

Notes

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Acrylic and Methacrylic Anhydrides

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Acrylic and methacrylic anhydrides have been prepared directly from the corresponding acids through the use of dehydrating agents such as acetic anhydride,¹ and indirectly from the reaction of the sodium salts of the acids with the corresponding acid chlorides.² The former method is complicated by the formation of difficultly separable mixed anhydrides and polymeric by-products and the latter process requires a separate synthesis of the acid chloride. A procedure similar to one previously described³ for the preparation of amino acid anhydrides, which were not isolated but used *in situ*, has been used for the preparation of polymer-free acrylic and methacrylic anhydrides.

when phosgene is used or sulfur dioxide when thionyl chloride is used is evolved on warming the solution to room temperature. After removal of the salt by filtration the resulting clear solution which contains the anhydride can be used *per se* in syntheses or the solvent can be removed and a refined product isolated. Comparable results were obtained when either benzene, acetone, or ethyl ether was used as solvent with acid concentrations of 10 to 35%.

EXPERIMENTAL⁴

Experimental data from several runs using different reaction conditions are summarized in Table I.

Typical acrylic anhydride preparation. A solution of 144 g. (1.95 moles) of acrylic acid in 1296 g. of benzene was treated with 202 g. (2 moles) of triethylamine at 0 to 10° over a period of 10 min. Hydroquinone (1.4 g.) was present in the solution as a polymerization inhibitor. With vigorous agitation, 99 g. (1 mole) of gaseous phosgene was added through a sparger placed near the bottom of the reactor. The phosgene

TABLE I
PREPARATION OF ANHYDRIDES

Acid, ^b moles	TEA, ^a moles	Phosgene Feed				Solvent	% Soln. by wt. of acid	% Yield of an- hydride
		Form	Feed rate, moles/hr.	Moles	Temp.			
Acrylic								
2.0	2.0	Liq.	1.5	1.0	-6 to 0	Acetone	35	73
1.95	2.0	Gas	2.0	1.0	5 to 18	Ether	25	50
1.95	2.0	Gas	0.82	0.82	-5 to 0	Ether	10	66
Methacrylic								
2.0	2.0	Gas	1.0	1.0	0 to 10	Benzene	11	90
Acrylic								
Thionyl Chloride Feed								
1.95	2.0	Liq.	1.2	1.0	0 to 5	Benzene	10	60

^a Triethylamine. ^b Containing 0.1% hydroquinone polymerization inhibitor.

The process involves the addition of thionyl chloride or phosgene (gaseous or liquid) to a non-aqueous solution of a carboxylic acid and at least an equivalent of triethylamine at -5 to 20°. Triethylammonium chloride precipitates during the acid chloride addition and either carbon dioxide

addition was completed in 65 min. with the temperature of the reaction mixture being maintained at 0 to 10° by external cooling. The resulting mixture was allowed to warm to room temperature and the triethylammonium chloride removed by filtration. The clear benzene filtrate was flash-distilled yielding 95 g. of crude product which was fractionally distilled through a column furnishing 89 g. (72.3%) of refined acrylic anhydride with a boiling point of 68°/9.7 mm. and n_D^{20} 1.4438.

Anal. Calcd. for C₆H₈O₃: C, 57.14; H, 4.76. Found: C, 57.31; H, 4.82.

Typical methacrylic anhydride preparation. The same general procedure was used as described for the preparation of acrylic anhydride except methacrylic acid was used in place of acrylic acid. A solution of 172 g. (2.0 moles) methacrylic acid, 202 g. (2.0 moles) of triethylamine, and 1.72 g. of hydroquinone in 1400 g. of benzene was treated with 99

(1) W. G. Lowe and W. D. Kenyon, U. S. Patent 2,319,070.

(2) C. Moreu, *Ann. Chim. and Phys.*, **7**, 2,167 (1894); British Patent 538,310; W. N. Haworth, H. Gregory, and L. F. Wiggins, *J. Chem. Soc.*, 488 (1946); A. A. Berlin and T. A. Makarova, *Zhur. Obschei. Khim. (J. Gen. Chem.)*, **21** 1267 (1945); *Chem. Abstr.*, **46**, 1996d (1952); C. E. Barnes, U. S. Patent 2,308,581.

(3) M. Brenner, Z. P. Zimmermann, P. Quitt, W. Schneider, and A. Hartmann, *Helv. Chem. Acta.* **40**, 604 (1957).

(4) All temperatures are uncorrected.

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^{20} 1.4492.

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

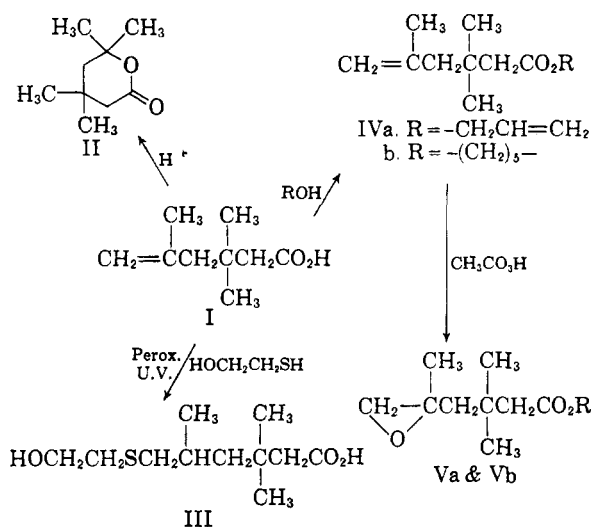
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Some Derivatives of 3,3,5-Trimethyl-5-hexenoic Acid

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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.



EXPERIMENTAL²

3,3,5-Trimethyl-5-hexenoic acid (I). The method of Finch¹ was employed to furnish a 41% yield of I (b.p. 121°/9 mm., n_D^{20} 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^{20} 1.4457, d_4^{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^{20} 1.5047).

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

(2) All temperatures are uncorrected.

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^{20} 1.4460, d_4^{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, 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^{20} 1.4620, d_4^{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^{20} 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^{20} 1.4650) whose infrared spectrum exhibited strong epoxide absorption and no unsaturation.

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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 series¹ 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,

(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).