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Abstract

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A New Method for the Synthesis of 2,2,6,6-Tetraalkyltetrahydropyrandiones-3,5

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The present work gives the results of an investigation of the reaction of diazomethane with monoketones and α-diketones of the furanidine series.

We have established that, under the action of diazomethane on 2,2,5,5-tetramethylfuranidone-3, 2,2,6,6-tetramethyltetrahydropyrone-3 is obtained, as well as traces of 2,2,6,6-tetramethyltetrahydropyrone-4; the best results are obtained when the reaction is carried out by the *in situ* method using N-nitroso-N-methylurethane or N-nitroso-N-methylurethylane, where the yield of the principal reaction product reaches 55–58%. Proof of the structure of 2,2,6,6-tetramethyltetrahydropyrone-3, a representative of the previously almost unknown class of tetrahydro-β-pyrones, was furnished by its oxidation with selenium dioxide to Δ^4-2,2,6,6-tetramethyldihydropyrone-3-ol-4, whose benzilic rearrangement led to 3-hydroxy-2,2,5,5-tetramethylfuranidyl-3-carboxylic acid, identical with the acid obtained from 2,2,5,5-tetramethylfuranidone-3.

[reaction scheme]

In a considerable number of examples we have shown that the interaction of 2,2,5,5-tetraalkylfuranidinediones-3,4 with an ethereal solution of diazomethane proceeds with expansion of the ring between the two carbonyl groups. The 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5 formed under the reaction conditions are enolized and methylated by excess diazomethane, as a result of which the reaction products are the methyl ethers of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5,

[reaction scheme]

The ethers of the enol form are readily hydrolyzed on heating with hydrochloric acid, giving 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5; this reaction may serve as a convenient method for the synthesis of the indicated β-diketones of the tetrahydropyran series.

The β-diketones of the tetrahydropyran series obtained by us readily form various derivatives; thus, for example, 2,2,6,6-tetramethyltetrahydropyrandione-3,5 gives a dioxime, the semibenzylidene derivative is methylated by diazomethane, and enters into an azo-coupling reaction ($^\frown$1). By reduction of the methyl ether of 2,2,6,6-tetramethyltetrahydropyrandione-3,5 with lithium aluminum hydride followed by hydrogenation over platinum, 2,2,6,6-tetramethyltetrahydropyrone-3 was obtained, identical with that obtained from 2,2,5,5-tetramethylfuranidone-3 and diazomethane.

The UV absorption spectra of methanolic solutions of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5 and their methyl ethers have an intense absorption maximum in the region of 250 mμ ($\lg\varepsilon$ 4.6), which indicates substantial enolization of these β-diketones in methanolic solutions and the absence of an intramolecular hydrogen bond. The UV absorption spectra of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5 in 0.01 *N* methanolic NaOH solution show an absorption maximum in the region of 280 mμ ($\lg\varepsilon$ 4.6), which indicates complete enolization of these diketones in methanol and complete dissociation in methanolic sodium ethoxide solution.

It should be noted that in all cases, with the exception of 2,2,5,5-tetramethylfuranidindione-3,4, good yields of the methyl ethers of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5 are obtained only when methanol (10% by volume) is added to the reaction mixture. Since in methanolic solutions 2,2,5,5-tetraalkylfuranidindiones-3,4 exist in the hemiketal form (2), we believe that only this form of the furanidindiones-3,4 is capable of reacting with diazomethane with ring expansion. The high yield of the methyl ether of 2,2,6,6-tetramethyltetrahydropyrandione-3,5, obtained even without addition of methanol, is explained by the fact that the starting furanidindione-3,4 is very hygroscopic (3) and always contains some amount of the hydrate form, constructed analogously to the hemiketal form.

It should be noted that, according to B. Eistert, ring expansion of triketohydrindane under the action of diazomethane proceeds only in the complete absence of water or alcohol (4).

Experimental Part

Methyl ethers of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5. To 300 ml (0.171 g-mol) of an ethereal solution of diazomethane at 0°, 30 ml of absolute methanol is added and, over 15 min with stirring, a solution of 0.05 g-mol of 2,2,5,5-tetraalkylfuranidindione-3,4 in 50 ml of absolute ether and 10 ml of absolute methanol is added. The mixture is left overnight and then the solvents are evaporated in vacuum. The residue is dissolved in petroleum ether; after cooling to −70°, the precipitate is separated. The constants and yields of the methyl ethers obtained are given in Table 1.

Table 1

Methyl ethers of 2,2,6,6-tetraalkyltetrahydropyrandiones-3,5	Yield, %	M.p., °C (after sublimation)	C, % found	C, % calc.	H, % found	H, % calc.
2,2,6,6-Tetramethyl ($C_{10}H_{16}O_3$)	46	74—75	65.2665.20	65.19	8.798.93	8.75
2,6-Dimethyl-2,6-diethyl ($C_{12}H_{20}O_3$)	44	69.8—71.3	67.6767.73	67.89	9.509.55	9.50
2,2,6,6-Bis-tetramethylene ($C_{14}H_{20}O_3$)	18.5	46—47	71.1571.20	71.16	8.658.51	8.53
2,2,6,6-Bis-pentamethylene ($C_{16}H_{24}O_3$)	51.5	124.5—126	72.4872.64	72.69	9.249.26	9.15

2,2,6,6-Tetraalkyltetrahydropyrandiones-3,5. A suspension of 1 g of the pure methyl ether of 2,2,6,6-tetraalkyltetrahydropyrandione-3,5 in 5 ml of 19% HCl is heated with frequent shaking on a water bath for several hours. After cooling, the diketone is separated. If the ether of the enol form is not isolated, but the crude reaction mass formed by the action of diazomethane on furanidindiones-3,4 is subjected to hydrolysis, these β-diketones can be obtained in higher yield, as is evident from the data given in Table 2.

Table 2

2,2,6,6-Tetraalkyltetrahydropyrandiones-3,5 (gross formula)	Yield from pure ether, on ether, %	Yield from pure ether, on α-diketone, %	Yield from crude ether to α-diketone, %	M.p., °C (after sublimation)	C, % found	C, % calcd.	H, % found	H, % calcd.
2,2,6,6-Tetramethyl($C_9H_{14}O_3$)	92.5	42.5	66	158—158.5	63.3163.51	63.54	8.428.54	8.29

2,2,6,6-Tetraalkyltetrahydropyrandione-3,5 (gross formula)	Yield from petro ether, on ether, %	Yield from pure ether, on α-diketone, %	Yield from crude ether to α-diketone, %	M.p., °C (after sublimation)	C, % found	C, % calcd.	H, % found	H, % calcd.
2,6-Dimethyl-2,6-diethyl($C_{11}H_{18}O_3$)	90	37	44	150.8—151.3	66.52 66.39	66.64	9.09 8.99	9.15
2,2-Dimethyl-6,6-tetramethylene($C_{11}H_{16}O_3$)	—	—	40	152.5—153.5	67.41 67.57	67.32	8.34 8.33	8.22
2,2,6,6-Bis-tetramethylene($C_{13}H_{18}O_3$)	96.5	18	38	169—170	70.32 70.17	70.24	8.17 8.23	8.16
2,2-Dimethyl-6,6-pentamethylene($C_{12}H_{18}O_3$)	—	—	41	161.5—162	68.85 68.90	68.54	8.79 8.69	8.63
2,2,6,6-Bis-pentamethylene($C_{15}H_{22}O_3$)	96	49.5	55	193	72.09 72.07	71.97	8.87 8.93	8.86

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Note: Figure translations are in progress. See original paper for figures.