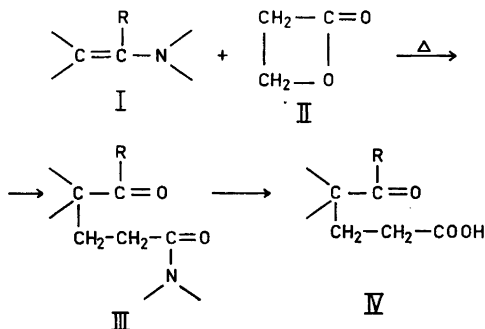


Enamine Chemistry

III.* A New Carboxyethylation
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The reaction of β -propiolactone with amines is complex and different types of reactions are observed depending upon such factors as the solvent, the amine used and the order in which the reactants are mixed.¹ It has now been found that an enamine I, which reacts as a nucleophile (for pertinent references, see Szmuszkovicz²) after being heated with β -propiolactone, II, smoothly and in high yields produces the corresponding δ -ketocarboxylic acid amide, III.

This new reaction, to our knowledge without precedent, implies that a rearrangement takes place as the enamine structure, I, is transformed to the carbonyl derivative, III, in the absence of water. The scope and mechanism of the reaction are now under active study and full details shall be published later. Below, a type-example is given:



Experimental. The Reaction between 1-morpholino-1-cyclohexene and β -propiolactone. 100 g (0.6 mole) of 1-morpholine-1-cyclohexene³ and 28.8 g (0.4 mole) of II in 100 ml of chlorobenzene were refluxed for 4 h (inner temperature 154–155°C). The solvent and excess of enamine were distilled off and the subsequent distillation gave the main fraction with b.p. 187–188°C/1 mm Hg; $n_D^{22} = 1.5090$. Yield 78 g (83 %). (Found: C 64.88; H 8.90; N 5.64; Calc.: for $\text{C}_{13}\text{H}_{21}\text{O}_3\text{N}$ (239.31): C 65.24; H 8.85; N 5.85). Mol. wt: 239 (mass spectrometry).

The 2,4-dinitrophenylhydrazone had mp. 153°C (ethanol and *o*-xylene). (Found: C 54.55; H 6.09; N 16.47; Calc.: for $\text{C}_{19}\text{H}_{25}\text{O}_6\text{N}_5$ (419.43); C 54.40; H 6.01; N 16.70). Mol. wt. (Rast): 428.

Basic hydrolysis of the morpholide gave a 77 % yield of 2-oxocyclohexanepropionic acid with m.p. 64°C. (Lit.⁴: m.p. 64°C). Hydrolysis of the crude reaction product gave an 81 % yield of the acid.

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