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HETEROCYCLIC ANALOGS OF 5,12-NAPHTHACENE-QUINONE. 4*. SYNTHESIS OF 4,11-DIMETHOXY-ANTHRA[2,3-*d*]ISOXAZOLE-5,10-DIONE

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A preparative synthetic method has been developed for 3-chloro-2-formyl-1,4-dimethoxyanthraquinone starting from available 2-methylquinizarine. The condensation of the α-chloroaldehyde obtained with acetone oxime gives 4,11-dimethoxyanthra[2,3-d]isoxazole-5,10-dione.

Keywords: acetone oxime, 3-chloro-1,4-dimethoxy-9,10-anthracenedione-2-carbaldehyde, 4,11-dimethoxyanthra[2,3-*d*]isoxazole-5,10-dione, nucleophilic aromatic substitution, transoximation.

We have already reported the synthesis of heterocyclic analogs of 5,12-naphthacenequinone containing methoxy groups in the α-positions of the anthraquinone system [2, 3]. Similar methoxy derivatives hold synthetic value since the demethylation of the methoxy groups permits the synthesis of hydroxy analogs of naphthacenequinone [4], many of which have extensive biological activity [5]. Furthermore, such methoxy derivatives may have interesting photochemical properties such as a large Stokes shift, as shown for 4,11-dimethoxynaphtho[2,3-*f*]indazole-5,10-dione and its derivatives [6]. Some derivatives of indoxazine (benzisoxazole) are used as drugs [7], leading to interest in the synthesis of isoxazole analogs of 5,12-naphthacenequinone. In the present work, we developed a synthesis of 4,11-dimethoxyanthra[2,3-*d*]-isoxazole-5,10-dione, whose derivatives have not yet been reported.

The synthesis of indoxazines (benzisoxazoles) is most commonly achieved by the cyclization of oximes of aromatic carbonyl compounds containing leaving groups such as halogen atoms in the *ortho* position in basic media [8-10]. This method proved inapplicable for the synthesis of 3-unsubstituted indoxazines in light of the instability of these compounds under basic cyclization conditions [11]. As a consequence, such indoxazines are synthesized from salicylaldehydes [12]. However, this method is not very suitable for the preparation of 4,11-dimethoxyanthra[2,3-*d*]isoxazole-5,10-dione due to the difficulty in obtaining the corresponding *o*-hydroxybenzaldehyde. Thus, for the synthesis of the desired compound, we studied the feasibility of a method based on the use of a "protected hydroxylamine," namely, acetone oxime. The anion obtained from acetone oxime predominantly attacks halogen atoms in *o*-halocarbonyl compounds and the acetone O-aryloximes obtained are converted upon hydrolysis into benzisoxazole derivatives due to subsequent intramolecular transoximation [13].

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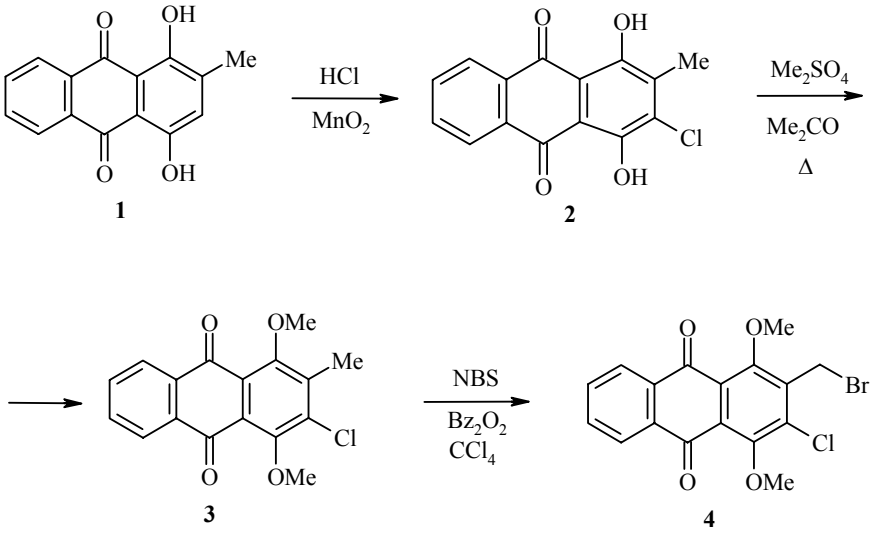
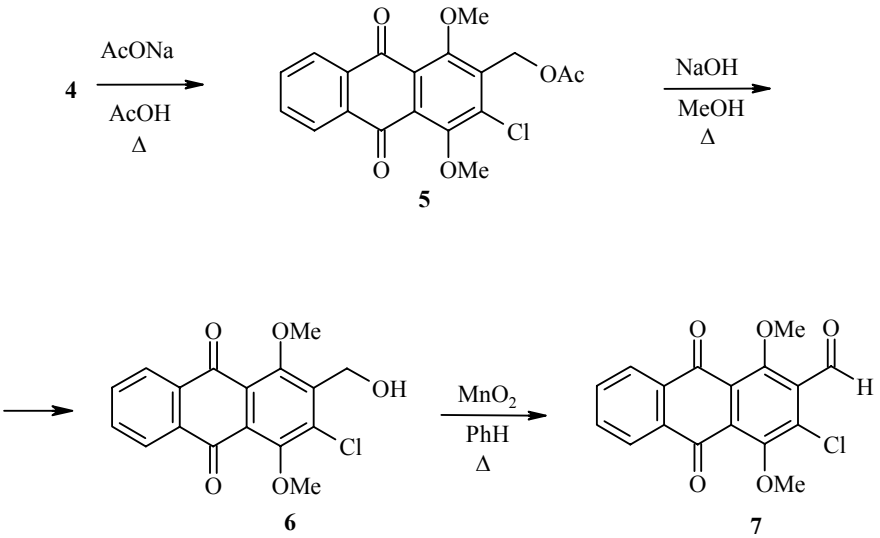
The first step in this synthesis of 4,11-dimethoxyanthra[2,3-*d*]isoxazole-5,10-dione required the development of a method for preparing the key compound, 3-chloro-2-formyl-1,4-dimethoxyanthraquinone. We attempted to use a method employed for the synthesis of 2-formyl-1,4-dimethoxyanthraquinone based on the hydrolysis of the corresponding geminal dihalide [14].

Available 2-methylquinizarine (**1)** synthesized using the Friedel–Crafts reaction [15] was selected as the starting compound. Chlorination of anthraquinone **1** by a method proposed by Gorelik for the chlorination of quinizarine [16] gave 3-chloro-2-methylquinizarine (**2)** in 81% yield. Methylation of the hydroxy groups in quinizarine **2** using dimethyl sulfate in acetone in the presence of potassium carbonate gave dimethoxy derivative **3** in 57% yield. In contrast to 1,4-dimethoxy-2-methylanthraquinone, whose bromination with excess N-bromosuccinimide (NBS) in the presence of benzoyl peroxide gives a dibromomethyl derivative [14], the bromination of **3** stops upon the formation of monobromomethyl derivative **4**, even with a large excess of N-bromosuccinimide. This discrepancy is probably a result of steric hindrance.



1 **2** **3** **4**

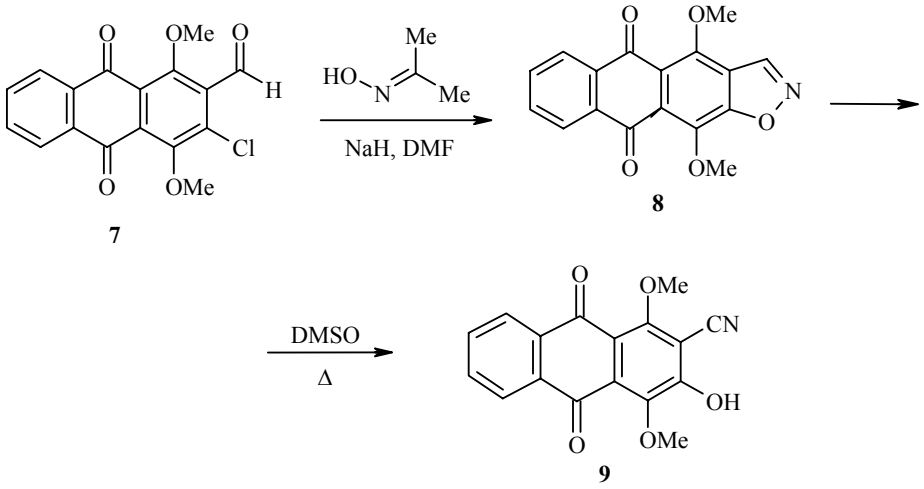
The replacement of the bromine atom in **4** by the action of acetate and subsequent hydrolysis of the resultant ester **5** leads to carbinol **6** in high yield. Oxidation of carbinol **6** by heating with MnO_2 in benzene at reflux gave the key compound for fusion of the isoxazole ring, *o*-halo aldehyde **7**.



5 **6** **7**

We should note some features of the UV spectra of the anthraquinones synthesized. The spectrum of 3-chloro-2-methylquinizarine **2** is virtually identical to the spectrum of quinizarine with a slight bathochromic shift of 3-4 nm of the long-wavelength bands. In contrast, comparison of the positions of the long-wavelength maxima in the spectra of 1,4-dimethoxyanthraquinone (λ_{max} 428 nm) and its derivatives **3-8** shows a significant hypsochromic shift of the absorption maxima by 60-65 nm for tetrasubstituted anthraquinones **3-8** and, thus, the position of the long-wavelength bands of these compounds is virtually identical to the band of monosubstituted 1-methoxyanthraquinone. This behavior indicates significant steric hindrance of the substituents in the β-positions of anthraquinones **3-8**, leading to extrusion of one of these methoxy groups from the molecular plane and its removal from conjugation. Such effects have previously been noted in the UV spectra of 1,2-disubstituted anthraquinones [17].

Arylation of the anion of acetone oxime by *o*-chloro aldehyde **7** proceeds under mild conditions in DMF at 0-5°C and is accompanied by intramolecular transoximation, giving rapid formation of the desired product, 4,11-dimethoxyanthra[2,3-*d*]isoxazole-5,10-dione (**8**), while the corresponding intermediate acetone O-aryloxime could not be observed.



The resultant anthraisoxazole **8** proved unstable under the synthesis conditions. An increase in the temperature or duration of the reaction leads to a significant drop in the yield of the desired product, which is in accord with the literature on the general instability of 3-unsubstituted isoxazoles toward the action of nucleophiles and bases [18]. As in the case of other indoxazines without a substitute in position 3 [19], naphthoindoxazine **8** isomerizes in the presence of NaOH or NEt_3 to give *o*-hydroxybenzonitrile **9**. However such an isomerization may also occur in the absence of base and heating anthraisoxazole **8** in DMSO leads to virtually quantitative isomerization to corresponding *o*-hydroxybenzonitrile **9**, which may be used for the preparative synthesis of this compound.

Fusion of the isoxazole ring and 1,4-dimethoxyanthraquinone leads to a bathochromic shift of the long-wavelength in the spectrum of anthraisoxazole **8** (λ_{max} 389 nm) in comparison with the spectrum of starting aldehyde **7**. Comparison of the absorption spectra of anthraisoxazole **8** and 1,4-dimethoxyanthraquinone indicates a considerable electron-withdrawing effect of the isoxazole ring, leading to a hypsochromic shift of the long-wavelength maximum by 40 nm. The isomerization of anthraisoxazole **8** to nitrile **9** leads to a significant bathochromic shift of the long-wavelength maximum (λ_{max} 450 nm) and drop in intensity.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on a Varian VXR-400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ (for **2-8**) and DMSO-d_6 (for **9**) using TMS as the internal standard. The mass spectra were taken on a Finnigan-MAT SSQ 710 GC/MS (USA) at 70 eV with direct introduction of the sample into the ion source. The sample was heated to 350°C and the temperature of the ionization chamber was 150°C. The absorption spectra were taken on a Hitachi-U2000 spectrometer. The reaction course and purity of the compounds were monitored by thin-layer chromatography on Silufol UV-254 plates. The preparative chromatography was carried out on Merck 60 silica gel.

3-Chloro-1,4-dihydroxy-2-methylanthracene-9,10-dione (2). 2-Methylquinizarine **1** (5.0 g, 20.0 mmol) was dissolved in glacial acetic acid (300 ml) and concentrated hydrochloric acid (30 ml) was added. Then, MnO_2 (3.2 g, 40.0 mmol) was added in small portions with stirring to the mixture at reflux. The mixture was heated at reflux for 30 min, and cooled. The reaction mixture was then poured into 1.0 liter water. The precipitate was filtered off, washed with water, dried, and recrystallized from toluene to give 4.6 g (81%) shiny red crystals; mp 250°C (subl.). UV spectrum (EtOH), λ_{max}, nm (log ε): 205 (4.3), (231), 252 (4.5), 292 (3.9), 325 (3.5), (460), 471 (3.8), 482 (3.9), 504 (3.8), 515 (3.7). ^1H NMR spectrum, δ, ppm: 13.64 (H, s, OH); 13.47 (1H, s, OH); 8.34 (2H, m, H-5,8); 7.85 (2H, m, H-6,7); 2.46 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 288 $[M]^+$ (100), 253 (84). Found, %: C 62.12; H 3.23. $C_{15}H_9ClO_4$. Calculated, %: C 62.41; H 3.14.

3-Chloro-1,4-dimethoxy-2-methylanthracene-9,10-dione (3). A mixture of 3-chloro-2-methyl-quinizarine **2** (3.5 g, 12.1 mmol), calcined potassium carbonate (15.2 g, 110 mmol), and freshly prepared dimethyl sulfate (10.0 ml, 100 mmol) in dry acetone (500 ml) was heated at reflux with vigorous stirring for 40 h in an argon stream. The reaction mixture was then filtered and the filtrate was evaporated in vacuum. The residue was washed with methanol, dried, and purified by chromatography on a silica gel column using benzene–ethyl acetate as the eluent (10:1→4:1) to give 2.2 g (57%) **3** as light-yellow crystals; mp 178-180°C (benzene). UV spectrum (EtOH), λ_{max}, nm (log ε): 210 (4.2), 258 (4.4), (274), 361 (3.7). ^1H NMR spectrum, δ, ppm: 8.18 (2H, m, H-5,8); 7.76 (2H, m, H-6,7); 4.01 (3H, s, OCH_3); 3.92 (3H, s, OCH_3); 2.50 (3H, s, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 316 $[M]^+$ (100), 299 (22), 287 (44), 269 (28). Found, %: C 64.54; H 4.25. $C_{17}H_{13}ClO_4$. Calculated, %: C 64.47; H 4.14.

2-Bromomethyl-3-chloro-1,4-dimethoxyanthracene-9,10-dione (4). A mixture of anthraquinone **3** (2.0 g, 6.3 mmol), N-bromosuccinimide (1.7 g, 9.4 mmol), and benzoyl peroxide (0.24 g, 1.0 mmol) in CCl_4 (100 ml) was heated at reflux with stirring for 5 h. The reaction mixture was cooled and filtered. The residue was washed with chloroform. The filtrate was evaporated in vacuum and the residue was recrystallized from toluene to give 2.1 g (84%) of bromomethyl derivative **4** as light-yellow crystals; mp 162-164°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 215 (4.3), 256 (4.4), (274), 362 (3.6). ^1H NMR spectrum, δ, ppm: 8.18 (2H, m, H-5,8); 7.77 (2H, m, H-6,7); 4.77 (2H, s, CH_2Br); 4.09 (3H, s, OCH_3); 4.03 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 181.90 (C=O), 181.63 (C=O), 155.86,* 152.89, 139.03, 138.20, 133.62; 133.53; 128.22; 125.24; 133.86 (CH), 133.83 (CH), 126.60 (CH), 126.55 (CH), 123.67 (CH2), 62.23 (CH3), 61.85 (CH3). Mass spectrum, *m/z* (I_{rel}, %): 396 $[M]^+$ (100), 315 (62), 285 (26), 257 (22). Found, %: C 51.45; H 3.14. $C_{17}H_{12}BrClO_4$. Calculated, %: C 51.61; H 3.06.

2-Acetoxymethyl-3-chloro-1,4-dimethoxyanthracene-9,10-dione (5). A sample of sodium acetate (4.0 g, 50 mmol) was added with stirring to a hot solution of bromomethyl derivative **4** (2.0 g, 5.1 mmol) in acetic acid (100 ml), heated at reflux for 1 h, cooled, and poured into water (300 ml). The precipitate was filtered off, washed with water, dried, and recrystallized from toluene to give 1.6 g (85%) ester **5** as light-yellow crystals; mp 174-176°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 217 (4.3), 256 (4.4), (273), 361 (3.7). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.16 (2H, m, H-5,8); 7.78 (2H, m, H-6,7); 5.38 (2H, s, CH_2O); 4.04 (3H, s, OCH_3);

* Here and subsequently, all signals without assignment belong to quaternary carbon atoms.

3.98 (3H, s, OCH_3); 2.12 (3H, s, OAc). ^{13}C NMR spectrum, δ, ppm: 181.99 (C=O), 181.72 (C=O), 170.37 (C=O), 156.73, 152.80, 139.32, 136.52, 133.69, 133.52, 128.72, 125.40, 133.88 (CH), 133.79 (CH), 126.59 (CH), 126.54 (CH), 58.43 (CH_2), 63.61 (CH_3), 61.83 (CH_3), 20.65 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 374 $[M]^+$ (67), 344 (22), 332 (58), 314 (100), 302 (81), 285 (57). Found, %: C 60.97; H 4.21. $C_{19}H_{15}ClO_6$. Calculated, %: C 60.89; H 4.03.

3-Chloro-2-hydroxymethyl-1,4-dimethoxyanthracene-9,10-dione (6). Acetate **5** (1.5 g, 4.0 mmol) was dissolved with heating in THF (30 ml) and methanol (20 ml) was added. Then, 20% aq. NaOH (5.0 ml) was added with stirring to the mixture at reflux. The mixture was heated at reflux for 30 min, cooled, and poured into a mixture of water (100 ml), ice (100 g), and concentrated hydrochloric acid (5.0 ml). The precipitate was filtered off, washed with water, dried, and recrystallized from toluene to give 1.1 g (85%) of carbinol **6** as yellow crystals; mp 160-162°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 215 (4.2), 258 (4.4), (274), 365 (3.6). ^1H NMR spectrum, δ, ppm: 8.18 (2H, m, H-5,8); 7.75 (2H, m, H-6,7); 4.95 (2H, s, CH_2O); 4.01 (3H, s, OCH_3); 3.99 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 181.90 (C=O), 181.85 (C=O), 156.07, 152.88, 141.03, 137.92, 133.65, 133.51, 127.86, 125.41, 133.78 (CH), 133.74 (CH), 126.56 (CH), 126.52 (CH), 57.73 (CH_2), 63.47 (CH_3), 61.73 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 332 $[M]^+$ (100), 317 (77), 302 (48), 273 (66), 257 (62). Found, %: C 61.30; H 3.77. $C_{17}H_{13}ClO_5$. Calculated, %: C 61.37; H 3.94.

3-Chloro-1,4-dimethoxyanthracene-9,10-dione-2-carbaldehyde (7). Carbinol **6** (1.0 g, 4.5 mmol) was dissolved in benzene (100 ml) with heating and MnO_2 (8.7 g, 100 mmol) was added with stirring. The mixture was heated at reflux for 1 h and filtered while hot. The precipitate was washed with hot ethyl acetate and the filtrate was evaporated in vacuum. The residue was recrystallized from toluene to give 0.73 g (73%) aldehyde **7** as light-yellow crystals; mp 210-212°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 220 (4.3), 256 (4.4), (271), 365 (3.6). ^1H NMR spectrum, δ, ppm: 10.46 (1H, s, CHO); 8.19 (2H, m, H-5,8); 7.82 (2H, m, H-6,7); 4.04 (6H, s, $2OCH_3$). ^{13}C NMR spectrum, δ, ppm: 181.75 (C=O), 181.24 (C=O), 157.85, 153.16, 136.88, 135.07, 133.68, 133.50, 130.84, 126.19, 188.48 (CHO), 134.14 (CH), 134.03 (CH), 126.71 (CH), 126.68 (CH), 64.72 (CH_3), 62.13 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 330 $[M]^+$ (100), 313 $[M - OH]^+$ (16), 283 (21), 273 (24). Found, %: C 61.71; H 3.39. $C_{17}H_{11}ClO_5$. Calculated, %: C 61.74; H 3.35.

4,11-Dimethoxyanthra[2,3-*d*]isoxazole-5,10-dione (8). Suspension of 60% NaH in mineral oil (0.16 g, 4.0 mmol) was added with stirring to a solution of acetone oxime (0.35 g, 4.5 mmol) in anhydrous DMF (30 ml) in an argon stream and maintained for 20 min at 50°C. The mixture was cooled to 0°C (using ice–NaCl) and a cooled solution of aldehyde **7** (0.50 g, 1.5 mmol) in anhydrous DMF (30 ml) was added rapidly with vigorous stirring to the cooled solution. The reaction mixture was stirred for 5 min and poured into a mixture of water (100 ml), ice (200 g), and concentrated hydrochloric acid (2.0 ml). The reaction product was extracted with ethyl acetate (3 × 40 ml). The extract was washed with water, 1% aq. NaOH (2 × 20 ml), and water. Then, the extract was dried over $MgSO_4$ and evaporated in vacuum. The residue was recrystallized from toluene to give 0.31 g (67%) of isoxazole **8** as yellow crystals; mp 170-172°C. UV spectrum (EtOH), λ_{max}, nm (log ε): 225 (4.2), 249 (4.4), (287), 389 (3.8). ^1H NMR spectrum, δ, ppm: 9.05 (1H, s, CH); 8.22 (2H, m, H-6,9); 7.78 (2H, m, H-7,8); 4.36 (3H, s, OCH_3); 4.27 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 181.90 (C=O), 181.63 (C=O), 158.70, 151.54, 150.04, 140.99, 134.34, 133.85, 125.96, 120.23, 145.65 (CH), 133.73 (CH), 133.52 (CH), 126.62 (CH), 126.55 (CH), 62.27 (CH_3), 61.85 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 309 $[M]^+$ (100), 294 $[M - CH_3]^+$ (21), 280 (19), 264 (18), 236 (10). Found, %: C 66.23; H 3.77; N 4.76. $C_{17}H_{11}NO_5$. Calculated, %: C 66.02; H 3.58; N 4.53.

3-Hydroxy-1,4-dimethoxyanthracene-9,10-dione-2-carbonitrile (9). A suspension of isoxazole **8** (100 mg, 1.2 mmol) in DMSO (5.0 ml) was stirred for about 10 min at 80-90°C until the solid was completely dissolved. The solution was cooled and poured with stirring into water (50 ml). The precipitate was filtered off, washed with water, and dried to give 94 mg (94%) of compound **9** as an amorphous brown powder; mp >250°C (dec.). UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.3), 253 (4.4), (272), 317 (4.0), 347 (3.7), 451 (3.6). ^1H NMR spectrum, δ, ppm: 8.07 (2H, m, H-5,8); 7.85 (2H, m, H-6,7); 3.95 (3H, s, OCH_3); 3.81 (3H, s, OCH_3).

^{13}C NMR spectrum, δ, ppm: 182.03 (C=O), 179.55 (C=O), 161.17, 159.81, 145.16, 133.58, 133.43, 129.48, 117.41, 112.93, 101.54, 133.21 (CH), 133.70 (CH), 126.20 (CH), 126.14 (CH), 62.58 (CH_3), 61.72 (CH_3). Mass spectrum, *m/z* (I_{rel}, %): 309 $[M]^+$ (100), 282 $[M - HCN]^+$ (18), 264 (26), 236 (20). Found, %: C 66.12; H 3.54; N 4.65. $C_{17}H_{11}NO_5$. Calculated, %: C 66.02; H 3.58; N 4.53.

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