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CARBONYLATION WITH INSERTION OF ACETYLENE : A NEW CLASS OF ε-LACTONES.

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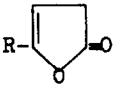
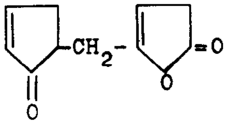
The formation of β, γ -unsaturated γ-lactones I and II :



I

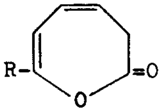


II

from acid halides RCOX or allyl halides $CH_2=CH-CH_2X$, acetylene and nickel carbonyl in ketonic solvents was recently reported (1, 2).

Working with acid halides at 40-50°C in other solvents such as esters or ethers (e.g. ethyl acetate, dioxan, ether, tetrahydrofuran) with the stoichiometric amount of nickel carbonyl and a slight excess of acetylene, and adding water at the end of the reaction, only small amounts of γ-lactones I are formed, the main products being anhydrides RCOOCOR. Of the latter, those fairly stable to hydrolysis have been isolated.

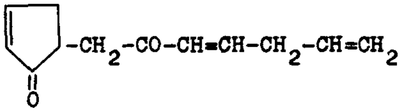
If in the above experiments, acetylene is passed through the solution at a rate sufficiently high to maintain a low concentration of carbon monoxide in the reaction medium, a new class of ε-lactones III having two double bonds in the ring may be obtained together with γ-lactones I and acid anhydrides as by-products.



III

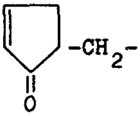
ε-Lactones III result from the addition of two molecules of acetylene and one of carbon monoxide to the acyl group, followed by lactonization.

Allyl halides, which under the conditions of our former experiments in ethers or esters gave mainly IV (3) :



IV

also form small amounts of ε-lactones of type III (with R = V) if in



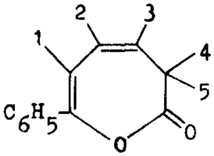
V

addition a large excess of acetylene is used.

The structure of the compounds thus obtained was inferred from the spectroscopic and analytical data and confirmed by transformation into known products.

Table I shows physical constants, elemental analysis, I.R. (stretching of the C=O group) and U.V. absorptions of the isolated compounds.

The NMR (4) spectrum of VI shows absorptions at

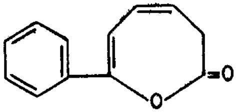
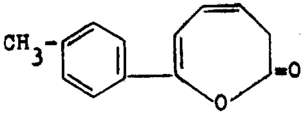
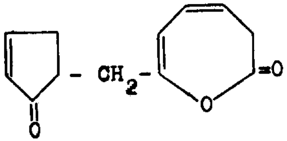


VI

τ 2.28-2.80 (phenyl group); τ 3.47-4.32 (H_1, H_2, H_3 : complex absorption, which by irradiation at τ 6.91 simplifies in ABX pattern); τ 6.91 (H_4, H_5 complex doublet).

In order to obtain the exact spectral parameters of the lactone ring protons, an analysis of the ABX pattern, obtained by irradiation, was made.

TABLE I

	ε-Lactones	I.R.(CCl_4)	U.V.(EtOH 95%)	Elemental analysis
VI	 b.p. 84-85°C/0.03 mm Hg	C = 0 1772 cm^{-1}	λ_{max} 280 mμ log ε = 4.232	found: C = 77.12 % H = 5.27 % calcd.for $C_{12}H_{10}O_2$ C = 77.40 % H = 5.41 %
VII	 m.p. 52-53°C	C = 0 1770 cm^{-1}	λ_{max} 284 mμ logε = 4.310	found: C = 77.89 % H = 6.05 % calcd.for $C_{13}H_{12}O_2$ C = 77.98 % H = 6.04 %
VIII	 m.p. 67-68°C	C=O(lactone) = 1774 cm^{-1} C=O(ketone) = 1714 cm^{-1}	λ_{max} 223 mμ logε= 4.200	found: C = 70.56 % H = 6.10 % calcd.for $C_{12}H_{12}O_3$ C = 70.57 % H = 5.92 %

The crude parameters obtained by this analysis, and the other ones directly extracted from the methylene band, were fed into LAOCOON program, which converged to give the following data (in cps units) :

$W_1 = 647.853 \pm 0.019$

$W_2 = 631.420 \pm 0.017$

$W_3 = 580.360 \pm 0.016$

$W_4 = W_5 = 308.962 \pm 0.014$

R.M.S. error = 0.110

$J_{12} = 5.585 \pm 0.024$

$J_{13} = 0.218 \pm 0.027$

$J_{14} = J_{15} = 0.534 \pm 0.014$

$J_{23} = 9.290 \pm 0.024$

$J_{24} = 0.479 \pm 0.014$

$J_{25} = 0.534 \pm 0.014$

$J_{34} = J_{35} = 6.609 \pm 0.020$

$J_{45} = 0.000$

The spectrum of compound VII reveals parameters of lactone ring protons resembling the corresponding ones of VI. This was observed by analysis of ABX pattern obtained by decoupling from methylene group, and by simple inspection of methylene absorption.

The NMR spectrum of VIII shows absorptions at τ 2.34 (β -olefinic proton of cyclopentenone : double triplet); τ 3.76-3.94 (α-olefinic proton of cyclopentenone and one olefinic proton of lactone:complex); τ 4.15-4.40 (remaining olefinic protons of lactone:complex); τ 6.96 (methylene of lactone:complex doublet); τ 7.07-7.89 (remaining protons:complex).

An additional proof of the structure of compound VI is based on its hydrogenation to ε -phenylcaproic acid, which was found identical with an authentic sample.

Authors thank prof. A.Quilico for the interest.

References

1. L.Cassar and G.P.Chiusoli, Tetrahedron Letters N°25, 2805 (1966)

2. L.Cassar and G.P.Chiusoli, Tetrahedron Letters N°37, 3295 (1965); Chimica e Industria 48, 323 (1966)

3. L.Cassar, G.P.Chiusoli and M.Foà, Tetrahedron Letters N°3, 285 (1967)

4. The NMR spectra were recorded at room temperature using a Varian HA 100 spectrometer; the absorption positions were determined with a Hewlett Packard 5512 A electronic counter. 10% solutions in $CDCl_3$ were used. Chemical shifts are relative to internal tetramethylsilane.