heated to from 80° to 100°. By means of a series of experiments at different temperatures within this range, the influence of temperature in accelerating the velocity of decomposition of the halogenoid may be strikingly demonstrated. In every case the sample may be observed to undergo incipient fusion and partial decomposition with evolution of gas before it explodes. The explosion usually consists of little more than a crackling or sputtering sound. The interval elapsing between the time of contact with the hot water and the time of explosion varies from about 10 to 12 seconds at 80°, to 4 to 6 at 85°, 2 to 3 at 90°, 1.5 to 2.5 at 95° and 1.0 to 1.5 at 100°.

(c) Arrange four portions of azido-carbondisulfide weighing approximately 0.02, 0.05, 0.15 and 0.4 g. about 10 cm. apart in a straight line on a wooden board. Direct a gentle stream of ammonia gas upon the samples in rapid succession, preferably beginning with the smallest. A series of explosions of increasing intensity will ensue.

Summary

The present article contains a brief description of several lecture experiments upon azido-carbondisulfide, $(SCSN_3)_2$, which serve to demonstrate (1) its halogenoid character, on the basis of its reaction with (a) sodium hydroxide, (b) potassium iodide and (c) silver nitrate; (2) its thermal decomposition, with formation of free thiocyanogen; (3) its sensitivity to (a) mechanical impact, (b) heat and (c) the chemical action of ammonia gas.

ITHACA, NEW YORK

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

OMEGA-CYCLOHEXYL DERIVATIVES OF VARIOUS NORMAL ALIPHATIC ACIDS. IV

BY G. S. HIERS[1] WITH ROGER ADAMS

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

In a recent paper[2d] it was pointed out that the cyclic structure present in chaulmoogric and hydnocarpic acids was, among others, an important factor in the bactericidal effect of these acids on *B. leprae*. As a consequence other acids containing a cyclic structure in the omega position have been studied. The κ-cyclohexyl-undecanoic acid and the μ-cyclohexyltridecanoic acid were described in a previous paper.[2d] This investigation

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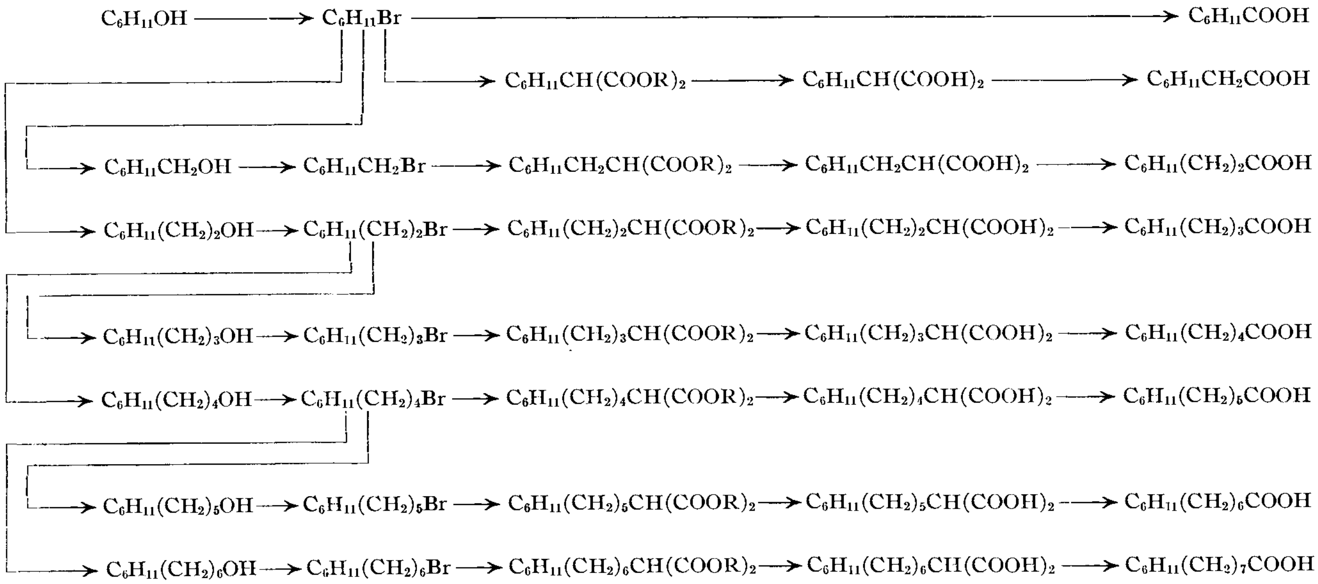
[1] This communication is an abstract of a portion of a thesis submitted by G. S. Hiers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] For previous papers in this field see (a) Shriner with Adams, THIS JOURNAL, **47,** 2727 (1925). (b) Noller with Adams, *ibid.*, **48,** 1074; (c) 1080 (1926). (d) Hiers with Adams, *ibid.*, **48**, 1089 (1926).

TABLE I

PREPARATION OF ω-CYCLOHEXYL ACIDS



describes the completion of the synthesis of all of the ω-cyclohexyl acids containing from 1 to 13 carbon atoms in the side chain.

The hexahydrobenzoic acid was prepared merely by the action of carbon dioxide on the Grignard reagent from cyclohexyl bromide. All the other acids containing from two to eight carbon atoms inclusive in the side chain were made by the malonic ester synthesis from the proper bromide; the bromides were in turn prepared from the corresponding alcohols. Cyclohexyl bromide was converted into the Grignard reagent and treated either with formaldehyde to give cyclohexyl-carbinol or with ethylene oxide to give β-cyclohexyl-ethanol. These alcohols were then converted into their bromides and condensed with malonic ester to give the 3- and 4-carbon side-chain acids. The β-cyclohexylethyl bromide was converted to the Grignard reagent and with formaldehyde or ethylene oxide yielded γ-cyclohexyl-propanol or δ-cyclohexyl-butanol, respectively; by conversion to the bromides and condensation with malonic ester, the 5- and 6-carbon side-chain acids were obtained. By a similar procedure δ-cyclohexylbutyl bromide was converted to ε-cyclohexylpentyl bromide and ζ-cyclohexylhexyl bromide and these to the 7- and 8-carbon side-chain acids. These reactions are summarized in Table I.

The acids with side chains having more than 8 carbon atoms were prepared by the condensation of the proper Grignard reagent with the aldehyde esters obtained by the ozonation of methyl oleate, methyl undecylenate or methyl erucate.[2b] The 9-carbon side-chain acid was obtained from cyclohexyl bromide and methyl η-aldehydo-octanoate, the 10-carbon side-chain acid from cyclohexyl bromide and methyl θ-aldehydo-nonanoate, the 11-carbon side-chain acid from β-cyclohexylethyl bromide and methyl η-aldehydo-octanoate, the 12-carbon side-chain acid from β-cyclohexylethyl bromide and methyl θ-aldehydo-nonanoate and finally the 13-carbon side-chain acid from cyclohexyl bromide and methyl λ-aldehydo-dodecanoate. The hydroxy esters thus produced were changed to the oxygen free acids by conversion of the hydroxy esters into the bromides, then to the unsaturated acids and finally to the saturated acids.

The bacteriological results will be reported in detail elsewhere. It is sufficient to mention here that β-cyclohexyl-propionic acid which has a 3-carbon side-chain did show a slight action against the *B. leprae* and other acid-fast bacteria, killing in a concentration of 1:1000. With increase in length of side chain the substances rapidly became more effective until a maximum was reached in the 9-carbon side chain and then again diminished in effectiveness until it appeared only slight in the 13-carbon side-chain acid. The hydroxy acids containing 12- and 13-carbon side chains were far more effective than the corresponding acids without the hydroxyl group. The malonic acid derivatives showed almost no action. These tests were kindly made by Mr. G. H. Coleman.

Experimental Part

Preparation of Alcohols by the Use of a Grignard Reagent and Formaldehyde.—By the reaction of the proper Grignard reagent and formaldehyde, cyclohexyl-methanol,[3] γ-cyclohexyl-propanol[4] and ε-cyclohexyl-pentanol were prepared; the amounts of the bromides for each run employed in the syntheses were 163 g. of cyclohexyl bromide, 105 g. of β-cyclohexylethyl bromide and 81.5 g. of δ-cyclohexylbutyl bromide, with the proper amounts of other reagents. The yields were 71–76, 79 and 58%, respectively.

The reaction was carried out by leading the formaldehyde under the surface of the Grignard solution which was efficiently stirred while the reaction was taking place. The formaldehyde was prepared from paraformaldehyde which had been previously dried for three days over phosphorus pentoxide. The dry paraformaldehyde was heated to 160–180° for about two hours in a round-bottomed flask carrying a delivery tube to the reaction mixture. The amount of paraformaldehyde used was about twice the calculated quantity and the excess that entered the reaction mixture did no harm. The reaction product was refluxed for an hour longer. The product was carefully decomposed in the usual way with 30% sulfuric acid and ice.

Preparation of Alcohols by the Use of a Grignard Reagent and Ethylene Oxide.—By the condensation of the proper Grignard reagent and ethylene oxide, β-cyclohexyl-ethanol,[2d] δ-cyclohexyl-butanol and ζ-cyclohexyl-hexanol were prepared; the amounts of bromide employed in individual runs were 489 g. of cyclohexyl bromide, 191 g. of β-cyclohexylethyl bromide and 43.8 g. of δ-cyclohexyl bromide, respectively, and the yields of product amounted to 52, 47–53 and 37%.

The procedure[2d] has been described in detail in a previous paper. The maximum yield was obtained when the temperature of rearrangement was 60–65°. In general, after the initial reaction had been run, the ether was distilled and benzene was added at such a rate as to keep the volume constant until the temperature of rearrangement was reached. Then the reaction mixture was refluxed for one to two hours.

Preparation of the Cyclohexyl Alkyl Bromides.—The formation of the bromides from the alcohols was best carried out either with hydrobromic acid and sulfuric acid or with phosphorus tribromide. The former was more suitable for β-cyclohexylethyl bromide[2d] and γ-cyclohexylpropyl bromide: in the latter preparation 48 g. of γ-cyclohexyl-propanol was used in individual runs with yields of 77% of product. On the other hand, the phosphorus tribromide method gave better yields in the preparation

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[3] Noller and Adams, "Organic Syntheses," J. Wiley and Sons, New York, **1926**, vol. 6, p. 22.

[4] Skita, *Ber.*, **48**, 1688 (1915).

of cyclohexyl bromide[5] (300g. runs of cyclohexanol with yields of 75–77% of product), cyclohexylmethyl bromide[6] (40g. runs of cyclohexyl-methanol with yields of 60% of product), δ-cyclohexylbutyl bromide, (78g. runs of δ-cyclohexyl-butanol with yields of 74% of product), ε-cyclohexylpentyl bromide (33g. runs of ε-cyclohexyl-pentanol with yields of 74% of product) and ζ-cyclohexylhexyl bromide (13.5g. runs of ζ-cyclohexyl-hexanol with yields of 83% of product).

Table II

Cyclohexyl Substituted Alcohols

Formula	Physical constants B. p., °C.	n_D^{25}	d_4^{25}	Analysis Carbon, % Calcd.	 Found	 Hydrogen, % Calcd.	 Found
$C_6H_{11}OH$[7]	67– 68 (23 mm.)	1.4642	0.9441				
$C_6H_{11}CH_2OH$[8]	88– 89 (22 mm.)	1.4640	.9215				
$C_6H_{11}(CH_2)_2OH$[9]	87– 89 (6 mm.)	1.4636	.9183				
$C_6H_{11}(CH_2)_3OH$[4]	91– 92 (5 mm.)	1.4624	.9061	75.98	75.73	12.77	12.70
$C_6H_{11}(CH_2)_4OH$	103–104 (4 mm.)	1.4632	.9015	76.85	76.62	12.91	12.89
$C_6H_{11}(CH_2)_5OH$	118–119 (4 mm.)	1.4638	.8959	77.56	77.34	13.03	12.98
$C_6H_{11}(CH_2)_6OH$	123–124 (4 mm.)	1.4648	.8963	78.18	77.97	13.13	13.00

The hydrobromic acid-sulfuric acid method was essentially that described by Kamm and Marvel[10] except that 40% hydrobromic acid was used.

The phosphorus tribromide method consisted in cooling the alcohol to —5° and then adding slowly during stirring, so that the temperature did not rise above 0°, 20% excess over one-third of one molecular equivalent of

Table III

ω-Cyclohexyl Substituted Alkyl Halides

Formula	Physical constants B. p., °C.	n_D^{25}	d_4^{25}	Analysis for Br, % Calcd.	 Found
$C_6H_{11}Br$[5a,b, 10]	69–71 (30 mm.)	1.4917	1.3128		
$C_6H_{11}CH_2I$[6]	106–108 (26 mm.)	1.4922	1.3751		
$C_6H_{11}CH_2Br$[6]	76–77 (26 mm.)	1.4889	1.2690	45.15	44.78
$C_6H_{11}(CH_2)_2Br$	70.5–71 (6 mm.)	1.4862	1.2096	41.83	41.58
$C_6H_{11}(CH_2)_3Br$	77–79 (4 mm.)	1.4848	1.1521	39.17	38.92
$C_6H_{11}(CH_2)_4Br$	91.6–92.2 (4 mm.)	1.4832	1.1350	36.65	36.24
$C_6H_{11}(CH_2)_5Br$	113–114 (5 mm.)	1.4814	1.1198	34.44	34.03
$C_6H_{11}(CH_2)_6Br$	124–125 (4 mm.)	1.4802	1.1073	32.47	32.25

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[5] (a) Freundler and Damond, *Compt. rend.*, **141**, 594 (1905). (b) Kohler and Burnley, *Am. Chem. J.*, **43**, 413 (1910).

[6] (a) Freundler, *Compt. rend.*, **142**, 344 (1906). (b) *Bull. soc. chim.*, [3] **35**, 544 (1906).

[7] (a) Frydlender, *Rev. prod. chim.*, **23**, 719 (1920). (b) Skrauth, *Z. angew. Chem.*, **35**, 25 (1922).

[8] Sabatier and Mailhe, *Compt. rend.*, **139**, 344 (1904).

[9] Zelinsky, *Ber.*, **41**, 2628 (1908).

[10] Kamm and Marvel, "Organic Syntheses, J. Wiley and Sons, New York, **1921**, vol. 1, p. 1.

pure phosphorus tribromide. The mixture was stirred at room temperature for two hours, then at 100° for one hour. Upon cooling, the product was extracted thrice with low-boiling petroleum ether, this extract washed with water, dried with calcium chloride and then washed once with a little cold, concd. sulfuric acid, dried again and distilled under diminished pressure.

Hexahydrobenzoic Acid.—This was prepared by the general procedure described by Gilman[11] from 571 g. of cyclohexyl bromide, 85 g. of magnesium and 1 liter of ether. There was obtained on the average 309–313 g. (69–70%) of hexahydrobenzoic acid.

Cyclohexyl Alkyl Malonic Esters.—The condensation of the cyclohexyl alkyl bromides with malonic ester was carried out in the usual way, taking particular care to have a high grade of absolute alcohol and to distil on a steam-bath, after the reaction had taken place, as much alcohol as possible before diluting the reaction mixture with water. It was generally desirable finally to extract the ester with a little ether as it did not always separate well from the aqueous suspension.

Cyclohexyl Alkyl Malonic Acids.[12]—These were prepared by adding the ester slowly during stirring to a hot 50% potassium hydroxide solution. The mixtures were then heated for eight hours on a steam-bath to distil all of the alcohol produced by saponification, then cooled and acidified with hydrochloric acid using Congo red paper as an indicator. During neutralization, the temperature was kept below 20°. The malonic acids were extracted with ether, the ether was evaporated and the products were purified from benzene.

TABLE IV

ω-CYCLOHEXYL SUBSTITUTED MALONIC ESTERS

Formula ($R = CO_2C_2H_5$)	Preparation Bromide used, g.	Preparation Yield of ester, %	Physical constants B. p., °C.	Physical constants n^{25}_D	Physical constants d^{25}_4	Analysis Carbon, % Calcd.	Analysis Carbon, % Found	Analysis Hydrogen, % Calcd.	Analysis Hydrogen, % Found
$C_6H_{11}CH(R_2)$[a]	62	44	122–123 (4 mm.)	1.4478	1.0228				
$C_6H_{11}CH_2CH(R_2)$[b]	24	71	135–136 (3 mm.)	1.4469	1.0059	65.58	65.32	9.44	9.51
$C_6H_{11}(CH_2)_2CH(R_2)$	32	50	139.8–140.2 (3 mm.)	1.4476	0.9956	66.61	66.53	9.70	9.69
$C_6H_{11}(CH_2)_3CH(R_2)$	42	53	153.5–154 (4 mm.)	1.4489	.9870	67.55	67.35	9.93	10.04
$C_6H_{11}(CH_2)_4CH(R_2)$	22	85	169–170 (5 mm.)	1.4500	.9787	68.40	68.18	10.14	9.98
$C_6H_{11}(CH_2)_5CH(R_2)$	30	79	186–187 (6 mm.)	1.4509	.9717	69.17	69.06	10.33	10.28
$C_6H_{11}(CH_2)_6CH(R_2)$	26	63	192–193 (4 mm.)	1.4522	.9647	69.88	69.69	10.50	10.40

[a] Ref. 6 a.

[b] Ref. 10.

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[11] Gilman and Parker, "Organic Syntheses," J. Wiley and Sons, New York, **1925,** vol. 5, p. 75.

[12] (a) Hope and Perkin, *J. Chem. Soc.*, **95,** 1363 (1909). (b) Sabatier and Murat, *Compt. rend.*, **156,** 426 (1913). Ref. 6. (c) J. Gutt, *Ber.*, **40,** 2067 (1907).

Decomposition of Cyclohexyl Alkyl Malonic Acids to Monobasic Acids.[13]—The malonic acids were heated in a small, round-bottomed flask at a temperature 20–30° above the melting point for two to three hours. The resulting acids were then distilled under diminished pressure. The yields are based on distilled product.

TABLE V

CYCLOHEXYL SUBSTITUTED MALONIC ACIDS

		Physical constants			Analysis			
					Carbon, %		Hydrogen, %	
Formula	Yield, %	M. p., °C.	Neut. equiv., found	Mol. wt., calcd.	Calcd.	Found	Calcd.	Found
$C_6H_{11}CH(CO_2H)_2$[a]	97	183–184	186.4	186.11				
$C_6H_{11}CH_2CH(CO_2H)_2$[b]	95	114–115	200.9	200.13	59.96	59.62	8.06	7.86
$C_6H_{11}(CH_2)_2CH(CO_2H)_2$	84	129–130	214.2	214.14	61.64	61.24	8.47	8.22
$C_6H_{11}(CH_2)_3CH(CO_2H)_2$	92	88–89	229.8	228.16	63.11	62.89	8.83	8.70
$C_6H_{11}(CH_2)_4CH(CO_2H)_2$	97	118–119	242.6	242.18	64.42	64.19	9.15	9.07
$C_6H_{11}(CH_2)_5CH(CO_2H)_2$	93	111–112	257.7	256.19	65.58	65.31	9.44	9.22
$C_6H_{11}(CH_2)_6CH(CO_2H)_2$	94	114–115	271.0	270.21	66.61	66.27	9.70	9.61

[a] Melting point reported as 176–178°. See Ref. 12 a.

[b] Melting point reported as 106.5°. See Ref. 13.

The Formation of Cyclohexyl Substituted Acids by the Condensation of the Proper Grignard Reagent with Various Aldehyde Esters.[14]—The general procedure for such condensations has been described in a previous paper.[2d]

θ-Cyclohexyl-θ-hydroxy-nonanoic Acid, θ-Cyclohexyl-nonanoic Acid.—From 80 g. of methyl η-aldehydo-octanoate[2b] and cyclohexylmagnesium bromide there was obtained after three fractional distillations 25 g. (23%) of methyl θ-cyclohexyl-θ-hydroxy-nonanoate; b. p., 186–192° at 5 mm. This was converted into the hydroxy acid by boiling with aqueous alcoholic potassium hydroxide. The hydroxy ester was converted into θ-cyclohexyl-nonanoic acid through the bromide and olefinic acid. No attempt was made to purify completely these last two intermediates. The final acid was purified by crystallization from 80% alcohol.

ι-Cyclohexyl-ι-hydroxy-decanoic Acid, ι-Cyclohexyldecanoic Acid.—From 48 g. of methyl θ-aldehydo-nonanoate[2b] and cyclohexylmagnesium bromide there was obtained after four fractional distillations 15.4 g. (23%) of methyl ι-cyclohexyl-ι-hydroxy-decanoate; b. p., 191–195° at

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[13] Zelinsky, *Ber.*, **41,** 2676 (1908).

[14] (a) Sabatier and Murat, *Compt. rend.*, **156,** 752 (1913). (b) Fokin and Willstätter, *Rec. trav. chim.*, **35,** 261, 285 (1916). (c) Ipatiew, *Ber.*, **42,** 2098 (1909).

4 mm. This was saponified and the corresponding hydroxy acid crystallized from acetone. The hydroxy ester was converted into ι-cyclohexyldecanoic acid which was purified from 70% alcohol and then from low-boiling petroleum ether.

λ-Cyclohexyl-ι-hydroxy-dodecanoic Acid, λ-Cyclohexyl-dodecanoic Acid.—From 47 g. of methyl θ-aldehydo-nonanoate[2b] and β-cyclohexylethylmagnesium bromide there was obtained after three fractional distillations 10 g. (14%) of methyl λ-cyclohexyl-ι-hydroxy-dodecanoate, b. p., 214–218° at 4 mm. The corresponding hydroxy acid proved to be difficult to purify. The hydroxy ester was converted into λ-cyclohexyl-dodecanoic acid which was crystallized from 75% alcohol, then from petroleum ether.

Table VI

ω-Cyclohexyl Substituted Hydroxy Fatty Acids

Formula	Physical constants			Analysis			
	M. p., ° C.	Neut. equiv., found	Mol. wt. calcd.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$C_6H_{11}CHOH(CH_2)_7CO_2H$	78–79	254.2	256.22	70.25	69.97	11.02	10.94
$C_6H_{11}CHOH(CH_2)_8CO_2H$	63–64	267.2	270.24	71.05	70.84	11.19	11.23
$C_6H_{11}(CH_2)_2CHOH(CH_2)_7$-$CO_2H$	75–76[2d]						
$C_6H_{11}(CH_2)_2CHOH(CH_2)_8$-$CO_2H$[a]	58–59	291.1	298.27				
$C_6H_{11}CHOH(CH_2)_{11}CO_2H$	72–73[2d]						

[a] The substance was difficult to purify and was, therefore, converted directly into the hydroxyl free acid.

Table VII

ω-Cyclohexyl Substituted Fatty Acids

Acid[a] R(R')nCOOH[a]	Yield, %	B. p., °C. 4 mm.	M. p., °C.	n^{36}_D 1.—	d^{38}_4	Neut. equiv. found	Mol. wt. calcd.	Analyses C., % Calcd.	C., % Found	H., % Calcd.	H., % Found
R[b]	70	105–6	29–30	4520	1.0251	128.3	128.1				
RR'[c]	88	116–7	29–30	4537	1.0020	141.5	142.1				
RR'_2[d]	88	125–6	15–16	4553	0.9848	154.9	156.1				
RR'_3	85	132–4[e]	29–30	4562	.9693	169.8	170.1	70.53	70.45	10.67	10.63
RR'_4	82	151–3[f]	6–8	4570	.9589	184.2	184.2	71.68	71.52	10.95	10.87
RR'_5	91	157–8	33–34	4580	.9506	196.5	198.2	72.66	72.58	11.19	11.13
RR'_6	93	171–2	25–26	4588	.9436	211.5	212.2	73.52	73.29	11.40	11.66
RR'_7	88	182–3	37–38	4598	.9359	224.3	226.2	74.27	74.01	11.59	11.32
RR'_8	..	...	45.5–6.5	...	...	242.2	240.2	74.93	75.10	11.75	11.80
RR'_9	..	...	52.5–3.5	...	...	253.6	254.2	75.52	75.70	11.89	11.74
RR'_{10}	..	...	58–59	...	...	267.1	268.2	...	...	...	...
RR'_{11}	..	...	61.5–2	...	...	280.2	282.3	76.52	76.36	12.14	12.07
RR'_{12}	..	...	63–64	...	...	297.9	296.3	...	...	...	...

[a] $R = C_6H_{11}$; $R' = CH_2$.

[b] Refs. 15, 11.

[c] Refs. 6 a, 12 a, 12 c.

[d] Refs. 10, 14 a.

[e] 3 mm. pressure.

[f] 5 mm. pressure.

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[15] Godchat, *Bull. soc. chim.*, [4] 9, 261 (1911). Grignard and Billet, *Compt. rend.*, **155**, 46 (1912).

Summary

1. A series of ω-cyclohexyl acids containing from 1 to 13 carbon atoms in the side chain have been prepared.

2. Those with from three to nine carbon atoms in the side chain show bactericidal action toward *B. leprae.*

3. A number of hydroxy-substituted acids of the above-mentioned series, formed as intermediates, also show bactericidal action.

URBANA, ILLINOIS

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

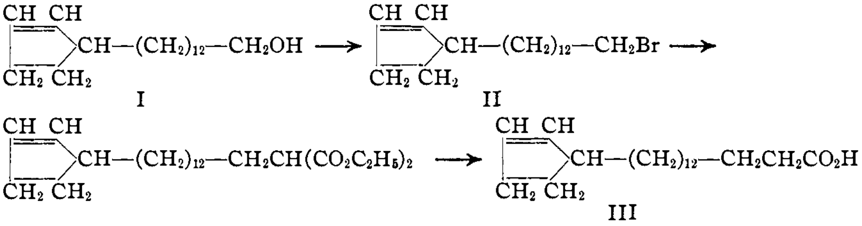
SYNTHESIS OF CHAULMOOGRYLACETIC ACID. V

BY RUSSEL H. VANDYKE[1] AND ROGER ADAMS

RECEIVED JUNE 7, 1926 PUBLISHED SEPTEMBER 4, 1926

Although it has been known for several years that hydnocarpic and chaulmoogric acids have a specific action against *B. leprae,* very few derivatives or compounds closely related to these two acids have been synthesized and studied. This paper describes the salts of chaulmoogryl acetic acid. Incidentally, the intermediates necessary for this synthesis are valuable for producing other compounds in which the chaulmoogryl nucleus is present.

The procedure was to esterify pure chaulmoogric acid to the ethyl ester. This latter compound was reduced to chaulmoogryl alcohol I by means of sodium and alcohol. The alcohol was converted to the bromide II and the bromide to chaulmoogrylacetic acid III by a malonic ester synthesis.



I II III

Experimental Part

Ethyl Chaulmoograte.—This was prepared according to the method of Power and Gornall.[2]

Chaulmoogryl Alcohol.—The reduction of ethyl chaulmoograte was attempted under a variety of conditions. The best yield was obtained by following the general procedure of Grün and Wirth.[3]

A 2-liter, round-bottom, 3-neck flask, fitted with a mechanical stirrer and long condenser was used. A solution of 70 g. of ethyl chaulmoograte in 230 cc. of absolute al-

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[1] This paper is an abstract of a portion of a thesis submitted by R. H. VanDyke in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Illinois.

[2] Power and Gornall, *J. Chem. Soc.,* **85,** 838 (1904).

[3] Grün and Wirth, *Ber.,* **55,** 2206 (1922).