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Free-Radical Rearrangements. II. Ketones and Esters from the Reactions of Aldehydes with Peroxides[1]

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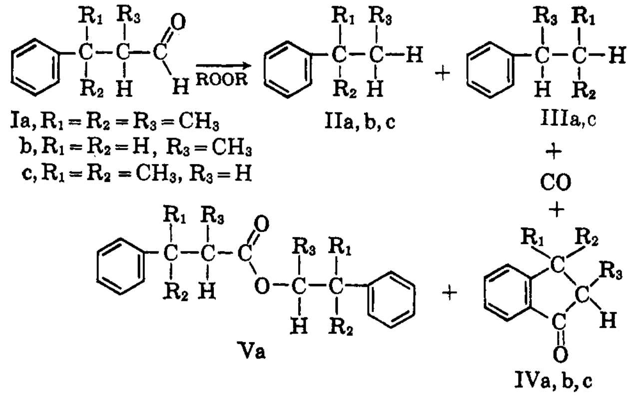
Striking changes occur when the reactions of *t*-alkyl peroxides with aralkanals are carried out at 100°. Carbonyl-containing products are formed indicating that the reactions of intermediate aralkanoyl radicals become more important at the lower temperature. For example, the reaction of *t*-amyl peroxide with 4-methyl-4-phenylpentanal (VI) at 100° gives 18% 4,4-dimethyl-1-tetralone (VIII) and 18% 4-methylvalerophenone (IX) and only 30% of the product of decarbonylation, 3-methyl-3-phenylbutane (VII). Structures with strong steric interactions have a similar effect. The reaction of 2,3-dimethyl-3-phenylbutanal (Ia) with *t*-butyl peroxide even at 140° produces 2,3-dimethyl-3-phenylbutyl 2,3-dimethyl-3-phenylbutyrate (Va, 67%), 2,3,3-trimethyl-1-indanone (IVa, 21%), and products of decarbonylation with partial rearrangement (7%)—carbon monoxide, 2-methyl-2-phenylbutane (IIa), and 2-methyl-3-phenylbutane (IIIa).

Previous studies of the free-radical reactions of aralkanals with *t*-butyl peroxide have stressed their decarbonylation to give aralkanes with their intermediate free-radical rearrangement (1,2-shift of aryl groups)[2-4] that is dominant above 130°. The influence of reaction temperature[2d,4a,d] and reactant concentrations,[2d,4d] as well as conformational[4b,c] and other structural effects,[2b,c,3a,b,4a,d] on the extent of rearrangement have been considered. In two prior studies, the formation of a tetralin[3a] and an indanone[4a] as minor products has indicated that intramolecular free-radical alkylation or acylation also occurs, and an example of 1,4-rearrangement has been observed.[3a]

The observation that the sterically congested aldehyde Ia with *t*-butyl peroxide, even at 140°, gives the tetralone VIa and its Tischenko ester Va as dominant products encouraged study of these reactions under conditions planned to favor the formation of such carbonyl-containing products. Previous research[5] with free-radical reactions of aldehydes and ketones has shown that yields of carbonyl products are enhanced at lower reaction temperatures as a consequence of the decreased rates of decarbonylation of intermediate alkanoyl radicals. Accordingly, reactions of the 3- and 4-phenyl alkanals Ib, Ic, and VII with *t*-amyl peroxide at 100° have been found (see Table I) to give increased yields of ketonic products, but esters were not observed (even qualitative tests were negative).



At 100° with *t*-amyl peroxide, 4-methyl-4-phenylpentanal (VI) gives 4,4-dimethyl-1-tetralone (VIII) and decarbonylation product VII. An interesting product of rearrangement, 4-methylvalerophenone (IX), also is formed (see p. 1664, col. 1).

In all experiments, carbon monoxide was obtained in a yield equal to that of the alkyl benzene product, and all reactions were continued until its evolution ceased. The time required to complete the reaction was longer, and the conversions of aldehyde to products were lower in the experiments at 100° (*cf.* experiments 2 and 3, and 4 and 5, Table I). Analysis of distillation

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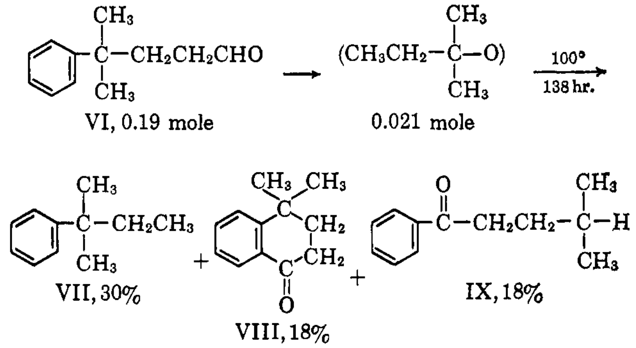
TABLE I

REACTION OF ARALKANALS WITH *t*-ALKYL PEROXIDES[a]

Expt.	Aldehyde (mole)	Peroxide[b]	Reaction time, hr.	% conversion	% yields[c] Hydrocarbon	Ketone	Other
1	Ia (0.095)	TBP	20	58	7, IIa, IIIa	21, IVa	67, Va
2	Ib (0.17)	TAP	84	32	81, IIb	6, IVb	*d*
3	Ib (0.058)	TBP	27	70	98, IIb	2, IVb	*d*
4	Ic (0.29)	TAP	24	58	62, IIc; 38, IIIc	5, IVc	*d*
5	Ic[e]	TBP		71	47, IIc; 53, IIIc	*f*	
6	VII (0.188)	TAP	138	58	30, VII	18, VIII	18, IX
7	Ia (0.053)[g]	TBP	48	75	8, IIa; 19, IIIa	*f*	46, Va
8	Ic[h]	TBP		57	15.9, IIc; 80.6, IIIc[i]	*f*	

[a] Experiments 1 to 6 without, and 7 and 8 with solvents. [b] In all experiments, approximately 10 mole % of peroxide was used: TAP denotes *t*-amyl peroxide at 100°, and TBP, *t*-butyl peroxide at 140°. [c] Based upon aldehyde consumed. [d] Corresponding 1,2-diketone was shown to be present in distillation residues. [e] Data from ref. 2d. [f] Ketone product was not isolated. [g] Ia was 0.90 *M* in chlorobenzene, 23 mole % *t*-butyl peroxide was used, and reaction temperature was 130°. [h] Data from ref. 4d. Ic was 1.01 *M* in *o*-dichlorobenzene, and reaction temperature was 129.7°. [i] Product contained 3–4% phenylisobutenes.


VI, 0.19 mole

0.021 mole

100° 138 hr.

VII, 30%

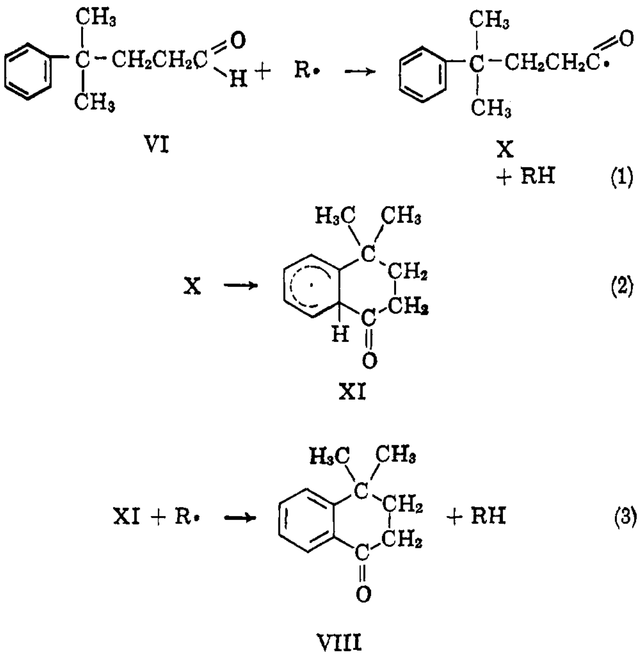
VIII, 18%

IX, 18%

residues showed that they contained the expected 1,2-diketones (RCHO → RCOCOR).

The free-radical chain reaction mechanism proposed[2–4] for this reaction must be supplemented with unit reactions of intermediate aralkanoyl radicals resulting in the formation of the ketonic products important at lower temperatures.

In this reaction of VI, the aralkanoyl radical X undergoes intramolecular free-radical acylation at either adjacent *ortho* position to give the intermediate radical XI (eq. 2, Ar_6^2 ring closure[3a]) that, when attacked by another free radical as in reaction 3, completes the formation of the tetralone VIII. Alternatively, the radical X effects ring closure to the 1-position (Ar_5^1) to give the spiro radical XII. Subsequent ring opening of XII may occur to regenerate X, but presumably reaction 5 is favored since the transition state leading to the more stable tertiary radical XIII is of lower energy. Reaction of XIII with another molecule of aldehyde gives 4-methylvalerophenone (IX) and another aralkanoyl radical X to continue the reaction chain.


VI

X

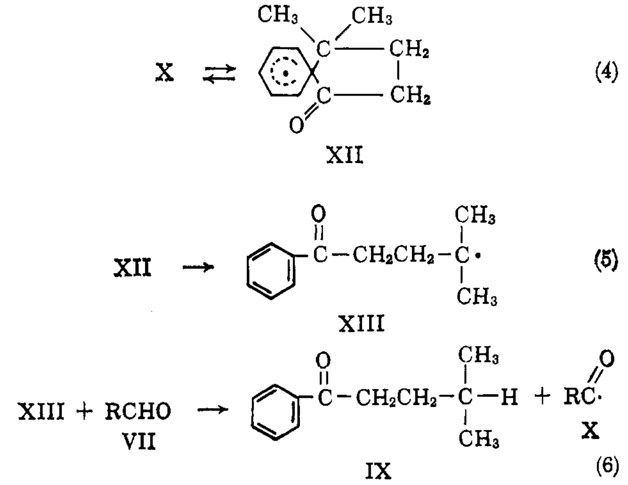
(1)

XI

(2)

VIII

(3)


XII

(4)

XIII

(5)

IX

(6)

Indanones[6] are formed in the reactions of aldehydes Ia, Ib, and Ic by a reaction sequence analogous to reactions 2 and 3. However, tetralones are obtained in higher yield than indanones when the reactions of homologous aldehydes are compared (*cf.* experiments 4 and 6, Table I). Yields of indanones are greater in the reactions of the more highly substituted 3-phenyl alkanals (*cf.* experiments 1 and 2 with 4, Table I) with a methyl group on the 2-carbon atom being as effective in increasing indanone formation as two methyl groups on the 3-carbon atom.

Even at 100° with Ib, Ic, and VII, decarbonylation of the intermediate aralkanoyl radicals is the dominant reaction.

No 3,3-dimethylindane is formed by XIV *via* intramolecular free-radical alkylation at its *ortho* position (the vapor phase chromatogram of the reaction product of 6, Table I, showed none, while the peak due to this

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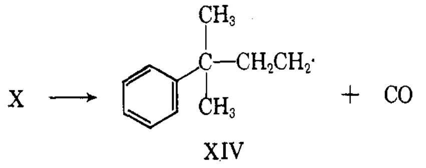
(6) Two such examples have been reported previously: 3,3-diphenylindanone (9%) from the reaction of 3,3,3-triphenylpropanal with benzoyl peroxide at 80°[4a]; and fluorenone from the reaction of 2-phenylbenzaldehyde with *t*-butyl peroxide at 140°. D. P. Denney and P. P. Klemchuk, *J. Am. Chem. Soc.*, **80**, 3289 (1958).



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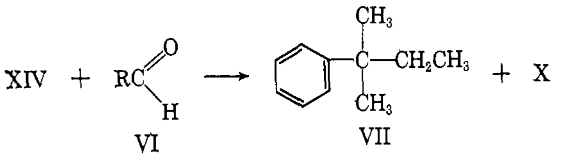

(8)

indane was visible in the chromatogram of a 1% solution of it in VII). However, the analogous formation of tetralins from 4-phenylbutyl radicals is well known.[3a,7] These observations, and the fact mentioned above that tetralones are obtained in higher yields than indanones (*cf.* 1 and 4, Table I), suggest that six-membered ring intermediates (such as XI) form more readily than the corresponding five-membered ring ones. Indanes are formed, however, in the reaction of alkylbenzenes with olefins at 400–485°, presumably *via* substituted 3-phenylpropyl radicals.[8]

That indanones are formed at 100–140° and indanes are not suggests that 3-phenylpropanoyl radicals undergo the ring-closure reaction more readily than 3-phenylpropyl radicals. An attractive hypothesis is that overlap of the π-orbitals of the carbonyl group of the former with those of the phenyl ring permits a transition state of lower energy than that for the ring closure of 3-phenylpropyl radicals. Another possibility is that the latter radicals undergo the competing attack upon aldehyde molecules (reaction 8) at a much faster rate than that of their ring closure.

Another limitation of the versatility of radical XIV is that it does not undergo 1,3-rearrangement. No 2-methyl-4-phenylbutane is observed (experiment 6, Table I). In contrast, the 1,2-shift is a common reaction of 2-phenylethyl radicals, and the 1,4-shift of a 4-phenylbutyl radical, 4-methyl-4-phenylpentyl, has been postulated[3a] for the formation of 2-methyl-5-phenylpentane in the reaction of *t*-butyl peroxide with 5-methyl-5-phenylhexanal.

With aldehyde Ic at 100°, the decarbonylation product contained 62% of IIc and 38% of the product of rearrangement, IIIc. This extent of rearrangement, that is lower than observed before,[2a,d,4d] may be attributed to two factors. During this reaction, the average concentration of Ic was higher than in former studies as a consequence of its low conversion (58%). Hence, the competing attack of the 2-methyl-2-phenylpropyl radical upon aldehyde prior to its rearrangement is favored. Further, Rüchardt[4d] has shown that the ratios of the rates of these competing reactions, rearrangement *vs.* attack upon aldehyde (Rüchardt's k_4/k_5), are 2.76 at 129.7° and 3.25 at 144.5°. It is likely that this rate ratio is lower ($k_4/k_5 \sim 2$) at 100°.

Even though the 2-phenylethyl radical undergoes 3.3–5.1% rearrangement in this reaction of 3-phenylpropanal (1 *M* in chlorobenzene),[3b'] the extent of rearrangement of such radicals (100% with $Ph_3CCH_2\cdot$)[2c] seems to depend upon the degree to which the rearranged radical is more stable than the unrearranged one. The rearrangement tendency of the 1,2-dimethyl-2-phenylpropyl radical (experiment 7, Table I, secondary radical rearranging to a tertiary one) is only a little less than that of the 2-methyl-2-phenylpropyl radical (primary giving a tertiary radical). This aspect of the reaction of *t*-butyl peroxide with aldehyde Ia was studied in chlorobenzene (0.90 *M* aldehyde) at 130°. With the lower aldehyde concentration, 27% of decarbonylation product was obtained. It contained 70% 2-methyl-3-phenylbutane (IIIa, rearrangement product) and 30% 2-methyl-2-phenylbutane (IIa). In a study of this reaction of Ic (experiment 8, Table I) at 129.7° in *o*-dichlorobenzene, Rüchardt[4d] found 80.6% of the rearrangement product IIIc, at an aldehyde concentration of 1.01, and 81.8% of it at 0.70 *M*.

In these reactions at 100°, chain-breaking events are profoundly changed. 1,2-Diketones were found to be present in distillation residues to suggest that dimerization, and probably cross dimerization, of both aralkyl and aralkanoyl radicals occurs. Most interesting is the fact that the formation of indanones and tetralones becomes an important chain-breaking reaction under these conditions. In the formation of each molecule of these products (reactions 2 and 3), two radicals are consumed. To illustrate the importance of such reactions, the yields of these cyclic ketones, based upon *t*-alkyl peroxide used, are listed in Table II.

TABLE II

Aldehyde (reaction temperature, °C.)	Ketone (% yield, based upon peroxide used)
Ib (140)	2-Methyl-1-indanone (9.3)
Ib (100)	2-Methyl-1-indanone (18)
Ic (100)	3,3-Dimethyl-1-indanone (23)
Ia (140)	2,3,3-Trimethyl-1-indanone (80)
VII (100)	4,4-Dimethyl-1-tetralone (90)

Even at 140° with Ia, this sequence is the dominant chain termination, but it is less important with Ib. With all of the aldehydes studied, its importance is increased at 100°. With Ia at 140° or VII at 100°, ring closure to form the indanone or tetralone is so efficient that little chain breaking occurs *via* other reactions.

The absence of esters among the products of the other reactions in this study emphasizes the uniqueness of the reaction of Ia with *t*-butyl peroxide at 140° to give 67% of the ester Va and 21% of IVa with only 7% of the products of decarbonylation and rearrangement—carbon monoxide, IIa, and IIIa. Va probably is formed by the two-step chain mechanism (reactions 9 and 10) in which aralkanoyl radical attack on the aldehyde carbonyl function involves addition to the oxygen atom. The limited number of prior examples of such presumed acyl radical addition to the carbonyl group involve obvious steric effects or resonance stabilization of the intermediate radical (enolate or benzyl radicals are formed). This type of reaction step is proposed[9] as part of a chain sequence for the photochemical reaction of benzaldehyde with phenanthraquinone to give the monobenzoate ester of phenanthracene-9,10-diol.[10]

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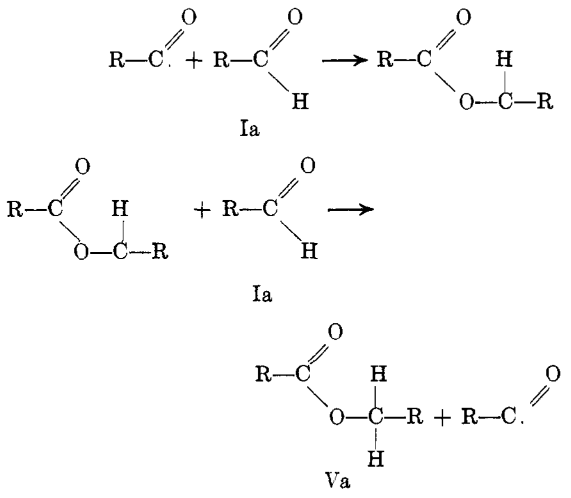


(9)

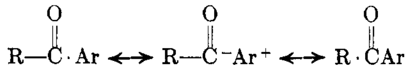
(10)

The quantum yield of this reaction is not known and it may be a nonchain photochemical process. Similar reaction steps have been proposed in the nonchain radical reactions: (1) perfluoro acid chlorides and nickel carbonyl with perfluoro 1,2-diketones to give the perfluoroenediol diesters[11]; (2) benzoyl peroxide with benzaldehyde to give *meso*[12] and *dl*[13] *sym*-diphenylethyleneglycol dibenzoate; and (3) *t*-butyl peroxide with benzaldehyde in pyridine to give 4-(α-benzoyloxybenzyl)pyridine.[14] The recently studied vapor phase photolysis of butanal to give *sym*-tripropyltrioxane (81%),[15] and of 3,4-hexanedione in propanal to give 4-oxo-3-hexanolpropionate[16] (54%), may again be reactions of photochemically excited states.

Free-radical, chain-addition reactions in which it is postulated that intermediate acyl radicals add to olefins[17] to give ketones and to azo compounds to give substituted hydrazines[18] as the eventual products are well known.

Steric effects and the tendency of radicals to form π-complexes with aromatic substances are probably responsible for the above reaction of Ia to give the ester Va and the indanone IVa, and for its diminished decarbonylation reaction. Study of the molecular model of the 2,3-dimethyl-3-phenylbutanoyl radical (from Ia) indicates that its most stable conformation is that in which the 2-methyl group is staggered between the two methyl groups on the 3-carbon atom. In this conformation, the acyl radical is forced toward one side of the phenyl ring. Hence, this radical may be stabilized against decarbonylation by π-complex formation. Addition of this radical to the oxygen atom of another aldehyde molecule on the side of the acyl group away from the phenyl ring (reaction 9) would lead to the ester-forming reaction, and formation of the σ-bond to the *ortho* carbon of the phenyl ring would lead to the formation of indanone product.

This intramolecular stabilization of intermediate acyl radical by π-complex formation is the converse of a suggestion by Walling[19] that such π-complex formation by *t*-butoxy radicals give enhanced β-scission. It is reasonable that a partial negative charge on oxygen atom in the *t*-butoxy aromatic complex should lower the energy of the transition state for β-scission to give acetone and a methyl radical. On the other hand, similar complex formation by alkanoyl radicals may be represented as follows.



$$R-\overset{O}{\overset{\|}{C}}\cdot Ar \longleftrightarrow R-\overset{O}{\overset{\|}{C}}{}^{-}Ar^{+} \longleftrightarrow R\cdot\overset{O}{\overset{\|}{C}}Ar$$

The partial negative charge on the carbonyl carbon of the complex may stabilize it against α-scission decarbonylation.

The decarbonylation of two aliphatic aldehydes, 2,3,3-trimethylbutanal and cyclopropylacetaldehyde, have given interesting results. With the former, only 2,2-dimethylbutane and carbon monoxide were obtained to indicate that there is no comparable rearrangement of aliphatic free radicals with a quaternary carbon atom. The peroxide-induced reaction of cyclopropylacetaldehyde gave only 1-butene and carbon monoxide. It is apparent that the intermediate cyclopropylcarbinyl radical undergoes a ring-opening reaction as a consequence of the strain in the cyclopropyl ring to give the but-3-enyl radical that abstracts the aldehydic hydrogen of another aldehyde molecule to give 1-butene.

Experimental

Preparation of VI.—The Grignard reagent was prepared from 1-chloro-2-methyl-2-phenylpropane (570.3 g., 3.37 moles, b.p. 65° at 2 mm., $n^{20}D$ 1.5250; prepared in 61% yield by the method of Whitmore)[20] with magnesium turnings (87.5 g., 3.65 g.-atoms) in anhydrous ether (950 ml.). Treatment of the reaction mixture with a large excess of Dry Ice and its acid hydrolysis gave 3-methyl-3-phenylbutanoic acid (493 g., 2.77 moles, m.p. 57–58°,[21] 82% yield). Reduction[22] of this acid with lithium aluminum hydride (119.8 g., 3.16 moles) in anhydrous ether (3.5 l.) gave 3-methyl-3-phenylbutanol (378.8 g., 2.31 moles, b.p. 137° at 16 mm., $n^{20}D$ 1.5228, 91% yield).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.4; H, 9.8. Found: C, 80.7; H, 9.8.

3-Methyl-3-phenylbutanol (378.4 g., 2.31 moles) with thionyl chloride (550 g., 4.60 moles; Matheson Coleman and Bell) gave 1-chloro-3-methyl-3-phenylbutane (314.7 g., 1.72 moles, b.p. 123° at 18 mm., $n^{20}D$ 1.5194, 75% yield). The Grignard reagent from this chloride (274 g., 1.5 moles) with magnesium turnings (40 g., 1.7 g.-atoms) in anhydrous ether (850 ml.) was treated with ethyl orthoformate (333 g., 2.25 moles) in anhydrous ether (370 ml.). Hydrolysis of the resulting acetal with sulfuric acid solution (5 *M*, 500 ml.), ether extraction, drying (sodium sulfate), and distillation gave VI (101 g., 0.57 mole, b.p. 123° a 10 mm., $n^{20}D$ 1.5109, 38% yield). Its 2,4-dinitrophenylhydrazone (m.p. 81° from ethanol) was prepared.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.7; H, 5.7; N, 15.7. Found: C, 60.4; H, 5.9; N, 15.8.

Reaction of VI with *t*-Amyl Peroxide.—In a nitrogen atmosphere, a solution containing VI (33.0 g., 0.188 mole) and the peroxide (3.6 g., 0.021 mole) was held at 100° for 138 hr. in a three-necked flask (50 ml.) equipped with a thermometer, a

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[21] A. Hoffman, *ibid.*, **51**, 2545 (1929).

[22] R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

nitrogen inlet tube, and a condenser (attached through a −80° trap to a Precision wet test meter). Carbon monoxide (0.85 l., 18%) was evolved.

Fractional distillation of the reaction mixture through a 3-ft. Podbielniak Heli-Grid column gave VII (4.4 g., 0.03 mole, b.p. 63–66° at 10 mm., $n^{20}\mathrm{D}$ 1.4995, 30% yield); unchanged VI (1.9 g., 0.011 mole, b.p. 123° at 10 mm., $n^{20}\mathrm{D}$ 1.5109); and a mixture of carbonyl compounds (12.7 g., b.p. 123–127° at 10 mm., $n^{20}\mathrm{D}$ 1.5149, infrared at 1725 and 1675 cm.$^{-1}$). Distillation then was continued in a molecular still to give another such mixture (6.0 g.; infrared at 1720, 1690 and 1675 cm.$^{-1}$). Quantitative analysis of these carbonyl-containing fractions by chromatography of a mixture of their 2,4-dinitrophenylhydrazones on silicic acid[23] gave unchanged VI (12.0 g., 0.068 mole, total recovery 42%), VIII (3.4 g., 0.020 mole, 17.5% yield), and IX (3.3 g., 0.019 mole, 17.5% yield).

A distillation residue (6.2 g., infrared at 1710 cm.$^{-1}$, no hydroxyl) remained, and part of it (1.0 g.) was chromatographed on neutral alumina. The first two fractions contained 2,9-dimethyl-2,9-diphenyl-5,6-decanedione (positive 2,4-dinitrophenylhydrazine and periodic acid tests; hydroxylamine–ferric chloride test for ester was negative; carbonyl content 105%, based on one carbonyl function per molecule as determined by the hydroxylamine hydrochloride method).[24]

Anal. Calcd. for $C_{24}H_{30}O_2$: mol. wt., 350. Found: mol. wt., 355.

Treatment of this residue with aqueous periodic acid gave 4-methyl-4-phenylpentanoic acid (melting point of its anilide, 165–166°; melting point of mixture with authentic sample, 166–167°).

VII was identified further by the preparation of its *p*-sulfonamide (m.p. 85–86°,[25] melting point of mixture with an authentic sample was undepressed). 1,1-Dimethylindane (b.p. 85° at 20 mm., $n^{20}\mathrm{D}$ 1.5150; prepared according to Bogert and Davidson)[26] was not a product of this reaction. This hydrocarbon and VII are separated by the v.p.c. method used (Fisher–Gulf partitioner; 11-ft. column packed with tricresyl phosphate on firebrick; isothermal, 120°; helium flow, 100 ml. per min.), but the chromatogram of the reaction product had no peak due to this indane.

The mixture of the three 2,4-dinitrophenylhydrazones obtained from the carbonyl-containing fractions was triturated with boiling ethanol, and the insoluble 2,4-dinitrophenylhydrazone of VIII (m.p. 224–226°; mixture melting point with authentic sample, 223–225°) was separated by filtration of the hot mixture.

Anal. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.0; H, 5.1; N, 15.8. Found: C, 61.1; H, 5.2; N, 15.9.

The 2,4-dinitrophenylhydrazone of IX (m.p. 177–179°, undepressed with a mixture with an authentic sample) recrystallized from the ethanol solution.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.7; H, 5.6; N, 15.7. Found: C, 60.7; H, 5.6; N, 15.5.

This derivative also gave the same X-ray diffraction pattern as an authentic sample [*d* 10.0 Å. (s); 7.5 Å. (w); 5.5 Å. (s); 4.8 Å. (m); 4.2 Å. (s); 3.5 Å. (m); 3.0 Å. (w); and 2.0 Å. (w)].[27]

IX (20.0 g., 0.11 mole, b.p. 143–145° at 20 mm., $n^{20}\mathrm{D}$ 1.5100,[24] 61% yield) was prepared by the reaction of 4-methylpentanoyl chloride (25.0 g., 0.19 mole, Eastman) with benzene (141 g., 1.8 moles) and aluminum chloride (30.0 g., 0.23 mole). After a 17-hr. reaction period, additional aluminum chloride (30.0 g., 0.23 mole) was added and stirring was continued for 2 hr. Its oxime (m.p. 70–71° from ethanol)[28] and its 2,4-dinitrophenylhydrazone (m.p. 180–181°) were prepared.

VIII was prepared by the reaction of 4-methyl-4-phenylpentanoic acid (17.6 g., 0.09 mole) in carbon disulfide (175 ml.) with phosphorus pentachloride (15.8 g.; 0.09 mole; Matheson Coleman and Bell) under vigorous stirring for 2 hr., and then aluminum chloride (30 g., 0.225 mole, Mallinckrodt A.R.) was added and the mixture was held at reflux for 2.5 hr. After hydrolysis of the reaction mixture with cold dilute hydrochloric acid, distillation gave VIII (3.17 g., 0.21 mole, b.p. 127–128° at 7 mm., $n^{20}\mathrm{D}$ 1.5502,[29] 24% yield). Its 2,4-dinitrophenylhydrazone (m.p. 125–126° from ethyl acetate), and its semicarbazone (m.p. 203–204° from aqueous ethanol) were prepared.

Preparation of Ic.—This aldehyde (46.3 g., 0.29 mole, b.p. 83–85° at 3 mm., $n^{20}\mathrm{D}$ 1.5148, 29% yield, 2,4-dinitrophenylhydrazone m.p. 120–122°) was prepared by the hydrolysis of its acetal with hydrochloric acid solution (5 *N*, 400 ml.). The acetal was prepared by the reaction of the Grignard reaction from 1-chloro-2-methyl-2-phenylpropane (170.0 g., 1.01 mole, b.p. 75° at 3 mm., $n^{20}\mathrm{D}$ 1.5252; prepared in 88% yield by the method of Kharasch and Brown)[30] with magnesium turnings (25.9 g., 1.11 g.-atoms) in ether (400 ml.) with ethyl orthoformate (148.0 g., 1.00 mole) in ether (150 ml.). The crude Ic from the acetal hydrolysis was treated with a saturated solution of sodium bisulfite. The precipitated bisulfite addition product was separated on a filter and was washed thoroughly with ether. Ic was recovered by treating the addition product with hydrochloric acid solution (1 *N*, 200 ml.).

Reaction of Ic with *t*-Amyl Peroxide.—In the apparatus previously described, Ic (46.3 g., 0.29 mole) and *t*-amyl peroxide (5.6 g., 0.032 mole) were held at a temperature of 100° for 24 hr. (swept with nitrogen). During this time, carbon monoxide (3.4 l., 52%) was evolved.

The gas chromatography (apparatus described above; isothermal, 220°) of the reaction mixture indicated that it contained 2-methyl-2-butanol and 2-butanone, a mixture of butylbenzenes (48.5%; retention time, 5 min.), unchanged Ic (42% recovered; retention time, 22 min.), and IVc (2.5%; retention time, 30 min.). Fractional distillation through a 3-ft. Podbielniak Heli-Grid column gave the following products: a mixture of 2-methyl-2-butanol and 2-butanone (5.0 g., b.p. 55–90°, $n^{20}\mathrm{D}$ 1.4918); a mixture of butylbenzenes (21.9 g., 0.163 mole, b.p. 58–60° at 20 mm., $n^{20}\mathrm{D}$ 1.4918–1.4873), shown to contain 62% IIc (13.8 g., 0.103 mole, 57% yield) and 39% IIIc (8.1 g., 0.060 mole, 33% yield) by comparison of the refractive index of each fraction obtained with a graph (refractive indices *vs.* per cent composition) from the known butylbenzenes (infrared spectra of fractions were identical with mixtures of the indicated composition); a mixture of carbonyl compounds (10.7 g., b.p. 60° at 1 mm., $n^{20}\mathrm{D}$ 1.5172) that contained unchanged Ic (9.5 g., 0.059 mole) and IVc (1.2 g., 0.007 mole, 5% yield); and a viscous residue (6.0 g., negative hydroxylamine–hydrochloride test, positive periodic acid test) that contained 2,7-dimethyl-2,7-diphenyl-4,5-octanedione.

Anal. Calcd. for $C_{22}H_{26}O_2$: mol. wt., 322. Found: mol. wt., 319.

The known *p*-sulfonamides[25] were prepared from the IIc (m.p. 134–136°) and the IIIc (m.p. 86–87°, mixture melting points with authentic samples were not depressed). A mixture of 2,4-dinitrophenylhydrazones was prepared from the above carbonyl fraction and the hydrazone of IVc (m.p. 265–267°, red crystals)[31] was obtained pure by trituration with boiling ethanol. Authentic IVc (1.6 g., 0.01 mole, b.p. 125° at 21 mm., $n^{20}\mathrm{D}$ 1.5408, 63% yield) was prepared by the reaction of aluminum chloride (2.7 g., 0.020 mole) under reflux for 2.5 hr. with a mixture obtained from 3-methyl-3-phenylbutanoic acid (2.6 g., 0.016 mole) and phosphorus pentachloride (3.4 g., 0.016 mole) in ligroin (20 ml., 90–100°) that had been stirred for 2 hr. Its semicarbazone (m.p. 205–207°),[31] and its 2,4-dinitrophenylhydrazone (m.p. 268° from ethyl acetate,[31] mixture melting point with above derivative showed no depression) were prepared.

Separation of the above 2,4-dinitrophenylhydrazone mixture with column chromatography on a 2:1 mixture of activated silicic acid and Celite (156-A)[23] gave the 2,4-dinitrophenylhydrazone of 3-methyl-3-phenylbutanal (m.p. 121–122°).[29] The reaction of the residue from the above distillation with an aqueous solution of periodic acid gave 3-methyl-3-phenylbutanoic acid (m.p. 56–57°).[21]

Preparation of Ib.—1-Phenyl-2-propanol (478.8 g., 3.53 moles, b.p. 95° at 7 mm., $n^{20}\mathrm{D}$ 1.5241; prepared in 47% yield by

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the method of Huston and Bostwick)[32] with thionyl chloride (905 g., 7.06 moles) gave 1-phenyl-2-chloropropane (386.9 g., 2.51 moles, b.p. 94° at 17 mm., $n^{22}\mathrm{D}$ 1.5196,[33] 71% yield). Ethyl orthoformate (296 g., 2.00 moles, Eastman) in anhydrous ether (400 ml.) was treated with the Grignard reagent prepared from the 1-phenyl-2-chloropropane (309.7 g., 2.00 moles) with magnesium turnings (53.5 g., 2.20 g.-atoms) in ether (950 ml.). The product acetal was hydrolyzed with hydrochloric acid (5 *N*, 200 ml.). The aldehyde–sodium bisulfite addition product was prepared. Its treatment with hydrochloric acid (1 *N*) gave Ib (57.0 g., 0.62 mole, b.p. 89–90° at 6 mm.,[34a] $n^{20}\mathrm{D}$ 1.5141, 31%). Its semicarbazone (m.p. 121–122°)[34a] and its 2,4-dinitrophenylhydrazone (m.p. 116–117°) were prepared.

Reaction of Ib with *t*-Amyl Peroxide.—Ib (25.0 g., 0.17 mole) and the peroxide (3.3 g., 0.019 mole, b.p. 51° at 13 mm., $n^{20}\mathrm{D}$ 1.4087) were held at 100° for 84 hr. in the apparatus described above.

During this reaction period, carbon monoxide (1.25 l., S.C.,[34b] 29% yield) was given off. Gas chromatographic analysis (Perkin-Elmer vapor fractometer, Model 154; 12-ft. column, 35% by weight Dow-Corning silicon oil no. 710 on 30–80-mesh firebrick; isothermal, 173°; helium flow, 100 ml. per min.) indicated peroxide decomposition products (2-methyl-2-butanol and 2-butanone); IIb (26%; retention time, 5 min.); unchanged Ib (72%; retention time, 23 min.); and IVb (2%; retention time, 37 min.). Authentic samples gave the same retention times. A known mixture of 2-phenylpropane (retention time, 4.5 min.) and IIb (retention time, 5.0 min.) was separated by this analysis. Hence, 2-phenylpropane is not a product of this reaction. Similarly, 2-methylpropiophenone (retention time, 25 min.) was shown to be absent from the product.

Fractional distillation (the Podbielniak Heli-Grid column, 50-plate) of this reaction mixture gave (1) a mixture of 2-methyl-2-butanol and 2-butanone (3.2 g., b.p. 55–90°); (2) IIb (5.0 g., 0.042 mole, b.p. 53° at 15 mm., $n^{20}\mathrm{D}$ 1.4740, 81% yield); (3) a mixture of carbonyl compounds (b.p. 90–95° at 7 mm., $n^{20}\mathrm{D}$ 1.5120, infrared at 1725 and 1690 cm.$^{-1}$) composed of Ib (17.1 g., 0.115 mole, 68% recovered) and IVb (0.5 g., 0.032 mole, 6%); and (4) a dark viscous residue (2.0 g., mol. wt. 325, infrared at 1705 cm.$^{-1}$ with no hydroxyl absorption, positive periodic acid test, and negative hydroxyl amine–ferric chloride ester test).

IIb gave its *p*-sulfonamide (m.p. 108–109°, mixture melting point with authentic sample the same).[25] Fraction 3 gave a mixture of 2,4-dinitrophenylhydrazones (red and yellow crystals). The red needles of the 2,4-dinitrophenylhydrazone of IVb (m.p. 201–203° from ethanol–ethyl acetate, m.m.p. 204–205°) were obtained by filtration when the mixture was triturated with boiling ethanol.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: N, 17.2. Found: N, 17.4.

The 2,4-dinitrophenylhydrazone of Ib (m.p. 116–117°) recrystallized as the ethanol solution cooled. IVb (13.4 g., 0.092 mole, b.p. 108° at 9 mm., $n^{20}\mathrm{D}$ 1.5550, 62% yield, semicarbazone m.p. 198–199°,[35] *p*-nitrophenylhydrazone m.p. 165–166°,[36] and 2,4-dinitrophenylhydrazone m.p. 207–208°) was prepared otherwise from the reaction of 2-methyl-3-phenylpropanoyl chloride (from the acid, 24.6 g., 0.15 mole, and phosphorus pentachloride, 31.2 g., 0.15 mole, in ligroin, 90°, 175 ml.) and aluminum chloride (40.0 g., 0.30 mole) at reflux for 2 hr. The 2-methyl-3-phenylpropanoic acid (59.1 g., 0.36 mole, b.p. 146° at 7 mm.,[37] $n^{20}\mathrm{D}$ 1.5186, 72% yield, amide m.p. 106°)[38] was prepared by the carbonation of the Grignard reagent obtained from 1-phenyl-2-chloropropane (77.2 g., 0.50 mole) with magnesium turnings (13.3 g., 0.55 g.-atom) in anhydrous ether (160 ml.).

Reaction of Ib with *t*-Butyl Peroxide.—Ib (8.5 g., 0.058 mole) and the peroxide (0.93 g., 0.0063 mole, b.p. 42° at 58 mm., $n^{20}\mathrm{D}$ 1.3889) were brought into reaction as previously described except that the reaction temperature was held at 140° for 27 hr. Gas (1.15 l., S.C.,[34b] 79%, carbon monoxide) was evolved. Chromatographic analysis, as before, showed (a) 2-methyl-2-propanol and acetone; (b) IIb (69%; retention time, 5 min.); (c) Ib (30% unchanged; retention time, 23 min.); and (d) IVb (1%; retention time, 37 min.).

Preparation of Ia.—This aldehyde was prepared by procedures as described above. from 2-bromo-3-methyl-3-phenylbutane. Bromine (48 g., 0.30 mole) was added in six portions to 2-methyl-2-phenylbutane[39] (160.0 g., 1.08 mole, $n^{20}\mathrm{D}$ 1.4960; purified by a previous bromination to remove 2-methyl-3-phenylbutane present)[40] irradiated with a 150-w. flood lamp for 6 hr. (50–60°). After a short induction period (20 min.), hydrogen bromide was evolved. After 6 hr., residual hydrogen bromide and bromine were removed through an aspirator as nitrogen was bubbled through the reaction mixture. Distillation gave unchanged 2-methyl-2-phenylbutane (123.9 g., b.p. 40–42° at 2 mm., $n^{20}\mathrm{D}$ 1.4958) and 2-bromo-3-methyl-3-phenylbutane (38.6 g., b.p. 78–80° at 2 mm., $n^{20}\mathrm{D}$ 1.5425, 71% yield based upon amylbenzene consumed).

Anal. Calcd. for $C_{11}H_{15}Br$: Br, 35.2. Found: Br, 35.1.

A residue (12.6 g.) of polybromides remained. This bromide was identified further by carbonation of its Grignard reagent to give 2,3-dimethyl-3-phenylbutanoic acid (m.p. 104–105° from aqueous ethanol; 91% yield).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.4. Found: C, 75.1; H, 8.5.

In addition this bromide was hydrogenated over palladium on calcium carbonate to give only 2-methyl-2-phenylbutane.

The Grignard reagent was prepared by the reaction of 2-methyl-2-phenyl-3-bromobutane (68 g., 0.30 mole, $n^{20}\mathrm{D}$ 1.5392) with magnesium (7.2 g.) in anhydrous ether (100 ml.). After the formation of the Grignard reagent was complete (addition of the halide, 2.5 hr.; reflux, 45 min.), ethyl orthoformate (redistilled Eastman, 44.0 g., 0.30 mole, $n^{20}\mathrm{D}$ 1.3920) in anhydrous ether (80 ml.) was added (over 20 min.; reflux, 12 hr.).

Work-up of the reaction mixture with hydrolysis of the acetal by hydrochloric acid and purification of the aldehyde through its bisulfite addition product were done as described above. Ia (29.4 g., 0.17 mole, 56% yield, b.p. 53–55° at 0.3 mm., $n^{20}\mathrm{D}$ 1.5289) was obtained by distillation.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.2. Found: C, 81.3; H, 9.0.

Its 2,4-dinitrophenylhydrazone (m.p. 223–224° from ethyl acetate), and its semicarbazone (m.p. 195–196° from aqueous ethanol) were prepared.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: N, 15.7. Found: N, 15.4.

The Reaction of Ia with *t*-Butyl Peroxide.—A solution of the peroxide (1.6 g., 0.011 mole) in Ia (16.7 g., 0.095 mole) was heated at 140° under a nitrogen atmosphere for 20 hr. After 12 hr., additional peroxide (0.5 g., 0.003 mole) was added. Little carbon monoxide (200 ml.) was evolved.

The reaction product was separated by fractional distillation to give a distillate (7.5 g., b.p. 70–75° at 1 mm.) and a viscous residue (8.4 g., infrared at 730 and 1690 cm.$^{-1}$). Analysis of the distillate (v.p.c., F & M, Model 500, temperature-programmed gas chromatograph, 2-ft. silicone rubber column; isothermal, 175°; helium flow, 100 ml. per min.) indicated a mixture of amylbenzenes (retention time, 1.7 min.; 0.5 g.; 0.004 mole; 7.2%) and unchanged Ia (retention time, 5.3 min.; 7.0 g.; 0.040 mole; 58% conversion). Recrystallization of the residue from ethanol gave Va (6.5 g., 0.018 mole, m.p. 186–187°, 67% yield).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 81.8; H, 9.1. Found: C, 81.4; H, 8.9.

Va was hydrolyzed with aqueous alcoholic potassium hydroxide solution (0.86 *N*; reflux, 24 hr.). The ethanol was removed under vacuum, and 2,3-dimethyl-3-phenylbutyric acid (m.p. 103.5–104.5° after sublimation; mixture melting point with authentic acid prepared as above, 104–105°) precipitated when the basic solution was made acidic. From the ether extract, 2,3-dimethyl-3-phenylbutanol (m.p. 108–109° from aqueous ethanol) was isolated.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.8; H, 10.2. Found: C, 80.7; H, 10.0.

An authentic sample of this alcohol (m.p. 108–109°, mixture melting point not depressed) was prepared by the reduction of the above aldehyde with lithium aluminum hydride.

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The ethanolic filtrate from the recrystallization of Va contained IVa (2.0 g., 0.011 mole, 21% yield). It was converted to its 2,4-dinitrophenylhydrazone [m.p. 75–77°, mixture melting point undepressed; ultraviolet spectrum was λ_{max} 390 μ (ϵ_{max} 1.92 × 10^4), and 266 (1.18 × 10^4)]. Authentic IVa was obtained from the reaction of 2,3-dimethyl-3-phenylbutanoic acid (5.0 g., 0.026 mole, prepared as above) with phosphorus pentachloride (5.5 g.; 0.026 mole; reflux, 1 hr.), and then aluminum chloride (6.9 g., 0.052 mole; reflux, 2 hr.) was added. Work-up of the reaction mixture with cold, dilute hydrochloric acid, drying, and then distillation gave IVa (3.2 g., 0.018 mole, b.p. 130–134° at 1 mm., n^{20}D 1.5437, infrared at 1690 cm.$^{-1}$). Its 2,4-dinitrophenylhydrazone (m.p. 76–77° from ethanol) was prepared.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.8. Found: N, 15.3.

To study the amylbenzenes obtained in the reaction of Ia with *t*-butyl peroxide, reaction conditions were modified. A solution containing Ia (9.3 g., 0.053 mole, n^{20}D 1.5287), the peroxide (1.02 g., 0.007 mole, n^{20}D 1.3893), and redistilled chlorobenzene (50 ml., n^{20}D 1.5248) was held at 130° for 24 hr. Then more peroxide (0.96 g.) was added, and the reaction was continued for another 24 hr. Carbon monoxide (515 ml., S.C.) was evolved.

The reaction mixture was distilled to give chlorobenzene (54.8 g., b.p. 71–72° at 112 mm., n^{20}D 1.5248); a mixture of hydrocarbons (2.18 g., b.p. 62–68° at 20 mm., n^{20}D 1.4931); and a residue (5.8 g.) from which Ia (4.3 g., m.p. 184–186°) was obtained. The infrared spectrum of the mixture of hydrocarbons was identical with a mixture of IIa (30%) and IIIa (70%). A mixture of *p*-benzamido derivatives was prepared from the hydrocarbon mixture (m.p. 104–118°). 2-Methyl-3-(*p*-benzamidophenyl)butane (m.p. 138–141°, after nine recrystallizations from aqueous ethanol; mixture melting point with authentic sample, 139–141°) was obtained.

Preparation of 2,3,3-Trimethylbutanal.—The Grignard reagent prepared from 2-chloro-3,3-dimethylbutane (56.0 g., 0.46 mole, n^{20}D 1.4180,[41] obtained by careful fractional distillation of the mixture products from the photochemical chlorination of 2,2-dimethylbutane)[42] with magnesium (12 g., 0.5 g.-atom) in anhydrous ether (125 ml.; addition, 4 hr.; reflux, 45 min.) was treated with ethyl orthoformate (Eastman, 96.0 g., 0.46 mole, b.p. 80° at 89 mm., n^{20}D 1.3920) in anhydrous ether (100 ml.; reflux, 16 hr.). The acetal product was hydrolyzed with hydrochloric acid, and the aldehyde formed was purified *via* the aldehyde–bisulfite addition product. The latter was treated with sodium carbonate solution, and the mixture was extracted with ether. The ether solution (dried over sodium sulfate) was distilled to give 2,3,3-trimethylbutanal (13.1 g., 0.11 mole, b.p. 66–68° at 69 mm., n^{20}D 1.4125).

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 72.9; H, 12.2.

Its 2,4-dinitrophenylhydrazone (m.p. 126–127° from aqueous ethanol) was prepared.

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: N, 19.0. Found: N, 18.8.

Reaction of 2,3,3-Trimethylbutanal with *t*-Butyl Peroxide.—A solution containing this aldehyde (3.54 g., 0.031 mole) and peroxide (0.56 g., 0.004 mole, b.p. 45° at 72 mm., n^{20}D 1.3889) was heated at 130° for 24 hr. Carbon monoxide (563 ml. S.C. 80% yield) was evolved. 2,2-Dimethylbutane (2.2 g., n^{20}D 1.3684,[43] 83% yield) was obtained by distillation of the reaction mixture and the contents of the −80° trap. Its infrared spectrum was identical with that of an authentic sample (Phillips 99% pure neohexane).

Preparation of Cyclopropyl Acetaldehyde.—Cyclopropanecarboxylic acid (51.6 g., 0.60 mole, prepared from γ-chlorobutyronitrile)[44] with thionyl chloride (84 g., 0.70 mole) gave cyclopropane carbonyl chloride (52.3 g., 0.50 mole, 83% yield).[45] This acid chloride (14.4 g., 0.14 mole) in ether (50 ml.) was added over a period of 45 min. to a stirred solution of diazomethane (0°, from 70 g. of nitrosomethylurea)[46] in anhydrous ether (700 ml.). The crude diazo ketone obtained by distillation of the reaction mixture was dissolved in absolute ethanol (200 ml.), and this solution was irradiated with a mercury resonance lamp. Over a period of 2 days, nitrogen (2.98 l., S.C., 0.133 mole) was collected. Distillation of the reaction mixture gave ethyl cyclopropylacetate (13.9 g., 0.11 mole, b.p. 86–88° at 75 mm., n^{20}D 1.4240).

Ethyl cyclopropylacetate (18 g., 0.14 mole) in anhydrous ether (50 ml.) was treated with an ether solution (100 ml.) of lithium aluminum hydride (5.0 g., 0.13 mole; addition, 45 min.; reflux, 2 hr.). Work-up gave 2-cyclopropylethanol (11.1 g.; 0.13 mole; b.p. 88–90° at 100 mm.; n^{20}D 1.4344; 93%; infrared at 3320, 3060, and 1050 cm.$^{-1}$).

Anal. Calcd. for $C_5H_{10}O$: C, 69.8; H, 11.6. Found: C, 69.4; H, 11.8.

The phenylurethane (m.p. 57–58° from aqueous ethanol), and α-naphthylurethane (m.p. 81–82° from 60° ligroin) of this alcohol were prepared.

Anal. Calcd. for $C_{12}H_{15}NO_2$: N, 6.9. Found: N, 6.9.

Anal. Calcd. for $C_{16}H_{17}NO_2$: N, 5.5. Found: N, 5.9.

2-Cyclopropylethanol (9.0 g., 0.10 mole) in anhydrous pyridine (40 ml., Baker) was oxidized with chromic anhydride–pyridine complex (120 ml.; prepared from anhydrous chromic anhydride, 12 g., and pyridine, 120 ml.).[47] After the reaction mixture had been allowed to stand for 12 hr., it was made acidic with dilute hydrochloric acid. It was then extracted with ether, and the ether solution (dried over sodium sulfate) was distilled to give cyclopropylacetaldehyde (4.03 g., 0.048 mole, b.p. 69–75° at 166 mm., n^{20}D 1.3891, 48% yield) and unchanged 2-cyclopropylethanol (4.01 g., b.p. 78–90° at 160 mm., n^{20}D 1.4290, 45% recovery).

Anal. Calcd. for C_5H_8O: C, 71.4; H, 9.5. Found: C, 70.8; H, 10.0.

The 2,4-dinitrophenylhydrazone of this aldehyde (m.p. 118–119° from aqueous ethanol) was prepared.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: N, 21.2. Found: N, 21.1.

Reaction of Cyclopropylacetaldehyde with *t*-Butyl Peroxide.—This aldehyde (4.14 g., 0.049 mole) and peroxide (1.07 g., 0.0073 mole, n^{20}D 1.3893) were heated at 130° for 27 hr. Gasses evolved were led through a trap (−80°, containing 20 ml. of ether) into a Precision wet test meter. Carbon monoxide (0.88 l., S.C., 0.393 mole, 80% yield) was measured on the meter. The decarbonylation product, collected in the ether in the −80° trap, was found to be 1-butene (retention time, 8 min.; Fisher–Gulf gas chromatograph; 10-ft. column, paraffin oil on Celite; isothermal, 35°; helium flow, 20 ml. per min.). Other possible products gave different retention times under the same column conditions (butane, 9 min.; *cis*-2-butene, 10 min.; *trans*-2-butene, 11 min.; methylcyclopropane, 10.5 min.; and cyclobutane, 18 min.), and their mixtures with 1-butene always gave the expected two peaks.

The ether solution of the 1-butene was treated with 2,4-dinitrobenzenesulfenylchloride in glacial acetic acid, and the reaction mixture was allowed to stand for 16 hr. 2-Chlorobutyl 2,4-dinitrophenyl sulfide (m.p. 77–78°, mixture melting point with authentic sample was undepressed) was obtained.[48]

The same reaction products were obtained when cyclopropyl acetaldehyde (2.01 g., 0.024 mole) and *t*-butyl peroxide (0.79 g., 0.0054 mole) in chlorobenzene (25.6 g., n^{20}D 1.5248) were held at 130–135° for 48 hr.

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