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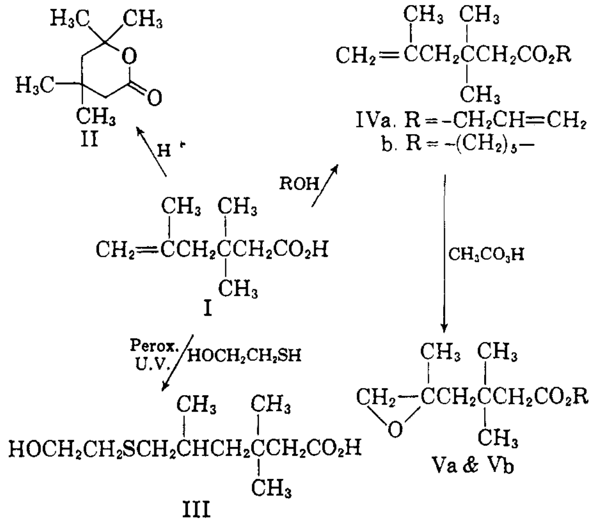
Alkali fusion of isophorone to give 3,3,5-trimethyl-5-hexenoic acid (I)[1] provides a facile synthesis of this terminally unsaturated acid. A variety of novel materials may be derived from I by simple procedures as is shown schematically below.



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.

Acknowledgment. The author is grateful to Mr. J. Smith, Jr. for technical assistance and to Mr. P. S. Starcher for synthesis of the epoxides.

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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

M. AVRAMOFF AND Y. SPRINZAK

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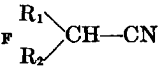
[1] (a) Y. Sprinzak, *J. Am. Chem. Soc.*, **80,** 5449 (1958); (b) E. Ghera and Y. Sprinzak, *J. Am. Chem. Soc.*, **80,** 4945 (1960); (c) M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, **80,** 4953 (1960).

TABLE 1

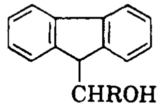
HYDROXYMETHYLATION OF



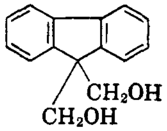
$$\begin{matrix} R_1 \searrow \\ CH{-}CN \\ R_2 \nearrow \end{matrix}$$

No.	R_1	R_2	Temp.	Time, hr.	Yield, %	Recrystallization Solvent	M.P.	Formula	Calcd. C	Calcd. H	Found C	Found H
1	C_6H_5	C_6H_5	25	22	94	Benzene–pet. ether (b.p. 60–90°)	65	$C_{15}H_{13}NO$	80.69	5.87	80.80	5.84
2	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$[a,b]	25	24	92	Heptane	97	$C_{17}H_{17}NO$	81.24	6.82	81.16	6.89
3	C_6H_5	α-$C_{10}H_7$[a,c]	25	18	95	Benzene-heptane	126–128	$C_{19}H_{15}NO$	83.49	5.53	83.45	5.63
4	C_6H_5	$C_6H_5CH_2$[d]	0	2	93	Ethyl acetate–pet. ether	89–90	$C_{16}H_{15}NO$	80.98	6.37	81.21	6.42
5	C_6H_5	α-$C_{10}H_7CH_2$[d]	25	16	95	Benzene	146–148	$C_{20}H_{17}NO$	83.59	5.96	83.61	5.96
6	$C_6H_5CH_2$	α-$C_{10}H_7$[d]	25	6	87	Benzene	122–124	$C_{20}H_{17}NO$	83.59	5.96	83.35	6.01
7	p-ClC_6H_4	p-$ClC_6H_4CH_2$[e,f]	25	48	44	Heptane	89–90	$C_{16}H_{13}Cl_2NO$	62.74	4.28	62.98	4.43
8	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4CH_2$[e,g]	25	48	45	Ether–pet. ether	75–76	$C_{18}H_{19}NO_3$	72.70	6.44	72.45	6.46
9	C_6H_5	$(C_6H_5)_2CH$[d]	25	16	91	Benzene-heptane	161–162	$C_{22}H_{19}NO$	84.31	6.11	84.25	6.22
10	$C_6H_5CH_2$	$C_6H_5CH_2$[h]	25	24	0							

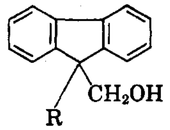
[a] Prepared according to the procedure of J. G. Burr, Jr., and L. S. Ciereszko [*J. Am. Chem. Soc.*, **74**, 5426 (1952)]. [b] M.p. 45–46°; reported 46.5–47° [R. F. Brown and N. M. van Gulick, *J. Am. Chem. Soc.*, **77**, 1083 (1955)]. [c] M.p. 94.5–96°; reported 95–96° [C. J. Collins, L. S. Ciereszko, and J. G. Burr, Jr., *J. Am. Chem. Soc.*, **75**, 405 (1953)]. [d] Ref. 3. [e] Prepared according to the procedure of Avramoff and Sprinzak.[3] [f] M.p. 90–91°; reported 91–92° [P. Weiss, M. G. Cordasco, and L. Reiner, *J. Am. Chem. Soc.*, **71**, 2650 (1949)]. [g] M.p. 117–118°; reported 117–118° [H. Köling and H. Lettré, Schenley Laboratories, Inc., U. S. Patent 2,691,044, October 5, 1954]. [h] H. Cassirer, *Ber.*, **25**, 3018 (1892).



I



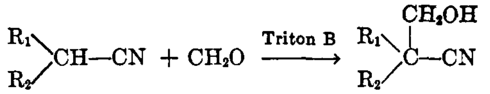
II



III

rather than their dehydration products. While formaldehyde reacted with fluorene with particular ease, affording both carbinol I (R = H) and glycol II, these products were accompanied by a considerable amount of a resinous material, presumably arising from the polymerization of dibenzofulvene, the dehydration product of the carbinol. The reaction occurred smoothly, however, with 9-alkylfluorenes, affording the corresponding hydroxymethylfluorenes (III) in quantitative yield.

The hydroxymethylation reaction has now been extended to acetonitrile derivatives[2] (Table I), including diarylacetonitriles and aryl-arylmethylacetonitriles.[3] Treatment of these compounds with paraformaldehyde in pyridine solution in the presence of Triton B affords α,α-disubstituted β-hydroxypropionitriles (Equation 1).



$$\begin{matrix}R_1\\ R_2\end{matrix}\!\!>\!CH{-}CN + CH_2O \xrightarrow{\text{Triton B}} \begin{matrix}R_1\\ R_2\end{matrix}\!\!>\!\overset{CH_2OH}{\overset{|}{C}}{-}CN \quad (1)$$

in yields ranging from 44 to 95%. It appears that the presence of an α-aryl group is essential for reaction to occur, as is indicated by the failure of dibenzylacetonitrile (No. 10) to react under the general reaction conditions. The reaction products, all of which are new compounds, were identified by elementary analysis and by their infrared spectra, showing the typical OH and $C{\equiv}N$ absorption bands in the 2.8 and 4.5 μ regions. The reaction product from diphenylacetonitrile (No. 1) was also identified by its benzoate ester.

Tertiary nitriles are known to be very resistant to hydrolysis.[4] Alkaline conditions could not be applied to the β-hydroxynitriles in question, as these are transformed, by reversal of their mode of formation and in complete analogy with β-hydroxyacids,[5] to the corresponding acetonitriles. Thus, prolonged refluxing of α,α-diphenyl-β-hydroxypropionitrile (No. 1) in ethanolic potassium hydroxide resulted in its conversion to diphenylacetic acid. A large quantity of the intermediate diphenylacetonitrile was isolated when the hydroxynitrile was kept at room temperature under similar conditions. α-Phenyl-α-benzyl-β-hydroxypropionitrile (No. 4) was the only hydroxynitrile that could be hydrolyzed to the corresponding hydroxyacid under acid conditions.

EXPERIMENTAL[6]

Pyridine was dried and a 40% solution of Triton B was prepared as described previously.[1a] The condensation reactions were performed in an atmosphere of nitrogen, the details being given in part II.[1b]

Hydroxymethylation of the nitriles (Table I). Triton B (0.5 ml.) was added to an ice cold, stirred solution of 0.005 mole of the nitrile in 10 ml. of pyridine, containing paraformaldehyde (0.6 g.; 0.02 mole) in suspension, and the stirred mixture was left at the appropriate temperature for the period indicated. The crude product obtained after treatment of the reaction mixture as described previously[1b] crystallized on trituration with petroleum ether. One recrystallization afforded the pure product.

β,β-Diphenyl-β-cyanoethyl benzoate. Refluxing α,α-diphenyl-β-hydroxypropionitrile (No. 1) with an excess of benzoyl chloride in pyridine solution for 30 min. gave the benzoate, m.p. 110° (from heptane).

Anal. Calcd. for $C_{22}H_{17}NO_2$: N, 4.28. Found: N, 4.23.

Alkaline hydrolysis of α,α-diphenyl-β-hydroxypropionitrile (No. 1). A solution of the nitrile (1.0 g.) in 20 ml. of ethanol and 2 g. of potassium hydroxide was refluxed for 20 hr. The acid fraction afforded 0.7 g., m.p. 130–140°. Recrystallization from 50% ethanol and then from a benzene-heptane mixture gave diphenylacetic acid, m.p. 139–142° and mixed m.p. 140–144°.

Reverse aldol reaction of α,α-diphenyl-β-hydroxypropionitrile (No. 1). A solution of the nitrile (1.0 g.) in 20 ml. of ethanol and 0.5 g. of potassium hydroxide was kept at room temperature for 48 hr. The mixture obtained after dilution with water was extracted several times with ether. The ethereal extract was washed with water, dried and evaporated to give 0.95 g. of residue, which was chromatographed on acid-washed alumina. The fraction (0.48 g.) obtained by elution with a 4:1 petroleum ether-benzene mixture was identified as diphenylacetonitrile, m.p. and mixed m.p. 72–75° (from petroleum ether). A fraction (0.35 g.) collected by elution with a 1:1 mixture of the same solvents proved to be the starting material.

α-Phenyl-α-benzyl-β-hydroxypropionic acid. One gram of the corresponding nitrile (No. 4) was refluxed for 30 hr. with a mixture of acetic acid (25 ml.), water (5 ml.), and concd. sulfuric acid (3 ml.). The mixture was poured into water, made alkaline with sodium hydroxide, the precipitate filtered, washed with water and with ether, then suspended in dilute hydrochloric acid, and extracted with ether. Evaporation of the dried ether solution afforded 0.35 g., m.p. 184–188°. Recrystallized from toluene, the acid melted at 190–193° (lit.[7] m.p. 188–189°).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.30; H, 6.45.

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(2) Phenylacetonitrile has been reported to form, by interaction with formaldehyde in methanolic sodium methoxide, a viscous oil, considered to be the hydroxymethylated nitrile; the product was dehydrated, without isolation, to α-phenylacrylonitrile (J. F. Walker, E. I. du Pont de Nemours and Co., U. S. Patent 2,478,990, August 16, 1949). A recent publication reports the formation of α,α,-diphenyl-α,α'-bishydroxymethylglutaronitrile, $NCC(C_6H_5)(CH_2OH)$-$CH_2C(C_6H_5)(CH_2OH)CN$, from the same reagents in toluene and sodium methoxide [H. Jäger, *Arch. Pharm.*, **289**, 165 (1956)].

(3) Chosen for their ready accessibility [M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 493 (1958)].

(4) See, *e.g.*, S. Rovira, *Ann. chim. (Paris)*, [11], **20**, 660 (1945).

(5) See, *e.g.*, C. S. Rondestvedt, Jr., and M. E. Rowley, *J. Am. Chem. Soc.*, **78**, 3804 (1956).

(6) Melting points are corrected. Infrared spectra were determined in chloroform solution on a Perkin-Elmer Infracord.

(7) F. F. Blicke and H. Raffelson, *J. Am. Chem. Soc.*, **74**, 1730 (1952).