Anal. Calcd. for $C_{18}H_{28}O_8$: 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° 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

IABLE III			
	Solvent (composition in wt. %)	Solubility of butadiene at 25° 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 tbutyl alcohol, acetic acid and propionic acid have been determined at 25° 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. WILMINGTON, DELAWARE

[Contribution No. 431 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

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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Received November 25, 1957

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 paper¹ 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 (\mathbb{R}) with a 1,3-diene (\mathbb{M}) to form the product \mathbb{R} - \mathbb{M} - \mathbb{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 tcycloalkyl hydroperoxides in the presence of a 1,3diene results in the formation of unsaturated longchain 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 Young² 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. Kharasch³ 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 α, ω -dicarboxylic acids.⁴

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

(1) D. D. Coffman and E. L. Jenner, THIS JOURNAL, 80, 2872 (1958).

(2) E. G. E. Hawkins and D. P. Young, J. Chem. Soc., 2805 (1950).
(3) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, J. Org.

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

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

yield of isomeric unsaturated C_{20} -diketones. One of the isomeric ketones separated as a crystalline product melting at 64–65°. By hydrogenation, the crystalline isomer was converted to the known 2,19-eicosanedione, m.p. 92–92.5°. This established the presence of an unbranched chain and indicated that the unsaturated diketone, m.p. 64–65°, 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 C₂₂-diketones from which a crystalline isomer, m.p. 71.5–72°, 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

TABLE I

(1)
$$(CH_{2})_{n+1} \xrightarrow{CH_3} CH_3 = CH_3CO(CH_2)_nCH_2 + Fe^{3+} + OH^-$$

(2) $A + CH_2 = CHCH = CH_2 \longrightarrow CH_3CO(CH_2)_nCH_2CH_2CH = CHCH_2 \cdot$
 $B \longrightarrow CH_3CO(CH_2)_nCH_2CH_2CH \cdot$
 $C \qquad CH = CH_2$
(3) $2B \longrightarrow CH_3CO(CH_2)_nCH_2(CH_2CH = CHCH_2)_2CH_2(CH_2)_nCOCH_3$
 D
(4) $B + C \longrightarrow CH_3CO(CH_2)_nCH_2CH_2CH = CHCH_2CHCH_2CH_2(CH_2)_nCOCH_3$
 $E \qquad CH = CH_2$

CH=CH₂

(5) $2C \longrightarrow CH_2CO(CH_2)_nCH_2CH_2CHCHCH_2CH_2(CH_2)_nCOCH_2$

F

CH=CH,

units terminated by 2-(2',2'-dimethyl-3'-acetylcyclobutyl)-ethyl groups. Oxidative cleavage of pinane has been reported⁵ to yield 1-acetyl-2,2dimethyl-3-ethylcyclobutane.

Experimental

I. Preparation of C_{20} -Diketones.⁶ A. 1-Methylcyclo-pentyl Hydroperoxide.—*CAUTION*. Reactions of 90% hydrogen peroxide should be carried out in preliminary trials on a small scale, and all experiments should be per-formed behind a heavy barricade. The apparatus consisted of a cylindrical jacketed flask (500 ml.) equipped with a stopcock drain and cooled by circulating chilled acetone. Additions to the reactor were made from dropping funnels tants were stirred with a stream of nitrogen. Into the reactor were introduced 100 ml. of 90% hydrogen peroxide⁷ and 30 drops of concentrated sulfuric acid. After cooling the reactor to -5 to 0°, 30 g. of molten 1-methylcyclopentanol⁸ was added dropwise to the stirred mixture. After stirring for one hour, the mixture was allowed to warm slowly to 15° over a period of 1.5 hours, and 50 ml. of purified lowboiling petroleum ether was added. The stirring was stopped. The lower hydrogen peroxide layer was with-drawn and diluted with 1 l. of distilled water. The petroleum ether solution of hydroperoxide was washed with water and dried with anhydrous magnesium sulfate. The petroleum ether was removed under reduced pressure, leaving almost colorless 1-methylcyclopentyl hydroperoxide (21.7 g.), n²⁵D 1.4530.²

Anal. Calcd. for C7H14O2: active O, 13.8. Found: active O, 13.3.

Addition of 5-Ketohexyl Radicals to 1,3-Butadiene. Β. A mixture of 25 ml. of nitrogen-saturated methanol and 60 ml. of liquid 1,3-butadiene was cooled to approximately -15° and rapidly stirred in a nitrogen atmosphere while a solution of 152 g. (0.545 mole) of ferrous sulfate heptahydrate in distilled water (total volume, 300 ml.) and 63.0 g. (0.543 mole) of 1-methylcyclopentyl hydroperoxide were (0.343 mole) of 1-methyleyclopentyl hydroperoxide were added simultaneously at equivalent rates over a period of about 10 minutes. Two additional portions (30 ml. each) of 1,3-butadiene were added after about $\frac{1}{3}$ and $\frac{2}{3}$ of the reac-tants had been added. The reaction was exothermic and required cooling with a solid carbon dioxide-acetone-bath to maintain the temperature below 0°. After stirring for 10 minutes, the reaction mixture was diluted with 100 ml. of water, and unreacted 1,3-butadiene was allowed to escape. The reaction mixture was extracted with one 300-ml. and two 50-ml. portions of ether. Removal of the ether gave 71.9 g. (86.6%) of crude product from which 25.4 g. (30.6%) of diketone, presumably 8,12-eicosadiene-2,19-dione, crys-

(5) D. Schochet, Bull. soc. chim. Belg., 44, 387 (1935); C. A., 30, 452 (1936).

(6) D. D. Coffman and H. N. Cripps, U. S. Patent 2,671,810, March 9, 1954.

(7) Buffalo Electrochemical Co.

(8) C. R. McClellan and W. R. Edwards, Jr., THIS JOURNAL, 66, 409 (1944).

tallized. After recrystallization from ethyl alcohol, the white plates melted at 64-65°.

Anal. Calcd. for C₂₀H₃₄O₂: C, 78.40; H, 11.20. Found: C, 77.86; H, 11.09.

The semicarbazone melted at 182-183°. Anal. Calcd. for C₂₂H₄₀N₆O₂: C, 62.80; H, 9.59; N, 20.00. Found: C, 62.68; H, 10.00; N, 19.75. The liquid isomers (46.5 g., 56%) solidified to a mixture

of isomeric diketones that were distilled through a 4-inch insulated Vigreux column under reduced pressure.

Fraction	°C. B.p.	Mm,	Weight, g.
1	31-140	2.5-0.7	1.6
2	151 - 162	0.7	5.4
3	167-169	0.6	20.1
4	170 - 175	0.6	15.2
R	Distillation Residue		3.1

Anal. Calcd. for C₂₀H₃₄O₂: C, 78.40; H, 11.20; quant. hydrogenation, 0.0131 g. H_2/g . Found for fraction 3: C, 78.05; H, 11.38; quant. hydrog., 0.0123 g. H_2/g . Found for fraction 4: C, 78.19; H, 11.38; quant. hydrog.,

0.0130 g. H_2/g . C. Preparation of 2,19-Eicosanedione.—A solution of C. **Freparation of 2,19-Elcosanedione**.—A solution of 8,12-eicosadiene-2,19-dione (3 g.) in 100 ml. of absolute ethyl alcohol was hydrogenated at 30-40 lb./sq. in. using platinum oxide catalyst (0.2 g.). Recrystallization of the crude product (m.p. 91-92.5°) gave 2,19-eicosanedione, m.p. 92-92.5°.⁹

Anal. Caled. for C₂₀H₃₅O₂: C, 77.40; H, 12.30. Found: C, 77.44; H, 12.39.

The oxime melted at 110-114°. Anal. Calcd. for C₂₀-H₄₀N₂O₂: C, 70.57; H, 11.83; N, 8.22. Found: C, 70.76; H, 11.89; N, 8.42. II. Preparation of C₂₂-Diketones. A. 1-Methylcyclo-hexyl Hydroperoxide.—1-Methylcyclohexyl hydroperoxide

was prepared using the apparatus and procedure described for 1-methylcyclopentyl hydroperoxide.

for 1-methylcyclopentyl hydroperoxide. B. Addition of 6-Ketoheptyl Radicals to 1,3-Butadiene.— 1,3-Butadiene (68 g.) was condensed in a 3-1. creased flask containing 50 ml. of distilled water and 50 ml. of methanol at -30 to -20° . The mixture was blanketed with nitrogen and maintained at -20 to -10° while solution of 1-methyl-cyclohexyl hydroperoxide (84.0 g., 0.65 mole) in methanol (total vol. 300 ml.) and 180 g. (0.65 mole) of ferrous sulfate heptahydrate in distilled water (total vol. 300 ml.) were heptahydrate in distilled water (total vol. 300 ml.) were added at equal rates with vigorous agitation over a period of 15 minutes. After 1/s and 2/s of the oxidation-reduction components had been added, an additional 50 ml. of liquid 1,3-butadiene was added. The reaction mixture was diluted with water (50 ml.), and an additional 50 g. of ferrous sulfate heptahydrate in 100 ml. of water was added to ensure complete destruction of peroxide.

The crude product was a mixture of oil and solid that was extracted from the reaction mixture with one 300-ml. and two 200-ml. portions of ether. The combined ether ex-

(9) M. Stoll, Helv. Chim. Acta, 34, 1817 (1951), reports m.p. 92-93°.

tract was washed with distilled water (100 ml.), 5% sulfuric acid (100 ml.) and again with distilled water (100 ml.). The ether solution was dried with anhydrous magnesium sulfate (10-15 g.) and concentrated to about 200 ml. After cooling to 34° for 24 hours, the mixture was filtered with suction. The crystalline solid, presumed to be 9,13-docosadiene-2,21-dione (22.0 g., 20.4%), melted at 71.5-72.0° after recrystallization from ethyl alcohol.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45; quant. hydrog., 0.0121 g. H_2/g . Found: C, 78.61; H, 11.31; quant. hydrog., 0.0128 g. H_2/g .

The semicarbazone melted at $163.5-165.0^{\circ}$ after recrystallization from ethyl alcohol. Anal. Calcd. for C₂₄H₄₄-N₈O₂: C, 64.25; H, 9.88; N, 18.74. Found: C, 64.13; H, 9.86; N, 19.04.

Hydrogenation of the unsaturated diketone in ethyl alcohol with platinum oxide catalyst gave 2,21-docosanedione, m.p. 89.5-90.5° after recrystallization from ethyl alcohol. 2,21-Docosanedione has been reported to melt at 94.5^{10} and 90-92°.¹¹ The bis-2,4-dinitrophenylhydrazone melted at 105-108° after recrystallization from acetic acid. The literature gives melting points of 107-109°10 and 95-101°.¹¹

The filtrate was concentrated to obtain 74.4 g. (68.9%) of isomeric diketones that were distilled through a 4-inch insulated still head under reduced pressure.

		B.p.,	
Fraction	°C.	Mm,	Weight, g.
1	30-70	18	9.7
2	43 - 180	1.3-0.9	3.8
3	181 - 193	0.8-1.0	22.8
4	195 - 198	1.0	20.9
5	199 - 205	1.0	5.4

Anal. Calcd. for $C_{22}H_{35}O_2$: C, 78.98; H, 11.45; mol. wt., 334.5; quant. hydrog., 0.0119 g. H_2/g . Found for fraction 3: C, 77.87; H, 11.26; mol. wt., 304; quant. hydrog., 0.0118 g. H_2/g . Found for fraction 4: C, 78.87; H, 11.59; quant. hydrog., 0.0118 g. H_2/g .

III. Reductive Cleavage of 1-Methylcyclopentyl Hydroperoxide in the Presence of Isoprene.—A solution of freshly distilled isoprene (34.1 g., 0.5 mole) in 50 ml. of nitrogen-saturated methanol was cooled to approximately -30° under a nitrogen atmosphere. Then 23.2 g. (0.2 mole) of 1-methylcyclopentyl hydroperoxide and an aqueous ferrous sulfate solution (120 ml. of a 1.66 M solution) of ferrous sulfate in nitrogen-saturated distilled water) were added at equivalent rates over a 10-minute period to the isoprene solution maintained at -20 to -10° . The reaction mixture was stirred for 10 minutes, and the system was evacuated with a water-pump to remove excess isoprene. After 100 ml. of distilled water had been added, the reaction mixture was extracted with one 100-ml. and three 50-ml. portions of ether. Removal of the ether left 25.7 g. of oil (77% yield assuming all of the product to be C₂₂-diketone). When cooled, 0.95 g. of a white solid (m.p. 58-62°) separated. The remainder of the product (24.6 g.) was a pale yellow oil. The white solid on recrystallization from ethyl alcohol gave a product melting at 66.5-68°. This material

was found to be 2,11-dodecanedione, reported by Hawkins² to melt at 67.5 to 68.5° . The semicarbazone melted at 202.5–204.5°.

The pale yellow oil was heated at 60° for 2 hours at approximately 20 mm. pressure to obtain 24.3 g. of residue.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45; carbonyl equiv., 167.3; mol. wt., 334.5; hydrog. equiv., 0.0121 g. H_2/g . Found: C, 75.58; H, 11.31; carbonyl equiv., 143.4; mol. wt., 248; hydrog. equiv., 0.0124 g. H_2/g .

An 8.2-g. sample of this residue was distilled through a 4inch Vigreux still under reduced pressure. Two highboiling fractions were collected and analyzed: fraction 1, b.p. 146-177° (0.5 mm.), n^{25} D 1.4658, 1.9 g.; fraction 2, b.p. 177-186° (0.5 mm.), n^{25} D 1.4740, 1.8 g.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45; inol. wt., 334.5. Found for fraction 1: C, 77.49; H, 11.57; mol. wt., 340. Found for fraction 2: C, 79.29; H, 11.67; mol. wt., 335.

The infrared spectrum of fraction 2 showed absorption for the carbonyl group $(5.82 \ \mu)$, for an internal double bond $(6.07 \ \mu)$ and for the methyl group $(7.35, 3.41, 3.49 \ \mu)$. A shoulder at 5.95 μ suggested the presence of some terminal double bonds. These data are in accord with a structure corresponding to that of an additive dimer as represented by D, Table I.

D, Table I. IV. Reactions of Radicals Derived from Pinane Hydroperoxide.—A mixture of 100 ml. of nitrogen-saturated methanol and 75 ml. (~1 mole) of 1,3-butadiene was cooled to -20° and rapidly stirred while a methanolic solution (total vol. 100 ml.) of 25 g. of 80% pinane hydroperoxide¹³ (0.12 mole) and an aqueous solution of 33.5 g. (total vol. 100 ml., 0.12 mole) of ferrous sulfate heptahydrate were added at equivalent rates in a period of about 3 minutes. The reaction mixture was diluted with 150 ml. of water and 10 ml. of concd. sulfuric acid. The organic layer was extracted using one 200-ml. and two 100-ml. portions of ether.

Removal of the ether left 29.1 g. of pale yellow oil that did not crystallize. A 26.0-g. sample of this was heated to 220° at 1 mm. The volatile material (5.8 g.) boiled from $50-110^{\circ}$ (1 mm.) and was not investigated further. The residue could not be distilled and was analyzed without further purification.

Anal. Caled. for C₂₈H₄₆O₂: C, 81.10; H, 11.18; mol. wt., 414.6. Found: C, 79.92; H, 11.05; mol. wt., 412.

The infrared spectrum showed strong carbonyl absorption at 5.85 μ and carbon-carbon double bond absorption at 6.1, 10.35, 10.1 and 11.0 μ . A hydroxyl impurity was indicated by a band at 2.9 μ .

A sample of this oil (2.8 g.) gave a semicarbazone (3.05 g., 85%) m.p. 152-157° after recrystallization from ethyl alcohol.

Anal. Calcd. for C₃₀H₅₂N₆O₂: C, 68.14; H, 9.91; N, 15.90. Found: C, 68.97; H, 9.99; N, 16.04.

WILMINGTON, DELAWARE

(12) The pinane hydroperoxide was obtained from the Southern Regional Research Laboratory, U. S. Dept. of Agriculture, Sample 2544-183. The preparation of this material is described by G. S. Fisher, L. A. Goldblatt, I. Kniel and A. D. Snyder, *Ind. Eng. Chem.*, 43, 671 (1951). Pinane hydroperoxide was shown to be primarily *cisi-L*pinane-2-hydroperoxide by G. S. Fisher, J. S. Stinson and L. A. Goldblatt, THIS JOURNAL, **76**, 3675 (1953).

⁽¹⁰⁾ L. Cannonica, M. Martinelli and T. Bacchetti, Atti. accad. nas. Lincei, Classe sci. fis. mat. e nat., 13, 61 (1952); C. A., 47, 11132 (1953).

⁽¹¹⁾ H. H. Gunthard, S. D. Heinman and V. Prelog, Helv. Chim. Acta, 36, 1147 (1953); C. A., 48, 8731 (1954).