

Anal. Subs., 0.2069: CO₂, 0.6068; H₂O, 0.1016. Calcd. for C₁₅H₁₂O₂: C, 80.32; H, 5.39. Found: C, 79.99; H, 5.49.

Decomposition of 4-Hydroxyphenyl-styryl Ketone.—Ten grams of this chalcone was refluxed with 200 cc. of 50% aqueous potassium hydroxide for eight hours. Ether extraction of the alkaline solution yielded a small amount of benzaldehyde, b. p. 175–180°, which was identified by means of its phenylhydrazone;¹¹ m. p. 153–154°. A very small amount of benzyl alcohol was also obtained. This was undoubtedly produced by the Cannizzaro reaction. The alkaline solution produced a brown precipitate on acidification which was dissolved in dilute alkali. The solution was saturated with carbon dioxide which caused the separation of some unreacted chalcone along with some amorphous polymerization products. These were filtered and the filtrate was extracted three times with 100-cc. portions of ether. The ether was distilled and the residue recrystallized from a small amount of water. Crystals of *p*-hydroxyacetophenone melting at 107° were obtained. It was identified by means of a mixed melting point and conversion to the phenylhydrazone,¹² which melted at 135–136°.

Summary

Concentrated potassium hydroxide splits simple chalcones into the corresponding aldehyde and ketone. The best conditions for accomplishing this degradation and procedures for isolating the products are given.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERICIDAL PROPERTIES OF CERTAIN PENTADECANOIC, HEPTADECANOIC AND NONADECANOIC ACIDS. XIX¹

BY C. M. GREER AND ROGER ADAMS

RECEIVED MARCH 10, 1930

PUBLISHED JUNE 6, 1930

In two previous papers covering the preparation and properties of certain dialkyl acetic acids, it was demonstrated that the hexadecanoic acids were more effective bactericidally to *B. Leprae* than the octadecanoic acids, and far more effective than the dodecanoic, the tridecanoic or the tetradecanoic acids. Representatives of the missing series, pentadecanoic, heptadecanoic and nonadecanoic acids have now been prepared. The bacteriological results of the specific compounds produced are given in Table I.

It is obvious that the C₁₅ and the C₁₇ acids are not as effective as the C₁₆, and the C₁₉ acids are less effective than the previously prepared C₁₈ acids. From the tables containing the data for all of the acids from C₁₂ to C₁₉, it may be concluded that the bactericidal action is zero for the C₁₂ acids, and practically nil for the C₁₃ acids. Beginning with the C₁₄ acids the

¹¹ Biltz, *Ann.*, 305, 171 (1899).

¹² Nencki, *Ber.*, 30, 1770 (1897).

¹ The previous paper in this series is XVIII, Armendt and Adams, 52, 1289 (1930).

TABLE I
BACTERIOLOGICAL TESTS TO *B. Leprae*
Dialkyl acetic acids containing C₁₅, C₁₇ and C₁₉

	Dilutions of sodium salts in thousands											
	5	25	50	62	74	85	100	125	155	192	250	333
Pentadecanoic Acids												
CH ₃ CH(CO ₂ H)C ₁₂ H _{26-n}	-	-	-	-	+	+	+	+	+	+	+	+
C ₂ H ₅ CH(CO ₂ H)C ₁₁ H _{23-n}	-	-	-	-	-	-	≠	≠	≠	+	+	+
C ₃ H ₇ CH(CO ₂ H)C ₁₀ H _{21-n}	-	-	-	-	-	≠	≠	+	+	+	+	+
C ₄ H ₉ CH(CO ₂ H)C ₉ H _{19-n}	-	-	-	-	-	≠	≠	+	+	+	+	+
C ₅ H ₁₁ CH(CO ₂ H)C ₈ H _{17-n}	-	-	-	-	-	≠	≠	+	+	+	+	+
C ₆ H ₁₃ CH(CO ₂ H)C ₇ H _{15-n}	-	-	-	-	-	-	+	≠	+	+	+	+
Heptadecanoic Acids												
CH ₃ CH(CO ₂ H)C ₁₄ H _{29-n}	-	-	≠	≠	≠	+	+	+	+	+	+	+
C ₂ H ₅ CH(CO ₂ H)C ₁₃ H _{27-n}	-	-	-	-	-	-	≠	+	+	+	+	+
C ₃ H ₇ CH(CO ₂ H)C ₁₂ H _{25-n}	-	-	-	+	≠	+	+	+	+	+	+	+
C ₄ H ₉ CH(CO ₂ H)C ₁₁ H _{23-n}	-	-	-	-	≠	+	+	+	+	+	+	+
C ₅ H ₁₁ CH(CO ₂ H)C ₁₀ H _{21-n}	-	-	-	-	-	≠	≠	+	+	+	+	+
C ₆ H ₁₃ CH(CO ₂ H)C ₉ H _{19-n}	-	-	-	≠	+	+	+	+	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₈ H _{17-n}	-	-	-	-	-	-	-	≠	+	+	+	+
Nonadecanoic Acids												
C ₃ H ₇ CH(CO ₂ H)C ₁₄ H _{29-n}	-	+	+	+	+	+	+	+	+	+	+	+
C ₅ H ₁₁ CH(CO ₂ H)C ₁₂ H _{25-n}	-	+	+	+	+	+	+	+	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₁₀ H _{21-n}	-	+	+	+	+	+	+	+	+	+	+	+

effectiveness reaches a maximum in the C₁₆ series, then drops off with a certain irregularity to a very low bactericidal value in the C₁₉ acids. Apparently the best combination of physical properties which are presumably causing the bactericidal action, appears in the hexadecanoic compounds. In Table II are given bacteriological results on individual members of the C₁₂ to C₁₉ acids tested all at one time. The maximum in the hexadecanoic acid is clean cut.

The various acids were prepared in a manner similar to those previously described from the proper disubstituted malonic esters.

TABLE II
BACTERIOLOGICAL TESTS TO *B. Leprae*. SERIES OF DIALKYL ACETIC ACIDS, C₁₂-C₁₉

	No. of C atoms	Dilution of sodium salts in thousands					
		5	50	100	155	250	500
C ₇ H ₁₅ CH(CO ₂ H)CH(CH ₃) ₂	12	+	+	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₄ H ₉	13	-	+	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₅ H ₁₁	14	-	-	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₆ H ₁₃	15	-	-	-	-	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₇ H ₁₅	16	-	-	-	-	-	+
C ₇ H ₁₅ CH(CO ₂ H)C ₈ H ₁₇	17	-	-	-	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₉ H ₁₉	18	-	-	+	+	+	+
C ₇ H ₁₅ CH(CO ₂ H)C ₁₀ H ₂₁	19	-	+	+	+	+	+

Experimental Part

 TABLE III
 CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, %	
				C	H
Diethyl dialkyl malonates (all alkyl groups normal)					
$\text{CH}_3\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{12}\text{H}_{25}$	161–164 (1.5–2.5 mm.)	1.4412	0.9217	70.01	11.1
$\text{C}_2\text{H}_5\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{11}\text{H}_{23}$	150–154 (0.2–1.0 mm.)	1.4420	.9262	70.16	11.25
$\text{C}_3\text{H}_7\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{10}\text{H}_{21}$	143–148 (0.1–1.0 mm.)	1.4416	.9256	70.02	11.12
$\text{C}_4\text{H}_9\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_9\text{H}_{19}$	143–147 (0.1–1.0 mm.)	1.4420	.9241	69.95	11.19
$\text{C}_5\text{H}_{11}\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_8\text{H}_{17}$	142–146 (0.1–1.0 mm.)			70.28	11.17
$\text{C}_6\text{H}_{13}\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_7\text{H}_{15}$	146–152 (0.1–1.0 mm.)	1.4412	.9231	70.14	11.18
Calcd. for each isomer of $\text{C}_{20}\text{H}_{38}\text{O}_4$				70.11	11.19
Pentadecanoic Acids					
$\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{C}_{12}\text{H}_{25}$	172–175 (2–3 mm.) m. p. 34–36			74.66	12.58
$\text{C}_2\text{H}_5\text{CH}(\text{CO}_2\text{H})\text{C}_{11}\text{H}_{23}$	160–163 (2–3 mm.)	1.4455	0.8821	74.24	12.42
$\text{C}_3\text{H}_7\text{CH}(\text{CO}_2\text{H})\text{C}_{10}\text{H}_{21}$	164–167 (2–3 mm.)	1.4450	.8819	74.32	12.51
$\text{C}_4\text{H}_9\text{CH}(\text{CO}_2\text{H})\text{C}_9\text{H}_{19}$	159–162 (2–3 mm.)	1.4459	.8824	74.20	12.46
$\text{C}_5\text{H}_{11}\text{CH}(\text{CO}_2\text{H})\text{C}_8\text{H}_{17}$	161–164 (2–3 mm.)			74.20	12.37
$\text{C}_6\text{H}_{13}\text{CH}(\text{CO}_2\text{H})\text{C}_7\text{H}_{15}$	156–159 (1–2 mm.)	1.4450	.8806	74.38	12.55
Calcd. for each isomer of $\text{C}_{15}\text{H}_{30}\text{O}_2$				74.31	12.48

 TABLE IV
 CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, %	
				C	H
Diethyl dialkyl malonates (all alkyl groups normal)					
$\text{CH}_3\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{14}\text{H}_{29}$	172–176 (0.5–1.0 mm.)	1.4436	0.9164	71.20	11.53
$\text{C}_2\text{H}_5\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{13}\text{H}_{27}$	178–181 (0.8–2.0 mm.)	1.4435	.9207	70.95	11.33
$\text{C}_3\text{H}_7\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{12}\text{H}_{25}$	173–177 (0.5–1.0 mm.)	1.4438	.9191	71.33	11.40
$\text{C}_4\text{H}_9\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{11}\text{H}_{23}$	171–176 (0.5–1.0 mm.)	1.4439	.9173	71.21	11.42
$\text{C}_5\text{H}_{11}\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_{10}\text{H}_{21}$	148–154 (0.1–0.8 mm.)			71.31	11.35
$\text{C}_6\text{H}_{13}\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_9\text{H}_{19}$	170–174 (0.5–1.5 mm.)	1.4441	.9178	71.20	11.39
$\text{C}_7\text{H}_{15}\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{C}_8\text{H}_{17}$	157–161 (0.2–1.0 mm.)	1.4436	.9171	71.40	11.36
Calcd. for each isomer of $\text{C}_{22}\text{H}_{42}\text{O}_4$				71.29	11.43
Heptadecanoic Acids					
$\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{C}_{14}\text{H}_{29}$	174–177 (1–2 mm.) m. p. 45.5–47.5°			75.77	12.67
$\text{C}_2\text{H}_5\text{CH}(\text{CO}_2\text{H})\text{C}_{13}\text{H}_{27}$	164–168 (1–2 mm.)	1.4480	0.8810	75.27	12.68
$\text{C}_3\text{H}_7\text{CH}(\text{CO}_2\text{H})\text{C}_{12}\text{H}_{25}$	183–187 (2.5–3.5 mm.)	1.4483	.8827	75.63	12.72
$\text{C}_4\text{H}_9\text{CH}(\text{CO}_2\text{H})\text{C}_{11}\text{H}_{23}$	174–177 (2–3 mm.)	1.4484	.8783	75.35	12.61
$\text{C}_5\text{H}_{11}\text{CH}(\text{CO}_2\text{H})\text{C}_{10}\text{H}_{21}$	177–182 (2–3 mm.)			75.94	12.50
$\text{C}_6\text{H}_{13}\text{CH}(\text{CO}_2\text{H})\text{C}_9\text{H}_{19}$	182–185 (2–3 mm.)	1.4489	.8821	75.31	12.59
$\text{C}_7\text{H}_{15}\text{CH}(\text{CO}_2\text{H})\text{C}_8\text{H}_{17}$	184–187 (2–3 mm.)	1.4483	.8780	75.44	12.71
Calcd. for each isomer of $\text{C}_{17}\text{H}_{34}\text{O}_2$				75.48	12.68

^a M. p. 54° according to Morgan and Holmes, *J. Soc. Chem. Ind.*, **46**, 152 (1927).

TABLE V
CONSTANTS OF ESTERS AND ACIDS

Compound	B. p., °C.	n_D^{20}	d_4^{20}	Found, %	
Diethyl dialkyl malonates (all alkyl groups normal)					
$C_3H_7C(CO_2C_2H_5)_2C_{14}H_{29}$	180-184 (0.2-1.0 mm.)	1.4459	0.9141	72.29	11.63
$C_5H_{11}C(CO_2C_2H_5)_2C_{12}H_{25}$	178-181 (0.2-1.0 mm.)	1.4460	.9112	72.30	11.58
$C_7H_{15}C(CO_2C_2H_5)_2C_{10}H_{21}$	182-186 (0.2-1.0 mm.)	1.4459	.9116	72.23	11.71
Calcd. for each isomer of $C_{24}H_{46}O_4$				72.29	11.64
Nonadecanoic Acids					
$C_3H_7CH(CO_2H)C_{14}H_{29}$	182-185 (0.5-1.5 mm.) m. p. 35-37			76.56	12.81
$C_5H_{11}CH(CO_2H)C_{12}H_{25}$	184-188 (0.5-1.5 mm.)	1.4508	0.8752	76.47	12.85
$C_7H_{15}CH(CO_2H)C_{10}H_{21}$	180-184 (0.5-1.5 mm.) m. p. 31.5-33.5			76.65	12.81
Calcd. for each isomer of $C_{19}H_{38}O_2$				76.43	12.84

Summary

A number of pentadecanoic, heptadecanoic and nonadecanoic acids have been prepared and tested bacteriologically toward *B. Leprae*. The C_{15} and the C_{17} acids are active but not to such a degree as the previously studied hexadecanoic acids. The C_{19} acids are very slightly bactericidal.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

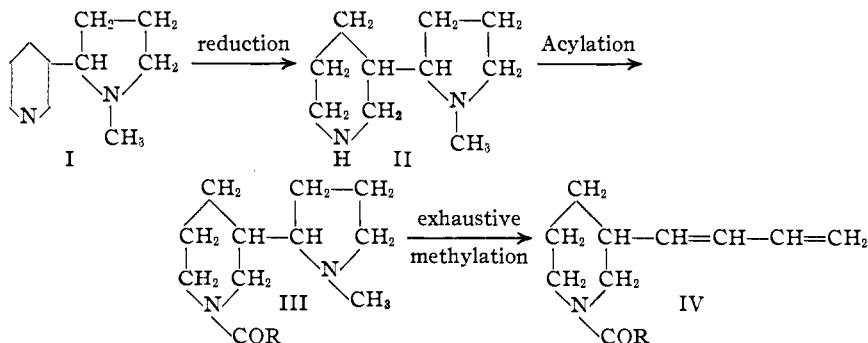
THE REDUCTION OF NICOTINE AND SOME DERIVATIVES OF HEXA- AND OCTAHYDRONICOTINES

BY WALLACE WINDUS AND C. S. MARVEL

RECEIVED MARCH 10, 1930

PUBLISHED JUNE 6, 1930

Nicotine (I) should be the cheapest basic product for the preparation of a piperidine ring with an unsaturated side chain in the beta position (IV), provided the following reactions proceed in the normal manner.



The reduction of nicotine by means of sodium and alcohol was first studied by Liebrecht,¹ who isolated a basic product which he called di-

¹ Liebrecht, *Ber.*, **18**, 2969 (1885); **19**, 2587 (1886).