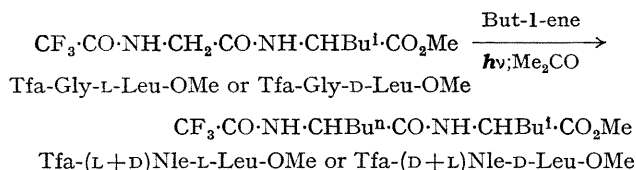
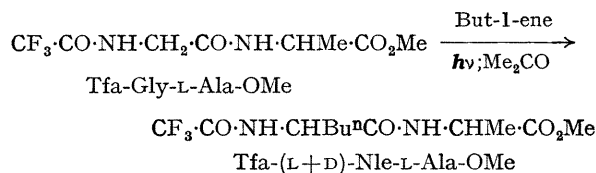


## 1,4-Asymmetric Induction in the Photoalkylation of Glycine Dipeptides

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PHOTOCHEMICAL alkylations of glycine dipeptide derivatives have been reported;<sup>1</sup> they involve the glycine residues in glycyL-alanine dipeptides selectively, leading to preferential conversion of the glycine residue into a branched  $\alpha$ -amino-acid residue. In glycine dipeptides the  $\alpha$ -carbon atoms of the two constituent amino-acids are in a 1,4-relationship with each other ( $-\text{NH}\cdot\overset{4}{\text{C}}\text{H}_2\cdot\overset{3}{\text{C}}\text{O}\cdot\overset{2}{\text{C}}\text{H}\cdot\overset{1}{\text{C}}\text{HR}\cdot\text{CO}-$ ). This leads to an asymmetric induction process,<sup>2</sup> with the chiral centre in the  $\alpha$ -carbon of the branched amino-acid residue as the asymmetric agent. We have found that formation of the norleucine residue in the acetone-initiated photoalkylation reactions of glycyL-alanine and glycyL-leucine dipeptide derivatives with but-1-ene involves the production of unequal amounts of the two enantiomers, *i.e.* the occurrence of asymmetric induction.



Since these photoalkylation reactions proceed *via* a free-radical mechanism,<sup>3</sup> the present results indicate a 1,4-asymmetric induction effect in a free-radical reaction.

The reactions were carried out according to the reported procedure.<sup>1</sup> The relative proportions of the two enantiomers were estimated by acid hydrolysis followed by digestion of the resulting amino-acids with L-amino-acid oxidase,<sup>4</sup> and determination of the intact amino-acids with an amino-acid analyzer. In the Tfa-Gly-L-Ala-OMe reaction the product was shown to consist of 54% of the L-(natural) enantiomer and 46% of the D-(unnatural) one, while the reaction of Tfa-Gly-L-Leu-OMe and but-1-ene led to 58.5% of the L- and 41.5% of the D-enantiomer. In a similar reaction with Tfa-Gly-D-Leu-OMe, the ratio of the L-product to D-product was 41:59. In the Tfa-Gly-L-Leu-OMe reaction, over 95% of the leucine residues remained in the original L-form as determined by digestion with L-amino-acid oxidase. This indicates that racemization of this residue took place to a very limited extent, and presents further confirmation of the selectivity of these reactions for glycine residues in glycine dipeptides.<sup>1</sup>

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