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Structural study of the acylation products of persubstituted para-nitrosophenols

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HIGHLIGHTS

- Ten new acyl derivatives of persubstituted para-nitrosophenols were synthesized.
- The oxygen atom of nitroso group is subjected to acylation.
- Quinonoid structure was proved for all products by NMR and X-ray diffraction.
- The acylation products crystallize in molecular structure with stacking columns.

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ABSTRACT

Acylation of potassium 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenolate with acetic anhydride and benzoyl chloride gave previously unknown 10 derived acyl compounds. ^{1}H NMR spectroscopy and X-ray diffraction data have been used to show that the oxygen atom of the nitroso group undergoes acylation to form the quinoid products. X-ray powder crystal structure analysis of 1-acetoxymino-3,5-di(methoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone, 1-acetoxymino-3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone and 1-benzoyloxymino-3,5-di(propoxycarbonyl)-2,6-dimethyl-1,4-benzoquinon revealed a planar structure of the molecules with quinoid ring as the central moiety. Alkyloxycarbonyl groups rotate in the range 94–101° relative to the plane of the molecule. Typical hydrogen bonds are absent. Molecules fill the unit cell following the closest packing principle in the form of the columns. The ^{1}H NMR spectroscopic data indicates that the direction of acylation and type of structure for the other members of the series of the studied compounds are the same.

1. Introduction

There are known a number of persubstituted nitrosophenols existing as salts in monomeric nitrosoform [1]. Hydrogenation of persubstituted nitrosophenols gives corresponding para-aminophenols [2]. Their some derivatives have been used in the pharmaceutical industry as anti-arrhythmic drugs [3]. Despite the practical importance of these para-nitrosophenols, their chemical properties are poorly understood. It is only known that they dimerize in neutral and mildly acidic medium [4] and their oxidation by hydrogen peroxide in alkaline medium leads to the formation of nitrophenols [5]. Recently, on the example of a structure of the product of alkylation it have been shown that alkylation brought the alkylesters of para-benzoquinonemonooximes [6]. The acylation of persubstituted nitrosophenols is interesting to further study of their reactivity. For conventional nitrosophenols, existing in two tautomeric forms as p-nitrosophenol and p-benzoquinonemonooxime (PQMO), the acylation may proceed both onto the hydroxyl and onto the oxime group depending on the conditions. For example, p-nitrosophenol in the reaction with benzoyl chloride in dioxane gives the p-nitrosophenylbenzoat [7,8]. The reaction of the potassium salt of p-nitrosophenol with acetic anhydride in acetonitril in the presence of crown ether (18-crown-6) proceeds similarly, giving p-nitrosophenylacetate [9]. At the same time, the p-benzoquinonemonooxime acetate was obtained by action of acetic anhydride on PQMO or acetyl chloride on the silver salt of PQMO [10]. The same result was obtained at the acylation of the series of substituted PQMO by acetyl chloride [11]. Similarly, PQMO benzoylation with benzoyl chloride in pyridine occurs at the oxime group with forming an ester [12] and in diethyl ether in the presence of triethylamine [13]. Conclusion about the structure of the acylation products was made using the of electronic spectroscopy data. The nitroso group remains intact in the case of the

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acylation reaction following the oxygen atom of the hydroxy group. Nitroso group has a characteristic absorption at 680–760 nm (n → π transition), causing the substance to be green [14]. At the formation of the oxime type product similar absorption band in the spectrum is missing. These data indicate the reactivity of the two groups, which complicates the prediction of the acylation direction for persubstituted nitrosophenols: on the oxygen atom of the hydroxy or nitroso groups.

In order to clarify the prefer directions of the carbonyl group joining to the persubstituted nitrosophenols, we carried out the reactions of the five potassium salts of 2,6-dialkoxycarbonyl-3,5-dimethyl-4-nitrosophenols (Ia–Ie) with different alkyl groups: methyl, ethyl, propyl, buthyl, amyl and acetic anhydride or benzoyl chloride as the acylating agents. As the result 10 new compounds were obtained: 1-acetoxymino-3,5-di(alkoxycarbonyl)-3,5-dimethyl-1,4-benzoquinones (IIa–IIe) and 1-benzoiloxymino-3,5-di(alkoxycarbonyl)-2,6-dimethyl-1,4-benzoquinones (IIIa–IIIe). In this paper we present the results of syntheses, identification of the products and some structural results obtained by X-ray powder diffraction analysis. The individuality of the compounds is also confirmed by ^{1}H NMR spectroscopy and mass spectrometry.

2. Experimental

2.1. Synthesis

2.1.1. Acylation of the substituted 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenols

Acylation of 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenols (Ia–Ie) were carried out at atmospheric pressure, stirring and heating. Potassium salt of persubstituted p-nitrosophenol (0.2 g) was suspended in absolute diethyl ether (2 ml) with addition acetic anhydride or benzoyl chloride in 1.1 fold molar excess relative to the potassium salt of p-nitrosophenol. The reaction was conducted in the presence of sulfuric acid. The reaction mixture was heated in a round bottom flask with reflux condenser and drying tube with stirring for 1.5–3 h. The product was passed into the diethyl ether solution, the reaction mixture color changed from green to yellow. Then the mixture was cooled to room temperature, poured into 10–15 ml water and the aqueous layer was separated from the organic in a separatory funnel. The aqueous layer was extracted 3 times with 10 ml diethyl ether. The ether extracts were combined with the organic layer and washed with 10% sodium carbonate solution, then with water. Ether was evaporated and the solid residue was dried for 1 h under vacuum in a desiccator over anhydrous sodium sulfate. Those products are isolated as an oil, first had been triturated with hexane and then the resulting crystals were dried under vacuum. The substances were purified by recrystallization from petroleum ether. Some products were obtained as yellow oil. Some of the individual physico-chemical properties of the synthesized compounds are presented below.

2.1.2. (**IIa**) 1-Acetoxymino-3,5-di(methoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{14}H_{15}NO_7$ (Scheme 1)

Yield 60%, yellow crystals, mp 185–187 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, NO—$COCH_3$), 3.93 s (6H, COO—CH_3). Mass spectrum, *m/z* ($I_{rel.}$, %): 309 (7) $[M]^+$, 267 (8), 147 (5), 121 (7), 67 (16), 43 (100), 39 (9).

2.1.3. (**IIb**) 1-Acetoxymino-3,5-di(ethoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{16}H_{19}NO_7$

Yield 50%, yellow crystals, mp 123–125 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.371 t (3H, $COOC_2H_5$), 1.378 t (3H, $COOC_2H_5$), 2.34 t (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.397 q (2H, $COOC_2H_5$), 4.401 q (2H, $COOC_2H_5$). Mass spectrum, *m/z* ($I_{rel.}$, %): 337 (6) $[M]^+$, 295 (20), 249 (6), 204 (5), 67 (13), 43 (100), 39 (5).

2.1.4. (**IIc**) 1-Acetoxymino-3,5-di(propyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{18}H_{23}NO_7$

Yield 53%, yellow crystals, mp 63–65 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (3H, $COOC_3H_7$), 1.02 t (3H, $COOC_3H_7$), 1.75–1.79 m (4H, 2 $COOC_3H_7$), 2.34 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.30 t (2H, $COOC_3H_7$), 4.32 t (2H, $COOC_3H_7$). Mass spectrum, *m/z* ($I_{rel.}$, %): 365 (9) $[M]^+$, 323 (10), 203 (5), 121 (5), 67 (18), 43 (100), 41 (33), 39 (14).

2.1.5. (**IId**) 1-Acetoxymino-3,5-di(butyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{20}H_{27}NO_7$

Yield 40%, yellow oil, fp 0–5 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.974 t (3H, $COOC_4H_9$), 0.975 t (3H, $COOC_4H_9$), 1.417–1.480 m (4H, 2 $COOC_4H_9$), 1.702–1.750 m (4H, 2 $COOC_4H_9$), 2.33 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.34 t (2H, $COOC_4H_9$), 4.35 t (2H, $COOC_4H_9$). Mass spectrum, *m/z* ($I_{rel.}$, %): 393 (2) $[M]^+$, 351 (7), 277 (23), 263 (11), 221 (20), 204 (11), 175 (7), 147 (13), 67 (21), 57 (59), 43 (83), 41 (100), 39 (22).

2.1.6. (**IIe**) 1-Acetoxymino-3,5-di(amyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{22}H_{31}NO_7$

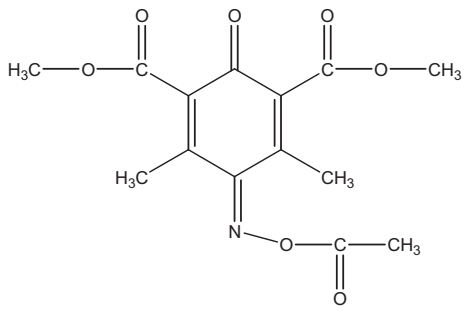
Yield 70%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, 2 $COOC_5H_{11}$), 1.36–1.38 m (8H, 2 $COOC_5H_{11}$), 1.72–1.74 m (4H, 2 $COOC_5H_{11}$), 2.32 c (3H, $PhCH_3$), 2.36 c (3H, $PhCH_3$), 2.46 s (3H, $NOCOCH_3$), 4.32 t (4H, 2 $COOC_5H_{11}$). Mass spectrum, *m/z* ($I_{rel.}$, %): 421 (3) $[M]^+$, 379 (10), 291 (27), 277 (6), 221 (26), 205 (13), 202 (23), 189 (11), 175 (8), 147 (23), 67 (34), 55 (40), 43 (100), 41 (85), 39 (27).

2.1.7. (**IIIa**) 1-Benzoyloxymino-3,5-di(methoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{19}H_{19}NO_7$

Yield 55%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (3H, $PhCH_3$), 2.60 s (3H, $PhCH_3$), 3.95 s (3H, $COOCH_3$), 4.04 s (3H, $COOCH_3$), 7.57 m (2H, NOCOPh), 7.72 m (1H, NOCOPh), 8.11 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 371 (15) $[M]^+$.

2.1.8. (**IIIb**) 1-Benzoyloxymino-3,5-di(ethoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_2{}^1H_{23}NO_7$

Yield 50%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (3H, $COOC_2H_5$), 1.39 t (3H, $COOC_2H_5$), 2.42 s (3H, $PhCH_3$), 2.59 s (3H, $PhCH_3$), 4.40 q (4H, 2 $COOC_2H_5$), 7.56 m (2H, NOCOPh), 7.71 m (1H, NOCOPh), 8.10 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 399 (3) $[M]^+$, 354 (6), 295 (7), 249 (6), 234 (6), 219 (22), 205 (18), 202 (12), 175 (8), 147 (22), 122 (30), 105 (65), 67 (66), 51 (60), 43 (22), 39 (32).



Scheme 1. Structural formula for $C_{14}H_{15}NO_7$ (**IIa**).