OPTICAL ACTIVITY OF MALAMIDE. 1859

CLXXX.—The Influence of various Substituents on the Optical Activity of Malamide.

By PERCY FARADAY FRANKLAND and EDWARD DONE, M.Sc.

THE results recorded in this paper form part of a systematic investigation which is being made by one of us on the rotation of the amides of optically active acids, in connexion with which papers have already appeared on some substitution derivatives of glyceramide (P. Frankland, Wharton, and H. Aston, Trans., 1901, 79, 266), and of tartramide (P. Frankland and Slator, Trans., 1903, 83, 1349; Ormerod, Trans., 1903, 83, 1342; and Twiss, preceding paper).

The present communication deals with the methylamide, ethylamide, normal- and *iso*-propylamide, allylamide, normal- and *iso*-butylamide, and normal heptylamide of ordinary *l*-malic acid, as well as with the piperidide, and phenylhydrazide of the same acid.

Of these derivatives, only the *n*-propylamide has been previously prepared (McCrae, Trans., 1903, 83, 1324), whilst the anilide and the three toluidides have been described by Guye and Babel (*Arch. Sci. phys. nat.*, 1899 [iv], 7, 23), and by Walden (*Zeit. physikal. Chem.*, 1895, 17, 264).

The alkylamides were all prepared by the interaction of the amine with diethylmalate, either alone or in alcoholic solution, and either in the cold or at a temperature not exceeding 100°. The yields were in most cases, and especially in the case of the higher amines in which no alcohol was used, very satisfactory. As in the corresponding

1860 FRANKLAND AND DONE: THE INFLUENCE OF VARIOUS

derivatives of tartramide, the poorest yield was obtained in the case of the *iso*propylamide.

The piperidide was prepared by the prolonged heating of diethylmalate with piperidine at 130° , whilst the phenylhydrazide was prepared, on the one hand by Bülow's method, in which malic acid and phenylhydrazine are heated together at $120-140^{\circ}$, and, on the other, by Fischer and Passmore's method, in which an aqueous solution of malic acid is heated on the water-bath with a solution of phenylhydrazine in acetic acid. The products obtained by each of these methods had substantially the same rotation, showing that no racemisation occurs at the higher temperature to which the mixture is heated in the case of Bülow's method.

The rotation was in all cases, excepting that of the phenylhydrazide, determined in pyridine, in methyl alcohol, and in glacial acetic acid solution. The rotation of the phenylhydrazide was determined in pyridine and in glacial acetic acid only, in consequence of its insolubility in methyl alcohol.

The results of the polarimetric determinations are summarised in the following table :---

		Malting	Pyri	dine.	Methy	l alcohol.	Gl aceti	acial c acid.
		point.	p.	[M] ^{20°} .	<i>p</i> .	[M] ^{20°} .	<i>p</i> .	[M] ^{20°}
Maldi	-amide *	157°	c = 1.998	-76·2°) <u> </u>		c=4.678	- 59.7
,,	methylamide	99	4.634	89.6	6.250	-109.6°	4.267	120.9
	•		10.080	90 .0	9.982	107.9	8.185	117.2
,,	ethylamide	122	4.319	90 ·6	4.984	110.3	4 170	116.0
	-		10.250	89.1	9.177	111.8	7.995	117.2
,,	<i>n</i> -propylamide .	126	4.530	90.5	5.020	114.3	4.278	115.4
			7.896	8.88	11.340	114.7	5.040	114.8
							9.048	112.8
,,	isopropylamide.	150-151	2.548	69·1	3.803	92.0	3.710	92.1
			3.986	69.0	6.039	90·3	6.284	92.5
,,	allylamide	117.5	4.639	72.7	4.804	102.5	4.492	86.9
			10.390	74.0	9.092	103.3	10.780	87.4
,,	<i>n</i> -butylamide	125	3.776	87·1	5.633	116.5	5.455	106.4
			10.850	86.3	10.540	112.0	9.718	104.9
,,	isobutylamide	121	5.394	86.9	5.316	117.4	5.492	106.2
	•		7 984	89.4	9.128	118.4	7.563	105.3
,,	n-heptylamide	131	5.166	88.6	6.001	116.1	4.492	103.2
			11.010	88.8			9.334	102.3
,,	benzylamide *	155.5	c = 4.855	101.1			c = 4.654	63 [.] 0
,,	piperidide	157.5	0.2981	55-2	4.975	73·7	3.575	+ 38 5
					8.845	73.6	6.531	+40.5
,,	phenylhydrazide	214	5.119	54.1			0.735	- 1 29 <i>`</i> 8
			7.175	55.0				

* McCrae (*loc. cit.*). In the case of the *n*-propylamide prepared by McCrae, our results corroborate those obtained by this author with pyridine solution, but our values, given in this table, for the glacial acetic acid solution of the *n*-propylamide are substantially higher than his, $[M]_{19}^{199} - 101^{-30}$, c=4.798. The temperatures at which McCrae's determinations were made were 20° for maldiamide in glacial acetic acid, and 15° in pyridine ; 22° for the dibenzylamide in glacial acetic acid, and 15° in pyridine.

SUBSTITUENTS ON THE OPTICAL ACTIVITY OF MALAMIDE. 1861

From the above table it will be seen how greatly the rotation is influenced by the solvent. Thus the alkylamides have a lower lævorotation in pyridine than in methyl alcohol or glacial acetic acid; on the other hand, the benzylamide and the aromatic amides have a higher lævorotation in pyridine than in glacial acetic acid solution. Again, whilst in the normal series of alkylamides in pyridine solution the lævorotation is almost unaffected in passing from the methylamide to the *n*-heptylamide, in methyl alcohol there is a slight rise, and in glacial acetic acid solution a distinct decline in the molecular rotation. The derivatives of malamide in this respect exhibit much less regularity than those of tartramide (compare Frankland and Twiss), for in the latter series there is a continuous rise in the molecular rotation from the methyl to the heptyl term in the normal series in pyridine, and probably also in methyl alcohol and in water solution.

In both the malic and the tartaric series the rotation of the normalis greater than that of the *iso*-propylamide, whilst the relative magnitudes of the rotation of the normal- and *iso*-butylamides in both series is dependent on the solvents, but in pyridine solution the *iso*butylamide, both malic and tartaric, has a higher rotation than the normal butylamide.

In both the malic and the tartaric series, the allylamide has a markedly lower molecular rotation, in all solvents, than the normal propylamide, thus showing that the presence of a double bond has not the invariable effect of increasing the optical activity as is often supposed.

Malic benzylamide, in pyridine solution, has a higher molecular rotation than the *n*-heptylamide in the same solvent, whilst in glacial acetic acid the relations are reversed. On the other hand, in pyridine solution, the molecular rotation of tartaric benzylamide is slightly inferior to that of the *n*-heptylamide.

The tartaric piperidide in pyridine solution is practically inactive, and therefore enormously less active than the *n*-heptylamide; similarly, the malic piperidide, in pyridine and in the methyl alcohol, is much less active than the *n*-heptylamide, although still strongly lævorotatory; in glacial acetic acid the difference is greatly further emphasised inasmuch as the piperidide is strongly dextrorotatory.

The phenylhydrazide, again, in both malic and tartaric series, has in pyridine solution a much lower molecular rotation than the *n*-heptylamide, but in glacial acetic acid solution malic diphenylhydrazide has a higher rotation than the heptylamide. We have also found that the rotation of tartaric diphenylhydrazide is much greater in glacial acetic acid than in pyridine solution (see Frankland and Twiss).

In both malic and tartaric series, again, the aromatic amides have a much higher molecular rotation than the alkylamides.

EXPERIMENTAL.

Maldimethylamide.

Twelve grams of diethyl malate and 21 grams of absolute alcohol were placed in a tall cylindrical bottle immersed in ice. Methylamine was liberated from Kahlbaum's 33 per cent. aqueous solution by heat, passed through a lime drying-tube, and then into the above mixture. When 6 grams of methylamine had been thus passed in, the bottle was stoppered and allowed to stand for three days. On evaporating the alcohol a yield of 50 per cent. was obtained.

The methylamide is very soluble in hot or cold water, methyl alcohol, glacial acetic acid, methylated spirit, ethyl acetate, or pyridine, sparingly so in chloroform, benzene, or ether, and insoluble in carbon disulphide or light petroleum. From acetone it was obtained in acicular prisms and plates melting at 99°.

0.1047 gave 15.4 c.c. moist nitrogen at 11° and 762 mm. N = 17.60. $C_6H_{12}O_3N_2$ requires N = 17.50 per cent.

Rotation of Maldimethylamide

p .	$d \ 20^{\circ}/4^{\circ}$.	I.	$a_{p}^{20^{\circ}}$.	$[\alpha]^{20^{\circ}}_{D}$.	[M] ^{20°} .			
		Pyridin	ne Solution.					
4.634	0.987	1.9984	- 5·12°	- 56·01°	- 89 ·6 °			
10.080	1.001	1.9984	11.35	56.27	90.0			
		Methyl Al	cohol Soluti	on.				
6.250	0.8143	1.9984	- 6·97°	68·50°	- 109.6°			
9 982	0.8280	1.9984	11.14	67.42	107.9			
	Gl	lacial Aceti	ic Acid Solı	ution.				
4.267	1.060	1.9984	- 6.83°	- 75·54°	- 120·9°			
8.185	1.070	1.0084	19.83	78.96	117.9			

Maldiethylamide.

Seven grams of ethylamine (Kahlbaum) in the form of vapour were passed into a mixture of 11 grams of diethyl malate and 13 grams of absolute alcohol cooled with a freezing mixture. On standing for some days in a stoppered bottle, the whole set into a solid mass of fine white, silky needles. Yield 90 per cent.

The ethylamide is very soluble in hot or cold water, methylated spirit, chloroform, pyridine, methyl alcohol, ethyl acetate, light petroleum, or

SUBSTITUENTS ON THE OPTICAL ACTIVITY OF MALAMIDE. 1863

carbon disulphide. From benzene it was obtained as white, shining plates and needles melting at 122°.

0.1067 gave 14.0 c.c. moist nitrogen at 12° and 735.1 mm. N = 15.05. $C_8H_{16}O_8N_2$ requires N = 14.89 per cent.

Rotation of Maldiethylamide.								
p.	$d \ 20^{\circ}/4^{\circ}$.	l.	$\pmb{\alpha}_{\mathrm{p}}^{20}$.	[α] ²⁰ [°] .	$[M]_{D}^{20^{\circ}}$.			
		Pyridin	e Solution.					
4·319 10·250	0 9854 0 9947	$1.9984 \\ 1.9984$	- 4·10° 9·66	-48.19° 47.41	- 90.6° 89.1			
		Methyl Al	cohol Soluti	o n .				
4·984 9·177	0.8054 0.8185	1·9984 1·9984	- 4.71° 8.93	- 58·69° 59·47	- 110·3° 111·8			
	Gi	lacial Acet	ic Acid Solv	ution.				
4·170 7·995	1.056 1.060	1·9984 1·9984	- 5·43° 10·56	- 61·70° 62·34	- 116·0° 117·2			

Maldi-n-propylamide.

Twelve grams of diethylmalate were added to 8 grams of n-propylamine (Kahlbaum), heat being evolved on mixing. On standing overnight the mixture had become almost solid. Yield 75 per cent. In order to obtain a theoretical yield, it is necessary to allow the mixture to stand for several days, or to heat on a warm water-bath for some hours.

The propylamide (m. p. 126°) is very soluble in water, benzene, alcohol, ethyl acetate, chloroform, pyridine, methyl alcohol, or glacial acetic acid, but insoluble in light petroleum or ether. It was purified by crystallisation from a mixture of benzene and light petroleum.

	Rota	tion of Mo	uldi-n - propy	lamide.	
v.	$d \ 20^{\circ}/4^{\circ}$.	l.	$a_{\mathbf{p}}^{20^{\circ}}$.	$[\alpha]^{20^{\circ}}_{p}$.	[M] ^{20°} .
		Pyridi	ne Solution.		
4.530	0.9833	1.9984	– 3·73°	- 41.90°	- 90.2°
7.896	0.9895	1.9984	6.42	41.11	88.8
		Methyl Al	cohol Soluti	on.	
5.020	0.8061	1.9984	-4·28°	-52.91°	- 114·3°
11.340	0.8260	1.9984	9.94	53.10	114.7
	G	lacial Acet	ic Acid Solu	tion.	
4.278	1.023	1.9984	-4.81°	– 53·43°	~ 115·4°
5.040	1.052	1.9984	5.63	53.14	114.8
9.048	1.055	1.9984	9.96	52.20	112.8

1864 FRANKLAND AND DONE: THE INFLUENCE OF VARIOUS

Maldiisopropylamide.

10.7 grams of diethylmalate were added to a solution of 5.8 grams of *iso*propylamine (Kahlbaum) in 8.4 grams of absolute alcohol, but the reaction takes place so slowly in the cold that even after five weeks only a small quantity of the amide had crystallised out. The mixture was therefore heated in a stoppered bottle in a steam oven for six days. The yield was only 20 per cent. The substance is very soluble in hot water, alcohol, ether, acetic acid, pyridine, methyl alcohol, benzene, ethyl acetate, or acetone, but crystallises from each of these solutions on cooling. It is insoluble in light petroleum, and only very slightly soluble in carbon disulphide. It crystallises from acetone in long, slender needles melting at $150-151^{\circ}$.

0.1355 gave 15.7 c.c. moist nitrogen at 15° and 738.4 mm. N = 13.17. $C_{10}H_{20}O_8N_2$ requires N = 12.96 per cent.

Rotation of M	Ialdi isopro	pylamide.
---------------	--------------	-----------

p.	$d 20^{\circ}/4^{\circ}$.	<i>l</i> .	$a_{p}^{20^{\circ}}$.	[α] ^{20°} .	[M] ^{20°} .
		Pyridin	ne Solution.		
2.548	0.9813	1.9984	-1.60°	-32.01°	- 69·1°
3.986	0.9828	0.999	1.25	31.93	69.0
		Methyl Al	cohol Soluti	on.	
3.803	0.8032	1.9984	- 2.60°	- 42·57°	– 92·0°
6.039	0.8091	0.999	2.04	41.79	90.3
	G	lacial Acet	ic Acid Solu	tion.	
3.710	1.020	0.999	1 .66°	-42.65°	- 92·1°
6.284	1.056	0.999	2.84	42.83	92.5

Maldiallylamide.

11.1 grams of diethylmalate were mixed with 6.4 grams of allylamine (Kahlbaum) and 8.4 grams of absolute alcohol. Heat was developed on mixing, and, after standing for two days, a nucleus was obtained by placing a little of the mixture in a vacuum desiccator. On adding this nucleus to the remainder, and allowing to stand for a few days longer, a crop of pure white needles separated out from which the alcohol was evaporated. Yield 90 per cent. The allylamide is very soluble in hot or cold water, methyl alcohol, methylated spirit, ethyl acetate, chloroform, glacial acetic acid, or benzene. It is almost insoluble in light petroleum. From a mixture of benzene and light petroleum it was obtained in needles melting at 117.5° .

0.1438 gave 16.3 c.c. moist nitrogen at 12° and 752.8 mm. N = 13.32. C₁₀H₁₆O₃N₂ requires N = 13.21 per cent.

87.4

SUBSTITUENTS ON THE OPTICAL ACTIVITY OF MALAMIDE. 1865

41.22

	n	otation of 2	matananyta	mae.	
ข.	d 20°/4°.	1.	$a_{\mathrm{p}}^{20^{\circ}}$.	$[\alpha]^{20^{\circ}}_{D}.$	$[M]_{\nu}^{20^{\bullet}}$.
		Pyridin	e Solution.		
4.639	0.9837	1.9984	– 3·13°	- 34·31°	-72.7°
10.390	0 9936	1.9984	7.20	34.89	74.0
		Methyl Al	cohol Soluti	on.	
4.804	0.8056	1.9984	– 3·74°	- 48·35°	-102.5°
9.092	0.8174	1.9984	7.24	48.72	103.3
	G	lacial Acet	ic Acid Solv	ction.	
4.492	1.060	1.9984	- 3.90°	- 40·99°	- 86·9°

Maldi-n-butylamide.

9.45

1.9984

1.064

10.780

10.2 grams of diethyl malate were mixed with 7.8 grams of normal butylamine (Kahlbaum). Heat was developed on mixing, and, after standing overnight the whole had set solid. The mixture was allowed to stand for a few days longer. Yield 100 per cent.

The *n*-butylamide is very soluble in alcohol, ethyl acetate, benzene, or chloroform, insoluble in light petroleum or cold water, but soluble in hot water. It was obtained from dilute alcohol in shining, silverwhite plates melting at 125°.

0.2278 gave 22.8 c.c. moist nitrogen at 12° and 746.7 mm. N = 11.67. C₁₂H₂₄O₃N₂ requires N = 11.48 per cent.

	Rot	ation of M	aldi-n -bu tyl	amide.	
<i>p</i> .	$d 20^{\circ}\!/4^{\circ}$.	1.	$\alpha_{\mathbf{p}}^{20^{\circ}}$.	$[\alpha]^{20^{\circ}}_{D}$.	[M] ^{20°} .
		Pyridin	re Solution.		
3.776	0.9804	1.9984	- 2·64°	- 35 .6 8°	- 87·1°
10.820	0.9860	1.9984	7.56	35.35	86.3
		Methyl Al	cohol Soluti	on.	
5.633	0.8037	1.9984	- 4·32°	- 47 ·74°	-116·5°
10.540	0.8160	1.9984	7.89	45.90	112.0
	G	lacial Acet	ic Acid Solu	tion.	
5.455	1.052	1.9984	-5.00°	- 43·59°	- 106·4°
9.718	1.052	1.9984	8.79	43.01	104.9

Maldiisobutylamide.

Ten grams of ethyl malate were added to 10 grams of *iso*butylamine (Kahlbaum), a little heat being evolved on mixing. After standing for a day and then warming on a water-bath for two hours, the mixture became solid, and a theoretical yield was obtained. The product is very soluble in hot water, ethyl or methyl alcohols, acetone, ethyl acetate, benzene, chloroform, ether, glacial acetic acid, or pyridine. It was crystallised from a mixture of benzene and light petroleum. Melting point 121°.

0.1456 gave 14.5 c.c. moist nitrogen at 14.5° and 755.8 mm. N = 11.63. $C_{12}H_{24}O_3N_2$ requires N = 11.48 per cent.

Rotation of Maldisobutulamide.

p.	$d 20^{\circ}/4^{\circ}$.	ι.	α ^{20°} .	$[\alpha]^{20^{\circ}}_{D}$.	[M] ^{20°} .
		Pyridin	ne Solution.		
5.394	0.9813	1.9984	- 3·77°	- 35·63°	- 86·9°
7 • 984	0.9837	1.9984	5.75	36.64	89.4
		Methyl Ald	ohol Soluti	on.	
5.316	0.8039	1.9984	4·11°	- 48·11°	- 117·4°
9.128	0.8123	1.9984	7.22	48 .53	118.4
	G	lacial Acet	ic Acid Solı	ution.	
5.492	1.051	1.9984	- 5·02°	- 43·51°	- 106·2°
7.563	1.051	1.9984	6.87	43.25	105.3

Maldi-n-heptylamide.

Sixteen grams of *n*-heptylamine (Kahlbaum) were added to 10 grams of diethyl malate, the mixture being accompanied by heat evolution. On standing overnight the whole had set to a solid mass. Yield 100 per cent.

The *n*-heptylamide is very soluble in hot alcohol, chloroform, pyridine, glacial acetic acid, or methyl alcohol, readily so in hot benzene or ethyl acetate. It is sparingly soluble in carbon disulphide, acetone, ether, or hot water. From methylated spirit it was obtained in beautiful white, shining plates melting at 130.5—131°.

0.2083 gave 15.6 c.c. moist nitrogen at 12.5° and 746.5 mm. N = 8.71. $C_{18}H_{36}O_3N_2$ requires N = 8.54 per cent.

	Rote	ation of Mo	aldi-n-hepty	lamid e.	
р.	d 20°/4°.	г.	$\alpha_{\rm p}^{20^{\circ}}$.	[a] ^{20°} .	[M] ²⁰ .
		Pyridin	ne Solution.		
5·166 11·010	0 •9792 0 •9804	1 •9984 1 •9984	-2.73° 5.84	$-27.01^{\circ}27.08$	- 88.6° 88.8
		Methyl Al	cohol Soluti	on.	
6· 0 01	0.8035	1.9984	- 3•41°	- 35·38°	– 116·1°
	A I	10 per cent. s	solution crysta	llised.	
	G	lacial Acet	ic Acid Solu	tion.	

4 · 497	1.020	1.9984	-2.97°	- 31 ·47°	-103.2
9.334	1.023	1.9984	6.13	31.20	102.3

Maldipiperidide.

Twelve grams of piperidine (Kahlbaum) were added to 10 grams of diethyl malate, and, although heat was evolved on mixing, only a 20 per cent. yield was obtained, even after keeping the mixture at 130° in an oil-bath for three days. A 50 per cent. yield was obtained by heating a similar mixture to the same temperature for ten days. The progress of the reaction is indicated by the contents of the flask becoming more and more solid on cooling. An attempt to prepare the piperidide by heating piperidine and malic acid together for several days proved unsuccessful.

The piperidide is very soluble in methylated spirit, but sparingly so in water, benzene, ethyl acetate, or pyridine. From a mixture of alcohol and acetone it was obtained in flat plates melting at 157.5°.

0.126 gave 11.2 c.c. moist nitrogen at 13° and 749.5 mm. N = 10.35. $C_{14}H_{24}O_3N_2$ requires N = 10.45 per cent.

Rotation of Maldipiperidide.

p.	$d \ 20^{\circ}/4^{\circ}$.	l.	α ^{20°} .	$[\alpha]^{20^{\circ}}_{\rm p}$.	$[M]^{20^{\circ}}_{D}$.
		Pyridin	ne Solution.		
0.5981	0.9794	3.899	- 0·47°	– 20·58°	- 55 *2*
		Methyl Al	cohol Solutio	on.	
4·975 8·845	0.8078 0.8200	1·9984 0·999	-2.21° 1.99	-27.51° 27.47	– 73'7° 73 '6
	G	lacial Acet	ic Acid Solr	tion.	
$3.575 \\ 6.531$	1·061 1·067	1 •9984 0 •999	$^{+1\cdot09^{\circ}}_{1\cdot05}$	+14·37° 15·08	+ 38 • 5° 40 • 5
VOL. LX	XXIX.				6 G

OPTICAL ACTIVITY OF MALAMIDE.

Maldiphenylhydrazide.

This compound was prepared, firstly, by Bülow's method (Annalen, 1886, 236, 194), which involves the use of a high temperature $(120-140^{\circ})$, and secondly, by Fischer and Passmore's method (Ber., 1889, 22, 2734), in which the reaction is carried out on the water-bath. As will be seen below, however, the products obtained by both methods were of substantially the same rotatory power, thus showing that the higher temperature does not lead to any racemisation.

Bülow's Method.-Twenty-eight grams phenyl of hydrazine (Kahlbaum) were added to 20 grams of finely powdered malic acid; the mixture which solidified with evolution of much heat was further heated to 120-140° for eight hours until no more steam was evolved. The heating must be begun with caution as there is a sudden evolution of a large amount of steam. The resulting mass, which was of a light brown colour, was first well washed with dilute acetic acid, and then with a solution of ammonium carbonate. The yield was 85 per cent. The substance is almost insoluble in water, methyl alcohol, or light petroleum, sparingly soluble in methylated spirit, and only slightly so in acetone, chloroform, carbon disulphide, ethyl acetate, ether, glacial acetic acid, or pyridine. It was obtained from alcohol in white shining plates melting at 214° with slight decomposition.

0.1232 gave 18.4 c.c. moist nitrogen at 11° and 764.2 mm. N = 17.91. $C_{16}H_{18}O_{3}N_{4}$ requires N = 17.83 per cent.

Fischer and Passmore's Method.—Twenty grams of dried malic acid were dissolved in 180 grams of water, and to this were added a solution of 22 grams of glacial acetic acid in 22 grams of water with 40 grams of phenylhydrazine, the whole being then heated on the water-bath in a flask provided with an air-condenser. The reaction took place suddenly after heating for 4 hours, much of the liquid being violently projected into the condenser. The light brown product was washed successively with water, dilute acetic acid, and ammonium carbonate solution. The yield was only 20 per cent. The product had to be crystallised three times from glacial acetic acid before being obtained in a state of chemical and optical purity. Melting point 214° .

THE ACTION OF POTASSIUM CYANIDE ON PULEGONE. 1869

27 1

	Kotat	ion of Ma	larphenyl	nyaraziae	•	
	p.	d 20°/4°.	1.	$\alpha_{p}^{20^{\circ}}$.	$[\boldsymbol{\alpha}]_{\mathbf{p}}^{20^{\circ}}.$	[M] ^{20°} .
		Pyridin	ne Solutio	n.		
Preparation by Bülow's method.	$inom{5.119}{7.175}$	0 •9929 0 •9987	1·9984 1·9984	$-\frac{1.75^{\circ}}{2.51}$	-17.22° 17.53	$-54.1^{\circ}55.0$
Preparation by Fischer and Pass- more's method.	$ \begin{cases} 4.809 \\ 6.390 \end{cases} $	0 9914 0 9960	1·9984 1·9984	- 1.65° 2.17	-17.28° 17.06	- 54·3° 53•6

. . . .

. .

. .

Glacial Acetic Acid Solution.

р.	d 20°/4°.	l.	$a_{p}^{20^{\circ}}$.	$[a]_{D}^{20^{\circ}}$.	[M] ^{20°} .
0.7350	1.054	0.999	- 0·32°	- 41·35°	- 129·8°

CHEMICAL DEPARTMENT, UNIVERSITY OF BIRMINGHAM.