[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Diacyl Peroxide Reactions. III. The Behavior of the Optically Active 3-Phenyl-2-propyl Free Radical[1]

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The thermal decomposition of (+)- and (−)β-phenylisobutyryl peroxide in carbon tetrachloride gives products analogous to those formed in the corresponding δ-phenylvaleryl peroxide reaction. Similar mechanisms can therefore be assumed. The 2-chloro-1-phenylpropane (accounting for 30–40% of the 1-phenyl-2-propyl groups) was optically inactive, and the alcohol portion of the ester, 1-phenyl-2-propyl β-phenylisobutyrate, showed about 75% retention of configuration. The formation of inactive alkyl chloride demonstrates the reaction of an alkyl (rather than of an acyloxy) radical with carbon tetrachloride. Since the ester probably arises from the geminate combination of a 1-phenyl-2-propyl radical and a β-phenylisobutyryloxy radical, the partial racemization of the alcohol portion indicates a very low activation energy for racemization of a free radical of the structure $R_1R_2R_3C\cdot$.

The possible existence of optically active free radicals $R_1R_2R_3C\cdot$ has been discussed for many years.[3] The problem has been a difficult one to study effectively since free radical reactions are complex even at best and since in many cases highly speculative reaction mechanisms have been assumed. In addition the preparation of intermediates which will give free radicals is fraught with some difficulty.

One of the first mechanistically sound approaches was that of Brown, Kharasch and Chao[4] who carried out the chlorination of (+)1-chloro-2-methylbutane and found that the 1,2-dichloro-2-methylbutane fraction was optically inactive. The interpretation of this result is somewhat uncertain inasmuch as the dichloro compound has not been prepared in optically active form and the magnitude of its rotation is therefore not known. If the rotation should be appreciable, the chlorination experiment shows that the 2-(1-chloro-2-methylbutyl) radical racemizes faster than it reacts with chlorine. If the rotation should prove to be very small, then the experiment is inconclusive.

The isolation in 70% yields of similar mixtures of *meso* and *dl-sym*-dimethyldiisobutylsuccinonitrile from both *meso*- and *dl*-2,2′-azo-bis-2,4-dimethylvaleronitrile has been cited[5] as evidence for the existence of free and of planar aliphatic free radicals. This evidence is of uncertain value. If there is no geminate ("cage") reaction so that all radicals are free, then the *dl*-azonitrile and the *meso*-azonitrile will give rise to similar members of *d*- and *l*-radicals. Combination of these in statistical fashion will give identical mixtures of *dl*- and of *meso*- products even if the radicals are optically stable. On the other hand the argument would have some merit if all of the product were produced in geminate reaction, for then *dl*-azonitrile should give only *dl*-product and *meso*-azonitrile *meso*-product if the radicals were stable. Such products might predominate even from planar radicals since radicals may be unable to achieve random orientation before undergoing geminate combination. The authors isolated the crossed dimer product from the decomposition of a mixture of 2,2′-azobisisobutyronitrile and 1,1′-azobis-1-cyclopentanenitrile thus showing that some of the radicals are free in these reactions. Further interpretation of this type of experiment would require precise product analyses and an independent estimate of the amount of geminate reaction.[6]

The decarbonylation of (−)methylethylisobutylacetaldehyde with *t*-butyl peroxide is reported to give inactive 2,4-dimethylhexane due to racemization of the methylethylisobutylmethyl free radical prior to its abstraction of the aldehyde hydrogen atom.[7]

Recently two reports have appeared of the use of optically active diacyl peroxides to produce optically active free radicals.[8] Kharasch, Kuderna and Nudenberg carried out the decomposition of (+)α-methylbutyryl peroxide in benzotrichloride. The ester, *sec*-butyl α-methylbutyrate, was isolated in 30–40% yield. Both the acid portion and the *sec*-butyl alcohol portion were optically active; the rotation of the alcohol indicated some racemization, the configuration being retained. No other products were reported. The interpretation of this result requires information about the mechanism of ester formation. The occurrence of induced peroxide decomposition leading to ester would be a possible complication needing investigation.

Greene[8] attempted to prepare the peroxide of optically active α-phenylpropionic acid, but the peroxide decomposed so rapidly that preparation and decomposition had to be carried out simultaneously. This was done in the presence of ether or without solvent. The careful product analysis showed a 20–35% yield of the α-phenylethyl ester of α-phenylpropionic acid and 5–8% yield of 2,3-diphenylbutane. The alcohol portion of the ester was optically active with retention of configuration and with about 20–50% racemization. The diphenylbutane was a mixture of *dl*- and *meso*-products, perhaps altogether two-thirds racemized. These products were attributed either to the formation of free radi-

(1) Paper II. D. F. DeTar and C. Weiss, THIS JOURNAL, **79**, 3041 (1957).

(2) Postdoctoral Research Associate supported by the Research Committee of the University of South Carolina.

(3) *Cf.*, *e.g.*, R. L. Shriner, R. Adams and C. S. Marvel in "Organic Chemistry," ed. by H. Gilman, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 383.

(4) H. C. Brown, M. S. Kharasch and T. H. Chao, THIS JOURNAL, **62**, 3435 (1940).

(5) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 4883 (1951); *Ann. Reps.*, **49**, 116 (1952).

(6) *Cf.*, G. S. Hammond, J. H. Sen and C. E. Boozer, *ibid.*, NAL, **77**, 3244 (1955).

(7) W. von E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, *ibid.*, **74**, 3000 (1952).

(8) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954); F. D. Greene, THIS JOURNAL, **77**, 4869 (1955).

cals which rapidly underwent geminate combination or else to a rearrangement reaction. The former alternative was preferred by Greene on the grounds that a rearrangement reaction should be stereospecific. The relative insensitivity of product ratios to reaction procedure was cited as evidence that induced decomposition was not important.

α-Phenylpropionic acid is not entirely satisfactory as a tool for investigation of the optical stability of free radicals for the following reasons: (1) It has not been possible to isolate the peroxide because of its great lability. On this account the interpretation of the results must of necessity be speculative. (2) Since this is a substituted phenylacetic acid, the possibility of ionic decomposition paths for the peroxide requires a careful evaluation that was not feasible.[9] (3) If formation of ester and hydrocarbon dimer occur by geminate reactions as appears likely, then the optical stability of an isolated free radical has not been investigated.

It was therefore our objective to carry out a diacyl peroxide decomposition which would correlate with the detailed studies of the δ-phenylvaleryl peroxide reaction[1] and which would involve a nongeminate reaction of an optically active free radical of the type

$$R^{*}\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3$$

The choice of diacyl peroxide imposed certain restrictions if mechanistically conclusive results were to be obtained. The peroxides of the convenient and extensively studied α-substituted arylacetic acids suffer from the twin disadvantage of being especially unstable and of being subject to heterolytic as well as homolytic cleavage.[9] The possible occurrence of heterolytic cleavage renders the details of the over-all results somewhat less certain with these peroxides than with other types. α-Methylbutyryl peroxide is satisfactory except for the experimental inconvenience of the low boiling points of the products. Other dialkyl-substituted acetic acids also could be used.

β-Phenylisobutyryl peroxide appears to be one of the best possibilities for the study of optically active radicals. The relative configurations of the key compounds are known, and the rotations are about twice as great as in the α-methylbutyric acid series. Furthermore there is a possibility that the peroxide can be obtained in crystalline form, although this was not achieved in the present work. Since β-phenylisobutyryl peroxide is closely related to the previously studied δ-phenylvaleryl peroxide,[1] it should be possible to evaluate the details of the reaction mechanism with reasonable certainty.

β-Phenylisobutyric acid has been resolved by several workers.[10,11] The maximum reported rotation is $\alpha^{24}D$ +21.6 and $[\alpha]^{21}D$ +17.9 (in ethanol). 1-Phenyl-2-propanol has $\alpha^{14}D$ 27.3°(l = 1),[11] and 1-phenyl-2-chloropropane of unreported optical purity had $[\alpha]_{5461}$ 25°(no solvent).[11] Kenyon, Phillips and Pittman[11] have related the configurations in this series by an unambiguous method: those compounds with the same sign of rotation have the same configuration.

β-Phenylisobutyryl peroxide undergoes decomposition in carbon tetrachloride with a half-life of about an hour at 40°.[12] It is therefore much less stable than δ-phenylvaleryl peroxide, and was not obtained in pure form except in one run that decomposed prematurely on attempted storage at 0°. It was noted that explosive decomposition of this peroxide did not destroy the container; the brisance seems to be low. Very few secondary peroxides have been reported; hexahydrobenzoyl peroxide is one example, and it appears to be relatively unstable.[13] The secondary α-phenylpropionyl peroxide is much less stable than phenylacetyl peroxide.[8] Incidentally phenylacetyl peroxide itself has a half-life of only about seven hours at 0° in toluene.[9] The preliminary study of the kinetics of the decomposition of β-phenylisobutyryl peroxide in carbon tetrachloride shows that the amount of induced decomposition is small.

The samples of (+)β-phenylisobutyryl peroxide used in the present study were about 60–70% pure; the principal impurities seem to have been solvent and possibly ester, 1-phenyl-2-propyl β-phenylisobutyrate. The optical purity of the (+)peroxide present in the samples was estimated as 42% by reducing a portion back to β-phenylisobutyric acid.

The products of the decomposition of a dilute solution of the peroxide in carbon tetrachloride are summarized in Table I. While the yields of many of the products are only approximations, it is clear that there is a great deal of similarity between this reaction and that of δ-phenylvaleryl peroxide previously reported.[1] In particular it seems reasonably certain that none of the 1-phenyl-2-chloropropane nor of the 1-phenyl-2-propyl β-phenylisobutyrate is derived from induced decomposition of the peroxide.

The 2-chloro-1-phenylpropane was formed in nearly the same yield as was 1-chloro-4-phenylbutane from δ-phenylvaleryl peroxide.[1] This 2-chloro-1-phenylpropane was optically inactive ($\alpha^{20}D$ 0.02 ± 0.02°, pure liquid, l = 1). If the rotation of the pure isomer for the D-line is estimated as 20° ($[\alpha]_{5461}$ 25),[11] then the rotation expected if no racemization had occurred would have been 8°. The racemization reaction is therefore 200 or more times faster than the chlorine abstraction reaction.

The free acid isolated from the reaction mixture had a rotation experimentally the same as that of the acid resulting from reduction of the peroxide. Since this acid is fairly stable toward racemization, such a result is expected. The ester, 1-phenyl-2-propyl β-phenylisobutyrate, was also active. The acid fraction obtained on hydrolysis had the same rotation as observed for the other acid samples. The alcohol portion was also optically active, the OH group being in the position previously occupied by the carboxyl function. However, the alcohol had a somewhat lower optical purity than the acid fractions, indicating some 20–26% of racemization during its formation.

(9) P. D. Bartlett and J. E. Leffler, This Journal, **72**, 3030 (1950).

(10) (a) F. S. Kipping and A. E. Hunter, *J. Chem. Soc.*, **83**, 1005 (1903); (b) R. H. Pickard and J. Yates, *ibid.*, **95**, 1019 (1909).

(11) J. Kenyon, H. Phillips and V. P. Pittman, *ibid.*, 1072 (1935).

(12) D. F. DeTar and R. C. Lamb, unpublished results.

(13) F. Fichter and W. Siegrist, *Helv. Chim. Acta*, **15** 1304 (1932).

TABLE I

THE THERMAL DECOMPOSITION OF (+)- AND (−)β-PHENYLISOBUTYRYL PEROXIDE IN CARBON TETRACHLORIDE[a]

Products	Yield[b]	Rotation	% Opt. purity	Yield[b]	Rotation	% Opt. purity
CO_2	1.41			1.60		
C_2Cl_6	0.2[c]					
$C_6H_5CH_2CHClCH_3$	.6[c]	0	0	0.8[c]	0	0
$C_6H_5CH_2CH(CH_3)COOH$	.04	+7.4[d]	41	.08	−7.3	41
$(C_6H_5C_3H_6CCl_3)$[e]	.15[e]	0	0	.07[e]	....	..
Ester	.6[c]	+9.6[f]	..	.8[c,g]	−9.5[f]	..
Acid from ester	...	+7.8[d]	44	...	−8.5[f]	46
Alcohol from ester	...	+8.6[f]	31[h]	...	−9.6[d]	35[i]
Starting Material						
$[C_6H_5CH_2CH(CH_3)COO]_2$, mmoles	(83.6)[j]	+7.5[d,k]	42	(59.4)[l]	(−)	..

[a] Reaction in 5 l. of CCl_4 at 60–77°; the amount of peroxide used is given at the bottom of the table. [b] Moles per mole of peroxide. [c] Approximate figure. [d] $[\alpha]^{20}D$ in ethanol. [e] The identity of this compound has not been established. [f] $\alpha^{70}D$ (l = 1, no solvent). [g] This figure is much too large and indicates presence of ester as impurity in the (−)peroxide used. [h] 31/42 or 74% retention. [i] 35/44 or 80% retention. [j] Based on 37.95-g. sample of 71.8% pure peroxide. [k] This applies to the β-phenylisobutyric acid obtained from reduction of the peroxide. [l] Based on 30-g. sample of 64.5% pure peroxide.

Although ester may have been present as an impurity in the (−)peroxide before decomposition in carbon tetrachloride, there does not seem to be any reason to suppose that ester arose from a source other than peroxide decomposition, though some of the decomposition may have taken place in a solvent medium other than carbon tetrachloride. The infrared curve of the (+)peroxide showed that ester was not present as an impurity in this sample.

Discussion

The fact that *dl*-1-phenyl-2-chloropropane is formed in the reaction of active β-phenylisobutyryl peroxide with carbon tetrachloride makes it possible to eliminate decarboxylative substitution as the mechanism of formation of the alkyl chloride. Such a reaction

$$RCOO\cdot + CCl_4 \longrightarrow RCl + CO_2 + \cdot CCl_3 \quad (1)$$

should be stereospecific irrespective of whether it occurs by inversion or by retention of configuration. This leaves halogen abstraction by the alkyl radical as the only route (eq. 2). The reasoning is as follows

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \quad (2)$$

The only potential direct precursors of RCl are the alkyl radical, the acyloxy radical or the peroxide. The peroxide is ruled out on the basis that induced decomposition is at most a minor process, and since the acyloxy radical has been eliminated, only the alkyl radical remains. There is at present no evidence to require consideration of less direct mechanisms.

The decarboxylative substitution step was proposed by Edwards and Mayo to explain an apparent discrepancy in the reactivity of alkyl radicals.[14] Edwards and Mayo developed a method for evaluating the relative reactivities of various solvents toward hydrogen abstraction by methyl radicals. A careful determination was made of the methane–methyl chloride ratio obtained in the decomposition of acetyl peroxide in solvent mixtures that had carbon tetrachloride as one component. It was possible to compare

$$CH_3\cdot + S_1H \longrightarrow CH_4 + S_1\cdot \quad (3)$$

$$CH_3\cdot + CCl_4 \longrightarrow CH_3Cl + \cdot CCl_3 \quad (4)$$

the reactivity of each solvent in the hydrogen abstraction reaction (eq. 3) with the reactivity of carbon tetrachloride in the chlorine abstraction (eq. 4). This led to a series of relative reactivities of methyl radicals with S_1H, S_2H, etc. The order of reactivities found was so different from the order obtained for other alkyl radicals (in polymerization systems) that it seemed advisable to speculate that the acetyl peroxide reaction involved decarboxylative substitution by acetoxyl radicals (eq. 1) rather than the expected methyl radical reactions. Since publication of this work, accurate estimates have become available for the rates of methyl radical reactions in the gas phase.[15] It has been shown that the methyl radical reactivities obtained in solution by Edwards and Mayo correlate very well with the gas phase values.[16] The main reason for postulating decarboxylative substitution has thus evolved instead into a reason for preferring the methyl radical reaction hypothesis.

There is now direct experimental evidence against decarboxylative substitution for three types of radicals: $CH_3COO\cdot$, $R_2CHCOO\cdot$ and $ArCOO\cdot$. The aryl group studied was the optically active 2-(2′-methyl-6′-nitrophenyl)-phenyl group.[17] The optically active peroxide reacted with carbon tetrachloride to give low yields of 2-chloro-2′-methyl-6′-nitrobiphenyl with partial racemization.

Since direct alkyl radical and aryl radical halogen abstraction has been demonstrated for three very different types of radicals, the method of Edwards and Mayo can be expected to be of great significance for obtaining relative radical reactivities.

(14) F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).

(15) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 552.

(16) A. F. Trotman-Dickenson, *Quart. Rev.*, **7**, 198 (1953).

(17) D. F. DeTar and J. C. Howard, THIS JOURNAL, **77**, 4393 (1955).

In considering the optical properties of a free radical such as the 1-phenyl-2-propyl radical the extreme possibilities appear to be either a planar symmetrical structure or else a pyramidal structure with an optical stability of the same order as the structurally similar amine, methylbenzylamine. The activation energy for inversion of an amine is not known accurately, but estimates range around 5 kcal.[18] The activation energy for racemization should therefore be in the approximate range of 0 to 10 kcal. A reasonable estimate of the activation energy of the chlorine abstraction step (eq. 2) is 12 kcal., on the assumption that chlorine abstraction and hydrogen abstraction (*cf.* eq. 3 and 4) have similar activation energies.[15] Since an activation energy for halogen abstraction that is about 3 kcal. greater than that for racemization will lead to the observed complete racemization, the formation of racemic 1-phenyl-2-chloropropane is not unexpected.

Further information can be obtained from a consideration of the ester, 1-phenyl-2-propyl β-phenylisobutyrate. In the present investigations induced peroxide decomposition can be excluded as a source of ester. Two possibilities remain: (1) a rearrangement process involving loss of carbon dioxide and (2) a radical combination reaction (eq. 5). Since rearrangement reactions are usually

$$RCOO\cdot + R\cdot \longrightarrow RCOOR \qquad (5)$$

stereospecific and since there seems to be no reason for anticipating more than one rearrangement path for the peroxide, it appears that at least some of the ester must have been formed by a non-rearrangement process in order to account for the partial racemization of the alcohol portion.

Evidence has been presented that all of the ester is formed by a geminate radical combination reaction,[1,19] rather than by rearrangements. In this case the racemization of the 1-phenyl-2-propyl radical is competing with a radical combination reaction and the activation energy for racemization would be of the order of 2 kcal. It is even possible that a planar free radical could give an optically active ester providing that random rotational orientation of the radical is slow compared to the geminate combination. While "asymmetric induction" could be invoked, it is unlikely that the configuration of the acyloxy radical would have much effect in a radical combination reaction.

Experimental

***dl*-β-Phenylisobutyric Acid.**[20]—To a solution of 24 g. of sodium in 410 ml. of absolute ethanol was added 174 g. of commercial diethyl methylmalonate. This was followed by dropwise addition of benzyl chloride during a period of two hours at a reaction temperature of 40°. After removal of the ethanol by distillation, the diethyl benzylmethylmalonate was extracted with ether, and after washing and drying was finally distilled, b.p. 127–133° at 1.5 mm.; yield 62 and 66% in two runs.

The ester (174 g.) was hydrolyzed by refluxing it with a solution of 110 g. of potassium hydroxide in 300 ml. of water and 120 ml. of methanol. After removal of the methanol, the benzylmethylmalonic acid was precipitated with acid and, after drying, recrystallized from a benzene–hexane mixture to give 130 g. (95%) of colorless crystals, m.p. 136–138°. This was raised to 138–139.5° after recrystallization; the reported m.p. is 135°.[20c] In precipitating the benzylmethylmalonic acid it is necessary to add the solution of the salt to a solution of hydrochloric acid since the reverse procedure leads to precipitation of the insoluble monopotassium salt.

The acid was decarboxylated in 90-g. portions at a temperature of 190–210°, and the resulting β-phenylisobutyric acid purified by distillation; b.p. 118–122° at 1 mm.

Resolution of β-Phenylisobutyric Acid.[10]—To a solution of 500 g. of quinine in 650 ml. of hot ethanol was added 250 g. of *dl*-β-phenylisobutyric acid. The solution was cooled to 30° and seeded with the pure *d*-salt (obtained from a previous small scale run). The crystallization was allowed to proceed at room temperature for 24 hours and at 5° for another 24 hours. Filtration gave 265 g. of dry salt, $[\alpha]^{20}D$ +110° (*c* 0.0203 g./cc., in ethanol). Three additional crops totaling 167 g. and having the same or slightly higher rotation were obtained by partial evaporation of the solvent and re-seeding. It is worth notice that the rotation of the quinine salt remained essentially constant even though the acid was not completely resolved.[10]

To 450 ml. of 10 *N* sulfuric acid was added 398 g. of the recrystallized *d*-salt. The liquid (+)β-phenylisobutyric acid was extracted with ether, washed, dried and distilled; yield 96%; $\alpha^{20}D$ +13.73° (*l* = 1), $[\alpha]^{20}D$ +11.5° (*c* 0.0327, ethanol, *l* = 2); reported $\alpha^{24}D$ +21.6° (no solvent),[11] $[\alpha]^{21}D$ + 17.87° (in ethanol[11]).

The (−)acid was obtained from the residue resulting from evaporation of the mother liquors to dryness, b.p. 123–124° at 1.5 mm.; $[\alpha]^{20}D$ −11.2° (*c* 0.0245, ethanol, *l* = 2).[21]

The *p*-bromophenacyl ester of the (+)acid was obtained in 0.83-g. yield from 0.4 g. of acid and 0.71 g. of *p*-bromophenacyl bromide; m.p. 54.5–56°; $[\alpha]^{21}D$ +23.8° (*c* 0.0136, ethanol, *l* = 2).

Anal. Calcd. for $C_{18}H_{17}BrO_3$: C, 59.8; H, 4.7; Br, 22.1. Found: C, 59.7, H, 5.0; Br, 22.0.

(+)- and (−)β-Phenylisobutyryl Chloride.[10,11]—A mixture of 85 g. of (+)β-phenylisobutyric acid, $[\alpha]^{20}D$ +19.7° (*l* = 2) and 110 g. of purified thionyl chloride was warmed on the water-bath for 70 min. and then distilled; b.p. 72–73° at 1 mm.; yield 92.5 g.; $\alpha^{20}D$ + 22° (*l* = 2, no solvent); reported $[\alpha]D$ +26.3°. The (−)acid chloride was prepared similarly, b.p. 110° at 1.5 mm., $\alpha^{20}D$ −25.2° (*l* = 2, no solvent).

(+)- and (−)β-Phenylisobutyryl Peroxide.—This peroxide proved to be much less stable than δ-phenylvaleryl peroxide. A number of samples decomposed spontaneously even when kept in the refrigerator, although the peroxide can be preserved at Dry Ice temperatures. It is more stable in carbon tetrachloride than in ether.

To a stirred mixture of 70 g. of ice, 70 g. of water, 10.5 g. of sodium peroxide and 50 ml. of pentane was added slowly a solution of 12 g. of (+)β-phenylisobutyryl chloride in 80 ml. of pentane. The temperature was maintained at 2–2.5° during the addition (15 min.) and for an additional half hour. The pentane layer was separated, washed, dried over sodium sulfate, and the solvent removed under reduced pressure. The resulting viscous oil had a peroxide titer corresponding to 74.8%. Carbon tetrachloride was added and removed under reduced pressure at −10 to 0°, and the titer then corresponded to 71.8% of peroxide. It is possible that solvent is still present. The ester peak at 5.77 μ was negligible in the spectra of a carbon tetrachloride solution.

The rotation was obtained in carbon tetrachloride solution for a 40-g. peroxide sample obtained by combining two preparations; $[\alpha]^{20}D$ + 69° (*l* = 2); 0.425 g. of peroxide of 71.8% purity corresponds to a concn. of 0.305 g. of peroxide in 15 ml. of carbon tetrachloride.

The (−)peroxide was similarly prepared from 40 g. of the (−)acid chloride and 34 g. of sodium peroxide to give a

(18) *Cf. e.g.*, J. F. Kincaid and F. C. Henriques, Jr., This Journal, **62**, 1474 (1940).

(19) For other evidence of geminate radical reactions see ref. 6 and A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955); J. Smid, A. Rembaum and M. Szwarc, *ibid.*, **78**, 3315 (1956).

(20) (a) F. Kenyon and W. A. Ross, *J. Chem. Soc.*, 3407 (1951); (b) A. W. Dox and L. Yoder, This Journal, **44**, 1144 (1922); (c) M. Conrad and C. A. Bischoff, *Ann.*, **204**, 177 (1880).

(21) L. W. Jones and E. S. Wallis, This Journal, **48**, 175 (1926).

sample containing 64.5% of (−)β-phenylisobutyryl peroxide.

A 0.7-g. sample of the above (+)β-phenylisobutyryl peroxide was reduced to the acid by treatment with 0.75 g. of potassium iodide and 3 ml. of water in 50 ml. of acetone. Sulfur dioxide was passed in to reduce the iodine, the acetone was evaporated, the oil treated with sodium carbonate and extracted with ether to remove neutral materials. The acid was recovered from the alkaline solution, the ether evaporated, and the residue kept *in vacuo* over phosphorus pentoxide for 24 hours; $[\alpha]^{20}D$ + 7.5° (*c* 0.0234, ethanol, *l* = 2), or 67% of that of the starting acid.

dl-1-**Phenyl-2-propanol.**[22]—Commercial phenylacetone was reduced in 96% yield with a suspension of lithium aluminum hydride in ether; b.p. 64–65° at 1 mm.; phenylurethan, m.p. 89.5–91° from hexane.

dl-1-**Phenyl-2-chloropropane.**—A solution of 50 g. of 1-phenyl-2-propanol in 100 ml. of benzene was added in dropwise fashion to a solution of 50 g. of purified thionyl chloride in 70 ml. of benzene maintained at gentle reflux. The solution was then warmed on a water-bath for another hour, poured into water, washed thoroughly, dried and distilled; b.p. 83–85° at 12 mm., yield 76%; reported b.p. 205–207°.[23]

dl-1-**Phenyl-2-propyl β-Phenylisobutyrate.**—This was prepared by direct esterification at 110° for 3 hours in the presence of sulfuric acid; b.p. 142–144° at 1 mm., $n^{25}D$ 1.5264, yield 87%.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.86. Found: C, 80.7; H, 7.9.

Decomposition of (+)β-Phenylisobutyryl Peroxide in Carbon Tetrachloride.—In a 5-l. flask with sealed-on reflux condenser and gas inlet tube was placed 5 l. of repurified carbon tetrachloride. About 50 ml. of this was distilled through the drained condenser while a stream of high purity nitrogen was passed in. The nitrogen stream was continued while the temperature was reduced to 20–25°. A 37.95-g. portion of the combined sample of (+)β-phenylisobutyryl peroxide described above (purity 71.8%, equivalent to 27.3 g. (0.0836 mole) of pure peroxide) was added, the temperature raised to 65–70° over a period of one hour and maintained there for four hours and then refluxed overnight. The carbon dioxide yield was 5.191 g. (1.41 mole per mole of "pure" peroxide). No phosgene was produced.

The solvent was removed through a column until the volume was reduced to 50 ml. Extraction with alkali gave 0.970 g. of (+)β-phenylisobutyric acid, $[\alpha]^{20}D$ +7.4° (*c* 0.0874, ethanol, *l* = 1) (0.037 mole per mole peroxide). The remainder of the solvent was removed with a small column and the residue fractionated through a small Vigreux column to give (1) 4.74 g. (mostly hexachloroethane), b.p. 60–66° at 12 mm.; (2) 3.25 g. of a hexachloroethane–2-chloro-1-phenylpropane mixture, b.p. 66–68° at 12 mm.; (3) 5.90 g. of 2-chloro-1-phenylpropane, b.p. 81–90° at 10 mm., and a residue of 17.70 g. of yellow oil. The hexachloroethane (3.25 g.) was frozen out of the first two fractions, and the remaining liquids redistilled to give 7.65 g. of 2-chloro-1-phenylpropane (0.59 mole per mole of peroxide). This had a $\alpha^{20}D$ +0.52°, but the infrared curve had some small peaks not present in 2-chloro-1-phenylpropane. After passage through a column of F-20 alumina, the extra peaks were no longer present and the rotation was nearly zero; $\alpha^{20}D$ +0.03 ± 0.01 (18 D.F.).

There was some evidence for the presence of allylbenzene in that the contents of the Dry Ice traps from the first vacuum distillation contained allylbenzene peaks in addition to those of CCl_4 and C_2Cl_6.

Since the residue showed incipient signs of decomposition on attempted distillation, it was instead purified by chromatography on a 17 × 550 mm. column of F-20 alumina (grade 1) using hexane as eluent. From 11.40 g. there was obtained 3.02 g. of pure 1-phenyl-2-propyl β-phenylisobutyrate and a larger less pure fraction. This impure remainder was rechromatographed. There was ultimately obtained 9.42 g. of ester and 1.58 g. of a chlorine-containing oil; the original 17.70 g. of residue therefore contained 15.2 g. of ester, (0.64 mole per mole "pure" peroxide) and 2.5 g. of chlorine-containing oil (0.15 mole per mole peroxide assuming it is $RCCl_3$), $[\alpha]^{20}D$ 0°.

Redistillation of the ester gave a fraction, b.p. 143–145° at 1 mm., $n^{25}D$ 1.5264, $\alpha^{20}D$ 9.65° (*l* = 1, no solvent), $[\alpha]^{20}D$ 15.1° (*c*, 0.046, ethanol, *l* = 1); the infrared curve matched that of the *dl*-ester. Hydrolysis of the ester at room temperature gave an acid (2.86 g.) with an infrared curve identical with that of β-phenylisobutyric acid; $[\alpha]^{20}D$ +7.8° (*c* 0.068, ethanol, *l* = 1) and an alcohol, b.p. 70–71° at 2 mm. (2.7 g.), $n^{25}D$ 1.5192, $\alpha^{20}D$ +8.55 (*l* = 1, no solvent); the infrared curve of the alcohol was identical with that of the *dl*-1-phenyl-2-propanol.

Decomposition of (−)β-Phenylisobutyryl Peroxide in Carbon Tetrachloride.—A 30-g. sample of the peroxide containing 64.5% or 19.35 g. (0.0594 mole) of pure peroxide was added to 5 l. of carbon tetrachloride prepared as described for the other run. The solution, initially at 25–30°, was heated at reflux overnight, and 4.168 g. of carbon dioxide was evolved (1.60 moles per mole of peroxide). From the solution there was obtained 1.62 g. of (−)β-phenylisobutyric acid, $[\alpha]^{20}D$ −7.3° in ethanol (0.084 mole per mole of peroxide); 7.85 g. of 2-chloro-1-phenylpropane, b.p. 90–91° at 15 mm., $n^{25}D$ 1.5152, and after passage through F-20 alumina the infrared curve was identical with that of an authentic sample, $\alpha^{20}D$ 0.00° (*l* = 1, no solvent) (0.85 mole per mole of peroxide); 13.30 g. of 1-phenyl-2-propyl β-phenylisobutyrate $\alpha^{20}D$ −9.50° (*l* = 1, no solvent), b.p. 150–151° at 1 mm., $n^{25}D$ 1.5266 (0.80 mole per mole of peroxide); and 0.87 g. of a chlorine-containing fraction. Saponification of the ester gave 4.7 g. of (−)β-phenylisobutyric acid, $[\alpha]^{20}D$ −8.5° in ethanol and 4.3 g. of 1-phenyl-2-propanol, b.p. 67–68° at 1 mm., $n^{25}D$ 1.5192, $\alpha^{20}D$ −9.55° (*l* = 1, no solvent). It is possible that ester was present as an impurity in the peroxide.

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