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Note

The Preparation and Properties of Some α -Arylureidoesters

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In connection with our work on β -ureidoesters^{1,2} some ethyl esters of α -ureido acids were required for comparative experiments. Although α -ureido acids, *i. e.* hydantoic acids, are standard compounds for the characterization of amino acids, very few of their esters, particularly arylureidoesters, have been prepared so far.

When equimolar amounts of α -aminoesters and phenyl- or α -naphthyl-isocyanate are mixed in absolute ether at 0°, the corresponding ureidoesters crystallize from the reaction mixture as well defined compounds in high yields (Tables I and II). Arylureidoesters prepared from optically active α -amino esters possess a high rotatory power; in all cases examined those derived from L-aminoesters have a positive, and those derived from D-aminoesters a negative value of rotation. In addition melting points of the racemic and optically active form of some ureidoesters differ considerably.

As α -amino acid ethyl esters are usually liquids, and some of them have very low rotation values, the above properties of their ureido derivatives might be very useful for their characterization. In this respect the α -naphthyl derivatives seem to be specially suitable.

EXPERIMENTAL

Melting points are not corrected.

Aminoesters were obtained^{3,4} by treating the corresponding amino acid in ethanolic hydrogen chloride; after removal of the solvent, the ester hydrochlorides were treated with triethylamine, and the liberated amino esters distilled *in vacuo*.

General procedure for the preparation of α -arylureidoesters

To a solution of aminoester (15 mmole) in absolute ether (30 ml.), a solution of phenyl- or α -naphthyl-isocyanate (15 mmole) in the same solvent (30 ml.) was added under shaking in several portions at 0°. After storage in refrigerator overnight, the crystals were filtered off, dissolved in hot chloroform and precipitated with petroleum ether. In general, after one recrystallization, α -naphthyl derivatives were analytically pure.

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TABLE I



No.	R	Yield %	M. p. °C	[α] _D CHCl ₃ c, 1.0-1.5	Molecular formula	Calc'd. %			Found %		
						C	H	N	C	H	N
1.	H	90	103-105		C ₁₁ H ₁₄ N ₂ O ₃	59.45	6.35	12.61	59.36	6.06	12.90
2.	DL-CH ₃	60	78-80						61.20	6.72	12.05
3.	L-CH ₃	63	90-92	+22.9	C ₁₂ H ₁₆ N ₂ O ₃	61.00	6.82	11.86	61.21	7.09	11.97
4.	D-CH ₃	64	90-92	-23.3					61.04	6.59	11.65
5.	DL-CH ₃ CH ₂	64	84-86						62.22	7.13	11.13
6.	L-CH ₃ CH ₂	62	99-101	+20.3	C ₁₃ H ₁₈ N ₂ O ₃	62.38	7.25	11.19	62.46	7.36	11.04
7.	D-CH ₃ CH ₂	68	99-101	-20.5					62.53	7.24	11.37
8.	DL-CH ₃ SCH ₂ CH ₂	92	68-70						56.87	6.73	9.47
9.	L-CH ₃ SCH ₂ CH ₂	80	103-105	+31.4	C ₁₄ H ₂₀ N ₂ O ₃ S*	56.73	6.80	9.45	56.44	6.53	9.46
10.	D-CH ₃ SCH ₂ CH ₂	82	103-105	-32.0					56.57	7.05	9.52
11.	DL-(CH ₃) ₂ CH	56	114-116		C ₁₄ H ₂₀ N ₂ O ₃	63.61	7.63	10.60	63.42	7.82	10.88
12.	DL-(CH ₃) ₂ CHCH ₂	70	90-92						64.87	8.24	10.10
13.	L-(CH ₃) ₂ CHCH ₂	71	64.5-65.5	+11.5	C ₁₅ H ₂₂ N ₂ O ₃	64.72	7.96	10.07			
14.	DL-C ₆ H ₅ CH ₂	90	173-175		C ₁₈ H ₂₀ N ₂ O ₃	69.21	6.46	8.97	69.19	6.15	9.13
15.	DL-EtO ₂ CCH ₂	90	99-101						58.71	6.25	9.30
16.	L-EtO ₂ CCH ₂	85	83-85	+61.5	C ₁₅ H ₂₀ N ₂ O ₅	58.43	6.54	9.09			
									58.56	6.85	9.30

* Calc'd: S, 10.82; found: S, No. 8, 11.06%; No. 9, 11.04%; No. 10, 11.02%.

TABLE II



No.	R	Yield %	M. p. °C	[α] _D CHCl ₃ c, 1.0-1.5	Molecular formula	Calc'd. %			Found %		
						C	H	N	C	H	N
1.	H	96	167-168		C ₁₅ H ₁₆ N ₂ O ₃	66.16	5.92	10.29	66.21	5.57	10.56
2.	DL-CH ₃	89	142-144						66.86	6.10	10.00
3.	L-CH ₃	94	175-177	+47.5	C ₁₆ H ₁₈ N ₂ O ₃	67.11	6.34	9.78	67.07	6.63	10.08
4.	D-CH ₃	95	175-177	-45.5					67.41	6.34	10.02
5.	DL-CH ₃ CH ₂	90	107-109						67.99	6.42	9.08
6.	L-CH ₃ CH ₂	95	140-142	+39.8	C ₁₇ H ₂₀ N ₂ O ₃	67.97	6.71	9.33	67.72	6.63	9.61
7.	D-CH ₃ CH ₂	95	140-142	-38.6					68.12	6.84	9.62
8.	DL-CH ₃ SCH ₂ CH ₂	95	140-142						62.51	6.15	7.87
9.	L-CH ₃ SCH ₂ CH ₂	96	146-148	+17.0	C ₁₈ H ₂₂ O ₃ N ₂ S*	62.40	6.40	8.09	62.21	6.33	8.29
10.	D-CH ₃ SCH ₂ CH ₂	90	146-148	-17.5					62.64	6.68	8.18
11.	DL-(CH ₃) ₂ CH	85	122-125		C ₁₈ H ₂₂ N ₂ O ₃	68.77	7.05	8.91	68.76	7.11	9.22
12.	DL-(CH ₃) ₂ CHCH ₂	85	111-113						69.60	7.66	8.54
13.	L-(CH ₃) ₂ CHCH ₂	81	109-110.5	+28.0	C ₁₉ H ₂₄ N ₂ O ₃	69.49	7.36	8.53			
14.	DL-C ₆ H ₅ CH ₂	90	150-153**		C ₂₂ H ₂₂ N ₂ O ₃	72.90	6.12	7.73	72.70	6.22	7.83
15.	DL-EtO ₂ CCH ₂	93	118-120						63.44	6.06	7.76
16.	L-EtO ₂ CCH ₂	90	108-110	+47.5	C ₁₉ H ₂₂ N ₂ O ₅	63.67	6.19	7.82			
									63.88	6.14	8.03

* Calc'd.: S, 9.26; found S: No. 8., 9.54%; No. 9., 8.89%; No. 10., 9.65%.
 ** Softening by 129°.

REFERENCES

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IZVOD

Priprava i svojstva nekih α -arilureidoestera

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Iz etilnih estera α -amino kiselina i fenil- odnosno α -naftil-izocijanata, nastaju odgovarajući ureidoesteri u vrlo dobrim iskorištenjima. Ti spojevi ako su pripremljeni iz optički aktivnih amino estera pokazuju visoke vrijednosti skretanja, a kod nekih je i razlika u talištima racemične i optički aktivne forme vrlo velika. Zbog tih svojstava arilureidoesteri mogu služiti kao vrlo pogodni derivati kod karakterizacije aminoestera.

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