube was 0.00°.

In an experiment employing *dl*-2-phenylbutane, the crude dimer, b.p. 137–139° (0.8 mm.), was subjected to infrared and elementary analysis.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.10; H, 10.19.

The infrared spectrum, recorded in carbon disulfide solution had (among others) a *broad* band at 13–13.1 μ. The semi-solid dimer was subjected to filtration, washed with absolute alcohol and recrystallized twice from the same solvent. This gave crystals melting at 99–100°. The infra-

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[13] All melting and boiling points are uncorrected. Infrared spectra were recorded on a Baird double-beam instrument by Mr. Rolland S. Ro. Mass spectra were recorded on a Consolidated 21-103A analytical mass spectrometer by Mr. George Young, except where noted otherwise. Deuterium analyses by Mr. Josef Nemeth, University of Illinois, Urbana, Ill., except when stated otherwise. Fractional distillations were carried out in a 40-cm. glass-helices packed column, unless otherwise indicated.

[14] E. L. Eliel, P. H. Wilken and F. T. Fang, *J. Org. Chem.*, **22**, 231 (1957).

[15] R. R. Dreisbach, "Physical Properties of Organic Compounds," American Chemical Society Advances in Chemistry Series, No. 15, Washington, D. C., 1955.

[16] This analysis was kindly carried out by Mr. Seymour Meyerson, Standard Oil Co. (Indiana), Whiting, Ind.

[17] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 198.

[18] This extent of ring deuteration does not appreciably affect the calculations of isotope effects. This is in contrast to the toluene-α-*d*[19] and *p*-xylene-α-*d*[7] prepared by other investigators using similar methods. These samples contained, respectively, 1.2 and 2.8% of ring monodeuterated species.

[19] D. Bryce-Smith, V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1954).

[20] Shown by infrared spectrum to be isomerically pure.

[21] H. Stephen, W. F. Short and G. Gladding, *J. Chem. Soc.*, **117**, 520 (1920).

[22] P. Shorygin and A. V. Bogdanova, *J. Appl. Chem.* (*U.S.S.R.*), **11**, 1217 (1938); *Chem. Zentr.*, **110** (2), 1277 (1939).

[23] R. L. Huang and L. Kum-Tatt, *J. Chem. Soc.*, 2570 (1954).

red spectrum of the solid in carbon disulfide had a sharp band at 13.01 μ.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.20; H, 9.95.

From these results it was inferred that the crude, semisolid material was a mixture of *meso*-3,4-dimethyl-3,4-diphenylhexane with the *dl*-isomer. This is in agreement with the finding of Huang and Kum-Tatt[23] that treatment of 2-phenylbutane with di-*t*-butyl peroxide at 140–150° gave a mixture of the *meso* dimer, m.p. 93° and its *dl*-isomer, m.p. 40–41°.

That the slight but significant racemization in these experiments was due to a hydrogen transfer reaction and not to a disproportionation of the type

$$2PhC(CH_3)C_2H_5 \rightarrow PhCH(CH_3)C_2H_5 + PhC(CH_3){=}CHCH_3\ [\text{or } PhC(C_2H_5){=}CH_2]$$

was shown by treating the recovered 2-phenylbutane with a solution of potassium permanganate in aqueous pyridine. No brown color developed. A blank of 2-phenylbutane containing 1.3% of α-methylstyrene produced a brown color very rapidly under the same conditions.

Decomposition of Acetyl Peroxide in a Mixture of 2-Phenylbutane and Cumene-α,β-d_2.—A 25% solution of acetyl peroxide (11.81 g., 0.1 mole) in dimethyl phthalate was introduced slowly beneath the surface of a mixture of 21.81 g. (0.1625 mole) of *dl*-2-phenylbutane and 32.30 g. (0.2643 mole) of cumene-α,β-d_2 with stirring and heating to maintain the reaction mixture at 125°. The addition took about two hours and the heating and stirring were continued for 15 more minutes. The reaction mixture was then distilled under reduced pressure to recover 40.3 g. of a mixture of hydrocarbons, b.p. 55.4–69.0° (25 mm.). Fractionation of this material led to the recovery of some 2-phenylbutane, b.p. 58.5–59.0° (24 mm.), $n^{20}D$ 1.4892 (lit.[24] $n^{20}D$ 1.4898) which was subjected to mass spectrometric analysis at reduced ionizing voltage.[11] Found: $C_{10}H_{14}$, 98.2 ± 0.2; $C_{10}H_{13}D$, 1.0 ± 0.2; $C_{10}H_{12}D_2$, 0.8 ± 0.2%.

The remainder of the reaction mixture was heated under reflux for four hours with a solution of 33.4 g. of potassium hydroxide in 225 ml. of methanol and 50 ml. of water, then freed of methanol by steam distillation, and extracted three times with ether. The combined ethereal solution was washed with water, dried over calcium chloride, freed of solvent, and then distilled *in vacuo* to give first a colorless liquid, b.p. 127–129° (1.0 mm.), which crystallized on standing. Two recrystallizations from ethanol produced 0.86 g. of deuterated 2,3-dimethyl-2,3-diphenylbutane as white needles, m.p. 114.5–115.5° (lit.[25] m.p. 115° for the hydrogen compound). Further distillation of the residue *in vacuo* yielded 1.34 g. of a slightly yellow viscous liquid, b.p. 114–115° (0.05 mm.), which, according to infrared spectrum, appeared to be a mixture of 3,4-dimethyl-3,4-diphenylhexanes.

Decomposition of Acetyl Peroxide in Toluene-α-*d*.—A 25% solution of acetyl peroxide (8.86 g., 0.0750 mole) in dimethyl phthalate was introduced slowly beneath the surface of 27.94 g. (0.3000 mole) of toluene-α-*d* (98.7% isotopic purity) with stirring and heating to maintain the reaction mixture at 125°. The addition took about 2.5 hours and the heating and stirring were continued for 15 minutes. Unreacted toluene-α-*d* was distilled out from the reaction mixture and then fractionated through a 20-cm. glass helices-packed column to recover 16.81 g. of the pure material, b.p. 109.0–110.0° (744 mm.), $n^{20}D$ 1.4953. Mass spectra of the starting and recovered materials failed to show any appreciable exchange of hydrogen isotopes.

The remainder of the reaction mixture was heated under reflux for three hours with a solution of 25.8 g. of potassium hydroxide in 175 ml. of methanol and 25 ml. of water, then freed of methanol by steam distillation, and extracted three times with ether. The combined ethereal solution was washed with water, dried over calcium chloride, freed of solvent, and then distilled *in vacuo* to give 0.48 g. of a slightly yellow liquid, b.p. 78–79° (0.04 mm.), which crystallized on cooling. Recrystallization from ethanol yielded a total of 91.8 mg. of deuterated bibenzyl, m.p. 51.5–52.5°. Pure bibenzyl has m.p. 52.0°.[24]

The bibenzyl sample was subjected to deuterium analysis.[26] Two different combustions in each of which the water was converted to hydrogen–deuterium mixtures, which were then subjected to duplicate mass spectrometric analysis gave values of 13.0, 13.2, 13.2 and 13.0 atom % of deuterium, corresponding to an isotope effect of 7.1.

In a second similar run, using toluene-α-*d* of 97.5% isotopic purity carried out in a closed system previously flushed with dry argon, the gaseous products were collected over water and several portions were analyzed mass spectrometrically. The percentage of deuteriomethane in the total methane produced gradually decreased as the reaction proceeded: 5.09, 4.44, 3.66, 3.48%. This may be interpreted as being due to the accumulation of dimethyl phthalate in the reaction flask. Hydrogen abstraction from the dimethyl phthalate, yielding methane, would tend to dilute the deuteriomethane formed. The apparent isotope effect in the formation of methane was thus calculated from the first figure reported.[27]

The bibenzyl, b.p. 73° (0.1 mm.), m.p. 51.5–52.5°, was isolated as described above; the yield of recrystallized material was 0.22 g.

Anal. Found: 12.84, 12.86 ± 0.1 atom % D corresponding to an isotope effect of 6.8.

Decomposition of Acetyl Peroxide (Dimethyl Phthalate-free) in Toluene-α-*d*.—Solutions of acetyl peroxide in toluene-α-*d* were prepared by the method of Price and Morita,[28] toluene-α-*d* being substituted for ethyl ether. The solutions were analyzed iodometrically by the method of Kokatnur and Jelling.[29] The apparatus utilized was a closed system consisting of a three-neck peak-shaped flask equipped with a gas inlet tube, a pressure-equalized addition funnel and a condenser. A thermometer reaching to the bottom of the flask was inserted through the condenser. All openings were channeled to a Dry Ice–acetone trap and from there to an inverted flask equipped at the top with a three-way stopcock by means of which gas samples could be withdrawn from the flask (using evacuated bulbs). Prior to each reaction the entire system was flushed with dry argon.

In the apparatus described, a 10.6% solution of acetyl peroxide in toluene-α-*d* (25.0 ml., containing 2.65 g., 0.0224 mole of acetyl peroxide) was added dropwise to 1.7 g. of refluxing toluene-α-*d* (total amount of toluene-α-*d*, isotopic purity 97.7%, 21.4 g., 0.23 mole). During the addition, which took 2.5 hours, several gas samples were withdrawn from the gas collection flask, the remainder of the gas being discarded. After the end of the addition, heating was continued for 1.5 hours. The toluene recovered upon fractionation, of the reaction mixture, 15.8 g., b.p. 104–108.5° (748 mm.), $n^{20}D$ 1.4891, was contaminated with acetic acid and acetic anhydride. The contaminants were removed prior to mass spectral analysis by heating a portion of the distillate with water and pyridine, shaking with dilute sulfuric acid, aqueous sodium carbonate and water. After drying over calcium chloride, the purified toluene-α-*d* was redistilled, b.p. 107.5–108° (748 mm.), $n^{20}D$ 1.4968. Comparison of the mass spectrum of this material with that of the starting material failed to show any isotopic exchange of hydrogens.

The remainder of the reaction mixture was refluxed for 4 hours with a solution of 7.5 g. of sodium hydroxide in 30 ml. of water. The mixture was then steam distilled and the solid recovered (by extraction of the steam distillate with ether, drying the ether extract, and removing the ether) was recrystallized from aqueous ethanol to give a total of 0.07 g. of deuterated bibenzyl, m.p. 51.5–52°. *Anal.* Found: 11.54 ± 0.1 atom % D corresponding to an isotope effect of 2.4. Mass spectrometric analysis of the gas samples taken showed the percentage of deuteromethane to be 4.77% (average).[27]

In a second run, 3.1 g. (0.026 mole) of acetyl peroxide was decomposed in 23.9 g. (0.26 mole) of toluene-α-*d* (isotopic purity 97.7%). After the addition of the peroxide

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[24] G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1946, Vol. 3.

[25] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

[26] We are greatly indebted to Dr. Kenneth E. Wilzbach, Chemistry Division, Argonne National Laboratories, for carrying out these analyses.

[27] The significance of the methane composition is discussed in paper II of this series: S. H. Wilen and E. L. Eliel, This Journal, **80**, 3309 (1958).

[28] C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[29] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

solution, heating was continued for six hours after which the reaction mixture was washed with aqueous sodium bicarbonate, water and dried over calcium chloride.

Upon fractionation, 13.2 g. of impure toluene-α-*d*, b.p. 107–108° (738 mm.), n^{20}D 1.4962, was recovered which was purified as in the previous run.

The residue from the fractionation was dissolved in petroleum ether (b.p. 30–60°) and chromatographed through a column of activated alumina (Aluminum Ore Co., Grade F-20). Deuterated bibenzyl was isolated from the eluate by removing the solvent over the water-bath and recrystallizing the residue from aqueous ethanol, m.p. 51.5–52.5°. The yield was 0.075 g.

Anal. Found: 12.43 ± 0.1 atom % D, corresponding to an isotope effect of 4.2.

The percentage of deuteromethane in the gas samples collected was found to be 5.21% (average) by mass spectral analysis.[27]

In an experiment in which 3.1 g. (0.026 mole) of acetyl peroxide was decomposed in 24.3 g. of ordinary toluene, the total volume of gas produced was measured and found to be 1460 ml. (at 23° and 737 mm.) of which 49.3% was methane. This corresponds to a yield of 0.029 mole of methane. The bibenzyl obtained in this run, which was isolated by the chromatographic method described above, amounted to 0.39 g. (0.0022 mole).

Decomposition of Acetyl Peroxide (Dimethyl Phthalate-free) in Toluene-α-*d* at High Concentration.—The concentration of a solution of acetyl peroxide in toluene-α-*d* (97.5% isotopic purity, see preceding experiment) was increased by utilizing the solution as the solvent for a repeat preparation of an acetyl peroxide solution. In this manner a 29.5% solution of acetyl peroxide in toluene-α-*d* was prepared. Using apparatus similar to that described in the preceding experiment[30] the 29.5% solution of acetyl peroxide in toluene-α-*d* (19 ml., containing 5.6 g., 0.048 mole of acetyl peroxide) was added dropwise to a dry flask maintained at 132–137°. Three gas samples were collected. The addition took 1 hour after which the reaction mixture was heated for an additional 2 hours. After cooling and without prior treatment, the reaction mixture was utilized as solvent for the preparation of an acetyl peroxide solution. The concentration of this solution was increased as above by utilizing the peroxide solution as solvent for a duplicate preparation of an acetyl peroxide solution whereupon the solution had a concentration of 31%.[31]

In the same apparatus (described above) and after flushing with dry carbon dioxide, the 31% peroxide solution (10 ml., 9.4 g., containing 3.1 g., 0.026 mole of acetyl peroxide) was added dropwise to 0.4 g. of boiling toluene-α-*d* (bath temperature 134–140°)[32] over the course of one hour.[33] During this time three gas samples were collected. The reaction mixture was heated for a further 1.5 hours and then the unreacted solvent was recovered by fractionation, b.p. 101–110° (746 mm.), 2.7 g. The recovered toluene-α-*d* was purified by heating with pyridine and water (see preceding experiment). Distillation of the purified material gave toluene-α-*d*, b.p. 110.5–113.5° (746 mm.), n^{20}D 1.4969, 1.0 g.; mass spectrometric analysis at reduced ionizing voltage: C_7H_8, 2.4 ± 0.2%; C_7H_7D, 97.2 ± 0.2%; $C_7H_6D_2$, 0.3 ± 0.2%. The mass spectrum also indicated the presence of a considerable quantity (of the order of 5% of the sample) of C_8-compounds.[34]

The residue from the fractionation was chromatographed on alumina, in petroleum ether (b.p. 39–69°) giving 0.7 g. of a liquid which was dissolved in 5 ml. of petroleum ether and chilled in a Dry Ice–acetone-bath. Upon scratching, a white solid precipitated. The liquid was removed with a fine dropper and the procedure was repeated with another 5 ml. of petroleum ether. The solid so recovered (0.1 g.) did not melt at room temperature and was recrystallized from aqueous ethanol leaving 66 mg. of product. The latter was purified by a combination of distillations and vacuum sublimations carried out in bulb tubes,[35] and recrystallizations from methanol carried out in small sealed tubes to minimize losses. The bibenzyl so obtained had m.p. 51–51.6° (Kofler block).

Anal. Found: 12.40 ± 0.1 atom % D, corresponding to an isotope effect of 4.4.

The methane in the six gas samples collected contained 5.08% (average) of methane-*d*.[27]

Decomposition of Benzoyl Peroxide in Toluene-α-*d*.—In a closed system consisting of a round-bottom flask equipped with a gas inlet tube, a thermometer and a condenser, the latter being in series with a bubbler through which gas could escape, a solution of 9.8 g. (0.038 mole) of benzoyl peroxide in 37.8 g. (0.406 mole) of toluene-α-*d* (97.7% isotopic purity) was flushed with dry argon and gradually heated until vigorous gas evolution was taking place. The solution was heated (116–117°) for an additional 24 hours, washed with 10% aqueous sodium bicarbonate and with water, dried over calcium chloride, and then fractionally distilled. There was recovered 23.2 g. of toluene-α-*d*, b.p. 107.9–108.6° (747 mm.), n^{20}D 1.4969. The residue was dissolved in petroleum ether (30–60°) and chromatographed through activated alumina. The eluate was freed of solvent by distillation; deuterated bibenzyl was isolated from the residual hydrocarbon mixture by the method of Rondestvedt and Blanchard.[36] The yield of deuterated bibenzyl, m.p. 51.5–52.5°, was 0.19 g.

Anal. Found: 12.00, 11.85 ± 0.1 atom % D, corresponding to an isotope effect of 3.0. Calcd. for $C_{14}H_{12.3}D_{1.7}$: C, 91.40; H, 7.8. Found: C, 91.69; H, 7.98.

The forerun from the fractional distillation in which toluene-α-*d* was recovered was carefully fractionated in a small glass spiral (vacuum jacketed) column (height 16 cm.). There was obtained in addition to more toluene-α-*d* a small fraction, b.p. 71–83° (749 mm.), n^{20}D 1.5007, which was analyzed mass spectrometrically at reduced ionizing voltage.[11] The fraction consisted of benzene, toluene and the corresponding monodeuterated species.

For benzene there was found 8.7% C_6H_5D and 91.3% C_6H_6.

Decomposition of Di-*t*-butyl Peroxide in Toluene-α-*d*.—The apparatus utilized in this experiment was similar to that used in the decomposition of acetyl peroxide in toluene-α-*d*, with the exception that the reaction flask was a round-bottom flask equipped with a gas inlet tube, a thermometer and a condenser. In this apparatus, a solution of 3.5 g. (0.024 mole) of di-*t*-butyl peroxide (Brothers Chemical Co., used as received) in 22.5 g. (0.242 mole) of toluene-α-*d* (97.7% isotopic purity) was flushed with dry argon and gradually heated until gas evolution had begun. The solution was heated for a total of 48 hours, during which time several gas samples were taken. Mass spectrometric analysis of these samples showed the presence of 6.2% (average) of deuteriomethane in the methane produced.[27] During the heating period, the temperature of the reaction mixture gradually dropped from 116 to 107° as acetone and *t*-butyl alcohol accumulated in the flask. Upon distillation of the reaction mixture, the following fractions were collected: (a) 4.9 g., b.p. 89–105° (739 mm.); (b) 12.7 g., b.p. 106–108° (739 mm.); and (c) 5.0 g., b.p. 108.5–109° (739 mm.). The distillate obtained upon vacuum distillation of the residue, b.p. 75° (0.09 mm.), solidified upon

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(30) The apparatus was modified as follows: A tube led from the top of the condenser to an inverted water-filled flask which served as a reservoir for the gas produced. Gas samples were withdrawn (using evacuated bulbs) through a stopcock-equipped side arm in the above-mentioned tube. Before the start of the experiment the apparatus was purged with carbon dioxide.

(31) Effectively, then, the same solvent served four times as medium for the preparation of acetyl peroxide solution. Accumulated products were not removed in order to magnify the effects of an identity reaction (if the latter were indeed taking place).

(32) This was preferable to adding the solution to a dry flask (as was done in the first part of the experiment). In this case this procedure proved to be too violent.

(33) The formal molar ratio of 1.4 listed for the over-all reaction in Table I was arrived at as follows: The molar ratio in the first part of the experiment was estimated to be *ca.* 2.5/1; that in the second part of the experiment (*i.e.*, the second decomposition) was found to be *ca.* 3/1. Since essentially the same solvent was used for both parts the molar ratio is stated as the average number of moles of solvent divided by the *total* number of moles of peroxide 2.75/2 ≈ 1.4/1.

(34) *Cf.* E. L. Eliel, K. Rabindran and S. H. Wilen, *J. Org. Chem.*, **22**, 859 (1957).

(35) See K. Ronco, B. Prijs and H. Erlenmeyer, *Helv. Chim. Acta*, **39**, 2088 (1956). We are indebted to Dr. Ralph G. Haber for assistance in carrying out these operations.

(36) C. S. Rondestvedt, Jr., and H. S. Blanchard, THIS JOURNAL, **77**, 1769 (1955).

cooling and was recrystallized from aqueous ethanol yielding 1.02 g. of deuterated bibenzyl, m.p. 51.5–52.5°.

Anal. Found: 12.15, 12.35 ± 0.1 atom % D corresponding to an isotope effect of 3.7. As in the case of the other decomposition reactions, the recovered toluene-α-*d*, (fraction c) had a mass spectrum essentially unchanged from that of the starting material. In this instance the fraction contained a small amount of di-*t*-butyl peroxide which did not, however, interfere in the mass spectral analysis.

Utilizing a closed system previously flushed with dry argon, an ether solution of fraction a, which contained the *t*-butyl alcohol formed in the reaction, was added to 0.10 mole of methylmagnesium iodide (from 14.3 g. of methyl iodide and 2.6 g. of magnesium turnings) in 50 ml. of ether. The methane produced was collected over water and several samples analyzed mass spectrometrically. The methane contained 8.3% (average) of deuteriomethane.[27]

Decomposition of Acetyl Peroxide in *p*-Xylene-α-*d*.—In an apparatus similar to that described for the decomposition of dimethyl phthalate-free acetyl peroxide in toluene-α-*d* previously flushed with dry carbon dioxide, a 15.4% solution of acetyl peroxide in *p*-xylene-α-*d* (26 ml., 22.9 g., 95.0% isotopic purity, containing 4.0 g., 0.034 mole, of acetyl peroxide) was added dropwise to 3.1 g. of refluxing *p*-xylene-α-*d* (total amount of *p*-xylene-α-*d* taken was 22.0 g., 0.205 mole). The addition took 1.25 hours (temperature range 122–124°) and heating was continued for two additional hours. Four gas samples were taken during the addition. Unreacted *p*-xylene-α-*d* was recovered by fractionating the reaction mixture, b.p. 136–137° (745 mm.), n^{20}_{D} 1.4953, 13.7 g.; mass spectrometric analysis at reduced ionizing voltage[11]: C_8H_{10}, 4.8 ± 0.2%; C_8H_9D, 95.2 ± 0.2%; $C_8H_8D_2$, 0.0 ± 0.2%.[16]

Deuterated 4,4′-dimethylbibenzyl was recovered from the fractionation residue by chromatography (alumina, petroleum ether of b.p. 30–60°) followed by distillation of the solid so obtained, b.p. 100–110° (0.15 mm.), 1.21 g. The solid was twice recrystallized from aqueous methanol and dried, m.p. 81.5–82.5° (lit.[37] 79–81°).

Anal. Found: 10.20, 10.27 ± 0.1 atom % D, corresponding to an isotope effect of 8.9.[38]

The percentage of deuteriomethane in the gas samples collected was 2.78% (average).[27]

Decomposition of Benzoyl Peroxide in *p*-Xylene-α-*d*.[7]—To 20.1 g. (0.188 mole) of *p*-xylene-α-*d* (95.0% isotopic purity) held at 80° (±3°) there was added 1.9 g. (0.0079 mole) of benzoyl peroxide portionwise in a period of 13 minutes. The solution was heated at 80 ± 3° for a total of 72 hours, then fractionated to recover unreacted *p*-xylene-α-*d*, b.p. 136–137° (743 mm.), n^{20}_{D} 1.4960, 15.2 g.; mass spectrometric analysis at reduced ionizing voltage[11]: C_8H_{10}, 5.1 ± 0.2%; C_8H_9D, 94.9 ± 0.2%.[16]

Chromatography (alumina, petroleum ether of b.p. 30–60°) of the residue from the fractionation, followed by distillation, (b.p. 87–127° (0.25 mm.)), gave a product part of which solidified upon cooling. The solid (*ca.* 0.3 g.) was separated from the liquid and twice recrystallized from aqueous methanol, then dried, m.p. 82–82.5°.

Anal. Found: 9.75, 9.82 ± 0.1 atom % D, corresponding to an isotope effect of 2.9.

Isotope Effect Calculations.—Isotope effects reported in this paper were calculated by means of the equations

Toluene-α-*d*–bibenzyl formation

$$i = \frac{7AP}{200P + 7AP - 2100A}$$

p-Xylene-α-*d*–dimethylbibenzyl formation

$$i = \frac{9AP}{500P + 9AP - 5400A}$$

i = isotope effect
A = atom per cent. deuterium in the bibenzyl or dimethylbibenzyl
P = isotopic purity of substrate

Acknowledgment.—This work is a contribution from the Radiation Project of the University of Notre Dame, supported in part under Atomic Energy Commission contract AT(11-1)-38 and Navy equipment loan contract Nonr-06900.

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[37] D. J. Cram and H. Steinberg, This Journal, **73**, 5691 (1951).

[38] This value is based on a deuterium content of the dimer of 10.23 atom % (average of two analyses) and an isotopic purity of the substrate of 95.05% (average of two mass spectrometric analyses). Unfortunately, when the isotope effect is larger than about 6, its exact value becomes extremely dependent on the analytical figures. Thus, in the above case, if one bases the isotope effect calculation on the lower of the two dimer analyses (10.20%) and the higher of the two substrate analyses (95.3%), the result is an isotope effect of 6.6. All one can say with some confidence is that the isotope effect is larger than 6.