azidothiophosphate in 5 ml of benzene. Immediately after adding the first drops of the azide a yellor color appears (formation of the triazene) and nitrogen is evolved vigorously. At the end of reaction the volatiles were vacuum-distilled and the residue was distilled to give 3.1 g of imidophosphate (IX).

CONCLUSIONS

1. Diphenoxythiophosphorylimidophosphorus trichloride undergoes thermal isomerization to diphenyl (dichlorothiophosphorylimido)chlorophosphate.

2. The reactions of diphenoxythiophosphorylimidophosphorus trichloride with phenol and dimethylamine were studied.

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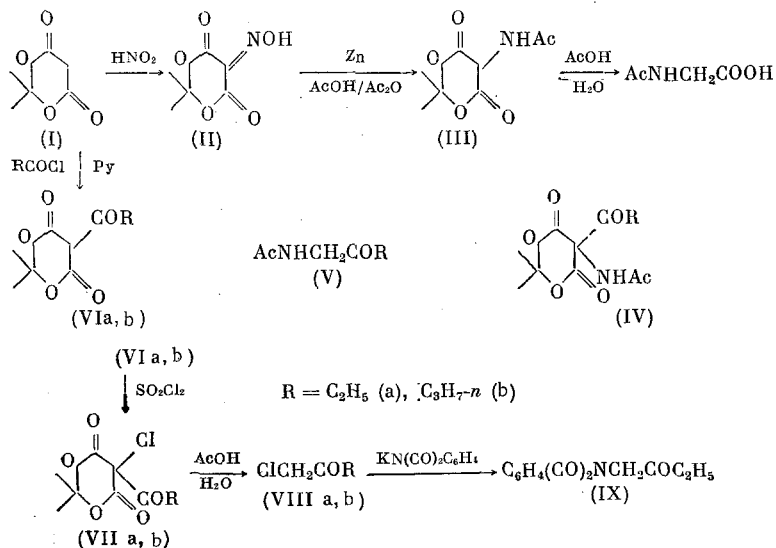5. A. A. Khodak, V. A. Gilyarov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 1117.

REGIOSELECTIVE SYNTHESES
OF α-FUNCTIONALLY SUBSTITUTED KETONES

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α-Functionally substituted ketones (FK) serve as important synthones for obtaining heterocyclic compounds. The most widely used method for synthesizing FK is based on the α-halogenation of ketones. A serious disadvantage of this method is the formation of mixtures of α-halo derivatives in the case of unsymmetrical ketones [1].

In the present paper we studied regioselective paths for the synthesis of FK using Meldrum's acid (I) [2].

$$(I) + (X \text{ a, b}) \rightarrow$$

COCHRN(CO)$_2$C$_6$H$_4$ (XI a, b)

$\xrightarrow[\text{H}_2\text{O}]{\text{AcOH}}$ C$_6$H$_4$(CO)$_2$NCHRCOCH$_3$ (XII a,(b).

$\xrightarrow[\text{H}_2\text{O}]{\text{HCl}}$ HCl·H$_2$NCHRCOCH$_3$ (XIII a, b)

(VI)–(VIII): R = C$_2$H$_5$ (a), n-C$_3$H$_7$ (b). ClCOCHRN(CO)$_2$C$_6$H$_4$ (X a,b). (X)–(XIII):
R = H (a), CH$_3$ (b).

The nitrosation of (I) with HNO$_2$ as described in [3] gives 2,2-dimethyl-4,6-dioxo-5-hydroxyimino-1,3-dioxane (II), the reduction of which with Zn in an AcOH/Ac$_2$O mixture leads to 2,2-dimethyl-4,6-dioxo-5-acetamido-1,3-dioxane (III). The structure of the latter was proved by the PMR spectrum and by hydrolytic cleavage to N-acetylglycine. The attempted C-acylation of (III) with AcCl or EtCOCl in the presence of pyridine (Py) as described in [4] in order to subsequently convert the C-acylation product (IV) to N-acetyl-α-amino-ketones (V) proved unsuccessful. The attempted C-nitrosation of the C-acyl derivatives (VIa, b), obtained by the reaction of (I) with RCOCl in the presence of Py as described in [4] with HNO$_2$ also proved unsuccessful. The chlorination of (VIa, b) with SO$_2$Cl$_2$ in CH$_2$Cl$_2$ gives the 5-chloro derivatives (VIIa, b), which in aqueous AcOH undergo cleavage and decarboxylation to chloromethyl alkyl ketones (VIIIa, b). The latter were identified by conversion to 1-phthalimido-2-butanone (IX) and the 2,4-dinitrophenylhydrazone of ketone (VIIIb).

The acylation of (I) with the acid chlorides of N-phthaloylglycine (Xa) and N-phthaloyl-α-alanine (Xb) respectively gave the 5-(N-phthaloylglycinyl)- and 5-(N-phthaloyl-α-alanyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxanes (XIa, b). The cleavage of (XIa, b) with either aqueous HCl or aqueous AcOH leads either to hydrochlorides of the aminoketones (XIIIa, b) or the N-phthaloyl derivatives (XIIa, b).

As a result, the use of Meldrum's acid (I) permits running a two-step conversion of the acid chlorides of carboxylic acids to FK with a fixed position of the functional substituents.

EXPERIMENTAL

The IR spectra were measured as a KBr pellet on a UR-20 spectrometer, and the PMR spectra were measured on a Tesla BS-497 instrument (100 MHz, internal standard = HMDS).

2,2-Dimethyl-4,6-dioxo-5-hydroxyimino-1,3-dioxane (II) was obtained as described in [3] with some modifications. To a solution of 12 g of Meldrum's acid (I) [2] in 60 ml of water were gradually added 12 g of Na$_2$CO$_3$ and then 4 g of NaNO$_2$, after which the mixture was cooled with ice and, with stirring, dilute HCl solution (1:1) was added in drops until the red color changed to pale yellow. The precipitate was filtered, washed with chilled water, and dried in the air. We obtained 2 g of (II) with mp 107–109°C. The aqueous mother liquor was treated with excess Na$_2$CO$_3$, kept for 3 h at 5°, and the red precipitate of the Na salt of (II) was filtered and then, with stirring and cooling with ice, was added to a mixture of 6 ml of conc. HCl and 20 ml of water. The (II) precipitate was filtered, washed with chilled water, and dried in the air. We obtained an additional 7.3 g of (II) with mp 107–109°. The total yield of (II) was 9.3 g (64%).

2,2-Dimethyl-4,6-dioxo-5-acetamido-1,3-dioxane (III). With stirring, to a solution of 3 g of oxime (II) in 20 ml of AcOH was gradually added 3 g of Zn dust, the mixture was stirred for another hour at 20°, 20 ml of Ac$_2$O was added, the mixture was stirred for 0.5 h, let stand in the air to evaporate the AcOH and Ac$_2$O, the residue was treated with water and dilute HCl solution (1:1), and the precipitate was filtered, washed with water, and dried in the air. We obtained 1.2 g (34%) of (III), mp 143–145° (decompn.) (from alcohol) [5]. PMR spectrum (Py, δ, ppm): 1.58 s (2CH$_3$), 1.98 s (CH$_3$CO). A mixture of 1 g of (III), 5 ml of AcOH, and 5 ml of water was heated for 1.5 h at 80–90°, then evaporated in vacuo, the residue was treated with chilled water, and the precipitate was filtered and dried in the air. We obtained 0.46 g (80%) of N-acetylglycine, mp 206–208° [6].

1-Chloro-2-butanone (VIIIa). With stirring and cooling, to a solution of 8.6 g of (I) in 20 ml of CH$_2$Cl$_2$ were added in succession 10 ml of Py and 6 ml of EtCOCl, the mixture was kept for 40 min at 5° and for 40 min at 20°, treated with water and dilute HCl solution (1:1), and the organic layer was separated, dried over Na$_2$SO$_4$, and evaporated in vacuo. The obtained 2,2-dimethyl-4,6-dioxo-5-propionyl-1,3-dioxane (VIa) (8.8 g) was used as such in the next step. With stirring, to 8.8 g of (VIa) was added in drops 4 ml of SO$_2$Cl$_2$ and the mixture was let stand overnight. We obtained 2,2-dimethyl-4,6-dioxo-5-chloro-5-propionyl-1,3-dioxane (VIIa) as an oil, which was dissolved in a mixture of 6 ml of AcOH and 10 ml of water, heated for 1.5 h at 80–85°, cooled, diluted with water, extracted 3 times with ether, and the extract was washed with NaHCO$_3$ solution and evaporated. After a double fractional distillation of the residue we obtained 1 g (21%) of (VIIIa), bp 128–131°, n_D^{20} 1.4340 [7]. PMR spectrum (CDCl$_3$, δ, ppm): 1.12 t (CH$_3$, J = 0.8 Hz), 2.60 q ($\underline{\text{CH}_2}$CH$_3$, J = 0.8 Hz), 4.20 s (Cl$\underline{\text{CH}}_2$CO).

A mixture of 1 g of (VIIIa) and 2 g of K phthalimide in 7 ml of DMF was stirred for 12 h at 20°, and then it was diluted with water, kept for 5 h at 20°, and the precipitate was filtered and subjected to low-temperature recrystallization from ether. We obtained 1.5 g (75%) of 1-phthalimido-2-butanone (IX), mp 106-107° [8]. PMR spectrum (CDCl$_3$, δ, ppm): 1.05 t (CH$_3$, J = 0.7 Hz), 2.50 q (CH$_2$CH$_3$, J = 0.7 Hz), 4.43 s (NCH$_2$CO), 7.50-7.90 m (aromatic ring).

1-Chloro-2-pentanone (VIIIb). The same as described above, from 2,2-dimethyl-4,6-dioxo-5-n-butyryl-1,3-dioxane (VIb) [4], via the intermediate 2,2-dimethyl-4,6-dioxo-5-n-butyryl-5-chloro-1,3-dioxane (VIIb) (oil), we obtained (VIIIb) in 20% yield, bp 150-152°, n$_D^{20}$ 1.4370 [9]. PMR spectrum (CDCl$_3$, δ, ppm): 1.10 t (CH$_3$, J = 0.8 Hz), 1.45 m (CH$_2$), 2.62 m (COCH$_2$), 4.20 s (ClCH$_2$CO). 2,4-Dinitrophenylhydrazone of (VIIIb), mp 138-139° [9].

The mixed melting point of the obtained 2,4-dinitrophenylhydrazone with an authentic sample [9] was not depressed.

2,2-Dimethyl-4,6-dioxo-5-(N-phthaloylglycyl)-1,3-dioxane (XIa). With cooling and stirring, to a solution of 3.5 g of (I) in 7 ml of CH$_2$Cl$_2$ and 6 ml of Py was gradually added a solution of 3.3 g of the acid chloride of N-phthaloylglycine (Xa) [10] in 7 ml of CH$_2$Cl$_2$, the mixture was kept for 3 h at 20°, evaporated in vacuo, the residue was treated with water and dilute HCl solution (1:1), and the precipitate was filtered, washed with water, and dried in the air. We obtained 3 g (67%) of (XIa), mp 237-238° (decompn.) (from alcohol). Infrared spectrum (ν, cm^{-1}): 1648, 1712, 1775; soluble in dilute KOH solution.

Phthalimidoacetone (XIIa). A mixture of 1.5 g of (XIa), 5 ml of AcOH, and 5 ml of water was heated until the CO$_2$ evolution ceased (3 h, 80-90°), and then it was diluted with water, kept for 12 h at 5°, and the precipitate was filtered, washed with water, and dried in the air. We obtained 0.8 g (92%) of (XIIa) with mp 121-123° [11]. The mixed melting point of the obtained (XIIa) with an authentic sample [11] was not depressed.

Aminoacetone Hydrochloride (XIIIa). A mixture of 1 g of (XIa) and 20 ml of 1:1 HCl solution was refluxed for 7 h, evaporated in vacuo to small volume, the phthalic acid was filtered, and the mother liquor was evaporated in vacuo to dryness. We obtained 0.3 g of (XIIIa) as a slowly crystallizing oil [12]. The obtained (XIIIa) was identified by conversion as described in [12] to 4,5-methylimidazolin-2-one, mp 195-197°.

3-Phthalimido-2-butanone (XIIb). The same as described above, from 3 g of (I) and 3 g of the acid chloride of N-phthaloyl-α-alanine (Xb) [10] we obtained the crude 2,2-dimethyl-4,6-dioxo-5-(N-phthaloyl-α-alanyl)-1,3-dioxane (XIb), which on hydrolysis with aqueous AcOH gave 1.8 g (40%) of (XIIb) with mp 84-86° [10]. The mixed melting point of the obtained (XIIb) with an authentic sample [10] was not depressed.

3-Amino-2-butanone Hydrochloride (XIIIb). The hydrolysis of (XIb) with HCl solution gave (XIIIb) [12] in 60% yield, which was identified by conversion as described in [12] to 4,5-dimethylimidazolin-2-one, mp 290° (decompn.).

CONCLUSIONS

1. The reduction of 2,2-dimethyl-4,6-dioxo-5-hydroxyimino-1,3-dioxane with Zn in an AcOH/Ac$_2$O mixture gives 2,2-dimethyl-4,6-dioxo-5-acetamido-1,3-dioxane, the cleavage of which with aqueous AcOH leads to N-acetylglycine.

2. The chlorination of the 5-acyl derivatives of Meldrum's acid with SO$_2$Cl$_2$ and subsequent hydrolytic cleavage of the intermediate 2,2-dimethyl-4,6-dioxo-5-chloro-5-acyl-1,3-dioxanes by aqueous AcOH give chloromethyl alkyl ketones.

3. The hydrolytic cleavage of the 2,2-dimethyl-4,6-dioxo-5-(N-phthaloyl-α-aminoacyl)-1,3-dioxanes by either aqueous AcOH or HCl leads to either α-phthalimido- or α-aminoketones.

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He(I) PHOTOELECTRONIC SPECTRUM

OF CYCLOPENTADIENYLMERCURY CHLORIDE

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Intramolecular rearrangements are characteristic for the η^1-cyclopentadienyl compounds of the transition and nontransition elements via the 1,2- shifts of the heteroorganic groups along the ring (1,5-sigmatropic rearrangements) [1-3].
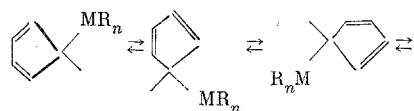
In the absence of other substituents in the ring the process represents a degenerate carbon−carbon metallotropism and frequently proceeds so rapidly that all of the ^1H and ^{13}C atoms appear in the NMR spectra as being equivalent. As a result, these compounds represent one of the classes of "stereochemically nonrigid" or "fluctuating" molecules [2]. Based on the parameters of the NMR spectra, which are averaged due to the rapid exchange process, they resemble the sandwich η^5-cyclopentadienyl compounds with delocalized metal−ligand bonds, which makes a determination of the type of structure difficult in a number of cases. In particular, the structure of dicyclopentadieneylmercury and the cyclopentadienylmercury halides was a subject of discussion [4, 5], and only a detailed study of the low-temperature NMR spectra [6] and IR spectra [7] conclusively proved the presence of a localized C−Hg bond in these molecules.

A study of the structure and rearrangement mechanism of the η^1-cyclopentadienyl compounds of the nontransition elements employing quantum chemical methods [8-12] leads to the conclusion that the main reason for the high lability of the element−carbon bond in these compounds is the σ,π conjugation, which leads to a noticeable delocalization of the electron pairs of the carbon−element bond on the adjacent π system. The migration rate of the organoelement groups MR_n correlates eith the perturbation value $b_1(\pi)$ of the orbital of the cyclopentadienyl ring in $\eta^1\text{-}C_5H_5MR_n$. This effect was observed when studying the photoelectronic spectrum (PES) of silylcyclopentadiene [9]. It is also distinctly manifested in the PES of the allyl compounds of Hg [12]. In the present paper we studied the He(I) photoelectronic spectrum of cyclopentadienylmercury chloride, which enabled us to quantitatively estimate the degree of σ, π conjugation in this molecule.

Cyclopentadienylmercury chloride was obtained and purified as described in [13]. The PES were recorded on the apparatus described in [12]. The He(I) photoelectronic spectrum of C_5H_5HgCl is shown in Fig.1.

To obtain information on the upper occupied MO in the given compound we will compare it with the PES of cyclopentadiene [14] and alkylmercury chlorides [15].

The first band in the cyclopentadiene spectrum (PI = 8.57 eV) corresponds to the ionization of the $1a_2(\pi)$ orbital. It correlates with the first band in the C_5H_5HgCl spectrum. An intense band with a maximum at 10.77 eV (see Fig. 1) corresponds to the ionization of the "unshared pairs" of chlorine (n_{Cl}).