

Fig. 1.— Δ , water vapor¹³; \circ , liquid water (solid line); 55.5 k (dotted line)¹⁴; \bullet , aq. formic acid (solid line); 0.1 k (dotted line).¹⁵

extinction coefficient and c_w , c_f ; concentrations of water and formic acid, respectively.) In Fig. 1, note that formic acid excitation dominates water excitation above 1800 Å. even in 0.1 M formic acid. Here $k_f c_f$ exceeds $k_w c_w$ by a factor of 100, which is far greater than the expected departure of the ratio of corresponding excitation probabilities from theory.¹⁰

The limits of this excitation effect can be estimated in 0.1 M formic acid by dividing $G(\text{CO})$ by the quantum yield, $\phi(\text{CO})$. One finds that the number of excitations/100 ev. varies from 1.7 for $\phi(\text{CO})$ equal to 0.14 at 2669 Å. to 0.40 for $\phi(\text{CO})$ equal to 0.58 at 1860 Å. Thus this effect is appreciable and supports Platzman's prediction⁸ that the subexcitation electron effect becomes significant at molar concentrations of the order of 0.1 and can attain a G value of the order of one.

If carbon monoxide originates from dissociation of formic acid by water subexcitation electrons, one may conclude that water contains no transitions below 6.85 ev. A transition to a low-lying level, if allowed for these slow electrons (even though optically forbidden) would channel energy very rapidly from the electron and formic acid would be largely unaffected in solutions as dilute as 0.1 M .

Acknowledgment.—The author wishes to thank M. S. Matheson, J. L. Weeks and R. L. Platzman for their coöperation and helpful discussions.

(13) K. Watanabe and M. Zelikoff, *J. Opt. Soc. Am.*, **43**, 753 (1953).

(14) L. H. Dawson and E. D. Hulbert, *ibid.*, **24**, 175 (1934).

(15) H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

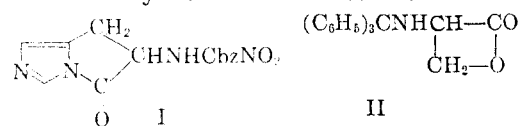
EDWIN J. HART

RECEIVED SEPTEMBER 3, 1959

ACTIVATED CYCLIC DERIVATIVES OF AMINO ACIDS Sir:

Many biologically important amino acids contain "extra" functional groups (e.g., hydroxyls, thiols, and potentially reactive heterocycles) which

may complicate peptide synthesis. These functions may be blocked as a separate operation or a "selective" condensing agent may be used. This communication reports attractive examples of reagents in which the "extra" group is "protected" while the carboxyl function is "activated."



Interaction of N-(*p*-nitrocarbobenzyloxy)-L-histidine¹ [m.p. 202–204°, α_D^{25} -22.6° (C , 1.6 in 6 N hydrochloric acid)] and N,N'-diisopropylcarbodiimide in dioxane solution afforded 60% of the crystalline cyclized product I [found: C , 53.00; H , 3.91; N , 17.41]; α_D^{25} -14.9° (C , 1.36 in tetrahydrofuran). Crystallization from tetrahydrofuran-hexane gave m.p. 186–187°; the infrared spectrum shows a strong band at 1775–1780 cm^{-1} attributable to an activated amide. The benzylamide, m.p. 190–191° (ethanol-ether), [found: C , 59.65; H , 5.33; N , 16.33], forms in nearly quantitative yield at room temperature on treatment with benzylamine; there is no band at 1775–1780 cm^{-1} .

Although a large number of β -lactones are known, no authentic synthesis from the corresponding hydroxy acid has been reported² until the past year.³

We have cyclized N-trityl-L-serine⁴ to a fully characterized crystalline β -lactone (II), using N,N'-diisopropylcarbodiimide, in 15% isolated yield; m.p. 193–194°, [α_D^{25} -62° (C , 0.5 in chloroform), $\nu_{\text{max}}^{\text{KBr}}$ 1820 cm^{-1} , attributable to a β -lactone group, and no hydroxyl absorption band (chloroform) [found: C , 79.83; H , 5.78; N , 4.36; mol. wt., 309 (Rast)]. Treatment of II with benzylamine gave, in 93% yield, the benzylamide, m.p. 146–147°, [α_D^{25} -114° (C , 0.5 in chloroform) [found: C , 79.62; H , 6.45; N , 6.29] identical with the benzylamide obtained directly from the condensation of N-trityl-L-serine and benzylamine in the presence of N,N'-diisopropylcarbodiimide. Treatment of II with L-alanine methyl ester hydrochloride⁵ in the presence of triethylamine gave, in 66% yield, N-trityl-L-seryl-L-alanine methyl ester, m.p. 149–150°, [α_D^{30} -41° (C , 1 in ethanol) [found: C , 72.27; H , 6.58; N , 6.51].

The possible utility of derivatives I and II as monomers is being investigated.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF
TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

JOHN C. SHEEHAN
KLAUS HASSPACHER
YING LIEH YEH

RECEIVED OCTOBER 1, 1959

(1) Prepared by the procedure described for the racemate, D. T. Gish and F. H. Carpenter, *THIS JOURNAL*, **75**, 950 (1953).

(2) H. E. Zaugg, "Organic Reactions," Vol. VIII, R. Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 307.

(3) In independent work which was published after the completion of our synthesis, yohimbic acid was cyclized to a β -lactone; P. A. Diassi and C. M. Dyllion, *ibid.*, **80**, 3746 (1958). See also J. C. Sheehan, Abstracts of Papers, 135th A. C. S. Meeting, April, 1959, p. 3-O.

(4) Prepared essentially by the method reported for N-trityl-D,L-serine, G. Amiard, R. Heymès and L. Velluz, *Bull. Soc. Chim. France*, 191 (1955). N-Trityl-L-serine was characterized as the crystalline diethylamine salt, m.p. 137–138°, [α_D^{25} -29° (C , 1 in methanol) [found: C , 74.19; H , 7.60; N , 6.84].

(5) Prepared by Fischer esterification, m.p. 110–110.5°, [α_D^{25} $+41^\circ$ (C , 1 in methanol) [found: C , 34.17; H , 7.16; N , 10.00].