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CYCLIZATION OF β-2-OXOCYCLOHEXYLPROPIONIC ACIDS LEADING TO BICYCLO[3-3-1]NONANE-4,9-DIONES

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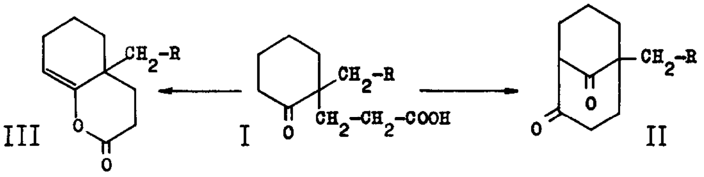
Two by-products obtained from the reaction, respectively, of acryloyl chloride and of cinnamoyl chloride with 4-cyclohex-1'-enylmorpholine were tentatively assigned the bicyclo[3-3-1] nonane-4,9-dione structure (1).

Reaction of methyl-vinylketone with cyclohexanone in the presence of a catalytic amount of ethanolic sodium ethoxide yielded various products; one of these products is probably a bicyclo[3-3-1] nonane derivative; however it was not isolated, but only identified by spectroscopic data (2).

In this report we describe cyclization of the β-2-oxocyclohexylpropionic acids and characterization of the resulting bicyclo[3-3-1] nonane-4,9-diones (II).



IIIa R = C_6H_5-
IIIb R = o-CH_3O-C_6H_4-

Ia R = C_6H_5-
Ib R = o-CH_3O-C_6H_4-
Ic R = o-Cl-C_6H_4-
Id R = p-Cl-C_6H_4-

IIa R = C_6H_5-
IIb R = o-CH_3O-C_6H_4-
IIc R = o-Cl-C_6H_4-
IId R = p-Cl-C_6H_4-

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The acids (I) were prepared from 2-benzylcyclohexanones via cyanoethylation and subsequent hydrolysis (3).

The acids (I) when subjected to dehydrating agents, such as acetic anhydride and acetyl chloride, yielded the corresponding enol-lactones III (4).

For example:

IIIa m.p. 69-70° (+) (from hexane) - Anal.: Calculated for $C_{16}H_{18}O_2$, C = 79,31; H = 7,49; Found C = 79,64; H = 7,41. The infra-red spectrum in carbon tetrachloride gives bands at 1745 cm^{-1} and 1665 cm^{-1}.

IIIb m.p. 81-83° (from hexane) - Anal.: Calculated for $C_{17}H_{20}O_3$, C = 74,97; H = 7,40; Found C = 75,09; H = 7,44. The infra-red spectrum in carbon tetrachloride gives bands at 1740 cm^{-1} and 1665 cm^{-1}.

Acids (I) were also dissolved in tetrahydro- or decahydronaphthalene in the presence of a catalytic amount of p-toluene-sulfonic acid, and the reaction mixture was slowly distilled in order to remove water formed during the reaction. After the usual procedure, a high yield (60-70%) of isomer compounds of the above enol-lactones was obtained. These products were assigned the bicyclic diketone structure II.

The compound IIa is a white solid melting at 81-82°; Anal.: Calculated for $C_{16}H_{18}O_2$, C = 79,31; H = 7,49; Found C = 79,56; H = 7,45.

The n. m. r. spectrum is in excellent agreement with structure IIa.

The infra-red spectrum in carbon tetrachloride shows two strong sharp bands at 1725 cm^{-1} and 1700 cm^{-1} as expected for the diketone structure.

In accordance with its diketone structure compound IIa with hydroxylamine gives a dioxime, m.p. 227-228° (from diluted dioxane) (Anal.: Calculated for $C_{16}H_{20}N_2O_2$, C = 70,56; H = 7,40; N = 10,29; Found C = 70,48; H = 7,47; N = 10,10); with sodium borohydride it gave a mix-

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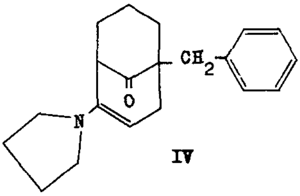
(+) = All melting points are uncorrected ture of stereoisomeric diols boiling at 183-185° (0,1 mm/Hg) (Anal.: Calculated for $C_{16}H_{22}O_2$, C = 78,01; H = 9,00; Found C = 78,33; H = 9,06); with pyrrolidine it gives an enamine, m.p. 96-98° (from hexane). (Anal.: Calculated for $C_{20}H_{25}NO$, C = 81,31; H = 8,53; N = 4,74; Found C = 81,11; H = 8,84; N = 4,64) which was assigned the structure IV for steric reasons.



IV

IIa with aqueous sodium hydroxide at room temperature, or with aqueous sodium carbonate on a steam bath for a short time, yielded Ia quantitatively.

Using the same procedure as for IIa diketones IIb, IIc and IId were also prepared with like yields: IIb, m.p. 87° (from hexane) Anal.: Calculated for $C_{17}H_{20}O_3$, C = 74,97; H = 7,40; Found C = 74,95; H = 7,37; dioxime m.p. 255-256° (from diluted dioxane) Anal.: Calculated for $C_{17}H_{22}N_2O_3$, C = 67,52; H = 9,27; Found C = 67,84; H = 7,37; N = 9,56.
IIc, m.p. 96° (from hexane) Anal.: Calculated for $C_{16}H_{17}ClO_2$, C = 69,43; H = 6,19; Found C = 69,64; H = 6,19; dioxime m.p. 236-237° (from diluted dioxane) Anal.: Calculated for $C_{16}H_{19}ClN_2O_2$, C = 62,63; H = 6,24; N = 9,13; Found C = 62,84; H = 6,24; N = 9,13.
IId m.p. 99° (from hexane) Anal.: Calculated for $C_{16}H_{17}ClO_2$, C = 69,43; H = 6,19; Found C = 69,33; H = 6,25; dioxime m.p. 234-235° (from diluted dioxane) Anal.: Calculated for $C_{16}H_{19}ClN_2O_2$, C = 62,63; H = 6,24; N = 9,13; Found C = 62,69; H = 6,24; N = 8,97.

The infra-red spectra in carbon tetrachloride of IIb, IIc and IId show the same two strong sharp bands as IIa at 1725 cm^{-1} and 1700 cm^{-1}.

A full and detailed account of this cyclization reaction of cycloalkanonpropionic acids will be published elsewhere.

Acknowledgment

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