known 4-methoxy-3-nitro compounds, *e.g.*, from the ester on pouring into cold water containing excess acid a white crystalline precipitate was obtained which melted sharply at 108°. On recrystallization from methanol the melting point was raised to 109° (lit. 108°, 109–110°).

Preparation of Materials. *o*-Chloronitrobenzene: the commercial product was recrystallized from ethanol; m.p. 32.5° (lit. 32°).

4-Chloro-3-nitrobenzoic Acid: from *p*-chlorobenzoic acid by the outline procedure of King and Murch.[4] The nitration was carried out at 65° then the mixture heated for a few minutes at 90° until all material went into solution; yield 90%, m.p. 183° (lit. 182.5°).

4-Chloro-3-nitrobenzamide: from the acid *via* the acid chloride according to the method of Montagne[5]; m.p. 156° (lit. 156°).

Methyl 4-chloro-3-nitrobenzoate: from the acid *via* the acid chloride by a standard procedure; yield 84%, m.p. 83° (lit. 83°).

4-Chloro-3-nitroacetophenone: from *p*-chloroacetophenone by the method of LeFèvre and LeFèvre[6]; m.p. 99–101° (lit. 99–101°).

4-Chloro-3-nitrobenzophenone: from the benzoyl chloride and benzene by the method of Montagne[7]; m.p. 104–105° (lit. 104–105°, 105.5°).

4-Chloro-3-nitrobenzaldehyde: from *p*-chlorobenzaldehyde by the method of Van der Lee[8]; m.p. 63° (lit. 61.5–62°, 64.5°).

4-Chloro-3-nitrobenzonitrile: from *p*-chlorobenzonitrile by the method of Mattaar[7]; m.p. 101° (lit. 101°).

Solvent: The solvent dried as in previous papers was shown by the method of Weaver[9] to contain not more than 0.001% water.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide- and Light-induced Additions of Alcohols to Olefins[1]

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α-C-Alkylation of primary and secondary alcohols results from their peroxide- and light-induced reactions with olefins. For example, this reaction with ethanol and ethene gives butanol-2, hexanol-2, octanol-2 and decanol-2 while that with propanol-2 and ethene yields 2-methylbutanol-2, 2-methylhexanol-2, 2-methyloctanol-2 and 2-methyldecanol-2. In each case, higher telomers also are formed. The peroxide initiation of these reactions shows an interesting specificity since alkyl peroxides are effective inducing agents while acyl peroxides are ineffective. The evidence suggests a free-radical, chain mechanism.

The peroxide- and light-induced additions of primary and secondary alcohols to olefins result in the replacement of a hydrogen atom attached to the hydroxyl-bearing carbon atom by an alkyl group to give secondary and tertiary alcohols, respectively. The free radical, chain mechanism in each such reaction leads to the formation of products (telomers: with 1:1, 2:1, 3:1 and higher whole number ratios of olefin to alcohol) of differing complexity in the alkyl group substituted. High yields of lower addition products (1:1 and 2:1) are favored by high alcohol to olefin concentration ratios.

In addition to the practical result that a variety of alcohols may be prepared conveniently from homologs of lower molecular weight, this work confirms two previous observations of theoretical importance in free radical chemistry. First, it clearly indicates that free radicals attack these alcohols to remove α-hydrogen atoms.[2] Second, it was predicted and then confirmed that in these reactions *t*-butyl peroxide is an effective initiator while benzoyl peroxide is not, in contrast to other addition reactions previously studied where either peroxide can be used. Previous work which suggested this outcome has shown that the former peroxide shows first-order kinetics with approximately the same rates of decomposition[3,4] in a wide range of organic solvents while the latter undergoes rapid chain decomposition in alcohols[5,6] (see Discussion).

The reactions of alcohols with olefins studied (induced by *t*-butyl peroxide at 125–130°) are summarized in Table I. The products listed were iden-

TABLE I

PRODUCTS IDENTIFIED IN PEROXIDE-INDUCED ADDITIONS OF ALCOHOLS TO OLEFINS[a]

Alcohol	Olefin	Products
Methanol	Octene-1	Nonanol-1
Ethanol	Ethene	Butanol-2, hexanol-2, octanol-2, decanol-2
Ethanol	Hexene-1	Octanol-2
Ethanol	Octene-1	Decanol-2
Propanol-2	Ethene	2-Methylbutanol-2, 2-methylhexanol-2, 2-methyloctanol-2, 2-methyldecanol-2
Propanol-2	Propene	2-Methylpentanol-2
Propanol-2	3-Hydroxypropene	4-Methylpentanediol-1,4
Propanol-2	Octene-1	2-Methyldecanol-2
Propanol-2	Dodecene-1	2-Methyltetradecanol-2
Butanol-1	Octene-1	Dodecanol-4
Butanol-2	Octene-1	3-Methylhendecanol-3
Cyclohexanol	Hexene-1	1-*n*-Hexylcyclohexanol
Cyclohexanol[b]	Octene-1	1-*n*-Octylcyclohexanol

[a] All reactions represented were obtained with *t*-butyl peroxide. [b] Induced by *t*-butyl peroxide, *t*-amyl peroxide and 2,2-bis-(*t*-butylperoxy)-butane.

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TABLE II

	Alcohol, moles	Olefin, moles	Initiator, mole	T, °C.	Olefin used, moles	Conversion to telemers,[a] % 1:1	2:1	3:1	4:1	Residue (telomer)[b]
1	Methanol (10.0)	Octene-1 (0.20)	0.031[g]	116–120	0.11	16	16			68 (3.8)
2	Ethanol (7.82)	Ethene ( )[c]	.061[g]	125–135	2.53	10	8	11	15	56 (9.4)
3	Ethanol (7.80)	Hexene-1 (.26)	[f]	30–35	0.088	13				87 (3.2)
4	Ethanol (7.82)	Octene-1 (.31)	.031[g]	115–118	0.26	28	12			60 (3.9)
5	Propanol-2 (7.07)	Ethene ( )[d]	.031[g]	125–130	2.37	36	18	14	10	22 (7.6)
6	Propanol-2 (4.00)	Propene ( )[e]	.031[g]	125–130		0.060[i]	0.062[i]			10[j]
7	Propanol-2 (5.00)	3-Hydroxypropene (.25)	.031[g]	125–130		0.078[i]				8.9[j]
8	Propanol-2 (5.95)	Octene-1 (.25)	.031[g]	120–125	0.204	46	25			29 (3.9)
9	Propanol-2 (3.32)	Octene-1 (.18)	[f]	30–35	.092	38	24			38 (3.2)
10	Propanol-2 (5.00)	Dodecene-1 (.16)	.031[g]	115–120	.12	51				49 (2.3)
11	Butanol-1 (7.85)	Octene-1 (.26)	.048[g]	117–118	.26	37	19			44 (3.1)
12	Butanol-2 (3.34)	Octene-1 (.24)	.037[g]	117–118	.19	37	22			41 (4.0)
13	Cyclohexanol (4.50)	Hexene-1 (.25)	.038[g]	125–135	.22	42				58 (3.4)
14	Cyclohexanol (6.00)	Octene-1 (.40)	.051[g]	128–130		0.127[i]				36[j]
15	Cyclohexanol (2.50)	Octene-1 (.10)	.026[h]	108–112		.026[i]				11.4[j]

[a] Percentage conversion to each telomer based upon olefin consumed. [b] Average number of olefin units per molecule of residue. [c] Pressure of ethene, 250–400 p.s.i. [d] Pressure of ethene, 200–300 p.s.i. [e] Pressure of propene, 120–150 p.s.i. [f] Ultraviolet light induced. [g] t-Butyl peroxide induced. [h] t-Amyl peroxide induced. [i] Conversion to products given in moles. [j] Residue yield in grams.

tified by the comparison of their physical properties, derivatives and infrared spectra with those of known alcohols prepared from Grignard reactions with the appropriate ketones.

Propanol-2 with octene-1 and ethanol with hexene-1 gave 2-methyldecanol-2 and octanol-2, respectively, in the presence of light. In all of the experiments listed higher boiling products (higher telomers) were obtained, but were not identified. Details are given in Table II.

The following reactions were attempted (with t-butyl peroxide at 130°) but failed to give identifiable amounts of addition products: (1) cyclohexanol with isobutylene, (2) benzyl alcohol with ethylene, (3) 2-phenylethanol with ethylene and (4) 2-methylpropanol-2 with octene-1. Benzoyl peroxide (at 80 and 140°), hexachloroethane (150°), 2,2′-azo-bis-isobutyronitrile (80°) and α-cumyl hydroperoxide (150°) failed to initiate addition reactions listed in Table I.

Discussion

A free-radical, chain mechanism for these reactions is suggested by the experimental observations: (1) small amounts of peroxide or light induce a disproportionately large amount of reaction, (2) no reaction occurs in the absence of these inducing agents or in the presence of inhibitors and (3) telomeric products are formed. The most probable mechanism for the t-butyl peroxide-induced reaction of ethanol with ethylene is

$$(CH_3)_3C{-}O{-}O{-}C(CH_3)_3 \longrightarrow 2(CH_3)_3C{-}O\cdot \quad (1)$$

$$(CH_3)_3C{-}O\cdot + CH_3CH_2OH \longrightarrow (CH_3)_3COH + CH_3\underset{\cdot}{C}HOH \quad (2a)$$

or

$$(CH_3)_3C{-}O\cdot + CH_3CH_2OH \longrightarrow CH_4 + CH_3COCH_3 + \underset{\text{I}}{CH_3\underset{\cdot}{C}HOH} \quad (2b)$$

$$CH_3\underset{\cdot}{C}HOH + CH_2{=}CH_2 \longrightarrow \underset{\text{II}}{CH_3CHOHCH_2CH_2\cdot} \quad (3)$$

$$CH_3CHOHCH_2CH_2\cdot + CH_3CH_2OH \longrightarrow CH_3CHOHCH_2CH_3 + CH_3\underset{\cdot}{C}HOH \quad (4)$$

$$CH_3CHOHCH_2CH_2\cdot + CH_2{=}CH_2 \longrightarrow \underset{\text{III}}{CH_3CHOHCH_2CH_2CH_2CH_2\cdot} \quad (5)$$

$$CH_3\underset{\cdot}{C}HOH + X \longrightarrow CH_3CHO + HX \quad (6)$$

Reactions 1 and 2 are chain initiating steps, reactions 3, 4 and 5 with analogous subsequent reactions to form higher telomers are chain propagating steps, and reaction 6 represents a probable chain termination (see below).

An interesting aspect of this work is the specificity of inducing agents observed. The alkyl peroxides, t-butyl peroxide, t-amyl peroxide and 2,2-bis-(t-butylperoxy)-butane, are effective initiation reagents while others useful in previous studies of free-radical olefin addition reactions, benzoyl peroxide (at 80 and 140°), α-cumyl hydroperoxide (150°), hexachloroethane (150°) and 2,2′-azo-bis-isobutyronitrile (80°) are ineffective.

The failure of benzoyl peroxide at 80° to initiate the addition reaction was not unexpected since it has been shown[5] that in alcohols this peroxide undergoes an accelerated chain decomposition which probably involves attack by the alcohol-derived free radicals on the peroxide. In view of the present results, which clearly indicate the site of attack by free radicals upon alcohols, this decomposition may be written as

$$(C_6H_5COO{-})_2 \longrightarrow 2C_6H_5COO\cdot \quad (a)$$

$$C_6H_5COO\cdot + RR'CHOH \longrightarrow C_6H_5COOH + RR'\underset{\cdot}{C}OH \quad (b)$$

$$RR'\underset{\cdot}{C}OH + (C_6H_5COO{-})_2 \longrightarrow RR'C(OH)OCOC_6H_5 + C_6H_5COO\cdot \quad (c)$$

$$RR'C(OH)OCOC_6H_5 \longrightarrow RCOR' + C_6H_5COOH \quad (d)$$

Apparently, benzoyl peroxide is rapidly consumed in this reaction with the alcohols and does not initiate the free-radical, chain addition to the olefins. These results suggest an interesting specificity in the reactions of the free alcohol-derived radical (I) since it seems to have an overwhelming tendency to react with benzoyl peroxide (reaction c) rather than the olefin present (reaction 3) even though the former is in relatively low concentration. The attempt to use benzoyl peroxide at 140° was suggested by the observation that its unimolecular decomposition is more important relative to the free radical-induced chain reaction at higher temperatures. However, even at 140° benzoyl peroxide was ineffective. Since similar free-radical, chain decompositions have been observed with other acyl peroxides,[6] it is suggested that these reagents will be equally ineffective in inducing the additions of alcohols to olefins.

With the other possible initiation agents which failed to induce the reaction, it is probable that free radicals produced in their decompositions gave reactions other than addition to the olefin present or abstraction of a hydrogen atom from the alcohol. The reaction with hexachloroethane gave no hydrogen chloride or chloroform, and, of course, no addition product. Tetramethylsuccinonitrile, the product of free radical dimerization, was isolated in the experiment in which 2,2′-azo-bis-isobutyronitrile was used.

The reactions of chain transfer (equation 4) and chain growth (equation 5) are in competition. In general reaction 4 is of relatively slow rate, and a higher molar ratio of addition reagent (alcohol) to olefin than in addition reactions previously studied has been necessary to favor the formation of lower telomers (1:1 and 2:1 addition products). A comparison of the reactions of various alcohols (Table II) shows that the relative rates of reactions 4 and 5 are markedly dependent upon the nature of the carbon to hydrogen bond broken in the chain transfer step 4. In the reactions of propanol-2 and butanol-2 with octene-1, a 40–50% conversion (based upon the olefin) to the 1:1 addition product is obtained with a 20–25:1 molar ratio of alcohol to olefin. With methanol, on the other hand, the corresponding conversion is 15% even when the alcohol–olefin molar ratio is 50:1.

A more quantitative estimate of the ratio of the rate of chain transfer (reaction 4) to that of chain growth (reaction 5) is obtained by a calculation of the transfer constants[7,8] for the reactions of various alcohols with ethene, hexene-1 and octene-1 (Table III). Although the values of the transfer constants calculated here are not reliable because of the low average molecular weights of the products, they are internally consistent and indicate semi-quantitatively the relative ease of chain transfer with different alcohols. As expected, the reactivities decrease in the order secondary alcohols to primary alcohols (ethanol and butanol-1) to methanol. No marked temperature effect is observed since the peroxide-induced reaction of propanol-2 with octene-1 at 130° (Table III, reaction 8) gives a transfer constant (0.052) approximately the same as that (0.063) for the light-induced reaction at 40° (Table III, reaction 9). These results also indicate that there is no marked change in transfer constant with chain length of the free radicals such as II and III or of the alcohol reactant.

In the additions of primary alcohols to olefins, products resulting from subsequent reactions of the telomers initially formed (secondary alcohols) are possible; but, in a careful fractional distillation of the product of the peroxide-induced reaction of ethanol with ethene, no such products were isolated. For example, this reaction of the initial products (butanol-2, hexanol-2, octanol-2 and decanol-2) with ethene probably gives the products (3-methylpentanol-3, 3-methylheptanol-3, 3-methylnonanol-3, 3-methylhendecanol-3 and higher telomers) in small amount. Calculation shows that the average amount of ethanol (7.475 moles) in the reaction mixture was so great compared with the average amount of butanol-2 present (0.125 mole) that even though the latter is roughly twice as reactive as the former the yield of 3-methylpentanol-3 expected (0.0075 mole, 0.75 g.) is indeed small. These products were probably formed in amounts too small to isolate under the conditions of our experiments, but in reactions carried to greater conversion with higher pressures of ethene such products should be observed.

TABLE III

TRANSFER CONSTANTS[a] FOR ALCOHOL–OLEFIN ADDITION REACTIONS

	Alcohol	Olefin	[M]/[S]	$\bar{P}$	C
1[b]	Methanol	Octene-1	0.015	2.42	0.011
2	Ethanol	Ethene	*ca.* .053	3.76	*ca.* .019
3	Ethanol	Hexene-1	.026	2.49	.017
4	Ethanol	Octene-1	.023	2.02	.023
5	Propanol-2	Ethene	*ca.* .047	1.82	*ca.* .057
8	Propanol-2	Octene-1	.025	1.48	.052
9	Propanol-2	Octene-1	.040	1.63	.063
11	Butanol-1	Octene-1	.017	1.63	.027
12	Butanol-2	Octene-1	.039	1.75	.052
13	Cyclohexanol	Hexene-1	.030	1.77	.039

[a] Transfer constants have been calculated according to the equation of Mayo: *viz.*, $\bar{P} = [M]/C[S] + 1$ where $\bar{P}$ is the average number of olefin units per molecule of product, C is the transfer constant and [M]/[S] is the average molar ratio of olefin to alcohol. [b] Numbers correspond to those of reactions listed in Table II.

Equation 6 in the reaction mechanism represents one way in which chain termination may occur. X could be a free *t*-butoxy radical, an intermediate free radical such as II or III, or some other hydrogen "acceptor" such as *t*-butyl peroxide. The occurrence of this reaction is indicated by the isolation of small amounts of acetaldehyde and cyclohexanone from the ethanol and cyclohexanol reactions, respectively. Further, in the peroxide-induced reaction of propanol-2 with ethene, acetone was obtained in greater amount (1.75 g.) than that expected from reaction as in 2b (0.3 g. of acetone was isolated in the ethanol–ethene experiment). This reaction 6 was apparently dominant in an attempted addition of benzyl alcohol (4.7 moles) to ethene (300–400 p.s.i.) in the presence of *t*-butyl peroxide (0.06 mole) at 130° since benzaldehyde (2.3 g., 0.02 mole) and benzoic acid (0.01 mole) were obtained, but no addition product was formed.

Experimental Part

Reagents.—*t*-Butyl peroxide (Shell Chemical Co., b.p. 49.5° at 77 mm., n^{20}_D 1.3893) was distilled in a 12-plate Fenske column. *t*-Amyl peroxide (b.p. 59.5° at 20 mm., n^{20}_D 1.4092) was prepared by the method of Milas and Sur-

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(7) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

(8) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

genor[9] from *t*-amyl alcohol, hydrogen peroxide and concentrated sulfuric acid, and was distilled in the same way.

The following reagents were distilled through a 50-plate Podbielniak column before use: propanol-2 (Carbide and Carbon, b.p. 82°, n^{20}_{D} 1.3779), butanol-2 (Eastman Kodak Co., b.p. 99°, n^{20}_{D} 1.3968), butanol-1 (Merck, b.p. 117.5°, n^{20}_{D} 1.3995), 2-methylpropanol-2 (Matheson, b.p. 82°, n^{20}_{D} 1.3878), cyclohexanol (Eastman Kodak Co., b.p. 106–107° at 105 mm., n^{25}_{D} 1.4650), benzyl alcohol (Eastman Kodak Co., b.p. 97° at 17 mm., n^{20}_{D} 1.5405), 2-phenylethanol (Eastman Kodak Co., b.p. 82.5° at 4 mm., n^{20}_{D} 1.5340), octene-1 (Humphrey-Wilkinson, b.p. 121°, n^{20}_{D} 1.4089), hexene-1 (Phillips, b.p. 63.8°, n^{20}_{D} 1.3875) and dodecene-1 (Humphrey-Wilkinson, b.p. 83° at 10 mm., n^{20}_{D} 1.4300). Hexachloroethane (m.p. 185°) was recrystallized three times from ethanol (95%). α-Cumyl hydroperoxide (commercial 72%, Hercules) was purified by the method of Hock and Lang,[10] and the final product distilled at reduced pressure (b.p. 60° at 0.2 mm.).

Benzoyl peroxide (Eastman Kodak Co.), ethanol (U.S.I. reagent grade), methanol (Merck reagent grade), ethene (Matheson C.P.), propene (Phillips Pure) and 2-methylpropene (Phillips Pure) were used without further purification.

Peroxide-induced Addition of Propanol-2 to Ethene.—In a glass-lined stainless steel autoclave equipped with a Magnedash stirrer, a solution containing propanol-2 (425 g., 7.07 moles) and *t*-butyl peroxide (4.5 g., 0.031 mole) was held at 125–130° for 20 hours under a pressure of ethene (200–300 p.s.i.). The approximate consumption of ethene (2.0 moles) was indicated by the cumulative pressure drop (1700–1800 p.s.i. free volume of 550 ml.).

The reaction mixture was distilled through a 50-plate Podbielniak column. A low boiling fraction (8.0 g., b.p. 50–80°) contained acetone (1.75 g., determined by the hydroxylamine hydrochloride method).[11] After unreacted propanol-2 and 2-methylpropanol-2 had distilled, the following fractions were obtained: (1) 2-methylbutanol-2 (75.9 g., 0.86 mole, b.p. 66° at 165 mm., n^{20}_{D} 1.4052); (2) 2-methylhexanol-2 (24.2 g., 0.21 mole, b.p. 82° at 80 mm., n^{20}_{D} 1.4180), (3) 2-methyloctanol-2 (16.0 g., 0.11 mole, b.p. 66° at 8 mm., n^{20}_{D} 1.4282) and 2-methyldecanol-2 (10.5 g., 0.06 mole, b.p. 75° at 0.3 mm., n^{20}_{D} 1.4368). A residue (18.5 g., average mol. wt. 274) remained.

Identification of Propanol-2–Ethene Addition Products.—The 2-methylbutanol-2 was converted to its 3,5-dinitrobenzoate (m.p. 116–117°) and its *p*-nitrobenzoate (m.p. 83.5–84.5°). The 2-methylhexanol-2 was identified by the preparation of its allophanate[12] (m.p. 153–154°, m.p. of its mixture with an authentic sample 153–154°).

Anal. Calcd. for $C_9H_{18}O_3N_2$: N, 13.84. Found: N, 13.90.

The 2-methylhexanol-2 for comparison (b.p. 90.5° at 120 mm., n^{20}_{D} 1.4180, m.p. of allophanate 153–154°) was prepared by the reaction of *n*-butylmagnesium bromide with acetone.

The allophanate of the 2-methyloctanol-2 (m.p. 113–113.5°, m.p. of its mixture with an authentic sample 112–113°) was prepared.

Anal. Calcd. for $C_{11}H_{22}O_3N_2$: N, 12.16. Found: N, 12.10.

2-Methyloctanol-2 (b.p. 79–80° at 12 mm., n^{20}_{D} 1.4280, m.p. of allophanate 112–113°) was also prepared from *n*-hexylmagnesium bromide and acetone. Our 2-methyldecanol-2 had the same physical properties and gave the same allophanate (m.p. 113–114°, m.p. of mixture 113.5–114.5°) as the alcohol (b.p. 50–52° at 1 mm., n^{20}_{D} 1.4358, m.p. of its allophanate 113.5–114°) prepared from *n*-octylmagnesium bromide and acetone.

Anal. Calcd. for $C_{13}H_{26}O_3N_2$: N, 10.85. Found: N, 10.54.

The melting point of a mixture of the allophanates of 2-methyloctanol-2 and 2-methyldecanol-2 gave a marked depression (m.p. 94–97°).

Peroxide-induced Addition of Ethanol to Ethene.—In the stainless steel autoclave, a mixture of ethanol (360 g., 7.82 moles) and *t*-butyl peroxide (9.0 g., 0.061 mole) was held at 125–135° under a pressure of ethene (250–400 p.s.i.) until absorption of the latter ceased (20 hours). The cumulative pressure decreases (2000 p.s.i., in a free volume of 550 ml.) indicated the approximate amount of ethene (2.5 moles) used.

The reaction mixture was distilled through the 50-plate Podbielniak column, and the initial fraction was found to contain acetaldehyde (0.7 g., m.p. of 2,4-dinitrophenylhydrazone 144–146°) and acetone (0.3 g., m.p. of 2,4-dinitrophenylhydrazone 123–125°) by the determination of total carbonyl with hydroxylamine hydrochloride and chromatographic separation of the 2,4-dinitrophenylhydrazones on silica gel. After the unreacted ethanol had distilled, the following reaction products were obtained: (1) butanol-2 (18.3 g., 0.25 mole, b.p. 61° at 140 mm., n^{20}_{D} 1.3978); (2) hexanol-2 (10.4 g., 0.10 mole, b.p. 54.5° at 17 mm., n^{20}_{D} 1.4154); (3) octanol-2 (12.3 g., 0.095 mole, b.p. 49–50° at 5 mm., n^{20}_{D} 1.4288); and (4) decanol-2 (14.5 g., 0.092 mole, b.p. 30–33° at 0.2–0.3 mm., n^{20}_{D} 1.4358). A high boiling residue (47 g., average mol. wt. 309) remained.

Identification of Ethanol–Ethene Addition Products.—The α-naphthylurethan of the butanol-2 (m.p. 97–98°, m.p. of mixture with authentic sample 97–98°) was prepared. The hexanol-2 was converted to its 3,5-dinitrobenzoate (m.p. 39.5–40.5°, m.p. of mixture with authentic sample 39–40°). The 3,5-dinitrobenzoate of the octanol-2 (m.p. 34–34.5°, m.p. of mixture with authentic sample 34–34.5°) was also prepared. The decanol-2 was further identified with the same derivative (m.p. 52.5–53.5°, m.p. of mixture with authentic sample 52–53°).[13]

Peroxide-induced Addition of Butanol-2 to Octene-1.—A solution containing butanol-2 (247 g., 3.34 moles), octene-1 (26.5 g., 0.236 mole) and *t*-butyl peroxide (5.5 g., 0.037 mole) was heated to 117–118° for 40 hours in the reaction flask of a special all-glass apparatus under a positive pressure of nitrogen (15 p.s.i.). One half of the peroxide was added at first and the remainder after 20 hours.

Distillation of the reaction mixture through a Vigreux gave, after removal of the low boiling products and unreacted butanol-2, a 1:1 addition product shown to be 3-methylundecanol-3 (13.3 g., 0.071 mole, b.p. 58–60°, at 0.1 mm., n^{20}_{D} 1.4418).

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.35; H, 14.07; mol. wt., 186. Found: C, 77.70; H, 14.18; mol. wt., 194.

This product had the same physical properties and infrared spectrum as 3-methylundecanol-3 prepared by the reaction of butanone-2 with *n*-octylmagnesium bromide (b.p. 63° at 0.1 mm., n^{20}_{D} 1.4416), and it gave the same allophanate (m.p. 76–77°, m.p. of mixture 76–78°).

Anal. Calcd. for $C_{14}H_{28}O_3N_2$: N, 10.29. Found: N, 10.44.

A second fraction (6.2 g., 0.021 mole, b.p. 150–160° at 0.1 mm., n^{20}_{D} 1.4552, mol. wt., 311) was presumed to be the 2:1 addition product (2 octene : 1 butanol, mol. wt. 298). A high boiling residue (10.4 g., mol. wt. 518) remained.

Peroxide-induced Addition of Butanol-1 to Octene-1.—A solution of octene-1 (29 g., 0.26 mole) and *t*-butyl peroxide (3 g.) in butanol-1 (581 g., 7.85 moles) was heated at its reflux temperature (117–118°) for 40 hours. Additional peroxide (2 g. after 5 hours, 2 g. after 18 hours, total: 7 g., 0.048 mole) was added.

Distillation of the reaction mixture through a 12-plate Fenske column gave *t*-butyl alcohol (3.3 g.) and unreacted butanol-1. The residue remaining was distilled through a Vigreux column to give an initial fraction shown to be dodecanol-4 (18 g., 0.097 mole, b.p. 83–84° at 1 mm., n^{20}_{D} 1.4409).

Anal. Calcd. for $C_{12}H_{26}O$: C, 77.35; H, 14.07; mol. wt., 186. Found: C, 77.64; H, 13.82; mol. wt., 192.

Dodecanol-4 (b.p. 83–84° at 1 mm., n^{20}_{D} 1.4409, m.p. of α-naphthylurethan 57–58°, 60% yield) was prepared by the reduction of dodecanone-4 (from the reaction of *n*-butyraldehyde with octene-1 in the presence of benzoyl peroxide, 60% yield)[14] with lithium aluminum hydride. Identity of the alcohol from the two sources was confirmed with

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the α-naphthylurethan (m.p. 57–58°, m.p. of mixture 57–58°).

Anal. Calcd. for $C_{23}H_{33}O_2N$: C, 77.70; H, 9.36. Found: C, 77.35; H, 9.58.

The 2:1 addition product (7.5 g., 0.025 mole, b.p. 120–145° at 1 mm., n^{20}D 1.4518, mol. wt. 297, calcd. mol. wt. 299) distilled next, and a high boiling residue (15 g., n^{20}D 1.4635, mol. wt. 421) remained.

Peroxide-induced Addition of Propanol-2 to Octene-1.—In the glass-lined, stainless steel autoclave, a solution of octene-1 (28 g., 0.25 mole) and *t*-butyl peroxide (4.5 g., 0.03 mole) in propanol-2 (357 g., 5.95 moles) was heated to 120–125° for 35 hours. The reaction mixture was distilled to give a low boiling fraction (3.9 g., b.p. 62–82°) containing acetone and *t*-butyl alcohol, unreacted propanol-2 and a fraction shown to be 2-methyldecanol-2 (16.5 g., 0.096 mole, b.p. 50° at 0.2 mm., n^{20}D 1.4359).

Anal. Calcd. for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.35; H, 13.80.

The infrared spectrum and other physical properties of this alcohol were identical with 2-methyldecanol-2 (b.p. 50° at 0.2 mm., n^{20}D 1.4358, m.p. of allophanate 113.5–114°) prepared from *n*-octylmagnesium bromide and acetone. The allophanates were identical (m.p. of mixture 113–114°). The next fraction (7.4 g., 0.026 mole, b.p. 120–130° at 0.1 mm., n^{20}D 1.4525, mol. wt. 263) was the 2:1 addition product (calcd. mol. wt. 284), and a residue (7 g., n^{20}D 1.4632, mol. wt. 499, average 3.9 octene : 1 propanol) was left in the still pot.

Light-induced Reaction of Propanol-2 with Octene-1.—A solution containing propanol-2 (199 g., 3.32 moles) and octene-1 (19.9 g., 0.178 mole) was illuminated internally with a quartz mercury resonance lamp in a special cylindrical apparatus for 96 hours. Distillation gave unreacted propanol-2 and octene-1, and 2-methyldecanol-2 (6.0 g., 0.035 mole, b.p. 50–52° at 0.2 mm., n^{20}D 1.4369, m.p. of allophanate 113–114°). The melting point of a mixture of this allophanate with that from authentic 2-methyldecanol-2 gave no depression. The 2:1 addition product (3.1 g., 0.011 mole, b.p. 120–125° at 0.1 mm., n^{20}D 1.4525) distilled, and a residue (4.7 g., average mol. wt. 422) remained.

Peroxide-induced Addition of Ethanol to Octene-1.—A solution of octene-1 (35 g., 0.31 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) in ethanol (360 g., 7.82 moles) was heated at 115–118° for 40 hours in the glass-lined, stainless steel autoclave. Acetone, *t*-butyl alcohol, unreacted ethanol and octene-1 were removed by distillation. The residue was distilled through a Vigreux apparatus to give decanol-2 (11.6 g., 0.074 mole, b.p. 52–54° at 1 mm., n^{20}D 1.4358, mol. wt. 152). It was converted to its α-naphthylurethan (m.p. 68–69°)[15] and its 3,5-dinitrobenzoate (m.p. 51.5–52.5°).[16] The 2:1 addition product (4.0 g., b.p. 120–126° at 1 mm., n^{20}D 1.4479, mol. wt. 268), presumed to be 4-*n*-hexyldodecanol-2 (mol. wt. 270), distilled next, and a residue (19 g., average mol. wt. 488) remained.

Peroxide-induced Addition of Methanol to Octene-1.—A methanol (320 g., 10 moles) solution of octene-1 (22 g., 0.195 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) was heated to 116–120° in the autoclave for 45 hours. After acetone, unreacted methanol, *t*-butyl alcohol and unreacted octene-1 had distilled, nonanol-1 (2.5 g., 0.017 mole, b.p. 108–112° at 20 mm., n^{20}D 1.4342) was obtained. Its α-naphthylurethan (m.p. 65–66°)[17] and 3,5-dinitrobenzoate (m.p. 51.5–52.5°) were prepared. An intermediate fraction (2.3 g., 0.009 mole, b.p. 145–155° at 0.2 mm., n^{20}D 1.4510, mol. wt. 254, mol. wt. calcd. for 2:1, probably 3-*n*-hexylundecanol-1, 256), and high boiling residue (9.0 g., mol. wt. 460) remained.

Peroxide-induced Addition of Cyclohexanol to Hexene-1.—A solution containing cyclohexanol (450 g., 4.50 moles), hexene-1 (21 g., 0.25 mole) and *t*-butyl peroxide (5.5 g., 0.038 mole) was heated in the autoclave at 125–135° for 45 hours. Distillation through the 50-plate Podbielniak column gave the following fractions: (1) acetone (trace) and hexene-1 (5.6 g., b.p. 55–75°); (2) cyclohexanone (0.48 g., m.p. of 2,4-dinitrophenylhydrazone 159–160°), *t*-butyl alcohol (b.p. 75–100°, 1.60 g.) and unreacted cyclohexanol. Higher boiling products were distilled through a Vigreux column to give 1-*n*-hexylcyclohexanol (17.14 g., 0.093 mole, b.p. 114–117° at 7 mm., n^{20}D 1.4645). This substance was converted to its phenylurethan (m.p. 88.5–89.2°, m.p. of mixture with authentic sample 88.7–89.5°).[18] 1-*n*-Hexylcyclohexanol (prepared from *n*-hexylmagnesium bromide and cyclohexanone, m.p. of phenylurethan 88.8–89.5°) had physical properties identical with those of the 1:1 addition product. A residue (14.5 g., mol. wt. 382) remained in the distilling flask.

Light-induced Addition of Ethanol to Hexene-1.—A solution of hexene-1 (22 g., 0.26 mole) in ethanol (360 g., 7.80 moles) was illuminated with the quartz mercury resonance lamp for 168 hours. After low boiling products and unreacted hexene-1 and ethanol had been distilled, octanol-2 (1.5 g., 0.0115 mole, b.p. 97–98° at 38 mm., n^{20}D 1.4290, identical in infrared spectrum with known octanol-2) was obtained. A residue (7.5 g., mol. wt. 318) was left.

Peroxide-induced Addition of Propanol-2 to Propene.—In the stainless steel autoclave, a solution with propanol-2 (240 g., 4.0 moles) and *t*-butyl peroxide (4.5 g., 0.031 mole) was held at 125–130° for 24 hours under a pressure of propene (120–150 p.s.i.). The absorption of propene (0.3 to 0.4 mole) was much less than that of ethene in a comparable experiment with the latter. Distillation of the reaction mixture gave 2-methylpentanol-2 (6.1 g., 0.060 mole, b.p. 79° at 150 mm., n^{20}D 1.4120), 2,4-dimethylheptanol-2 (4.5 g., 0.03 mole, b.p. 110–120° at 100 mm., n^{20}D 1.4300) and a residue (10 g.).

Peroxide-induced Addition of Propanol-2 to 3-Hydroxypropene.—A solution of 3-hydroxypropene (14.5 g., 0.25 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) in propanol-2 (300 g., 5.0 moles) was held at 125–130° in the autoclave for 36 hours. Low boiling products and unreacted propanol-2 were distilled at atmospheric pressure, and the residue remaining was distilled at reduced pressures to give 4-methylpentanediol-1,4 (9.12 g., 0.078 mole, b.p. 127–128° at 22 mm., n^{20}D 1.4449) which was converted to its di-*p*-nitrobenzoate (m.p. 158–158.5°, m.p. of mixture with an authentic sample 157–158°). This substance was prepared for comparison by the reaction of methylmagnesium bromide with γ-butyrolactone,[19] residue 8.9 g.

Peroxide-induced Addition of Propanol-2 to Dodecene-1.—Dodecene-1 (27 g., 0.16 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) in propanol-2 (300 g., 5.0 moles) were heated in the autoclave at 115–120° for 44 hours. Distillation gave unreacted propanol-2, dodecene-1 (6.0 g.) and 2-methyltetradecanol-2 (13.85 g., 0.061 mole, b.p. 115–117° at 0.2 mm., n^{25}D 1.4447). This substance (b.p. 104° at 0.1 mm., n^{20}D 1.4437, m.p. of allophanate 113–114°) was prepared by the reaction of *n*-dodecylmagnesium bromide with acetone. The melting point of a mixture of the allophanates gave no depression (115°).

Anal. Calcd. for $C_{17}H_{34}O_3N_2$: N, 8.91. Found: N, 8.94.

A residue (11.5 g., mol. wt. 453) was left in the still pot.

Peroxide-induced Addition of Cyclohexanol to Octene-1.—A solution of octene-1 (45 g., 0.40 mole) and *t*-butyl peroxide (7.5 g., 0.051 mole) in cyclohexanol (600 g., 6.0 moles) was heated for 48 hours at 128–130°. The reaction mixture was distilled, and after unreacted cyclohexanol (b.p. 100° at 70 mm.) had been removed, 1-*n*-octylcyclohexanol (27.13 g., 0.127 mole, b.p. 87–91° at 1 mm., n^{20}D 1.4645) was obtained. The phenylurethan of this alcohol (m.p. 75.5–76°, m.p. of mixture with authentic sample 75.5–76.5°)[18] was prepared. This alcohol prepared by the Grignard reaction (*n*-octylmagnesium bromide with cyclohexanone) had similar physical properties (b.p. 106° at 2 mm., n^{25}D 1.4625) and gave the same phenylurethan (m.p. 76.5–77°), residue 36 g.

This reaction was also induced with *t*-amyl peroxide and with 2,2-bis-(*t*-butylperoxy)-butane. A solution containing cyclohexanol (250 g., 2.50 moles), octene-1 (11.2 g., 0.10 mole) and *t*-amyl peroxide (4.5 g., 0.026 mole) was heated to 108–112° for 43 hours. 1-*n*-Octylcyclohexanol (5.6 g., 0.026 mole, b.p. 87–91° at 1 mm., n^{20}D 1.4637) was obtained as described above. A residue (11.4 g.) remained. A mixture of cyclohexanol (125 g., 1.25 moles), octene-1 (6 g., 0.054 mole) and 2,2-bis-(*t*-butylperoxy)-butane (1.4 g., 0.006 mole) was heated at 100° for 42 hours. Distillation

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[17] G. B. Malone and E. E. Reid, *ibid.*, **51**, 3426 (1929).

[18] H. B. Williams and W. R. Edwards, *ibid.*, **69**, 336 (1947).

[19] M. S. Newman, W. S. Fones and W. T. Booth, *ibid.*, **67**, 1053 (1945).

gave unreacted octene-1 (3.5 g.), cyclohexanol, 1-*n*-octylcyclohexanol (1.8 g., b.p. 105–115° at 1 mm., $n^{25}D$ 1.4628) and a residue (3 g.).

Attempted Additions with Other Free Radical Initiators.—A number of possible free radical initiators gave negative results in test systems containing cyclohexanol (250 g., 2.50 moles) and octene-1 (11.2 g., 0.10 mole): (1) α-cumyl hydroperoxide (4.5 g.) at 150° for 48 hours; (2) hexachloroethane (2.4 g.) at 150° for 48 hours; and (3) a solution of benzoyl peroxide (2.4 g.) in chlorobenzene (20 ml.) added over 8 hours at 140° (12 hours at 140° after addition). In all cases the cyclohexanol and octene-1 were recovered quantitatively, and no residues were obtained.

A solution of benzoyl peroxide (2 g.) and octene-1 (26.5 g., 0.22 mole) in propanol-2 heated under reflux (80–81°) for 24 hours gave no addition product. Acetone (0.45 g.) was obtained. Propanol-2 and octene-1 in the same amount with 2,2′-azo-bis-isobutyronitrile (1.6 g.) at 80° for 20 hours gave no addition reaction. A small residue (0.5 g.) obtained after distillation contained tetramethylsuccinonitrile (m.p. 166–168° after recrystallization from ethanol, 80%).[20] A small amount of acetone (0.1 g.) was also found.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rate Data for the Bimolecular Elimination Reactions of the *t*-Amyl Halides. Further Evidence for the Concerted Nature of Bimolecular Eliminations

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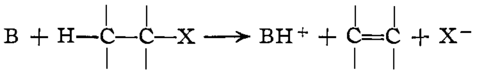
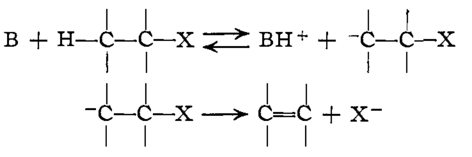
The first-order reactions of *t*-amyl bromide with methyl, ethyl, isopropyl and *t*-butyl alcohols have been investigated and compared with the second-order reactions with the corresponding potassium alkoxides in the same solvents. The reaction with potassium *t*-butoxide in *t*-butyl alcohol is considerably faster than the first-order reaction in that solvent. This reaction therefore furnishes a convenient procedure for investigating bimolecular eliminations involving tertiary halides. The rate constants ($k_2 \times 10^6$, l. mole^{-1} sec.$^{-1}$) vary markedly with the halogen: *t*-amyl chloride, 0.00583; bromide, 0.338; iodide, 2.34. These results can best be explained by the simultaneous loss of hydrogen and halogen and are therefore consistent with the concerted mechanism for bimolecular elimination in tertiary halides.

Considerable interest has been expressed in whether bimolecular eliminations involve one- (I) or two-stage (II) processes.[2]



$$B + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \longrightarrow BH^{+} + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + X^{-} \tag{I}$$

or



$$B + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \rightleftarrows BH^{+} + {}^{-}\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \tag{II}$$
$$ {}^{-}\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \longrightarrow \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + X^{-}$$

Skell and Hauser[3] and Shiner[4] utilized deuterium in a study of this question in the elimination reactions of β-phenylethyl and isopropyl bromides. They concluded that the elimination process is concerted. In the course of an extended study of bimolecular eliminations in benzene hexachloride and various *cis–trans* isomeric compounds, Cristol and his co-workers have concluded that a concerted mechanism is involved when the hydrogen and halogen undergoing elimination are *trans* and can assume a planar transition state.[5]

Barton and his co-workers have reached the same conclusions as a result of his investigations of conformational effects in steroid systems.[6] Finally, Doering and Meislich observed that in optically active trimethyl-β-phenylisopropylammonium ion racemization did not accompany elimination and concluded that a concerted process was also involved in bimolecular eliminations in these compounds.[7]

These studies have largely dealt with eliminations from primary and secondary alkyl groups: $C_6H_5CH_2CH_2Br$,[3] $CD_3CHBrCD_3$,[4] $C_6H_6Cl_6$[5] and $C_6H_5CH_2CH(N^{+}Me_3)CH_3$.[7] In the course of a study we have been making of the effect of steric strains in directing the course of elimination reactions, we had developed an improved procedure for following the rates of bimolecular elimination reactions of tertiary halides. It appeared that a kinetic study of the rates of elimination of selected tertiary halides might provide an answer to the question whether the one-stage process is also involved in bimolecular elimination of such compounds. Accordingly, a kinetic study was undertaken of bimolecular elimination in *t*-amyl chloride, bromide and iodide.

Results and Discussion

In the case of secondary alkyl halides, the rates of bimolecular elimination are usually followed by observing the reaction of the halide with ethoxide ion in absolute ethanol.[4,8] This procedure offers difficulties in the case of tertiary halides. With these compounds the solvolysis reaction is so fast that the bimolecular elimination reaction with the base becomes the predominant reaction only at very high concentrations of the base. With increasing steric requirement of the alkyl groups attached to the central atom, R_3CX, the rate of the solvolytic reaction increases[9] and that of the bimolec-

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[1] O. N. R. Post-doctorate Fellow at Purdue University, 1951–1953.

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