Figure 1 is an Arrhenius plot showing these data and ours. Our lowest temperature data are the least accurate; Taylor and Feltis claim least accuracy at their highest temperature. It is seen that the agreement is excellent in the region where high accuracy is claimed for both results. Better agreement would require better temperature measurements, since our temperatures are measured with a mercury thermometer calibrated by the National Bureau of Standards, with corrections listed to the nearest 0.1°. If we choose to ignore the advantage of the concurrency of the pairs of runs, we get the average $k_H = 2.518 \times 10^{-4}$ with a mean deviation of 0.025×10^{-4}; the average k_D then is 2.562×10^{-4} with a mean deviation of 0.019×10^{-4} and the ratio k_H/k_D is then 0.983. This includes all runs at 52.8°, including one made as much as a year before the final ones in a somewhat different thermostat (the last one in the table at this temperature). No reasonable selection of individual runs or combinations thereof will significantly change this ratio.

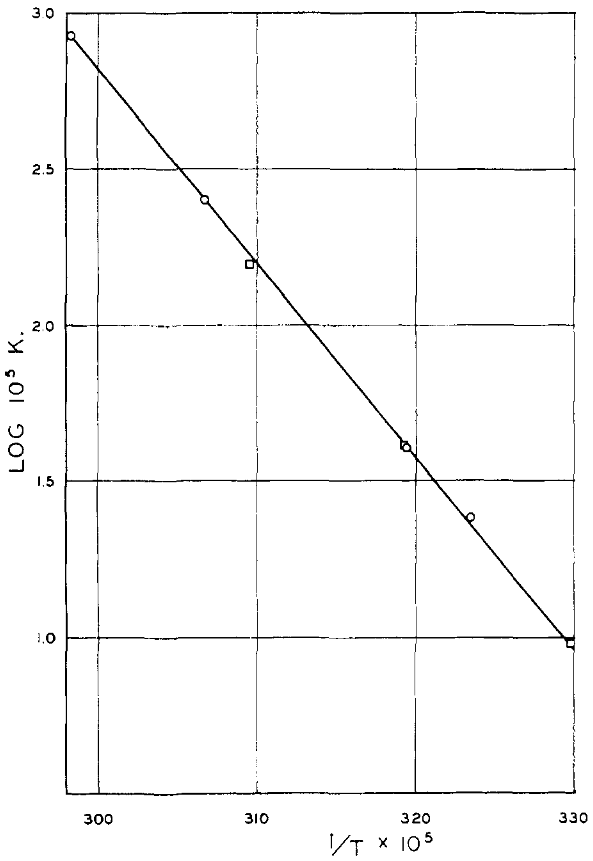

Fig. 1.—Arrhenius plot for the decomposition of *p*-toluenediazonium ion; data of Taylor and Feltis □; this work O.

While we cannot consider the ratio established to high accuracy the value 1.00 for the ratio is very improbable, being indicated in fact by only the one of the six values of k_H, the one which gave an unusually high value of k_D in the concurrent experiment. The value $k_H/k_D = 0.990 \pm 0.005$ covers the most reliable data combinations. The conclusions drawn at the beginning of this discussion are therefore justified, and both the connection between isotope effect and hyperconjugation and the suggested mechanism of diazonium salt decomposition can be considered to be confirmed by this unusual isotope effect.

Acknowledgment.—We wish to thank the Robert A. Welch Foundation for support of this work. We also thank Dr. R. B. Williams of Humble Oil and Refining Co. for the nuclear magnetic resonance spectra.

Houston, Texas

[Contribution from the Department of Chemistry of the University of South Carolina]

The Products of the Thermal Decomposition of Bis-δ-phenylvaleryl Peroxide in Carbon Tetrachloride and in Benzene

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The thermal decomposition of bis-δ-phenylvaleryl peroxide has been studied in solution in carbon tetrachloride and in benzene. By use of dilute solutions (4–16 mmolar) and of an aliphatic type of peroxide, complicating induced decomposition reactions have been minimized. The expected δ-phenylbutyl radical intermediate is structurally capable of cyclizing to give tetralin; tetralin was formed in 30% yield in benzene but was absent from reactions in carbon tetrachloride. In carbon tetrachloride the products were CO_2 (84%), phenylvaleric acid, 4-phenyl-1-chlorobutane, δ-phenylbutyl δ-phenylvalerate, 1,8-diphenyloctane, 1,1,1,3-tetrachloro-5-phenylpentane (addition of CCl_4 to 4-phenyl-1-butene), hexachloroethane and phosgene. A careful search showed that the intramolecular chain transfer product, *o*-chloro-*n*-butylbenzene, was absent and also that 1,1,1-trichloro-5-phenylpentane was absent. This latter result is most significant, for it shows that there is no cross-coupling of 4-phenyl-1-butyl radicals with trichloromethyl radicals, although the products of separate coupling, hexachloroethane and 1,8-diphenyloctane, are formed. Such a result can be accounted for if the 1,8-diphenyloctane and the δ-phenylbutyl δ-phenylvalerate result form radical dimerization occurring in a solvent "cage" and if all 4-phenyl-1-butyl radicals which escape react to give 4-phenyl-1-chlorobutane. On this hypothesis more than 50% of the reaction in carbon tetrachloride occurs by primary or secondary recombination reactions.

The thermal decomposition of diacyl peroxides has been studied extensively by many investigators[2–8] because of the importance of this type of reaction as a source of free radical intermediates. In spite of the studies there remain a great many perplexing features about the mechanisms of the peroxide reactions. The difficulty stems from the fact that under most conditions a number of plausi-

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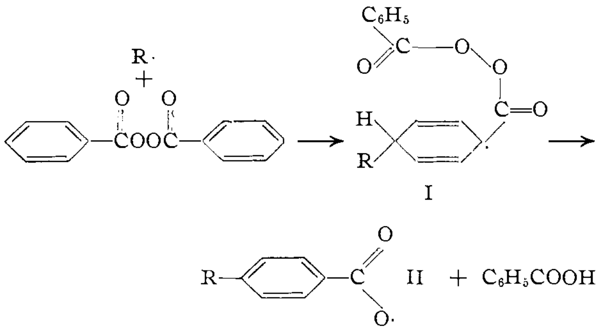
[1] Post-doctoral Research Associate. This work was supported by National Science Foundation Grant NSF G439.

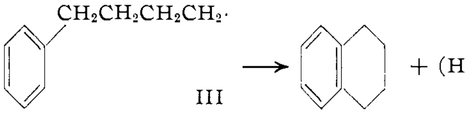
ble reaction paths can be written for each product, and there is no clear guide as to the actual paths taken by the reaction.

One of the principal sources of difficulty in work on the mechanisms of the diacyl peroxide reactions has been the occurrence of induced decomposition arising from attack on the peroxide by radicals derived from peroxide, from solvent or from products.[3,4] A number of attempts have been made to utilize inhibitors to prevent such induced decomposition, particularly in connection with rate studies.[7,8] We have chosen an approach to this problem which appears to have been very much neglected in previous work. By use of dilute solutions in a moderately reactive solvent, it should be possible to reduce the importance of the induced decomposition steps. A study of reaction products at a series of dilutions should provide additional evidence as to the success of the approach, and under favorable circumstances it may be possible to evaluate the products that would be formed at infinite dilution.

A review of the reactions of benzoyl peroxide suggests that this peroxide and other peroxides derived from aryl carboxylic acids may be capable of a special type of induced decomposition involving attack on the ring. Thus Cass[4] reports that one of the significant reaction products formed in the reaction of benzoyl peroxide in dioxane is a compound that is probably a dioxanylbenzoic acid. With dioxane there is a great deal of induced decomposition, but the acylal type of product formed in diethyl ether seems to be present in rather small amounts. One hypothesis to account for such results is that the induced decomposition reaction consists of attack of a dioxanyl radical at a ring carbon atom to give the intermediate radical I, which in turn undergoes decomposition to give a substituted aroyloxy radical II and benzoic acid. Examination of a scale model of I utilizing various approximations for the substituted ring indicates that it is possible to put the carbonyl oxygen atom in contact with the hydrogen atom as shown (for *meta* and *ortho* attack as well). The proposed induced decomposition is thus one that involves a reasonable intermediate. Another example of ring attack that may occur similarly has been reported for the reaction of benzoyl peroxide in acetic acid, a reaction which yields homoterephthalic, and *p*-phenylbenzoic acids among other products.[9] The formation of 1,4-naphthalenedicarboxylic acid occurs when α-naphthoyl peroxide reacts with carbon tetrachloride and the products are hydrolyzed. The suggestion of Kharasch and Dannley[6] that the precursor may have been 4-trichloromethyl-1-naphthoic acid seems most reasonable.



Because of the possibility of the above complications, an aliphatic type of radical was considered desirable for present purposes. Furthermore since we have been interested in intramolecular free radical reactions,[10] we selected δ-phenylvaleryl peroxide as an especially appropriate compound for a detailed study. The δ-phenylbutyl radical III resulting from the peroxide is structurally capable of cyclizing to tetralin. Carbon tetrachloride and benzene were selected as solvents for the preliminary product study in the present report, these being solvents which might be expected to react at quite different rates with the δ-phenylbutyl radical III.[11]



(1)

The present paper reports a semi-quantitative investigation of the reaction products obtained by actual isolation and by preliminary infrared analyses. In addition a search was made for a number of products that might have been formed but which proved to be absent. The results of reaction in carbon tetrachloride are summarized in Table I in terms of both mmoles of reactant and of products and in terms of a material balance for the phenylbutyl groups and the CO_2 groups of the peroxide and for the chlorine atoms and the trichloromethyl groups of the reacted solvent. The results of reaction in benzene are similarly summarized in Table II.

The reaction products can be accounted for in terms of the mechanism steps given in eq. 1–11. While these steps necessarily represent a somewhat arbitrary selection from some 60 or more fairly

$$[C_6H_5(CH_2)_4COO]_2 \longrightarrow 2[C_6H_5(CH_2)_4COO\cdot] \qquad (2)$$

$$[C_6H_5(CH_2)_4COO\cdot]_{cage} \longrightarrow [C_6H_5(CH_4)_4\cdot] + CO_2 \qquad (3)$$

$$C_6H_5(CH_2)_4\cdot + CCl_4 \longrightarrow C_6H_5(CH_2)_4Cl + \cdot CCl_3 \qquad (4)$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6 \qquad (5)$$

$$2[C_6H_5(CH_2)_4\cdot]_{cage} \longrightarrow C_6H_5(CH_2)_8C_6H_5 \qquad (6a)$$

$$2[C_6H_5(CH_2)_4\cdot]_{cage} \longrightarrow C_6H_5(CH_2)_3CH_3 + C_6H_5(CH_2)_2CH{=}CH_2 \qquad (6b)$$

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(2) For bibliographies see W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, Oxford, 1946; A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

(4) W. E. Cass, *ibid.*, **69**, 500 (1947).

(5) P. F. Hartman, H. G. Sellers and D. Turnbull, *ibid.*, **69**, 2416 (1947).

(6) M. S. Kharasch and R. L. Dannley, *J. Org. Chem.*, **10**, 406 (1945); *cf.* also the many other papers by M. S. Kharasch and his coworkers.

(7) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

(8) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(9) M. T. Gladstone, *ibid.*, **76**, 1581 (1954).

(10) D. I. Relyea and D. F. DeTar, *ibid.*, **76**, 1202 (1954).

(11) For a summary of chain transfer data see F. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

$$\left[\begin{matrix}C_6H_5(CH_2)_4\cdot \\ C_6H_5(CH_2)_4COO\cdot\end{matrix}\right]_{cage} \longrightarrow C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5 \quad (7a)$$

$$\left[\begin{matrix}C_6H_5(CH_2)_4\cdot \\ C_6H_5(CH_2)_4COO\cdot\end{matrix}\right] \longrightarrow C_6H_5(CH_2)_4COOH + C_6H_5CH_2CH_2CH{=}CH_2 \quad (7b)$$

$$\cdot CCl_3 + C_6H_5(CH_2)_2CH{=}CH_2 \longrightarrow C_6H_5(CH_2)_2CHCH_2CCl_3 \quad (8)$$

$$C_6H_5(CH_2)_2\underset{\cdot}{C}HCH_3CCl_3 + CCl_4 \longrightarrow C_6H_5(CH_2)_2CHClCH_2CCl_3 + \cdot CCl_3 \quad (9)$$

$$2CCl_3\cdot + O_2 \longrightarrow CCl_3OOCCl_3 \text{ or } 2COCl_2 + Cl_2 \text{ or } ClCOOCCl_3 + Cl_2 \quad (10)$$

$$C_6H_5(CH_2)_4COOCl_3 + H_2O \longrightarrow C_6H_5(CH_2)_4COOH + COCl_2 + HCl \quad (11)$$

Plausible reaction steps which probably do not occur.

$$C_6H_5(CH_2)_4\cdot + \cdot CCl_3 \longrightarrow C_6H_5(CH_2)_4CCl_3 \quad (12)$$

$$C_6H_5(CH_2)_4\cdot \longrightarrow o\text{-}CH_3(CH_2)_3C_6H_4\cdot \quad (13)$$

TABLE I

THE PRODUCTS OF THE THERMAL DECOMPOSITION OF BIS-δ-PHENYLVALERYL PEROXIDE IN CARBON TETRACHLORIDE AT REFLUX TEMPERATURE[a]

Substance	Mmoles	$C_6H_5(CH_2)_4$ groups, %	CO_2, %	Cl, meq.	CCl_3, meq.
Peroxide taken	14.9	100	100	..	..
Products					
CO_2	25	...	84	..	..
$COCl_2$[b]	1.1	...	..	..	1.1
HCl[b]	(3.6)	...	..	..	..
C_2Cl_6	2.7[c]	...	..	..	5.4[c]
$C_6H_5(CH_2)_4COOH$	1.1	4	4	..	..
$C_6H_5(CH_2)_4Cl$	12.2	41	..	12.2	..
$C_6H_5(CH_2)_4COO(CH_2)_4C_5H_5$	2.6	17.5	9	..	..
$C_6H_5(CH_2)_8C_6H_5$	3.2	21.5	..	..	..
$C_6H_5(CH_2)_2CHClCH_2CCl_3$	1.6	5.5	..	1.6	1.6
Total		89.5	97	13.8	8.1

Compounds not present: $C_6H_5(CH_2)_4CCl_3$, tetralin, *o*-$ClC_6H_4(CH_2)_3CH_3$; 1-phenylbutane and 4-phenyl-1-butene were not detected. [a] 4000 ml. of solvent used. [b] Phosgene was obtained as diphenylurea by reaction with aniline. The HCl represents total chloride ion present in the aniline trap; two moles came from each mole of diphenylurea formed, the balance was presumably evolved as HCl gas. [c] Test of the isolation procedure on a known mixture containing hexachloroethane showed that the procedure used with this run was not quantitative for hexachloroethane.

TABLE II

THE PRODUCTS OF THE THERMAL DECOMPOSITION OF BIS-δ-PHENYLVALERYL PEROXIDE IN BENZENE AT THE REFLUX TEMPERATURE[a]

Substance	Mmole	$C_6H_5(CH_2)_4$ groups, %	CO_2, %
Peroxide taken	82	100	100
Products			
CO_2	127		78[b]
$C_6H_5(CH_2)_4COOH$	6.5	4	4
$C_6H_5(CH_2)_3CH_3$	3.8	2.3	..
$C_6H_5(CH_2)_2CH{=}CH_2$	5.9	3.6	..
Tetralin	46	28	..
$C_6H_5(CH_2)_8C_6H_5$	26	32	..
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	15.2	18	9
Total		88	91

[a] 5000 ml. of solvent used. [b] In another run 31 mmoles of peroxide in 3700 ml. of benzene gave 84% of CO_2.

plausible possibilities, they do nevertheless represent a considered selection.[12] Induced decomposition is believed to be absent in the run reported in Table I because examination of the CO_2 yield as a function of initial peroxide concentration showed that as the initial peroxide concentration decreased, the CO_2 yield increased to a limiting maximum of 83–84%. The reduced yield at higher concentrations is attributed to the onset of induced decomposition.

The key result of the present study is the absence of 1,1,1-trichloro-5-phenylpentane (eq. 12), the product expected from combination of a 4-phenylbutyl radical with a trichloromethyl radical. Although this compound is a bit hard to detect in the presence of 1,1,1,3-tetrachloro-5-phenylpentane (eq. 9), a careful and extensive search showed that within the experimental error it was in fact absent. A 2% yield is distinguishable, and this figure is believed to represent an upper limit of the amount that could have formed. Since reaction 12 could also give chloroform and 4-phenyl-1-butene by disproportionation, a careful search was made for chloroform by examining the first few ml. of distillate from the various runs. Small amounts of chloroform in carbon tetrachloride are readily detectable with an infrared spectrophotometer. No chloroform was present in the first fractions.

On the other hand, the formation of hexachloroethane is almost certainly due to dimerization of trichloromethyl radicals (eq. 5) and the formation of 1,8-diphenyloctane is probably due to dimerization of 4-phenyl-1-butyl radicals (eq. 6a), since induced decomposition, which is the only other likely mechanism of formation, has been largely suppressed by working in dilute solution as mentioned above. The problem arises, then, of accounting for the absence of formation of the cross-combination product while permitting formation of the two simple combination products. An explanation based on a large difference in radical reactivity is most unlikely; in fact there seems some tendency for unlike radicals to react more rapidly than like radicals.

The simplest hypothesis seems to be that the 4-phenyl-1-butyl radical combination is a "cage" reaction[13] and that the trichloromethyl radical combination is a non-cage reaction. The reaction of escaped 4-phenyl-1-butyl radicals with carbon tetrachloride to give 4-phenyl-1-chlorobutane (eq. 4) is then so rapid that the concentration of free 4-phenyl-1-butyl radicals is negligible. In fact, the absence of tetralin and of *o*-chloro-*n*-butylbenzene shows that cyclization to tetralin (eq. 1) and the intramolecular chain transfer reaction (eq. 13)[10] are also negligible compared with chlorine abstraction from carbon tetrachloride (eq. 4).

The above reasoning also requires that the formation of the ester, δ-phenylbutyl δ-phenylvalerate be a cage combination reaction (eq. 7a). The formation of 1,1,1,3-tetrachloro-4-phenylpentane is due to addition of the elements of carbon tetrachloride to 4-phenyl-1-butene (eq. 8 and 9). Free 4-phenyl-1-butene is not present in detectable amounts in the

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[12] *Cf.* D. F. DeTar and J. C. Howard, THIS JOURNAL, **77**, 4393 (1955).

[13] R. M. Noyes, *ibid.*, **77**, 2042 (1955).

reaction mixture, and the 6% yield of the tetrachloro compound shows that the formation of the 4-phenyl-1-butene is not a very important reaction. The most likely origin is either reaction 6b or 7b. Since 1-phenylbutane appears to be absent, reaction 7b is considered the more likely source.

Preliminary experiments showed that small amounts of phosgene were formed, and by passing the gases evolved from the reaction through an aniline solution the phosgene was converted to diphenylurea. One mole of peroxide gave about 0.07 mole of diphenylurea as shown in Table I. The origin of the phosgene can probably be attributed to either reaction 10 or 11. It was first considered that the trichloromethyl ester of eq. 11 was produced by an induced attack of the trichloromethyl radical on the peroxide and that the ester underwent hydrolysis (only 20 mg. of water would be required for eq. 11). Since HCl was another product, the contents of the aniline trap were titrated for chloride ion. Equation 11 would require 3 chloride ions per diphenylurea molecule, and the observed ratios were about 3:1 with considerable scatter. The results given in Table I are typical. On the other hand, additional experiments have shown the amount of phosgene does not correlate well with the amount of peroxide used and furthermore the failure of 1-phenylbutane to show up tends to require the δ-phenylvaleric acid yield as a product of eq. 7b. The stoichiometry indicated in eq. 10 represents an alternative route to phosgene. Although some effort was made to remove oxygen by sweeping with nitrogen, the reaction given in Table I was certainly not carried out under oxygen-free conditions. Equation 10 would require 2.5 chloride ions per diphenylurea molecule (after reaction of the chlorine with the aniline), and the experimental results are rather too erratic to distinguish between a ratio of 2.5:1 and one of 3:1.

According to the above hypotheses the results given in Table I indicate a "cage" reaction of about 55% (49/90) at the reflux temperature of carbon tetrachloride. This is a larger amount of primary and secondary combination[13] than has been observed previously. The hypotheses also require that the decarboxylation of the δ-phenylvaleryloxy radical (eq. 3) must be a very fast reaction indeed. The problem of a distinguishing between the two-step mechanism (eqs. 2 and 3) and between a single step cleavage of the peroxide molecule into four fragments [$(RCOO)_2 \rightarrow 2R\cdot + 2CO_2$] will require additional evidence.

The reaction in benzene has been less extensively investigated. The products given in Table II are similar in many respects to those in Table I. The formation of tetralin involves intramolecular attack of an aliphatic radical on an aromatic ring. This represents one of the few examples where the product of a reaction of an aliphatic radical and an aromatic ring has been definitely identified. The fate of the hydrogen atom is somewhat of a mystery; the yields of δ-phenylvaleric acid and of 1-phenylbutane are too small to account for all of it. A search was made for 1,4-diphenylbutane which could arise from attack of the 4-phenyl-1-butyl radical on the solvent. This compound is difficult to distinguish from 1,8-diphenyloctane when present in small amounts. On the basis of distillation of the 1,8-diphenyloctane fraction, it seems reasonably certain that no more than 2 or 3 mmoles of 1,4-diphenylbutane could have been present. There is no way of estimating very exactly the amount of cage reaction. The tetralin and the 1-phenylbutane appear to be formed outside the cage, judging from the carbon tetrachloride results. This sets an upper limit of 57/88 or 65% for the cage reaction. The actual amount could be much smaller.

Experimental

δ-Phenylvaleric Acid.—This compound was prepared from commercially available γ-phenylpropyl bromide by the malonic ester synthesis.[14]

Bis-δ-phenylvaleryl Peroxide.—To a stirred mixture of 300 g. of ice and 300 ml. of ice-water was added 48 g. of sodium peroxide reported to contain 91% active peroxide (0.55 mole). A solution of 59 g. (0.30 mole) of distilled δ-phenylvaleryl chloride in 180 ml. of dry ether was added slowly, maintaining a temp. of 3–5°, and the reaction then stirred for 20 minutes longer. The ether layer was separated, the aqueous layer extracted with ether, the ether solutions washed with water, dried over sodium sulfate and the solvent removed under reduced pressure. The oil crystallized upon addition of an ethyl acetate–hexane mixture (1:20). After a recrystallization from this solvent mixture, the purified peroxide was recrystallized from hexane (temp. not over 40–45°), as colorless plates, m.p. 33–34°. This procedure gave consistently good results. The peroxide titer was determined[7] for many samples of the peroxide and was found to be 99.5 ± 0.5%.

An alternate procedure that also gave satisfactory results is as follows: To a solution of 18 g. of δ-phenylvaleryl chloride in 45 ml. of ether cooled to −5° was added 11 ml. of 30% aq. hydrogen peroxide over a period of 4 minutes. This was followed by dropwise addition of a solution of 8.5 g. of potassium hydroxide in 20 ml. of water at such a rate as to maintain a temperature of −3 to −1°. After an additional 10 minutes of stirring, the mixture was worked up as described above.

4-Phenyl-1-butene.[15]—This compound was obtained in 70% yield by reaction of the Grignard reagent from benzyl chloride with freshly distilled allyl bromide. The dried butene was purified by distillation from sodium. It had b.p. 178–179° at 760 mm., n^{25}_D 1.5066. The ultraviolet absorption curve showed that no appreciable isomerization to 1-phenyl-1-butene could have occurred, and infrared spectra on various fractions indicated the presence of only one olefin, the absorption at 994 and 912 cm.$^{-1}$ indicating a terminal methylenic group.

1-Phenylbutane.—This compound was obtained by catalytic hydrogenation of 4-phenyl-1-butene in methanol at room temperature and atmospheric pressure with Adams catalyst, b.p. 180–181° at atm. press.[16]

1,4-Diphenylbutane.—This was prepared in 30% yield (*pure*) by oxidation of the Grignard reagent derived from β-phenylethyl bromide with anhydrous cupric chloride, m.p. 52–53° from ethanol.[17]

1,8-Diphenyloctane.[18]—1,8-Diphenyloctatetraene was prepared from succinic acid, cinnamaldehyde, acetic anhydride and lead oxide by the method of Kuhn in 15% yield, m.p. 231–232°. A 3-g. sample suspended in 130 cc. of glacial acetic acid and with 0.8 g. of 5% palladium-on-charcoal present was reduced with hydrogen at 2 atm. absolute. The colorless 1,8-diphenyloctane had a b.p. of 125–127° at 1 mm.

4-Phenyl-1-butanol.—A 43-g. sample of γ-phenylbutyric acid was esterified with diazomethane. The pure methyl ester (96% yield) was reduced by adding it to 11.2 g. of lithium aluminum hydride in 600 cc. of anhydrous ether at a temperature of −70 to −65°. The mixture was kept at −30° for another hour, and excess hydride was decomposed with 5 g. of ethyl acetate. After hydrolysis the organic

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(14) J. von Braun, *Ber.*, **45**, 386, 2178 (1912).

(15) A. Wilkinson, *J. Chem. Soc.*, 3057 (1931).

(16) A. Klages, *Ber.*, **37**, 2312 (1904).

(17) E. E. Turner and F. W. Bury, *J. Chem. Soc.*, **123**, 2490 (1923).

(18) R. Kuhn, *Helv. Chim. Acta*, **11**, 93, 138 (1928).

layer was dried and distilled, giving a 97% yield of 4-phenyl-1-butanol, b.p. 94–95° at 1 mm., m.p. of phenylurethan 51–52°, reported m.p. 52°.[19a]

4-Phenyl-1-chlorobutane.[19]—A 6-g. sample of 4-phenyl-1-butanol was refluxed for 10 hours with concd. aq. hydrochloric acid in an apparatus permitting some distillation of water. The 4-phenyl-1-chlorobutane had a b.p. of 95–96° at 3 mm., n^{25}_{D} 1.5182.

1,1,1,3-Tetrachloro-5-phenylpentane.[20]—A mixture of 33 g. (0.25 mole) of 4-phenyl-1-butene, 200 cc. of carbon tetrachloride and 5 g. of dibenzoyl peroxide was refluxed for 12 hr., an additional 0.5 g. of the peroxide being added after 10 hr. Distillation gave carbon tetrachloride, unchanged 4-phenyl-1-butene, a crystalline material, m.p. 125° (from hexane), and then a fraction containing 60 g. of colorless 1,1,1,3-tetrachloro-5-phenylpentane; a redistilled sample had a b.p. of 111–112° at 0.2 mm.

Anal. Calcd. for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.23; Cl, 49.58. Found (for above sample): C, 46.78; H, 4.29; Cl, 49.20. Found (for redistilled sample): C, 46.56; H, 4.18; Cl, 49.80. Found (for sample prepared using acetyl peroxide as initiator): C, 46.13; H, 4.20; Cl, 49.43. Found (for sample isolated from δ-phenylvaleryl peroxide decomposition): C, 47.12; H, 4.66; Cl, 48.18.

Although the isolated sample had an infrared curve superposable on that of the best analytical samples, it may have contained a small amount of diphenyloctane. The analysis of the isolated sample is consistent with that of a mixture containing 3% of the diphenyloctane.

Evidence Regarding Structure of 1,1,1,3-Tetrachloro-5-phenylpentane.—A solution of 5.66 g. of the tetrachloride and 1.14 g. of potassium hydroxide in 30 ml. of absolute ethanol was allowed to stand overnight at room temperature. This gave 1.41 g. of potassium chloride, 95% of the expected amount for the loss of one molecule of hydrogen chloride and 4.51 g. (92%) of 1,1,1-trichloro-5-phenyl-2-butene, which on distillation had a b.p. of 112–113° at 1.5–2 mm. and n^{25}_{D} 1.5438. The product decolorized bromine in carbon tetrachloride and aqueous potassium permanganate solutions. Analysis showed that the sample was not quite pure.

Anal. Calcd. for $C_{11}H_{11}Cl_3$: C, 52.94; H, 4.45; Cl, 42.62. Found: C, 53.55; H, 4.71; Cl, 41.44.

A 1.9-g. sample of the trichloro compound was ozonized in 30 ml. of ethyl acetate at −80°, the solvent removed under reduced pressure and water added. From the hexane extract a 2,4-dinitrophenylhydrazone was obtained, m.p. 149–150.5°. The reported m.p. of hydrocinnamaldehyde 2,4-dinitrophenylhydrazone is 149°.[21]

1,1,1-Trichloro-5-phenylpentane.—A mixture of 17 g. of 4-phenyl-1-butene, 120 cc. of chloroform and 2 g. of dibenzoyl peroxide was refluxed for 20 hr. at an excess pressure of 220 mm. A 26% yield of 1,1,1-trichloro-5-phenylpentane, b.p. 90–91° at 0.2 mm., n^{25}_{D} 1.5281, was obtained

Anal. Calcd. for $C_{11}H_{13}Cl_3$: C, 52.53; H, 5.17; Cl, 42.30. Found (2 different samples): C, 53.20, 53.44; H, 5.45, 5.44; Cl, 41.55, 41.50.

1-(2′-Chlorophenyl)-butane.—The reaction of *o*-chlorobenzaldehyde with *n*-propylmagnesium bromide gave 1-(2′-chlorophenyl)-1-butanol which was only partly purified. This was dehydrated by distillation from sodium bisulfate at atmospheric pressure, the alcohol being added in a dropwise fashion. The resulting olefin mixture[22] had a b.p. of 65–66° at 3 mm. and n^{25}_{D} 1.5530. This was hydrogenated in acetic acid over commercial platinum oxide at room temperature and 10 p.s.i. A small but detectable amount of dehydrochlorination occurred. Redistillation under reduced pressure gave a colorless liquid, b.p. 53–54° at 2 mm., n^{25}_{D} 1.5087 which did not decolorize bromine in carbon tetrachloride nor aqueous potassium permanganate.

Anal. Calcd. for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77; Cl, 21.02. Found: C, 71.04; H, 8.31; Cl, 20.72.

1,2-Dibromotetralin.[23]—This was obtained in low yield from the reaction of 18 g. of bromine and 7.5 g. of tetralin at 90–100°, m.p. 70–71° from ethanol–chloroform.

δ-Phenylbutyl δ-phenylvalerate.—A mixture of 4 g. of 4-phenyl-1-butanol, 5 g. of δ-phenylvaleric acid and 3 drops of concd. sulfuric acid was heated on the water-bath for 6 hr. The acid was extracted out with aqueous sodium bicarbonate and the ester isolated in 85% yield by distillation, b.p. 83–85° at 0.2 mm., n^{25}_{D} 1.5282.

Anal. Calcd, for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.51; H, 8.22.

The Decomposition of Bis-δ-phenylvaleryl Peroxide in Carbon Tetrachloride.—The apparatus consisted of a 5-l. flask with a sealed-on bulb type (Allihn) condenser and a sealed-in gas inlet tube. Attached to the upper end of the condenser by means of ground joints were a small bubble trap containing a 30% solution of aniline in benzene–ethanol, a cold trap maintained at the solid carbon dioxide temperature and two Ascarite (sodium hydroxide on asbestos) tubes in series.

The carbon tetrachloride was purified by stirring with approximately 50% sodium hydroxide at 60°, followed by extraction with concd. sulfuric acid and by distillation from phosphorus pentoxide. The solvent (4000 ml.) was refluxed *in situ* and small amounts distilled (condenser drained) while a slow stream of high purity tank nitrogen was swept through. This procedure gave a reflux ring showing no traces of water droplets and it also removed most of the oxygen. A solution of 5.26 g. of bis-δ-phenylvaleryl peroxide was then added and the mixture swept with a very slow stream of nitrogen and refluxed for 50 hr., at which time carbon dioxide evolution had nearly closed. The products of this run are reported in Table I.

Identification of Products from the Carbon Tetrachloride Runs.—A number of runs were carried out using various quantities of the peroxide. The product isolation and identification below was carried out on rather larger quantities than would be available in a 5-g. run. With the small-scale runs the products were identified and determined in a reasonably quantitative fashion by a combination of distillation, chromatography and quantitative infrared techniques and by other methods as described below.

The bulk of the solvent was removed by distillation through an 18-in. helices packed column operated at low reflux ratio.

δ-Phenylvaleric Acid.—The residual 50–100 ml. of solution was extracted with alkali, the alkaline solution treated with decolorizing carbon, evaporated nearly to dryness, acidified and the mixture extracted with ether. Evaporation gave nearly pure δ-phenylvaleric acid, m.p. 52–56°, without recrystallization. This procedure served for both the qualitative and the quantitative determination.

Hexachloroethane.—Most of the remaining solvent was removed by distillation through a small column, and the residue (10–15 g.) was distilled at 1–3 mm. from a Claisen-type flask into a cooled receiver backed by traps at −80°. The oil-bath temperature was kept below 130° to avoid decomposition of some unidentified reaction product present in small amounts. This distillation gave three "fractions," residue, distillate and trap contents. Hexachloroethane was isolated from the trap contents by redistillation at atmospheric pressure to remove carbon tetrachloride. On recrystallization from ethanol–ether, it had a m.p. of 186° (sealed capillary). For quantitative determinations (carbon tetrachloride solutions) the infrared peak at 678 cm.$^{-1}$ was used. In some runs the trap also contained small amounts of 4-phenyl-1-chlorobutane; this was determined by the infrared peaks at 807, 1272 and 1305 cm.$^{-1}$.

4-Phenyl-1-chlorobutane.—This compound was the principal constituent of the distillate. It was isolated in pure form by redistillation and identified on the basis of the b.p., refractive index and comparison of the infrared curve with that of an authentic sample. The principal impurity removed by the distillation was hexachloroethane. For quantitative determinations a carbon disulfide solution was used and the peaks at 807, 1272, 1305 cm.$^{-1}$ (4-phenyl-1-chlorobutane) and at 678 and 744 cm.$^{-1}$ (hexachloroethane) were used.

δ-Phenylbutyl δ-Phenylvalerate.—The ester was a component of the residue. It was isolated by distillation; it was also isolated by chromatographic separation from 1,8-di-

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[19] (a) J. von Braun, *Ber.*, **44**, 2872 (1911); (b) S. S. Rossander and C. S. Marvel, This Journal, **50**, 1495 (1928); (c) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 242 (1924).

[20] M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

[21] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[22] We are indebted to Mr. B. James for preparing the olefin mixture.

[23] J. von Braun and G. Kirschbaum, *Ber.*, **54**, 601 (1921).

phenyloctane and from 1,1,1,3-tetrachloro-5-phenylpentane on neutral alumina (Merck) using hexane[24] as the solvent. The ester was much more strongly adsorbed than the other compounds. Alkaline alumina could not be used if the ester was to be recovered since it caused hydrolysis. The pure isolated ester was identified on the basis of the b.p., the infrared curve and by hydrolysis to the acid (identified by m.p. and mixed m.p.) and the alcohol (identified by m.p. of the phenylurethan). The quantitative determination of the ester was accomplished by two independent methods. The first was based on the strong infrared peak at 1742 cm.$^{-1}$ at which frequency the other components of the mixture did not interfere. The second was based on a quantitative application of the chromatographic procedure described above.

1,8-Diphenyloctane.—This was relatively difficult to identify in mixtures since its infrared curve has no strong peaks not masked by other constituents. By prolonged chromatography on alkaline alumina a pure sample was isolated as an oil which had only those peaks observed for authentic 1,8-diphenyloctane. For quantitative determination the residue from the distillation was chromatographed to remove ester as described above, and the mixture of 1,8-diphenyloctane and of 1,1,1,3-tetrachloro-5-phenylpentane was analyzed in carbon disulfide solution by use of the infrared peaks at 721 and 744 cm.$^{-1}$ (for dimer) and at 797, 931 and 1006 cm.$^{-1}$ (for the tetrachloride).

1,1,1,3-Tetrachloro-5-phenylpentane.—Fractions from the chromatographic separation were obtained which had all the infrared peaks of authentic 1,1,1,3-tetrachloro-5-phenylpentane and no others.

Phosgene.—From the aniline trap diphenylurea was obtained and identified by its m.p. For quantitative determination an excess of hexane was added, the mixture of diphenylurea and aniline hydrochloride separated by filtration and aniline hydrochloride removed by washing with water. The residue was weighed.

Absence of 1,1,1-Trichloro-5-phenylpentane.—This compound would appear in the 1,8-diphenyloctane fraction. Infrared curves were obtained for carbon disulfide solutions of binary mixtures of 1,8-diphenyloctane and 1,1,1,3-tetrachloro-5-phenylpentane. They were also obtained for a mixture containing in addition 1,1,1-trichloro-5-phenylpentane and δ-phenylbutyl δ-phenylvalerate. A comparison of the infrared curves of the various fractions from the chromatographic separation showed that the first fractions were richer in 1,8-diphenyloctane and the middle fractions richer in 1,1,1,3-tetrachloro-5-phenylpentane. A minor amount of an unidentified compound (less than 1% by weight of total products) was present as a separate later fraction. However, the peaks present in the major fractions were the same as those present in the binary mixtures and in particular the 1042 and 1068 cm.$^{-1}$ peaks of 1,1,1-trichloro-5-phenylpentane were absent.

Absence of Tetralin.—The infrared curves of the carbon disulfide solutions of the 4-phenyl-1-chlorobutane fraction did not have the strong tetralin peaks at 804 and 1111 cm.$^{-1}$. The 1111 cm.$^{-1}$ peak was also absent in a carbon disulfide solution of the trap contents of some of the runs.

Absence of *o*-Chloro-*n*-butylbenzene.—This compound would appear with the 4-phenyl-1-chlorobutane. The appropriate carbon disulfide solution had only those peaks characteristic of 4-phenyl-1-chlorobutane and of hexachloroethane. There were no extraneous peaks; in particular the strong 1050 cm.$^{-1}$ peak of *o*-chloro-*n*-butylbenzene was absent. Considering the intensity of the peak, an amount of 2–4% could be detected if present.

1-Phenylbutane and 4-Phenyl-1-butene.—These compounds probably are not present. Phenylbutane is difficult to detect in the presence of the other compounds, and a fair amount could escape spectroscopic detection. Careful distillation of the products of a large run failed to yield any 1-phenylbutane. At most only traces of 4-phenyl-1-butene are present.

TABLE III

APPLICATION OF THE ANALYTICAL PROCEDURES TO A KNOWN MIXTURE

Substance	Weight, g. Taken	Weight, g. Found
CCl_4	300 ml.	
$C_6H_5(CH_2)_4COOH$	0.210	0.210
C_2Cl_6	.930	.88
$C_6H_5(CH_2)_3CH_3$	.365	.39
$C_6H_5(CH_2)_4Cl$	1.520	1.41
$C_6H_5(CH_2)_8C_6H_5$	0.792	0.80
$C_6H_5(CH_2)_2CHClCH_2CCl_3$	.446	.48
$C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$	.900	.89

Identification of Products from the Benzene Runs.—The procedure for the decomposition was similar to that used for the carbon tetrachloride runs. The aniline trap was not needed. The benzene was reagent-grade material distilled from phosphorus pentoxide.

4-Phenyl-1-butene.—This was obtained in fractions of b.p. 185–203° at atmospheric pressure in a small column; it was accompanied by tetralin and 1-phenylbutane (infrared curve). A sample of the mixture was ozonized in ethyl acetate at 0°, the solvent removed, potassium iodide in acetic acid added to reduce the ozonides and the neutral materials extracted with ether. Chromatography on alkaline alumina with hexane as the solvent gave a mixture of tetralin and 1-phenylbutane (infrared curve) and a more strongly adsorbed oil stripped from the column with methanol–ether. This oil gave a *p*-nitrophenylhydrazone mixture from which could be obtained a reddish-brown material of high melting point and a yellow crystalline material, m.p. 124–126° (from ethanol). Hydrocinnamaldehyde *p*-nitrophenylhydrazone has a m.p. of 125°.

Tetralin.—Fractions of b.p. 203–207° at atmospheric pressure had an infrared curve identical with that of tetralin. The 1,2-dibromotetralin was prepared from 1.6 g. of the material as described for tetralin above, m.p. and mixed m.p. 69.5–70.5°.

1-Phenylbutane.—This has been identified on a basis of the infrared spectra.

Ester and Dimer.—These were isolated and identified as described above for the carbon tetrachloride runs.

Absence of 1,4-Diphenylbutane.—The 1,8-diphenyloctane sample after chromatographic separation from the ester (6.95 g.) was distilled under reduced pressure. It boiled at a constant temperature of 125° at 1 mm. Two arbitrary fractions were collected, the first one 1.5 g. and the second 5.0 g. The infrared curves were identical with each other and with that of 1,8-diphenyloctane. Since the 1,4-diphenylbutane has no especially characteristic peaks not masked by 1,8-diphenyloctane peaks, the evidence for the absence of 1,4-diphenylbutane consists of the absence of a forerun in the distillation.

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[24] Phillips Commercial grade.