Unter gleichen Bedingungen wird Poly-C in einer Halbwertszeit von 8 Std. zur CDP abgebaut (s. Abb. 2).


4. Zusammenfassung


Substituted Gamma-Lactones. XII

Synthesis of Maculine

By Hans Zimmer and R. Walter

Department of Chemistry, University of Cincinnati
Cincinnati, Ohio


We are presently engaged in synthesizing linearly condensed heterocyclics by utilizing certain substituted 2-benzylidene-γ-butyrolactones of the following type as starting materials:

\[
\begin{align*}
\text{R} & \quad \text{O} \quad \text{X} \\
\text{C} & \quad \text{YH} \\
\text{O} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

1 Y = NH,O; X = H,Br,OMe; R = numerous substituents.

In this communication we wish to report the synthesis of maculine (V), an alkaloid occurring in the bark of several Flindersia species. This publication is prompted by an article by Y. Kubayama, who reported the preparation of dihydrodictamine, a compound structurally related to V. This author used a method similar to the one employed by the present authors.

The synthesis of V reported here proceeded according to the following scheme:

1 Part XI of this series. H. Zimmer and R. Walter, Naturwissenschaften, 50, 531 [1963].
8 T. Okita and Y. Mori, C. A. 56, 4806 [1962].
9 Y. Kubayama, C. A. 57, 16554 g [1962].
Acetylbutyrolactone was condensed with 2-nitro-4,5-methylene-dioxybenzoyl chloride\(^{10}\) to give II, m.p. 153—5°, yield 36%, based on 2-nitro-4,5-methylene-dioxybenzoyl chloride (IR-spectrum \(\nu_{\text{C=O}}\) (lactone) at 5.65 \(\mu\) and \(\nu_{\text{C=O}}\) (ketone) at 5.9 \(\mu\)); anal. calcd. for \(\text{C}_{15}\text{H}_{13}\text{NO}_{7}\): C, 51.62; H, 3.25; N, 5.12; found: C, 51.40; H, 3.37; N, 5.02). The acyllactone II reacted with diazomethane to give the trans-lactone III, m.p. 183—4°, yield 91% (IR-spectrum \(\nu_{\text{C=O}}\) (lactone) at 5.75 \(\mu\); \(\nu_{\text{C=C}}\) at 6.05 \(\mu\)); anal. calcd. for \(\text{C}_{13}\text{H}_{11}\text{NO}_{7}\): C, 53.24; H, 3.78; N, 4.78; found: C, 53.29; H, 3.88; N, 4.68). Upon reduction of the \(\text{NO}_2\)-group of III by \(\text{Pd}\) on charcoal in the presence of methanolic \(\text{HCl}\) rearrangement to dihydroramiculine (IV) occurred smoothly in agreement with the general principle of this type of reaction. IV was obtained in 72% yield, m.p. 196—8° (IR-spectrum did not show any functional groups); anal. calcd. for \(\text{C}_{13}\text{H}_{11}\text{NO}_{4}\): C, 63.67; H, 4.52; N, 5.71; found: C, 63.73; H, 4.70; N, 5.90). IV was dehydrated by refluxing and radiating it with \(\text{UV-light}\) in the presence of an equivalent amount of \(\text{N-bromosuccinimide in CCl}_4\), evaporating this solvent and refluxing the remainder with an excess of collidine\(^{11}\). After chromatographic purification the synthetic alkaloid V was found to be identical in every respect to the authentic material, m.p. 197°, mixed melting point was not depressed and the \(\text{UV-spectra}\) of the natural product and the synthetic sample were superimposable.

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\(^{10}\) W. Repe\ et al., Liebigs Ann. Chem. \textbf{596}, 185 [1955].