g. (1.0 mole) of gaseous phosgene. Distillation of the benzene solution furnished 139 g. (90.3%) of methacrylic anhydride with a boiling point of 82°/9.4 mm. and n_D^{30} 1.4492.

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.30; H, 6.50. Found: C, 61.98; H, 6.45.

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Some Derivatives of 3,3,5-Trimethyl-5-hexenoic Acid

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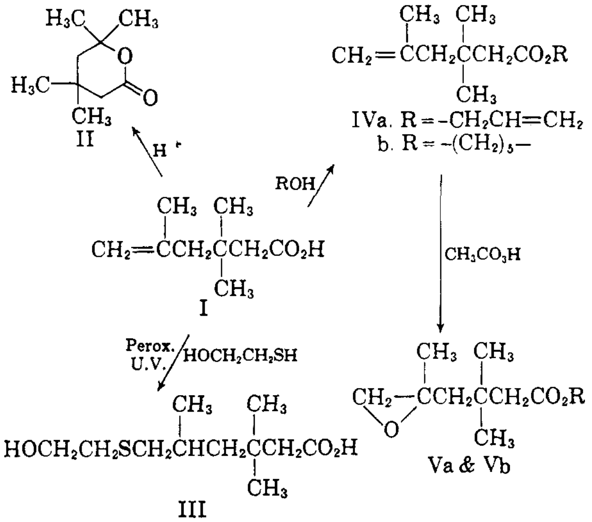
Alkali fusion of isophorone to give 3,3,5-trimethyl-5-hexenoic acid (I)[1] provides a facile synthesis of this terminally unsaturated acid. A variety of novel materials may be derived from I by simple procedures as is shown schematically below.



EXPERIMENTAL[2]

3,3,5-Trimethyl-5-hexenoic acid (I). The method of Finch[1] was employed to furnish a 41% yield of I (b.p. 121°/9 mm., n_D^{30} 1.4495, 98.6% purity by sodium hydroxide titration).

4,4,6,6-Tetramethylvalerolactone (II). A mixture of 156 g. (1.0 mole) of I, 1.6 g. of *p*-toluenesulfonic acid and 300 ml. of benzene was refluxed for 36 hr. The cooled mixture was neutralized with sodium acetate, filtered, and distilled to furnish an 89% yield of II (b.p. 99°/6 mm., n_D^{30} 1.4457, d_{20}^{20} 0.9667, 97.7% purity by saponification).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.25. Found: 69.1; H, 10.48.

9-Hydroxy-7-thia-3,3,5-trimethylnonanoic acid (III). A mixture of 172 g. (1.1 moles) of I, 78 g. (1.0 mole) of 2-mercaptoethanol and 1.26 g. of benzoyl peroxide was stirred at 70° for 10 hr. under irradiation from a General Electric Company Sunlamp. The reaction mixture was stripped of volatiles to a flask temperature of 205° at 1.5 mm. The residual amber oil amounted to 39% of III (n_D^{30} 1.5047).

Anal. Calcd. for $C_{11}H_{22}O_3S$: C, 56.1; H, 9.41; S, 13.66. Found: C, 56.48; H, 9.36; S, 14.8.

Allyl. 3,3,5-trimethyl-5-hexenoate (IVa). A mixture of 75.3 g. (0.46 mole) of I, 58 g. (1.0 mole) of allyl alcohol, 1.35 g. of *p*-toluenesulfonic acid and 265 ml. of benzene was refluxed for 11 hr. while water was removed azeotropically. The mixture was washed with 10% sodium carbonate solution and water and then distilled to furnish an 84% yield of IVa (b.p. 83°/4.5 mm., n_D^{30} 1.4460, d_{20}^{20} 0.9084, 99.3 purity by saponification).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.50; H, 10.2. Found: C, C, 73.34; H, 10.17.

1,5-Pentamethylene bis(3,3,5-trimethyl-5-hexenoate) (IVb). A mixture of 234 g. (1.5 moles) of I, 52 g. (0.5 mole) of 1,5-pentanediol, 1.4 g. of *p*-toluenesulfonic acid, and 400 ml. of benzene was refluxed for 28 hr. while water was removed azeotropically. The mixture was neutralized with sodium acetate, filtered, and distilled to furnish a 95% yield of lactone II (based on excess I) and a 98% yield (based on glycol) of IVb as a residual oil (n_D^{30} 1.4620, d_{20}^{20} 0.9521.

Anal. Calcd. for $C_{23}H_{40}O_4$: C, 72.70; H, 10.51. Found: C, 72.62; H, 10.50.

Allyl 5,6-epoxy-3,3,5-trimethylhexanoate (Va). To 218 g. (1.11 moles) of IVa was added with cooling to maintain 40° temperature 346 g. of 26.8% peracetic acid in ethyl acetate over 2-hr. period. The mixture was stirred for an additional 6 hr. at 40° to complete reaction. The mixture was fed into refluxing ethylbenzene to remove acetic acid and excess peracetic acid and was then distilled to furnish 81 g. of refined product (b.p. 93°/5 mm., n_D^{30} 1.4499).

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 68.0; H, 9.45. Found: C, 68.3; H, 9.7.

1,5-Pentamethylene bis(5,6-epoxy-3,3,5-trimethylhexanoate) (Vb). The procedure described above was employed to furnish a pale yellow residual oil (n_D^{30} 1.4650) whose infrared spectrum exhibited strong epoxide absorption and no unsaturation.

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[1] H. Finch, K. E. Furman, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 4299 (1951).

[2] All temperatures are uncorrected.

Reactions of Active Methylene Compounds in Pyridine Solution. IV. A New Synthesis of β-Hydroxypropionitriles

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In the previous parts of this series[1] reactions of hydrocarbons of the cyclopentadiene type have been discussed. In particular,[1b] the high reactivity observed in pyridine solution in the presence of benzyltrimethylammonium hydroxide made possible the use of lower temperatures in the reaction with aldehydes and thereby the isolation of primary reaction products, *e.g.* carbinols of structure I from fluorene,

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[1] (a) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958); (b) E. Ghera and Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 4945 (1960); (c) M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 4953 (1960).