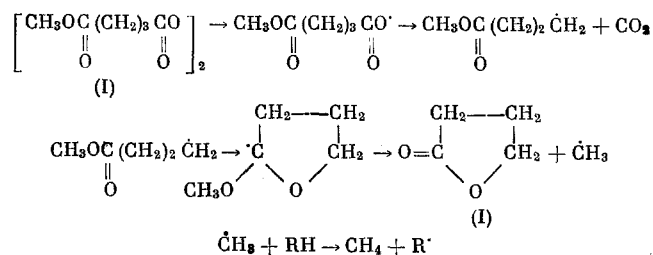


CYCLIZATION REACTION OF  $\gamma$ -CARBOMETHOXYPROPYL  
RADICAL TO  $\gamma$ -BUTYROLACTONE

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While studying the thermal and photolytic decomposition of the dimethyl ester of peroxydiglutamic acid (I) in solution we discovered a new homolytic cyclization reaction. The  $\gamma$ -carbomethoxypropyl radical, generated from (I), is cyclized to  $\gamma$ -butyrolactone (II). The reaction possibly proceeds via the intermediate  $\alpha$ -methoxy- $\alpha$ -tetrahydrofuryl radical, which then undergoes  $\beta$ -decomposition with the elimination of the  $\dot{\text{C}}\text{H}_3$  radical



(II) was identified by GLC and IR spectroscopy ( $\nu_{\text{C}=\text{O}}$  of lactone  $1780 \text{ cm}^{-1}$ ). The radical mechanism of the reaction for the formation of (II) is confirmed by the identification of methane (by GLC) in the decomposition products of (I), and by the observance of a chemical polarization of the nuclear spins (CPN) in the NMR spectrum of the (II) obtained in the decomposition process of (I). The CPN effect, relating to the protons of the  $\beta$ - and  $\gamma$ - $\text{CH}_2$  groups of (II), is found to be in full agreement with the theory given in [1], which postulates transitions between the singlet and triplet ( $T_0$ ) states in the radical pair.

When (I) was subjected to thermal ( $90^\circ\text{C}$ ) and photolytic ( $10^\circ$ ) decomposition in acetic acid the amount of formed  $\gamma$ -butyrolactone was respectively 0.35 mole/mole of (I) and 0.22 mole/mole of (I), and 0.40 mole/mole of (I) when the thermal ( $75^\circ$ ) decomposition was run in benzene. The reactions were run in an argon atmosphere, and the concentration of (I) was 0.15 M/liter. Besides (II), other transformation products of the  $\text{CH}_3\text{OOCCH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$  radicals were observed.

LITERATURE CITED

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