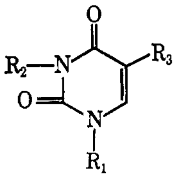
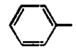
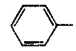
TABLE I[a]



No.	R$_1$	R$_2$	R$_3$	Time, hr	Temp, °C	% yield	Mp, °C	Recrystn solvent	R_f (solvent)
I	2′-dR	C_2H_5	CH_3	40	130	38	Gum		0.84 (A)
II	H	C_2H_5	CH_3			90	202.5	Water	0.84 (A)
III[b]	2-dR	—CH$_2$	CH_3	40	130	32	167–168	Water	0.84, 0.70 (A, B)
IV[b]	H	—CH$_2$	CH_3			85	207	Water	0.84 (A)
V	2′-dR	$CH_3(CH_2)_2CH_2$	CH_3	40	130	31	Gum		0.84 (A)
VI	H	$CH_3(CH_2)_2CH_2$	CH_3			75	73	Ether–petroleum ether	0.84 (A)
VII	2′-dR	$CH_3(CH_2)_6CH_2$	CH_3	66	140	2.2	Gum		0.70 (A)
VIII	CH_3	CH_3	CH_3	30	100	71.5	155	Ethanol	0.86 (A)
IX	C_2H_5	C_2H_5	CH_3	47	130	83	56–57	Water	0.86 (A)
X	C_2H_5	H	CH_3			10	223	Water	0.77 (A)
XI	Rb	CH_3	H	20	90	18	115–116	Methanol–ethyl acetate, petroleum ether	0.68 (A)
XII[c]	H	CH_3	H			75[d]	184[d]	Ethanol	
XIII	Rb	$CH_3(CH_2)_2CH_2$	H	40	130	17	Gum		0.42, 0.76 (A, B)
XIV[c]	H	$CH_3(CH_2)_2CH_2$	H			73[e]	152–153[e]	Ethyl acetate	0.75, 0.83, 0.72 (A, B, C)
XV	Rb	—CH$_2$	H	40	130	7	174–175	Ethyl acetate, ether–petroleum ether	

[a] Abbrevations: 2′-dR, 2′-deoxyribose; Rb, ribose. A, B, and C refer to chromatographic solvents used (see Experimental Section). [b] The benzyl derivatives are strongly retained by resins particularly by Dowex-1. The yields can be increased if the excess benzyl alcohol is extracted with petroleum ether and the use of resins avoided. [c] Prepared by hydrolysis of XI and XIII, respectively, for 1 hr in 70% perchloric acid 100°. [d] lit.[19] 184.0–184.5°; see ref 19 and A. Benitez, L. O. Ross, L. Goodman, and B. R. Baker, *J. Amer. Chem. Soc.*, 82, 4585 (1960). [e] lit.[20] 152.3°.

paper with water; the water eluates were concentrated. When necessary these were percolated through Dowex-1-Acetate and Dowex-50-H$^+$ resins. The products were isolated either as chromatographically pure gums or where possible, they were crystallized. A summary of the pertinent data is presented in the accompanying table. This general procedure was used to synthesize the following compounds: 3-ethylthymidine (I), 3-benzylthymidine (III), 3-(*n*-butyl)thymidine (V), 3-(*n*-octyl)-thymidine (VII) (5.3 mg was obtained; structure was assumed from uv spectrum), 1,3-dimethylthymine[5,6,15] (VIII), 1,3-diethylthymine[9] (IX), 1-ethylthymine[19] (X) (as a by-product of synthesis of IX), 3-methyluridine[20,21] (XI), 3-(*n*-butyl)-uridine (XIII), 3-benzyluridine (XV).

Anal. Calcd for $C_{12}H_{18}N_2O_5$ (I): C, 53.32; H, 6.71. Found: C, 53.46; H, 6.92.

Anal. Calcd for $C_{17}H_{20}N_2O_5$ (III): C, 61.44; H, 6.07; N, 8.43. Found: C, 60.86; H, 6.06; N, 7.45.

Anal. Calcd for $C_{14}H_{22}N_2O_5$ (V): C, 56.36; H, 7.43; N, 9.39. Found: C, 53.89; H, 7.84; N, 9.22. Recalcd for $C_{14}H_{22}N_2O_5 \cdot H_2O$: C, 53.15; H, 7.65; N, 8.86. On this basis it is assumed that the derivative contains one water of crystallization.

Anal. Calcd for $C_{13}H_{20}N_2O_6$ (XIII): C, 51.99; H, 6.71; N, 9.33. Found: C, 53.93; H, 7.25; N, 9.38.

Anal. Calcd for $C_{16}H_{18}N_2O_6$ (XV): C, 57.48; H, 5.43; N, 8.38. Found: C, 57.34; H, 5.56; N, 8.10.

The following substituted pyrimidines were prepared from the parent pyrimidine nucleosides by hydrolysis in glacial acetic acid–concentrated hydrochloric acid (2:1, v/v) for 1 hr in a boiling-water bath: 3-ethylthymine (II) from I, 3-benzylthymine[22] (IV) from III, 3-(*n*-butyl)thymine (VI) from V.

Anal. Calcd for $C_7H_{10}N_2O_2R$ (II): C, 54.53; H, 6.54; N, 18.17. Found: C, 54.40; H, 6.64; N, 18.48.

Anal. Calcd for $C_9H_{14}N_2O_2$ (VI): C, 59.32; H, 7.74; N, 15.37. Found: C, 59.09; H, 7.71; N, 15.58.

Registry No.—I, 21473-40-5; II, 21473-20-1; III, 21473-21-2; IV, 21473-22-3; V, 21473-41-6; VI, 5564-91-0; VII, 21473-42-7; VIII, 4401-71-2; IX, 21472-93-5; X, 21472-94-6; XI, 2140-69-4; XIII, 21473-43-8; XV, 14985-34-3; dicyclohexylcarbodimide, 53-87-50; thymine, 65-71-4; uracil, 66-22-8; thymidine, 50-88-4; uridine, 58-96-8.

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[19] W. Schmidt-Nickels and T. B. Johnson, J. Amer. Chem. Soc., 52, 4511 (1930).

[20] J. A. Haines, C. B. Reese and Lord Todd, *J. Chem. Soc.*, 1406 (1964).

[21] D. W. Visser, G. Barton and R. Beltz, *J. Amer. Chem. Soc.*, 75, 2017 (1953).

[22] T. B. Johnson and J. H. Derby, *Am. Chem. J.*, 40, 456 (1908).

Hydrodimerization of Acrylic Acid by Sodium Amalgam

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Electrolytic hydrodimerization of unsaturated acids was reported by Wilson and Wilson.[1] They have shown that sorbic and cinnamic acids can undergo a hydrogenative dimerization to produce a mixture of isomeric saturated dicarboxylic acids.[1] Being conjugated acids, the reduction potentials of these compounds are much lower than that of a proton. In acrylic acid (AA), however, the double bond is not so easily reduced, and one would expect hydrogen evolution or reduction to propionic acid. This is indeed the case when electrolysis of acrylic acid is carried out in aqueous solution or in an ether solvent.

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[1] C. I. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, 80, 139 (1941); 84, 153 (1943).

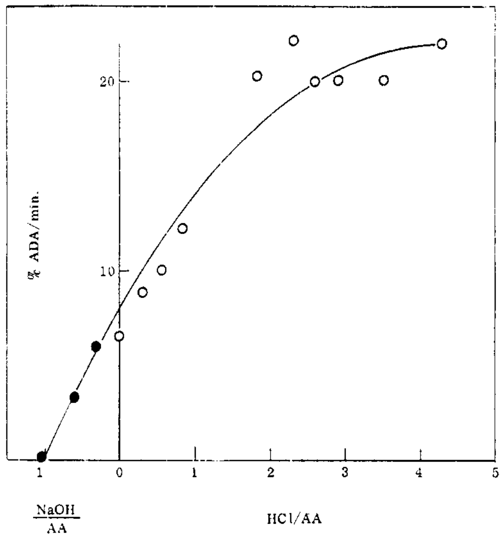


Figure 1.—Hydrogenative dimerization of acrylic acid (AA). Dependence of rate on molar ratio of AA to NaOH and HCl.

As part of our study on the hydrodimerization of acrylic monomers by means of alkali metal amalgams,[2,3] we have also attempted to dimerize acrylic acid. When the reaction was carried out in water, dioxane, or diglyme, the only product was propionic acid (PA). However, when dimethyl sulfoxide (DMSO) was used as solvent, adipic acid (ADA) was the main product.

The reaction was carried out by stirring a solution of 2–5% AA and 10% water in DMSO with a sodium amalgam. To achieve high conversion, it was necessary to add hydrochloric acid during the reaction. Under these conditions, it was possible to obtain a yield of about 70% ADA, and as by-product 20–25% propionic acid. The interesting point is that the addition of hydrochloric acid increased the rate of the reaction but did not increase the PA/ADA ratio.

The following standard technique was used to measure the reaction rate. A sodium amalgam (60 ml, the sodium content being 15 mmol/100 g of mercury) was placed into a reaction flask equipped with an efficient mechanical stirrer. To this was then introduced 50 ml of a DMSO solution containing 5% AA and 10% water, and stirring was continued for 30 additional sec. The amalgam was then separated and the acids formed were esterified with a boron trifluoride–methanol mixture and injected into an F & M gas chromatograph (column, LAC 446 polyester on Chromosorb W).

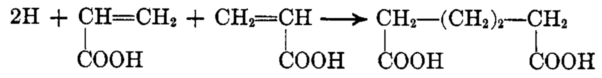
The results may be seen from Figure 1.

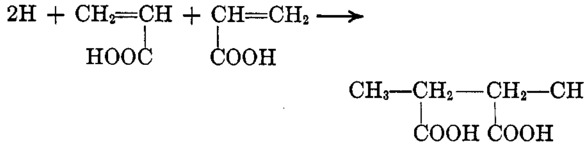
When sodium acrylate is the reacting species, no reaction is occurring. However, upon addition of hydrochloric acid to the medium, the rate of reaction gradually increases due to the equilibrium

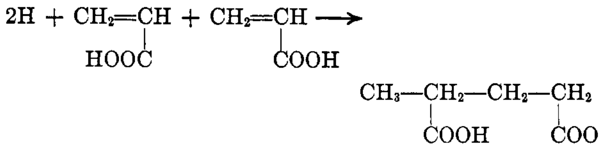
$$\text{acrylate}^- + \mathrm{H}^+ \rightleftarrows \text{acrylic acid}$$

The large excess of hydrochloric acid is required because of the strongly alkaline conditions existing at the double layer. This shows clearly that the active species interacting with the amalgam is the undissociated acid and not the acrylate anion.

Hydrodimerizations were also carried out with methacrylic and crotonic acids. In these cases, however, one does not obtain the tail-to-tail addition that was the exclusive reaction made for AA (eq 1), but mainly head-to-head (eq 2) and head-to-tail (eq 3) addition.


$$2\mathrm{H} + \underset{\mathrm{COOH}}{\mathrm{CH}}{=}\mathrm{CH_2} + \mathrm{CH_2}{=}\underset{\mathrm{COOH}}{\mathrm{CH}} \longrightarrow \underset{\mathrm{COOH}}{\mathrm{CH_2}}{-}(\mathrm{CH_2})_2{-}\underset{\mathrm{COOH}}{\mathrm{CH_2}} \qquad (1)$$


$$2\mathrm{H} + \mathrm{CH_2}{=}\underset{\mathrm{HOOC}}{\mathrm{CH}} + \underset{\mathrm{COOH}}{\mathrm{CH}}{=}\mathrm{CH_2} \longrightarrow \mathrm{CH_3}{-}\underset{\mathrm{COOH}}{\mathrm{CH_2}}{-}\underset{\mathrm{COOH}}{\mathrm{CH_2}}{-}\mathrm{CH_3} \qquad (2)$$


$$2\mathrm{H} + \mathrm{CH_2}{=}\underset{\mathrm{HOOC}}{\mathrm{CH}} + \mathrm{CH_2}{=}\underset{\mathrm{COOH}}{\mathrm{CH}} \longrightarrow \mathrm{CH_3}{-}\underset{\mathrm{COOH}}{\mathrm{CH_2}}{-}\mathrm{CH_2}{-}\underset{\mathrm{COOH}}{\mathrm{CH_2}} \qquad (3)$$

Codimerizations of these two acids with AA were also carried out to yield mixtures of isomeric saturated dicarboxylic acids.

Sorbic acid can also be hydrodimerized in DMSO by the use of sodium amalgam to yield three different isomeric dicarboxylic acids. This, however, can be accomplished in an ether solvent such as diglyme as well as in DMSO, which emphasizes the effect of DMSO on the reduction potential of the unconjugated acids.

The effect of DMSO is probably due to its donor character. It is known that DMSO can bind acids through strong hydrogen bonding. It thus avoids the direct reduction of the acid and enables it to undergo hydrodimerization. The detailed mechanism of the reaction is at present under study.

Registry No.—Acrylic acid, 79-10-7.

Acknowledgment.—The authors are indebted to U. C. B. (Union Chimique-Chemische, Bedrijven) S. A., Brussells, Belgium, for financial support of this work.

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[2] Y. Arad, M. Levy, I. R. Miller, and D. Vofsi, *J. Electrochem. Soc.*, **114**, 889 (1967).

[3] Y. Arad, M. Levy, H. Rosen, and D. Vofsi, *J. Polym. Sci.*, in press.

Acid-Catalyzed Reactions of 1,4-Dihydro-1-methyl-4-oxo-1-naphthonitrile. Self-Condensation to a 13-Oxapicene Derivative[1]

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Certain cyclohexadienones have been found to undergo the dienone–phenol rearrangement with difficulty or with the formation of unusual reaction products if one of the *gem* substituents is an electron-attracting group.[2] We now find that another similarly con-

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[1] The author is indebted to Lafayette College for a 1968 Summer Research Fellowship. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (1905-B) of this research.

[2] (a) T. G. Miller, *J. Org. Chem.*, **27**, 1549 (1962). (b) H. Pleininger and T. Suehiro, *Chem. Ber.*, **89**, 2789 (1956). (c) M. S. Newman and L. L. Wood, Jr., *J. Amer. Chem. Soc.*, **81**, 6450 (1959).