

A higher boiling fraction (b.p. 90–130° (0.3 mm.)) appears to be cyclopentanonylcyclopentanone.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: C, 72.26; H, 8.49; carbonyl, 83.1. Found: C, 72.79; H, 8.69; carbonyl, 89.0.

An unidentified intermediate fraction (b.p. 69–90° (0.5 mm.)) was obtained as a crystalline solid. The total yield of acid and diketone was 36%.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 430 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

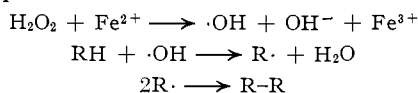
## Syntheses by Free-radical Reactions. II. Additive Dimerizations Effected by Hydroxyl Radicals

BY D. D. COFFMAN AND E. L. JENNER

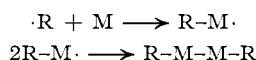
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A new one-step synthesis that yields long-chain, unsaturated dicarboxylic acids, diketones, glycols and other difunctional compounds has been found in the reaction of a 1,3-diene, a monofunctional compound, and hydroxyl radicals generated from hydrogen peroxide with ferrous sulfate. The products have the structure R-M-M-R in which R is a radical generated from the monofunctional compound by hydrogen abstraction and M is an unsaturated unit of composition corresponding to the 1,3-diene.

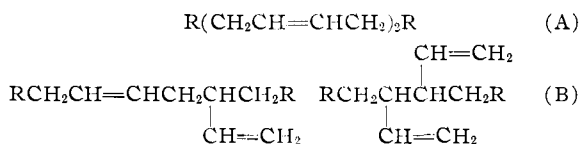
The action of hydroxyl radicals on saturated aliphatic compounds has been shown to bring about oxidative coupling.<sup>1</sup> This synthesis requires the removal of a hydrogen atom to form a carbon radical that dimerizes. The hydroxyl radicals were generated by reaction of ferrous sulfate with hydrogen peroxide.



**Additive Dimerization.**—It has now been found that the action of similarly generated hydroxyl radicals on saturated aliphatic compounds in the presence of a 1,3-diene yields novel long-chain products incorporating both components. In this new synthesis, the aliphatic free radical adds to the diene to produce a new free radical which dimerizes. The series of reactions may be represented as



This sequence, in which the unsaturated compound (M) is converted to a dimer containing residues (R) of the saturated compound as terminating groups, is called *additive dimerization*. The products of this reaction sequence, *i.e.*, the additive dimers, comprise straight-chain (A) and branched-chain (B) compounds formed by 1,4- and 1,2-incorporation of the diene.



It is likely that the preferential formation of dimers comes about through a gradation of radical reactivities. The hydroxyl radical is extremely reactive and relatively non-selective. It extracts a hydrogen atom from the saturated organic reactant which, except for water, is the most abundant species (1–10 M) in the system. The aliphatic radical so obtained adds rapidly to the diene (present at

concentrations of 0.01–0.1 M) to form a resonance-stabilized radical of greatly reduced reactivity. The new radical does not abstract a hydrogen atom and adds another butadiene molecule only reluctantly. The very high rate of radical generation employed (on the order of 2 moles of radicals per liter per hour) leads to a high concentration of substituted butenyl radicals. As a result, dimerization becomes almost the exclusive reaction of these radicals. The reaction system differs from polymerization systems in that here the steady state concentration of radicals is very much higher.

Related syntheses have been described by Kharasch<sup>2</sup> who utilized radicals generated from organic peroxides. Thus, the reductive cleavage of *t*-hydroperoxides in the presence of butadiene gave unsaturated diethers,<sup>2</sup> and reaction of cyclohexanone peroxide with ferrous sulfate in the presence of butadiene gave long-chain, unsaturated  $\alpha,\omega$ -dicarboxylic acids.<sup>3</sup> Similarly, the reduction in the presence of 1,3-dienes of cyclic *t*-hydroperoxides and of peroxides derived from keto acids has given long-chain diketones and dicarboxylic acids.<sup>4</sup>

The use of radicals generated by the action of hydroxyl radicals on saturated organic compounds affords a convenient route to additive dimers with a wide selection of terminal functionalities derived from commonly available organic compounds. The preparation of an organic hydroperoxide is not required. The additive dimerization is brought about safely and rapidly by simply adding equimolar quantities of hydrogen peroxide and ferrous sulfate to an aqueous system containing the aliphatic reactant and the 1,3-diene.

Butadiene has been used chiefly as the unsaturated component, but chloroprene, isoprene and cyclopentadiene react similarly, and even acrylonitrile and maleic acid will function as the unsaturated component. Saturated aliphatic reactants have included ketones, acids, alcohols, esters, acetaldehyde, propionitrile and cyclohexylamine. The scope of this synthesis with respect to the

(2) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).


(3) M. S. Kharasch and W. Nudenberg, *ibid.*, **19**, 1921 (1954).

(4) D. D. Coffman and H. N. Cripps, *THIS JOURNAL*, **80**, 2877, 2880 (1958).

(1) D. D. Coffman, E. L. Jenner and R. D. Lipscomb, *THIS JOURNAL*, **80**, 2864 (1958).

TABLE I  
 ADDITIVE DIMERIZATION OF BUTADIENE

These reactions were carried out at approximately 0° by the addition of butadiene, hydrogen peroxide, and ferrous sulfate to an aqueous solution of the saturated compound (see text for description of experiment employing *t*-butyl alcohol and butadiene).

Saturated compound	Yield (based on H <sub>2</sub> O <sub>2</sub> ), %	Structure of product <sup>a</sup> XC <sub>4</sub> H <sub>6</sub> C <sub>4</sub> H <sub>6</sub> Y	Formula	C	H	Mol. wt.	Other
Cyclopentanone	70		Calcd. Found	78.79 76.67	9.55 9.76	274 302	137 145 Carbonyl equiv. Carbonyl equiv.
<i>t</i> -Butyl alcohol	64	HOCH <sub>2</sub> CH <sub>2</sub> <sup>b</sup>   (CH <sub>3</sub> ) <sub>2</sub>	Calcd. Found	75.53 74.98 <sup>c</sup>	11.89 11.84 <sup>c</sup>	254 250	200 205 Iodine number Iodine number
<i>n</i> -Butyl alcohol	47	HOC <sub>4</sub> H <sub>9</sub> -	Calcd. Found	75.53 73.14	11.89 12.09	254 278	
Isopropyl alcohol	13	HOC <sub>3</sub> H <sub>7</sub> -	Calcd. Found	74.28 72.21	11.58 11.27	226 220	113 127 Unsatn. equiv. (hydrogenation) Unsatn. equiv. (hydrogenation)
Ethyl alcohol	12	HOC <sub>2</sub> H <sub>5</sub> - <sup>b</sup>					
Acetic acid	..	HO- and-CH <sub>2</sub> COOH <sup>b</sup>					
Propionic acid	77	HOCC <sub>2</sub> H <sub>4</sub> -	Calcd. Found	66.11 65.10	8.72 8.53		127 127 160 139 93 186 106 198 Neut. equiv. Unsatn. equiv. (hydrogenation) Neut. equiv. Unsatn. equiv. (hydrogenation) Neut. equiv. Unsatn. equiv. (hydrogenation)
Glutaric acid	30	(HOOC) <sub>2</sub> C <sub>3</sub> H <sub>6</sub> -	Calcd. Found	58.36 58.51	7.08 7.39		93 186 106 198 Unsatn. equiv. (hydrogenation) Unsatn. equiv. (hydrogenation) Neut. equiv. Unsatn. equiv. (hydrogenation)
Methyl acetate	27	CH <sub>3</sub> OCOCH <sub>2</sub> - and CH <sub>3</sub> COOCH <sub>2</sub> -	Calcd. Found	66.11 65.80	8.72 8.81	254 296	127 152 Sapn. equiv. Sapn. equiv.
Methyl formate	27	CH <sub>3</sub> OCO- and -CH <sub>2</sub> OCHO <sup>b</sup>	Calcd. Found	63.70 64.85	8.02 8.63	226 265	113 147 Sapn. equiv. Sapn. equiv.
Acetaldehyde	7	-CH <sub>2</sub> CHO and C <sub>2</sub> H <sub>5</sub> CO- <sup>b</sup>	Calcd. Found	74.19 72.89	9.34 9.84	194 208	
Acetone	51 g. (per mole H <sub>2</sub> O <sub>2</sub> )	CH <sub>3</sub> -, CH <sub>3</sub> COCH <sub>2</sub> -and HO- <sup>b</sup>					

<sup>a</sup> All products are of the form XC<sub>4</sub>H<sub>6</sub>C<sub>4</sub>H<sub>6</sub>Y, where C<sub>4</sub>H<sub>6</sub> is a butadiene residue, corresponding to either 1,4- or 1,2-addition; X and Y are as indicated below. Where only one group is given, X and Y are the same; where more than one group is shown, the product contains all possible combinations of the groups. <sup>b</sup> See text for further characterization. <sup>c</sup> Determined on distilled product.

saturated reactant is similar to that of the couplings effected by hydroxyl radicals,<sup>1</sup> with the additional qualification that the saturated reactant should possess a solubility in water sufficient to increase appreciably the solubility of the 1,3-diene in the aqueous reaction mixture. Accordingly, most of the reactants were monofunctional compounds that contained from 2-5 carbon atoms and had water solubilities of at least 10% (many were miscible with water).

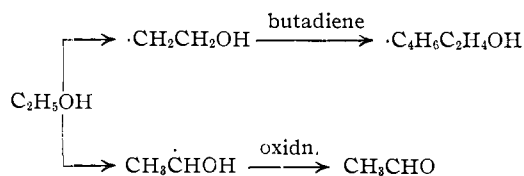
**Illustrative Syntheses.**—The effectiveness of this new synthesis is revealed by the formation of additive dimers in upwards of 60% yield based on hydrogen peroxide, in reactions involving butadiene with *t*- and *n*-butyl alcohol, propionic acid and cyclopentanone (Table I) and from *t*-butyl alcohol with chloroprene and with acrylonitrile. The additive dimers so formed comprised a mixture of 1,4- and 1,2-adducts in which the former predominated. There was little evidence for the formation of compounds containing but a single butadiene unit. Products containing more than two butadiene units have been estimated at less than 10% of the total product. Thus, the synthesis highly favors the production of dimers. Among the side-products of the synthesis are hydroxy compounds which can arise by the direct addition

of hydroxyl radical to an unsaturated carbon atom. Since these side-products are usually present as contaminants in the additive dimers, the presence of hydroxy compounds explains the low carbon content generally encountered in the analysis of the additive dimers (*cf.* Table I).

In the additive dimerization of butadiene with *t*-butyl alcohol, the chemistry was not complicated by the formation of isomeric radicals from hydroxyl radical attack at various sites on the alcohol since all of the hydrogen atoms are equivalent. The major product was the glycol formed by 1,4-addition of the two butadiene units. It was an unsaturated, waxy-crystalline solid which upon hydrogenation gave the corresponding crystalline saturated glycol, 2,13-dimethyl-2,13-tetradecane-diol (m.p. 50-52°). Similarly, with *n*-butyl alcohol, butadiene gave unsaturated C<sub>16</sub>-glycols, but in this case a mixture of isomers was obtained. Reactions of butadiene with isopropyl alcohol and with ethyl alcohol gave the dimers in low yields. In these instances, considerable attack by hydroxyl radical occurred on the α-hydrogens, and the free radicals so formed oxidized rapidly to the corresponding carbonyl compounds<sup>5</sup> and hence did not react appreciably with butadiene.

(5) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S-15 (1949).

The use of such lower aliphatic monocarboxylic acids as propionic and the butyric acids affords a route to unsaturated dicarboxylic acids in the 14-16 carbon range. The product from propionic acid and butadiene was principally the unsaturated C<sub>14</sub>-dicarboxylic acids. It was a mixture of isomers due to  $\alpha$ - and  $\beta$ -attack on the propionic acid<sup>1</sup> and the 1,2- and 1,4-addition of butadiene. The use

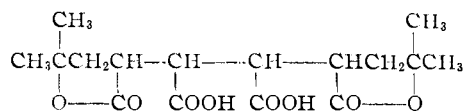


of glutaric acid in additive dimerization gave a C<sub>18</sub>-tetracarboxylic acid. The product from acetic acid and butadiene was chiefly a hydroxy monocarboxylic acid. In other studies,<sup>1,5</sup> acetic acid was found to be comparatively unreactive toward hydroxyl radicals. This accounts for the reluctance of acetic acid to participate in additive dimerization and the resulting direct addition of hydroxyl radical to butadiene.

Additive dimers have been prepared from butadiene with methyl acetate and with methyl formate. In each case attack by hydroxyl radical occurred on both the alcohol and acid portions of the ester. Hydrolysis of the ester obtained from methyl acetate showed that about 80% of the attack was on the alcohol moiety and 20% on the acyl portion of methyl acetate. With methyl formate about 25% of the attack was on the alcohol moiety and 75% was on the hydrogen atom of the formyl group. If the hydrogen atom of the methoxy group is taken as a standard, then the formyl group appears to be about 12 times as susceptible to hydroxyl radical attack as is the acetyl group. This correlates well with the ease of oxidation of formic acid and its derivatives.

Additive dimerization involving butadiene, acetaldehyde and hydroxyl radicals, gave a mixture of carbonyl-containing products having terminal groups derived from acetaldehyde. Attack by hydroxyl radical on the carbonyl hydrogen of the aldehyde would give an acetyl radical leading to a methyl ketone, whereas attack on the methyl group would give an aldehyde precursor. The additive dimers obtained were oxidized by Tollens reagent and also gave a positive iodoform test. This behavior and also the infrared spectrum indicated the presence of both aldehyde and acetyl groups and supported the view that the hydroxyl radical attacked both the methyl hydrogen and the carbonyl hydrogen of acetaldehyde.

The additive dimer from maleic acid and *t*-butyl alcohol would be expected to be dihydroxytetracarboxylic acid. Instead, a lactonic acid was isolated directly from the reaction mixture. Its mode of formation, elemental analysis, neutral and saponification equivalents, and infrared spectrum support the structure



This structure was confirmed by the preparation and characterization of the dimethyl ester of the lactonic acid.

**Competitive Reactions.**—The products from hydroxyl radicals, acetone and butadiene merit detailed description. Their structures indicate the complicated and varied free-radical chemistry that can occur under synthesis conditions—given the proper combination of reactants.

Surprisingly, a major product was 3,7-decadiene. This was formed by the attack of a methyl radical on butadiene followed by dimerization of the resulting pentenyl radical. Lesser amounts of isomeric branched-chain C<sub>10</sub>-dienes were formed also. Other products included a C<sub>9</sub>-alcohol, a C<sub>12</sub>-ketone and a higher-boiling hydroxy-ketone and diketone.

Detailed characterization of the C<sub>10</sub>-hydrocarbons showed that the principal mode by which butadiene was incorporated resulted in dimers containing 1,4-units. Thus, distillation of the product (Table II) indicated less branched product (fractions 2 and 3, 9.9 g., branched C<sub>10</sub>-dienes) than straight-chain isomer (fractions 4 and 5, 12.7 g., decadiene). Furthermore, the majority of the branched-chain product contained one 1,4-unit and one 1,2-unit. Thus, about 75% of the butadiene was incorporated as 1,4-units. The infrared spectra of additive dimers from other saturated components indicated that the major product contained 2-butenylene units.

The array of products from acetone, butadiene and hydroxyl radicals was rationalized by assuming that the hydroxyl radical attacked acetone either by hydrogen extraction to give acetyl radicals or by cleavage to form acetic acid and methyl radicals.<sup>1</sup> (It is possible that the latter fragments could have arisen from the ketone peroxide 2-hydroxy-2-hydroperoxypropane by reductive cleavage to the intermediate 2-hydroxy-2-propoxy radical.) The addition of the various free radicals in the system to butadiene would form butenyl radicals bearing on one end a methyl, acetyl or hydroxyl group. The dimerization or cross-combination of these radicals would result in the products isolated.

### Experimental

**The Additive Dimerization of Butadiene with *t*-Butyl Alcohol.**<sup>6</sup>—The reaction vessel was charged with 1500 ml. of water, 750 ml. of *t*-butyl alcohol and 27 ml. of sulfuric acid. The three reactants, butadiene (158 ml., 2 moles), hydrogen peroxide (34 g., 1 mole) in 118 g. of water and ferrous sulfate heptahydrate (278 g., 1 mole) dissolved in 575 ml. of water and 55 ml. of sulfuric acid, were added over a 12-minute period while the mixture was maintained at 5°. Three specially calibrated burets were used to add the liquids simultaneously and equivalently. The two layers which resulted were separated, the aqueous layer was extracted three times with ether, and the combined organic layer and ether extract was washed with aqueous bicarbonate solution. The ether and *t*-butyl alcohol were distilled, and the residue was heated to 70° under a pressure of 1 mm. whereupon 81 g. (64% yield) of the unsaturated C<sub>16</sub>-glycol was obtained (see Table I for analysis). The infrared spectrum of this material showed the presence of hydroxyl groups and of carbon-carbon unsaturation. The latter was partly internal and partly terminal.

A sample of the crude unsaturated glycol was fractionally distilled to separate low-boiling branched-chain and high-boiling straight-chain glycols. The principal fraction, b.p.

(6) E. L. Jenner, U. S. Patent 2,757,210, July 31, 1956.

TABLE II  
 DISTILLATION OF ADDITIVE DIMERS FROM BUTADIENE AND ACETONE

Fraction	Weight, g.	B.p. °C.	Mm.	$n_D^{20}$	C	H	Characterization
1	7.5	33-44	26	1.3921	...	...	Neut. equiv. 92; mixt. of acid and hydrocarbons; acid identified as acetic by Duclaux numbers
2	3.8	47-61	26	1.4291	84.7	12.7	Chiefly hydrocarbon
3	6.1	63-67	26	1.4321	86.4	13.2	Infrared spect. indicates both terminal and internal unsatn.; probably is 3-ethyl-1,5-octadiene
4	8.5	44-46	4.5	1.4351	86.4	13.1	Hydrogenation equiv., 74; calcd. for decadiene, 69; infrared spect. indicates all unsatn. is internal; identified as 3,7-decadiene <sup>a</sup>
5	4.2	46	4.5	1.4365	...	...	Gave same tetrabromide obtained from fract. 4
6	3.6	78-89	4.5	1.4551	78.3	11.7	Hydroxyl equiv., 231; hydrogenation equiv., 72; hydrogenated material had odor similar to <i>n</i> -octyl alcohol; gave a 3,5-dinitrobenzoate which did not crystallize
7	4.4	88-89	4.5	1.4589	78.44	11.37	Hydrogenation equiv., 82; carbonyl equiv., 495; hydroxyl equiv., 263; fract. is mixt of ketone and alcohol
8	3.3	74-79	1.5	1.4571	79.00	11.33	
9	4.3	80-82	1.5	1.4549	80.8	11.5	Hydrogenation equiv., 88; carbonyl equiv., 214
10	4.7	87-89	1.5	1.4561	...	...	Hydrogenation equiv., 95; carbonyl equiv., 204; prepared dinitrophenylhydrazone <sup>b</sup> of the hydrogenated ketone
11	3.3	88-101	0.3	1.4630	78.16	11.06	
12	2.9	100-111	0.3	1.4742	75.43	10.26	Hydrogenation equiv., 97; carbonyl equiv., 179; hydroxyl equiv., 353; mixt. of glycol, diketone and hydroxy ketone
13	1.0	110-120	0.3	1.4735	...	...	
Residue	3.0						
Total	60.8						

<sup>a</sup> A 1.8-g. sample was treated with bromine in carbon tetrachloride (required, 0.95 ml. bromine; calcd., 1.00 ml. bromine). Evaporation of solvent gave crystalline tetrabromide. Recrystallization from hexane gave 3,4,7,8-tetrabromodecane, m.p. 68-69°. C. Prevost and G. Richard, *Bull. soc. chim.*, **49**, 1368 (1931), reported a melting of 70-71°. *Anal.* Calcd. for  $C_{10}H_{18}Br_4$ : C, 26.23; H, 3.96; Br, 69.81. Found: C, 26.39; H, 4.26; Br, 68.91. <sup>b</sup> Dinitrophenylhydrazone had m.p. 78-79°. *Anal.* Calcd. for  $C_{18}H_{28}N_2O_4$ : C, 59.3; H, 7.74; N, 15.4. Found: C, 58.7; H, 7.63; N, 15.5.

80° (0.08 mm.) ( $n_D^{20}$  1.4773), was the straight-chain glycol 2,13-dimethyl-5,9-tetradecadiene-2,13-diol. The infrared spectrum of this material showed hydroxyl groups and internal carbon-carbon unsaturation. The fraction partially crystallized upon standing.

The crude glycol mixture was hydrogenated in dioxane solution at 30° over a palladium-on-charcoal catalyst. The resulting saturated glycol was distilled from a spinning cone molecular still. The majority of the distillate possessed  $n_D^{20}$  1.4570-1.4595. The higher-boiling fractions (b.p. 70° (0.02 mm.)) crystallized on standing. The solid glycol thus obtained was recrystallized from ether to yield 2,13-dimethyl-2,13-tetradecanediol, m.p. 50-52°.

*Anal.* Calcd. for  $C_{18}H_{34}O_2$ : C, 74.35; H, 13.26. Found: C, 74.01; H, 13.19.

In another similar experiment, one mole each of freshly distilled chloroprene (2-chloro-1,3-butadiene), hydrogen peroxide, ferrous sulfate and sulfuric acid were added to a solution of 27 ml. of sulfuric acid and 750 ml. of *t*-butyl alcohol in 1500 ml. of water maintained at 25°. The product was isolated by ether extraction, and 0.1 g. of phenothiazine was added to the extract to prevent polymerization of residual chloroprene. Distillation of the ether and chloroprene to a temperature of 80° at a pressure of 1 mm. gave the additive dimer, an unsaturated dichloro glycol, in 76% yield.

*Anal.* Calcd. for  $C_{18}H_{28}O_2Cl_2$ : C, 59.44; H, 8.73; Cl, 21.93; mol. wt., 323. Found: C, 59.95; H, 8.64; Cl, 20.59; mol. wt., 350.

Under similar conditions using *t*-butyl alcohol as the reactive solvent, additive dimers were obtained from isoprene, cyclopentadiene and acrylonitrile in yields of 46, 20 and 54%, respectively.

**The Additive Dimerization of Butadiene with Ethyl Alcohol.**—Two additive dimerizations were conducted by procedures similar to that described for *t*-butyl alcohol. In the preliminary experiment, two moles of butadiene and one mole each of hydrogen peroxide and of ferrous sulfate were added to a solution of 27 ml. of sulfuric acid and 500 ml. of water in 2000 ml. of ethyl alcohol. A large portion of the ferrous sulfate remained at the end of the reaction. In the other

experiment, only 0.5 mole of ferrous sulfate was used with 1.0 mole of hydrogen peroxide. Even in this case, however, an excess of ferrous ion remained. At the end of the addition period, a clear solution was obtained, and no water-insoluble phase separated. The addition of ether for extraction of the product brought about the precipitation of ferrous sulfate from the reaction mixture. The unsaturated glycol obtained weighed 13.2 g., 12% yield. It was hydrogenated over a palladium-on-charcoal catalyst. The resulting saturated glycol was distilled through a spinning-band column. The high-boiling fraction, b.p. 136° (0.8 mm.), believed to be principally the straight-chain isomer dodecamethylene glycol, partially crystallized upon standing.

*Anal.* Calcd. for  $C_{12}H_{26}O_2$ : C, 71.23; H, 12.95. Found: C, 70.49; H, 12.82.

**The Additive Dimerization of Butadiene with Cyclopentanone.**—This additive dimerization was carried out by a procedure similar to that described for the reaction of butadiene with *t*-butyl alcohol. Two moles of butadiene and one mole each of hydrogen peroxide, ferrous sulfate and sulfuric acid were added to a solution of 27 ml. of sulfuric acid and 250 ml. of cyclopentanone in 2200 ml. of water. At the end of the reaction the additive dimer was extracted by ether. The ethereal solution of the product was washed with an aqueous bicarbonate solution to remove carboxylic by-products. The unsaturated diketone was obtained as a very pale viscous liquid (see Table I for analysis). The infrared spectrum showed that the unsaturation was part internal and part terminal.

The unsaturated diketone was hydrogenated at room temperature and 2000 lb./sq. in. over a palladium catalyst. The saturated ketone (b.p. 138-142° (0.25 mm.)) was obtained as a pale yellow viscous liquid.

*Anal.* Calcd. for  $C_{18}H_{30}O_2$ : C, 77.64; H, 10.86; mol. wt., 278; carbonyl equiv., 139. Found: C, 76.51; H, 11.15; mol. wt., 281; carbonyl equiv., 146.

**The Additive Dimerization of Butadiene with Acetic Acid.**—A procedure similar to that described for *t*-butyl alcohol

was used. The product, extracted with ether, was obtained as a viscous amber distillation residue. It was soluble in aqueous alkali. A portion of the product was dissolved in aqueous alkali and was hydrogenated at 60° over a palladium-on-charcoal catalyst at 2000 lb./sq. in. The saturated acid was isolated by treating the solution with excess sulfuric acid, and the crude product was esterified in refluxing ethyl alcohol in the presence of a trace of sulfuric acid. The acid catalyst was neutralized with potassium acetate, and the excess alcohol was distilled. The crude ester was dissolved in toluene to separate it from inorganic salts. After removing the toluene, the ester was distilled, b.p. 150–180° (0.3 mm.). The analysis of the distillate corresponded approximately to that of the ethyl ester of a 10-carbon saturated hydroxy acid.

*Anal.* Calcd. for  $C_{12}H_{24}O_3$ : C, 66.63; H, 11.18; sapon. equiv., 216; hydroxyl equiv., 216. Found: C, 67.09; H, 10.43; sapon. equiv., 220; hydroxyl equiv., 235.

**The Additive Dimerization of Butadiene with Glutaric Acid.**—The additive dimerization was conducted at 25° in a solution prepared from 880 g. of glutaric acid, 27 ml. of sulfuric acid and 1500 ml. of water. To this were added simultaneously 2 moles of butadiene and solutions containing one mole of hydrogen peroxide and one mole of ferrous sulfate and of sulfuric acid, respectively. The reaction mixture was extracted twice with ether. The ether extract was concentrated to about 400 ml., and the solution was subjected to countercurrent liquid-liquid partition between ether and water according to the procedure described by Marvel and Richards.<sup>8</sup> Approximately 600 ml. each of ether and water were employed for each extraction, and a 4 × 4 diamond array was used. Figure 1 indicates the de-

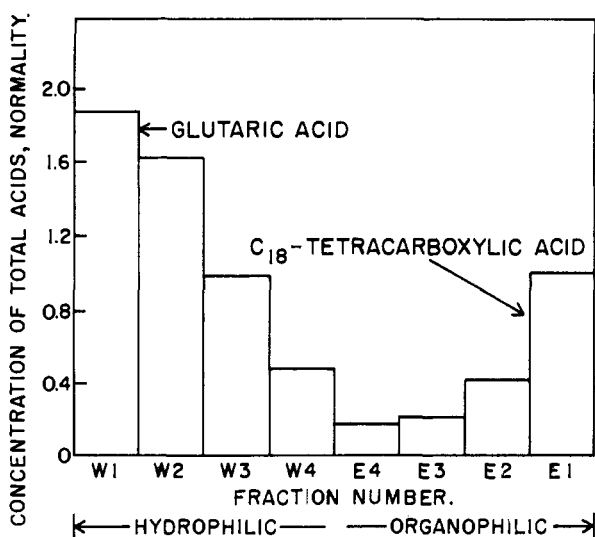


Fig. 1.—Countercurrent partition between water and ether of additive dimer from butadiene and glutaric acid.

gree of separation achieved and the titer of total acid present in each fraction. From these data the ether-water partition coefficients of glutaric acid and of the additive dimer were calculated to be approximately 0.28 and 9.0, respectively. These partition coefficients would predict that fraction E-1 would contain less than 2% glutaric acid and fraction E-2 would contain approximately 10% glutaric acid. The yield of additive dimer based on these assumptions was 30%. Removal of the solvent from fraction E-1 (pot temperature of 70° under a pressure of 1 mm.) left a residue (34.2 g.) of a very viscous pale liquid. The additive dimer thus obtained was a  $C_{18}$ -tetracarboxylic acid containing two double bonds (see Table I for analysis). Removal of the solvent from fraction E-2 furnished an additional 24 g. of additive dimer.

**The Additive Dimerization of Butadiene with Methyl Acetate.**—The reaction vessel was charged with 750 ml. of methyl acetate, 27 ml. of sulfuric acid and 1800 ml. of water. The additive dimerization was carried out as described for

*t*-butyl alcohol. Because of the limited water solubility of methyl acetate, two phases were present throughout the reaction. The organic layer was separated, and the aqueous phase was extracted with ether. The ether extracts were combined with the organic layer. The crude ester solution was washed with sodium carbonate, and the methyl acetate and ether were distilled. The distillation flask was heated to 105° (2 mm.) whereupon 34.2 g. of additive dimer was obtained (see Table I for analysis).

The ester was hydrolyzed, and the acidic and neutral fractions were examined to indicate the position of hydroxyl radical attack upon methyl acetate. A 15.2-g. sample of ester was heated on a steam-bath with 80 ml. of ethylene glycol and 10 ml. of 20 *M* NaOH. The water, methanol and ethylene glycol were removed by heating the flask to 105° (5 mm.). Water was added to the residue, and the resulting solution was extracted with ether. After distillation of ether, 2.4 g. of  $C_{10}$ -glycol, b.p. 115–130° (1 mm.), was obtained.

The aqueous fraction was acidified by the addition of sulfuric acid and was extracted 10 times with ether. The ether extracts required 75 ml. of 1 *M* NaOH for neutralization. The aqueous solution of the sodium salt was acidified with excess sulfuric acid, and the volatile acid was distilled. The Duclaux numbers demonstrated that the volatile acid was acetic acid; found 6.5, 6.8, 7.0; Shriner and Fuson<sup>9</sup> give 6.8, 7.1 and 7.4 for acetic acid. The volatile acid totaled 42 milliequivalents and the non-volatile acid 12 milliequivalents. This indicates that the attack of hydroxyl radicals on methyl acetate was approximately four times as extensive on the alcohol portion as on the acyl portion.

**The Additive Dimerization of Butadiene with Methyl Formate.**—The additive dimerization was carried out like that described for *t*-butyl alcohol. The dimer was obtained in 27% yield by extraction followed by distillation of the solvent. Saponification of the additive dimer and separation of the resulting acids into volatile and non-volatile fractions showed that about 25% of the acid was volatile and 75% was non-volatile (*i.e.*, high boiling). This indicated that hydroxyl radical attack on methyl formate occurred on the formate and methyl portions, respectively, in a ratio of approximately 3:1.

**The Additive Dimerization of Butadiene with Acetaldehyde.**—The procedure for *t*-butyl alcohol was followed, and the additive dimer was isolated in 7% yield. The low yield was anticipated in view of the known susceptibility of acetaldehyde to oxidation. The additive dimer which was obtained as a distillation residue was the expected dicarbonyl compound (see Table I for analysis).

The additive dimer gave both a positive iodoform test and a positive reaction with Tollens reagent. This indicated the presence of both formyl and acetyl groups. The infrared spectrum confirmed the presence of both types of carbonyl groups. Thus, hydroxyl radical attack on acetaldehyde occurred on both the methyl and formyl hydrogen atoms.

**The Additive Dimerization of Maleic Acid with *t*-Butyl Alcohol.**—This additive dimerization followed the standard procedure, employing one mole each of maleic acid, hydrogen peroxide and ferrous sulfate in a large excess of *t*-butyl alcohol. The product was isolated by extracting the reaction mixture with nine 1-liter portions of methyl ethyl ketone. Upon concentration of the combined extracts, 53 g. of a light tan solid precipitated. Recrystallization from water gave a white solid, m.p. 180–220° dec., which is the bislactone of the dihydroxytetracarboxylic acid formed by additive dimerization.

*Anal.* Calcd. for  $C_{18}H_{22}O_8$ : C, 56.13; H, 6.48; neut. equiv., 171; sapon. equiv., 86. Found: C, 54.37; H, 6.43; neut. equiv., 171; sapon. equiv., 85.

The infrared spectrum of the bislactonic acid showed the presence of carboxyl and of  $\delta$ -membered lactone carbonyl.

In a second similar experiment, the product was isolated directly by concentration of the reaction mixture under reduced pressure to obtain the additive dimer in 24% yield. The lactonic acid was converted to the dimethyl ester by reaction with diazomethane. The dimethyl ester of the dilactone melted at 173–175°.

(9) R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 147.

(8) C. S. Marvel and J. C. Richards, *Anal. Chem.*, **21**, 1480 (1949).

*Anal.* Calcd. for  $C_{18}H_{26}O_8$ : C, 58.4; H, 7.1; mol. wt., 370. Found: C, 58.16; H, 7.23; mol. wt., 365.

**Additive Dimerization of Butadiene with Acetone.**—To 600 ml. of acetone and 150 ml. of water in a 3-necked flask equipped with a thermometer and an efficient stirrer were added 125 ml. (1.2 moles) of 30% hydrogen peroxide, 189 ml. (2.4 moles) of butadiene and 1200 ml. of a solution one molar in ferrous sulfate and one molar in sulfuric acid. Three calibrated burets were used to add the solutions simultaneously and equivalently during 20 minutes. The temperature of the mixture was maintained at  $-5^\circ$  by means of a solid carbon dioxide-acetone bath. At the end of the addition, two layers were present. These were separated, and the aqueous layer was extracted four times with ether. The organic layer was added to the ether extracts, and excess acid was neutralized with sodium bicarbonate. The solution was dried over magnesium sulfate, and the ether and excess acetone were distilled. The product was then fractionally distilled through a 24-inch Vigreux column (Table II).

TABLE III

Solvent (composition in wt. %)	Solubility of butadiene at $25^\circ$ and 1 atm. (vol. of gas/vol. of solvent)
Water	0.3
33% Acetic acid	0.87
33% Propionic acid	1.4
33% <i>t</i> -Butyl alcohol	3.5

**Solubility of Butadiene in Aqueous Systems.**—The solubilities of butadiene in water and in aqueous solutions of *t*-butyl alcohol, acetic acid and propionic acid have been determined at  $25^\circ$  and atmospheric pressure by measuring the quantity of gaseous butadiene required to saturate a measured volume of solvent. The butadiene was added from a gas buret. It is seen (Table III) that the organic cosolvents, particularly *t*-butyl alcohol, are very effective in increasing the solubility of butadiene in aqueous systems.

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### Syntheses by Free-radical Reactions. III. Unsaturated Long-chain Diketones from Cyclic *t*-Hydroperoxides and 1,3-Dienes by Additive Dimerization

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Unsaturated long-chain bis-(methyl ketones) have been synthesized in high yields by reduction of *t*-cycloalkyl hydroperoxides with ferrous salts in the presence of 1,3-dienes. The products can be represented as R-M-M-R in which R- is a ketoalkyl group derived from the hydroperoxide and -M- is a butenylene unit of composition corresponding to that of the 1,3-diene.

A preceding paper<sup>1</sup> has described a convenient synthesis by which a variety of long-chain, unsaturated, terminal difunctional compounds can be prepared in one step. This synthesis, called additive dimerization, is based on the reaction of a free radical (R·) with a 1,3-diene (M) to form the product R-M-M-R. The principles involved in additive dimerization have now been extended to the synthesis of new long-chain unsaturated bis-(methyl ketones).

It has been found that reductive cleavage of *t*-cycloalkyl hydroperoxides in the presence of a 1,3-diene results in the formation of unsaturated long-chain diketones in high yields. The transformations involved are represented in Table I. The individual reactions that comprise the sequence in the synthesis have been reported previously. Thus, Hawkins and Young<sup>2</sup> found that ferrous salt reduction of cyclic 1-alkyl 1-hydroperoxides gave diketones *via* dimerization of an intermediate ketoalkyl radical A derived from the hydroperoxide. Kharasch<sup>3</sup> has shown that alkoxy radicals add to conjugated systems to yield bis-(alkoxy) products structurally similar to D and E. Also, the reductive cleavage of cycloalkyl hydroxy hydroperoxides in the presence of butadiene has been found to yield long-chain  $\alpha,\omega$ -dicarboxylic acids.<sup>4</sup>

In the studies here reported, ferrous sulfate reduction of 1-methylcyclopentyl hydroperoxide in aqueous methanol containing butadiene gave a 90%

yield of isomeric unsaturated  $C_{20}$ -diketones. One of the isomeric ketones separated as a crystalline product melting at  $64-65^\circ$ . By hydrogenation, the crystalline isomer was converted to the known 2,19-eicosanedione, m.p.  $92-92.5^\circ$ . This established the presence of an unbranched chain and indicated that the unsaturated diketone, m.p.  $64-65^\circ$ , was D and not E or F. Fractional distillation of the liquid products suggested that at least two isomeric unsaturated diketones were present as major components.

The reaction of isoprene with 5-ketohexyl radicals from 1-methylcyclopentyl hydroperoxide gave isomeric unsaturated  $C_{22}$ -diketones which corresponded approximately to additive dimers in composition.

The reductive cleavage of 1-methylcyclohexyl hydroperoxide in the presence of butadiene gave an 80% yield of isomeric unsaturated  $C_{22}$ -diketones from which a crystalline isomer, m.p.  $71.5-72^\circ$ , was isolated in amount corresponding to 23% of the ketonic products. Hydrogenation converted the crystalline, unsaturated diketone to the known 2,21-docosanedione, thereby establishing the straight-chain structure of the crystalline, unsaturated diketone. Fractional distillation of the remaining ketones indicated the presence of two liquid isomers, each in amount corresponding to 20-22% of the product.

Pinane hydroperoxide underwent reductive cleavage and additive dimerization with butadiene to form unsaturated diketones which have not been fully characterized but which corresponded in composition to a chain comprised of two butenylene

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