

*Anal.* Calcd. for  $C_{18}H_{26}O_2$ : 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

(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. Chem.*, **16**, 1556 (1951).

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



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° after recrystallization from ethyl alcohol. *Anal.* Calcd. for  $C_{24}H_{44}N_6O_2$ : 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<sup>10</sup> and 90–92°.<sup>11</sup> The bis-2,4-dinitrophenylhydrazone melted at 105–108° after recrystallization from acetic acid. The literature gives melting points of 107–109°<sup>10</sup> and 95–101°.<sup>11</sup>

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.

Fraction	°C.	B.p.,	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  $C_{22}H_{38}O_2$ : 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  $C_{22}$ -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

(10) L. Cannonica, M. Martinelli and T. Bacchetti, *Atti. accad. naz. 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).

was found to be 2,11-dodecanedione, reported by Hawkins<sup>2</sup> 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 4-inch Vigreux still under reduced pressure. Two high-boiling fractions were collected and analyzed: fraction 1, b.p. 146–177° (0.5 mm.),  $n_D^{25}$  1.4658, 1.9 g.; fraction 2, b.p. 177–186° (0.5 mm.),  $n_D^{25}$  1.4740, 1.8 g.

*Anal.* Calcd. for  $C_{22}H_{38}O_2$ : C, 78.98; H, 11.45; mol. 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  $\mu$  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.

**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 hydroperoxide<sup>12</sup> (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° (1 mm.) and was not investigated further. The residue could not be distilled and was analyzed without further purification.

*Anal.* Calcd. for  $C_{26}H_{46}O_2$ : 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  $\mu$  and carbon-carbon double bond absorption at 6.1, 10.35, 10.1 and 11.0  $\mu$ . A hydroxyl impurity was indicated by a band at 2.9  $\mu$ .

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  $C_{30}H_{52}N_6O_2$ : C, 68.14; H, 9.91; N, 15.90. Found: C, 68.97; H, 9.99; N, 16.04.

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(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 *cis*-L-pinane-2-hydroperoxide by G. S. Fisher, J. S. Stinson and L. A. Goldblatt, *THIS JOURNAL*, **76**, 3675 (1953).