833. *Optical Rotatory Dispersion. Part XXI.* Azomethines. (I.) N-Neopentylidene Derivatives of α-Amino-acid Esters*

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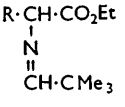
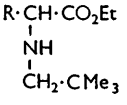
The preparation and properties of some *N*-neopentylidene derivatives of α-amino-acid esters are described. These compounds show anomalous dispersion curves with the first extremum in the 250 mμ region, and in certain cases the complete Cotton effect curves can be observed. In all examples so far examined, the derivative of L-configuration shows a negative Cotton effect, and the derivative of D-configuration a positive one.

The unconjugated azomethine group in an aliphatic environment ($R^1R^2C{:}NR^3$) shows a weak band [1,2] in the ultraviolet region ($\lambda_{max.}^{EtOH}$ ~235 mμ, log ε ~2) which appears to be analogous to the $n \rightarrow \pi^*$ band of the carbonyl group. It has been suggested [1] that the mutarotation observed when α-amino-acid esters are dissolved in ketones [3] is due to anomalous dispersion associated with the azomethine chromophore and further evidence for this view is now furnished by the isolation and examination of azomethine derivatives of several α-amino-acid esters in both configurations. *N*-Neopentylidene derivatives (I) were selected because they contain no strongly-absorbing group and because it seemed likely that the absence of a hydrogen α to the carbon atom of the azomethine linkage would make the compounds more amenable to study since aldol-type condensation is precluded.



(I)



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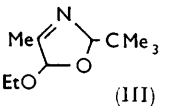

(III)

Although the *N*-neopentylidene derivatives of amino-acid esters do not appear to have been reported, other azomethines, especially those derived from the amino-acid salts, have attracted some attention. The earliest studies appear to be those of Schiff [4] who examined the reaction with formaldehyde, and this aspect remains of interest insofar as the chemistry of the Sørensen titration is concerned. Bergmann, Ensslin, and Zervas [5] isolated benzylidene and trichloroethylidene derivatives of α-amino-acids (as their barium or brucine salts), and related compounds have found some application as intermediates.[6] Gulland and Mead isolated similar derivatives of glycine, and reported polarimetric studies with (+)-phenylalanine buffered in the presence of aromatic aldehydes.[7] Mutarotation was observed, but the nature of the product was not settled. The reaction of certain aromatic aldehydes (notably *o*-hydroxyaldehydes) with free amino-acids has been examined.[8] Biochemical transamination involving pyridoxal and an α-amino-acid in presumably a related reaction.[9]

* Part XX, B. A. Shoulders, W. W. Kiwe, W. Klyne, and P. D. Gardner, *Tetrahedron*, 1965, **21**, in the press.

[1] R. Bonnett, N. J. David, J. Hamlin, and P. Smith, *Chem. and Ind.*, 1963, 1836.

[2] R. Bonnett, *J.*, 1965, 2313.

[3] F. Bergel, G. E. Lewis, S. F. D. Orr, and J. Butler, *J.*, 1959, 1431; cf. also F. Bergel and M. A. Peutherer, *J.*, 1964, 3965.

[4] H. Schiff, *Annalen*, 1901, **319**, 59.

[5] M. Bergmann, H. Ensslin, and L. Zervas, *Ber.*, 1925, **58**, 1034.

[6] E.g., T. Wieland and W. Schäfer, *Annalen*, 1952, **576**, 104; B. Bezas and L. Zervas, *J. Amer. Chem. Soc.*, 1961, **83**, 719; P. Quitt, J. Hellerbach, and K. Vogler, *Helv. Chim. Acta*, 1963, **46**, 327; J. C. Sheehan and V. J. Grenda, *J. Amer. Chem. Soc.*, 1962, **84**, 2417; R. G. Hiskey and J. M. Jung, *ibid.*, 1963, **85**, 578.

[7] J. M. Gulland and T. H. Mead, *J.*, 1935, 210.

[8] F. C. McIntire, *J. Amer. Chem. Soc.*, 1947, **69**, 1377; D. Heinert and A. E. Martell, *ibid.*, 1963, **85**, 183.

[9] B. E. C. Banks, A. A. Diamantis, and C. A. Vernon, *J.*, 1961, 4235; D. E. Metzler, M. Ikawa, and E. E. Snell, *J. Amer. Chem. Soc.*, 1954, **76**, 648.

Rather less work has been reported on the azomethine esters. Some arylidene derivatives have been made, but *N*-benzylideneglycine ethyl ester, first reported in 1963, appears to be particularly sensitive to heat and moisture.[10] Azomethines derived from β-diketones [11] and β-keto-esters [12] have been described. The mutarotation of amino-acid esters when dissolved in aliphatic monoketones has been ascribed to azomethine formation,[1,3,13] and in one case the azomethine has been isolated as a crystalline solid (*N*-cyclopentylidene-L-tyrosine ethyl ester [3]).

When pivaldehyde ($Me_3C{\cdot}CHO$) was allowed to react with an equimolar amount of freshly prepared alanine ethyl ester, either pure or in a small volume of anhydrous ether, reaction occurred within a few minutes and water separated. The reaction could conveniently be driven to completion over a small quantity of molecular sieve, and the product could be obtained directly by fractional distillation as a colourless liquid. That this product was correctly formulated as the azomethine (I; R = CH_3) was confirmed by (i) elemental analysis, (ii) the infrared spectrum, which showed bands at 1740 (ester) and 1665 cm.$^{-1}$ (azomethine), but no band which could be ascribed to the NH stretching mode, and (iii) the nuclear magnetic resonance (n.m.r.) spectrum in which signals appeared at 2·47 τ (singlet, C*H*=N; cf. ref. 14), 5·85 τ (quartet, $CH_3{\cdot}CH_2O$), 6·16 τ (quartet, CH_3CHN–), 8·63 τ (doublet, CH_3CH–N), 8·77 τ (triplet, partly obscured, CH_3CH_2O–), and 8·93 τ [singlet, $(CH_3)_3C$]. The areas under the three groups of signals at 2·5, 6, and 9 τ were in the ratio of *ca.* 1 : 3 : 15. The infrared and n.m.r. spectra eliminated the oxazoline structure (III). Hydrolysis regenerated alanine (isolated), while treatment of the azomethine with Brady's reagent gave the 2,4-dinitrophenylhydrazone of pivaldehyde. Catalytic reduction of the azomethine (I; R = CH_3) over Adams platinum oxide gave the dihydro-compound (II; R = CH_3), the infrared spectrum of which, as expected, had no azomethine band but did show NH absorption at 3340 cm.$^{-1}$.

TABLE 1

N.m.r. spectral data for the *N*-neopentylidene derivatives (I)

L-Amino-acid	Chemical shifts * (τ values)						
	C*H*=N	CH_2O †	NC*H*CO	OCH_2CH_3 ‡	t-Bu §	Other	
Alanine	2·47(s)	5·85	6·16(q)	8·77	8·93	CH_3CHN	8·63(d)
Valine	2·48(s)	5·81	6·65(d)	8·75	8·91	$(CH_3)_2CH$	7·78(m)
						$(CH_3)_2CH$	9·10(d)
							9·16(d)
Leucine	2·45(s)	5·84	6·21(bt)	8·77	8·91	$(CH_3)_2CH$	~9·1(m)
Isoleucine	2·50(s)	5·82	6·55(d)	8·77	8·91	CH_3–C	~9·1(m)
Aspartic acid ¶	2·36(s)	5·82	~5·8	8·76	8·94	$CO{\cdot}CH_2CH$	6·99
		5·87					7·30
						J_{AB} = 17 c./sec.	
Glutamic acid ¶	2·45(s)	5·84	6·27(bt)	8·78	8·92		
		5·89					
Methionine	2·42(s)	5·83	6·12(m)	8·76	8·91	CH_3S	7·92(s)
Lysine ‖	2·47(s)	5·85	6·33(bt)	8·77	8·91	CH_2N	6·67(t)
	2·53(bs)				8·95		
Phenylalanine	2·83(s)	5·79	6·10(q)	8·74	9·05	Ph	2·81
						$PhCH_2$	6·76 6·87

* s = singlet, d = doublet, t = triplet, q = quartet, b = broadened, m = multiplet. † Quartets throughout. ‡ Triplets throughout. § Singlets throughout. ¶ Diethyl ester. ‖ $N\alpha N\epsilon$ Dineopentylidene derivative.

A series of analogous azomethine esters was prepared and n.m.r. spectral data are recorded in Table 1. The compounds were liquids which could be distilled under reduced pressure without apparent decomposition. Nevertheless hydrolysis occurred quite readily and it appears that the azomethine group is hydrolysed much more rapidly than the ester

[10] O. Gerngross and A. Olcay, *Chem. Ber.*, 1963, **96**, 2550, and references therein.
[11] F. Bergel and J. Butler, *J.*, 1961, 4047.
[12] A. Treibs and A. Ohorodnik, *Annalen*, 1958, **611**, 139.
[13] H. E. Smith, M. E. Warren, and A. W. Ingersoll, *J. Amer. Chem. Soc.*, 1962, **84**, 1513.
[14] J. F. King and T. Durst, *Canad. J. Chem.*, 1962, **40**, 882.

function. The spectral properties in the series are quite uniform. Thus each compound shows infrared ester (1735—1745 cm.$^{-1}$) and azomethine (1660—1665 cm.$^{-1}$) bands. In the n.m.r. spectrum of *N*-neopentylidenephenylalanine ethyl ester the azomethine proton, and to a lesser extent the protons in the t-butyl group, are somewhat shielded, presumably by the phenyl ring. In this case, and also with the aspartic acid derivative, an ABX system, arising from the $RCH_2{\cdot}CHN$ grouping, is identifiable in the spectrum. In the lysine derivative both *N*-neopentylidene groups are revealed, although one of the azomethine signals is rather broad.

The *N*-neopentylidene derivatives of simple α-amino-acid esters do not show absorption maxima in the 235 mμ region; instead, broad end-absorption with an apparent maximum at ~220 mμ (ε ~300) is found. It is possible that the ester and azomethine chromophores are interacting in some way by orbital overlap. Alternatively, the observed spectrum may simply represent the envelope of the two bands. Some support for the latter view comes from the presence of a long tail to the absorption curve for the azomethine (I; R = CH_3, $\varepsilon_{245} = 120$) which is much less prominent in the spectrum of the reduced derivative (II; R = CH_3, $\varepsilon_{245} = 65$), and from the observation that even in the lysine derivative, which has two azomethine groups, a separate peak still does not occur although a weak inflection is observed (Figure 1, $\varepsilon_{245} = 230$).

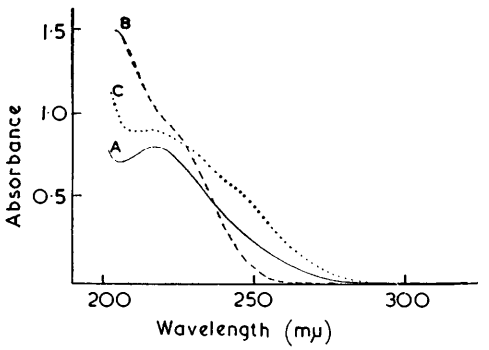

FIGURE 1. Ultraviolet spectra in hexane

A, *N*-Neopentylidene-L-alanine ethyl ester (I; R = CH_3; 12·5 mg. in 25 ml.). *B*, *N*-Neopentyl-L-alanine ethyl ester (II; R = CH_3; 14·0 mg. in 25 ml.). *C*, $^{\alpha}NN^{\epsilon}$-Dineopentylidene-L-lysine ethyl ester (18·5 mg. in 25 ml.).

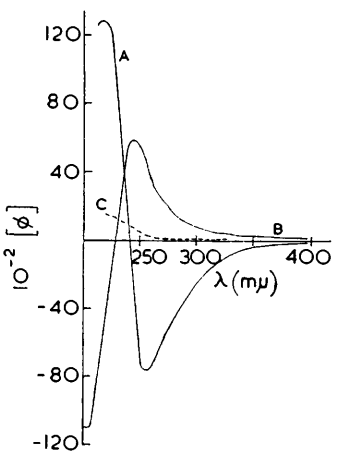

FIGURE 2. Optical rotatory dispersion curves (measured in methanol)

A, *N*-Neopentylidene-L-isoleucine ethyl ester. *B*, *N*-Neopentylidene-D-alanine ethyl ester. *C*, L-Alanine ethyl ester.

The results of optical rotatory dispersion measurements are summarised in Tables 2, 3, and 4, and some representative curves are given in Figure 2. The azomethine esters give Cotton effects in the range 210—250 mμ; derivatives of L- and D-α-amino-acids give negative and positive Cotton effects, respectively. It is noteworthy that these Cotton effects are of opposite sign to those of the free amino-acids and their esters. The observed curves are thought to be primarily associated with the absorption band [1] of the C=N group at about 235 mμ, although in the low-wavelength region at least both chromophores presumably make some contribution and for the methionine derivative a weak partial rotation would be expected from the dialkyl sulphide chromophore. At any event the resulting Cotton effects are characterised by large amplitudes. There are in some cases rather large experimental differences in amplitude between samples of enantiomers. Such

differences may be ascribed to the ready hydrolysis of the Schiff bases to amino-acid esters of lower rotatory power, and, probably to a greater extent, to racemisation occurring in the system $C{:}N{\cdot}\overset{*}{C}HR{\cdot}CO_2Et$ during the preparation. Such racemisation has a biochemically-important analogy in the pyridoxal-catalysed racemisation of α-amino-acids.[15] The amplitudes given in the Tables are therefore subject to this limitation. Preliminary experiments on thermal racemisation indicate that the alanine derivative is much more optically labile than the isoleucine one. A similar observation has been made for the pyridoxal-catalysed racemisation.[15]

Some generalisations can be made regarding the wavelengths of the Cotton effects. Both in methanol and in hexane there is a shift of the extrema towards higher wavelengths as branching at the β-carbon atom increases. The extremum at longer wavelength is about 7 mμ higher in hexane than in methanol. However, the extremum at shorter wavelength is 10 mμ lower in hexane, *i.e.*, the Cotton effect is appreciably broader in hexane than in methanol.

Optical rotatory dispersion curves for an extensive range of free amino-acids have already been reported from one of our laboratories and by others.[16,17] These curves show Cotton effects at ~225 mμ due to the carboxyl group. For comparison with these and with the present results the curves for a few amino-acid esters have been measured (Table 4). The curves are of the same sign, and the extrema are at approximately the same wavelength as those for the free acids; the rotations at the first extremum however are roughly

TABLE 2

N-Neopentylidene derivatives of α-amino-acid esters [$R{\cdot}CH(CO_2Et){\cdot}N{:}CH{\cdot}CMe_3$] optical rotatory dispersion data. Solvent: methanol

(Partial racemisation may have occurred in certain instances; see text.)

		Extrema				Amplitude
α-Amino-acid	R	[φ]	λ (mμ)	[φ]	λ (mμ)	*a*
D-Alanine	CH_3	+6000	244	−11,000	204	+170
L-Valine	$(CH_3)_2CH$	−5800	256	+9000	217	−148
D-Valine	,,	+6530	255	−10,400	218	+169
L-Leucine	$(CH_3)_2CH{\cdot}CH_2$	−6500	250	+5450 !	222	−120 !
D-Leucine	,,	+5430	251	−7300	214 infl.	+127
L-Isoleucine	$C_2H_5{\cdot}CH(CH_3)$	−7860	256	+13,000	219	−209
D-Isoleucine	,,	+6150	256	−9350 !	208	+156 !
L-Aspartic acid	$EtO_2C{\cdot}CH_2$	−4650	244	+3800 !	213	−85 !
L-Glutamic acid	$EtO_2C{\cdot}CH_2{\cdot}CH_2$	−3880	250	+4300 !	217	− 82 !
L-Methionine	$CH_3S{\cdot}CH_2{\cdot}CH_2$	−2200	252	+1800 !	214	−40 !
L-Lysine	$Me_3C{\cdot}CH{:}N[CH_2]_4$	−5800	250	+7320 !	212	−120 !

! Rotation at lowest wavelength reached; not an extremum (also in Tables 3 and 4).

TABLE 3

N-Neopentylidene derivatives of α-amino-acid esters [$R{\cdot}CH(CO_2Et){\cdot}N{:}CH{\cdot}CMe_3$]. Optical rotatory dispersion data. Solvent: hexane

		Extrema				Amplitude
Amino-acid	R	[φ]	λ (mμ)	[φ]	λ (mμ)	*a*
L-Alanine	CH_3	−7600	250	+13,000	202	−206
D-Alanine	,,	+7200	250	−13,000	202	+202
D-Leucine	$(CH_3)_2CH{\cdot}CH_2$	+6320	259	−11,100	205	+174
L-Isoleucine	$C_2H_5{\cdot}CH(CH_3)$	−7640	263	+11,400!	206	−190!
D-Isoleucine	,,	+5540	263	−6950sh	206	+125
L-Lysine	$Me_3C{\cdot}CH{:}N[CH_2]_4$	−6750	256	+10,300!	205	−155!
L-Phenylalanine	$C_6H_5{\cdot}CH_2$	−8700	250	0!	225	−87!

[15] J. Olivard, D. E. Metzler, and E. E. Snell, *J. Biol. Chem.*, 1952, **199**, 669.

[16] J. P. Jennings, W. Klyne, and P. M. Scopes, *J.*, 1965, 294; A. Kjaer, W. Klyne, P. M. Scopes, and D. R. Sparrow, *Acta Chem. Scand.*, 1964, **18**, 2412.

[17] W. Gaffield, *Chem. and Ind.*, 1964, 1460; I. P. Dirkx and F. L. J. Sixma, *Rec. Trav. chim.*, 1964, **83**, 522.

TABLE 4

Esters of α-amino-acids. Optical rotatory dispersion data. Solvent: methanol

Amino-acid ethyl ester	[φ]	λ (mμ)
L-Alanine	+1640!	222
D-Valine	−3300 tr	227
	−2800!	222
N-Neopentyl-D-valine	−710 tr	221
	−685!	219

double those of the corresponding α-amino-acids, but are still, of course, much smaller than the rotations of the azomethine esters (Tables 2 and 3). It is of interest that certain simple azomethines having no other chromophore show Cotton effects with small amplitudes (*e.g.*, $Me_3C{\cdot}CH{:}N{\cdot}\overset{*}{C}HMe{\cdot}Et$ in methanol,[1] *a* ~12). The large amplitudes found for the azomethine esters thus appear to be due to some interaction between the azomethine and ester chromophores.

The optical rotatory dispersion curves of the azomethine esters could clearly prove useful in certain cases for assigning configuration in the α-amino-acid series. The uniformity shown in Table 2 (negative Cotton effect, L-configuration; positive Cotton effect, D-configuration) certainly suggests such a possibility, but an estimate of the scope of such an application must await the results of present experiments with more complex α-amino-acids.

EXPERIMENTAL

Infrared spectra were measured on liquid films (Unicam S.P. 200, polystyrene calibration). N.m.r. spectra (Varian A60) refer to ~10% solutions in deuterochloroform with tetramethylsilane as internal reference. Optical rotatory dispersion measurements were made at 20—25° with the Bellingham and Stanley/Bendix and Ericsson spectropolarimeter " Polarmatic 62 " (cf. ref. 16). Concentrations were in the range *ca.* 0·1 mg./ml. to *ca.* 2·6 mg./ml. α-Amino-acids were obtained from the following sources, and were used without further purification: D- and L-alanine, L-valine, L-isoleucine, L-aspartic acid, L-glutamic acid, L-methionine, and L-lysine monohydrochloride from British Drug Houses Ltd.; L-phenylalanine from Aldrich Chemical Co.; D-valine, L- and D-leucine, and D-isoleucine from L. Light and Co.

N-*Neopentylidene-amino-acid Ethyl Esters*.—Two methods of preparation were employed: the first (*A*), illustrated for valine, involved isolation of the amino-acid ethyl ester; in the second (*B*), illustrated for phenylalanine, the crude ester was used directly.

(*A*) N-*Neopentylidene-*D-*valine ethyl ester*. D-Valine ethyl ester (4 g., prepared by the general method described by Fischer [18]) was treated carefully with freshly-distilled pivaldehyde (5 g.). The lower aqueous layer which separated after a short time was removed and the organic phase was kept overnight with molecular sieve (0·5 g., Linde 4A). Distillation gave a colourless *oil* (6·1 g., 96%), b. p. 85—86°/8 mm. (Found: C, 67·8; H, 10·7; N, 6·7. $C_{12}H_{25}NO_2$ requires C, 67·6; H, 10·9; N, 6·6%).

(*B*) N-*Neopentylidene-*L-*phenylalanine ethyl ester*. L-Phenylalanine (2·2 g.) was refluxed in saturated anhydrous ethanolic hydrogen chloride (50 ml.) for 4 hr. The solvent was removed (reduced pressure, bath ~40°) and the residue was treated at once with ice-cold saturated aqueous potassium carbonate and extracted rapidly with portions of ice-cold ethyl acetate. The organic extract was dried ($MgSO_4$; 20 min.) and filtered, and the solvent was removed under reduced pressure. The crude amino-acid ester was treated at once with a slight excess of freshly-distilled pivaldehyde (1·2 g.). Water separated and was removed; if an emulsion formed it was broken with a little ether. Drying over molecular sieve as before, and distillation, gave 2·1 g. (60%) of N-*neopentylidene-*L-*phenylalanine ethyl ester*, b. p. 121°/2 mm. (Found: C, 73·6; H, 8·7; N, 6·1. $C_{16}H_{23}NO_2$ requires C, 73·5; H, 8·9; N, 5·4%).

The following compounds were prepared by method (*A*): N-*Neopentylidene-*L-*alanine ethyl ester*, b. p. 72°/8 mm., (76%) (Found: C, 64·4; H, 10·2; N, 7·5. $C_{10}H_{19}NO_2$ requires C, 64·8; H, 10·3; N, 7·6%), $\lambda_{max.}^{hexane}$ 217 mμ; log ε 2·46. $N^{\alpha}N^{\epsilon}$-*dineopentylidene-*L-*lysine ethyl ester*, b. p. 121—122°/0·9 mm. (76%) (Found: C, 69·6; H, 11·0; N, 9·1. $C_{18}H_{34}N_2O_2$ requires C, 69·6; H, 11·0; N, 9·0%), $\lambda_{infl.}^{hexane}$ 215, 245 mμ; log ε 2·59, 2·36.

[18] E. Fischer, *Ber.*, 1901, **34**, 433.

The following compounds were prepared by method (*B*): N-*Neopentylidene*-D-*leucine ethyl ester*, b. p. 113°/11 mm. (40%) (Found: C, 68·5; H, 11·0; N, 6·3. $C_{13}H_{25}NO_2$ requires C, 68·7; H, 11·1; N, 6·2%); N-*neopentylidene*-D-*isoleucine ethyl ester*, b. p. 97—98°/8 mm. (52%) (Found: C, 68·6; H, 10·95; N, 6·4%); N-*neopentylidene*-L-*aspartic acid diethyl ester*, b. p. 99°/0·4 mm. (51%) (Found: C, 60·7; H, 8·9; N, 5·5. $C_{13}H_{23}NO_4$ requires C, 60·7; H, 9·0; N, 5·4%); N-*neopentylidene*-L-*glutamic acid diethyl ester*, b. p. 104°/0·4 mm. (41%) (Found: C, 61·6; H, 9·1; N, 5·4. $C_{14}H_{25}NO_4$ requires C, 62·0; H, 9·3; N, 5·2%); N-*neopentylidene*-L-*methionine ethyl ester*, b. p. 114—116°/1·5 mm. (33%) (Found: C, 58·7; H, 9·4; N, 5·9. $C_{12}H_{23}NO_2S$ requires C, 58·7; N, 9·45; N, 5·7%).

The derivatives of D-alanine, L-leucine, L-isoleucine, and L-valine were also made by this method. The n.m.r. spectral data of these compounds are in Table 1.

N-*Neopentyl*-D-*valine Ethyl Ester*.—*N*-Neopentylidene-D-valine ethyl ester (2·0 g.) was hydrogenated at atmospheric pressure (ethanol; PtO_2; 5 hr.). The filtered solution was concentrated and distilled to give 1·0 g. (50%) of N-*neopentyl*-D-*valine ethyl ester*, b. p. 88°/7 mm. (Found: C, 67·1; H, 11·5. $C_{12}H_{25}NO_2$ requires C, 66·9; H, 11·7; N, 6·5%), $\nu_{max.}$ 3330w, 1725s cm.$^{-1}$. Similarly, catalytic reduction of *N*-neopentylidene-L-alanine ethyl ester gave N-*neopentyl*-L-*alanine ethyl ester* (64%), b. p. 73—74°/8 mm., $\nu_{max.}$ 3340w, 1725s cm.$^{-1}$, τ 5·79 (quartet, $-O\cdot CH_2-$); 6·70 (quartet, α–CH); 7·41 (broad, NH); 7·63, 7·80 (AB quartet, J = 11 c. sec., $-N-CH_2-$); ~8·7 (multiplet, $-CH-CH_3$); 9·09 (singlet, $-CMe_3$) (Found: C, 64·1; H, 11·2; N, 7·4. $C_{10}H_{21}NO_2$ requires C, 64·1; H, 11·3; N, 7·5%); $\lambda_{infl.}^{hexane}$ 220 mμ log ε 2·52.

Hydrolysis of N-*Neopentylidene*-L-*alanine Ethyl Ester*.—(i) The azomethine ester (0·27 g.) was heated in aqueous ethanol (1 : 1 v/v, 2 ml.) on a water-bath. A strong smell of pivaldehyde was detected in the early stages of hydrolysis, but the basicity of the solution decreased only slowly until after 3 hr. the solution was nearly neutral (indicator paper). The residue was crystallised from aqueous ethanol to give 84 mg. (65%) of alanine, identified by infrared comparison with an authentic sample. (ii) On treatment with Brady's reagent the azomethine ester at once gave pivaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 210—212° (lit.,[19] 211·5—212°).

We thank Mr. R. J. Swan for measuring optical rotatory dispersions and Miss Joan Godfrey for preparing the L-leucine derivative. The financial support of the D.S.I.R., Imperial Chemical Industries Limited, and the Smith, Kline and French Research Institute is gratefully acknowledged.

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[*Received, December* 23*rd*, 1964.]

[19] E. E. Smissman, R. H. Johnsen, A. W. Carlson, and B. F. Aycock, *J. Amer. Chem. Soc.*, 1956, **78**, 3395.