# Derivatives of 4-Hydroxy-6-methyl-pyran-2-one (Triacetic Lactone)

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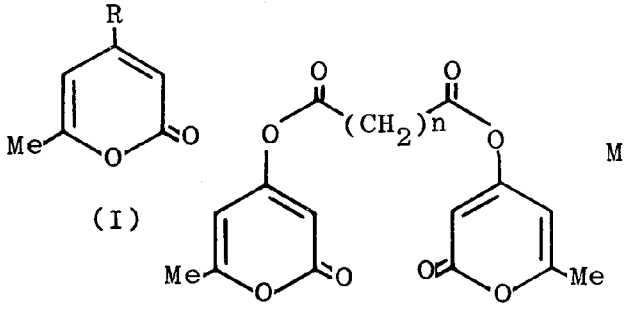
**Summary:** Acylation, using aliphatic dicarboxylic acid chlorides of triacetic lactone (1) has led to the formation of bispyran-2-ones of type (II). The bispyrones (IIa) and (IIb) on treatment with hydrochloric acid gave bispyran-4-ones (IVa) and (IVb) respectively. The action of methyl amine on (IIa,b) yielded the corresponding bispyridones (Va,b). Reactions of (1) with other electrophilic reagents such as thionyl chloride, Vilsmeyer formylation mixture (dimethyl formamide and phosphoryl chloride) and benzene diazonium chloride have resulted in the formation of (VIIa), (VIIIa) and (VIIIb) respectively. 3-Amino-derivatives (VIIId) and (VIIIe) have also been prepared. The 3-position of (1) has been found out to be the exclusive site of electrophilic substitution reactions. The spectroscopic data of the compounds has also been recorded.

**Triacetic lactone** (4-hydroxy-6-methyl-2H-pyran-2-one, 1) was originally prepared by Collie[1]. A controversy arose concerning its tautomeric forms which was finally resolved by the Polish workers[2]. Subsequently the chemistry of this compound was studied extensively. Previously reported reactions of triacetic lactone(1)with electrophilic reagents include bromination[3], nitration[3] and acylation[4] at the 3-position, O-alkylation[5] and O-acylaction 4f at the 4-postion and condensation[5a,6] at the 6-methyl position. Recent interest in the chemistry of triacetic lactone (1) and its derivatives has stemmed from their utility in the synthesis of natural products[5,7], polypyrones[8], polyketide anthracene derivatives[9] and naturally occuring saturated lactones[10]. In view of the synthetic importance of the compounds of triacetic lactone (1), we describe here the preparation of a number of triacetic lactone derivatives, in particular the bisacylated products (II) which can Potentially serve as precursors for the preparation of bispolypyrones and biogenetic-type[11] synthesis of phenolic compounds.

Acylation of (1) using monocarboxylic acid chlorides or acid anhydride has been reported by a number of workers[4]. However the use of aliphatic dicarboxylic acid chlorides as acylating agent for (1) has not been iinvestigated. Literature survey reveals a single instance where dipicolinic acid chloride and dinicotinicacid chloride have been used by Dallacker[12] et al. to bisacylate (1). In the present investigation the bisacylation of triacetic lactone (1) using aliphatic dicarboxylic acid chlorides alongwith other electrophilic substitution reactions have been described.

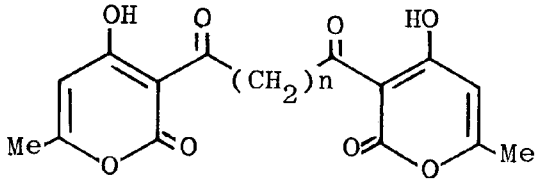
Two equivalent of triacetic lactone (1) on refluxing with one equivalent of appropriate aliphatic diacarboxylic acid chloride in trifluoroacetic acid gave the corresponding bispyran-2-ones of the type (II). The products are characterised by their positive ferric chloride test, elemental analysis and spectroscopic data (Table-1). The acylation of (1) can possibly give either the C-acylation products of type (II) or O-acylation products of type (III). The persistent appearance of enolic pro-



(I)



(III)



(II)

| | | | |
|---|---|---|---|
| a | n=3 | e | n=7 |
| b | n=4 | f | n=9 |
| c | n=5 | g | n=10 |
| d | n=6 | | |

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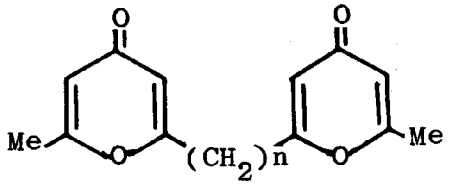
tons at 16.68-16.88 ppm (4,4,-positions) in the nmr spectra (Table-I) confirms structure (II) and eliminates the possibility of the alternative sturcture (III) for these products. The signals at 5.9 ppm are appropriately placed for allylic protons (5, 5'-positions) and unambigously show that the site of acylation in these reactions is the 3-position of triacetic lactone (I).

3-Acyl-4-hydroxy-6-methyl-pyran-2-ones[13] are known to undergo decarboxylation and rearrangement to 2-substituted-6-methyl-pyran-4-ones in the presence of concentrated hydrochlorc acid. Analogoue to these reactions, the bispyrones (IIa) and (IIb) on refluxing with concentrated hydrochloric acid yielded the bis-pyran-4-ones (IVa) and (IVb) respectively. This re-arrangement further substantiate the formulation (II) for the acylation products.



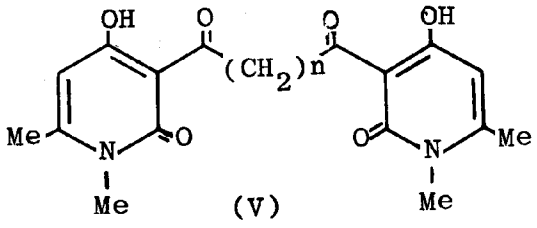
(IV)

a n=3

b n=4

In conformity with their bispyran-2-one structures, the compounds (IIa,b) on treatment with methylamine at room temperature afforded the corresponding bis-pyridone (Va,b) which on deacylation yielded the 4-hydroxy-l, 6-dimethyl-2-pyridone[14] (VI)

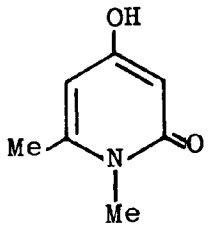
The mode of acylation of (l) using monocarboxylic acid chlorides has been reported[4e,f] to proceed either directly to form 3-acylderivatives or through the formation of enolester which subsequently rearranges to give the 3-acylderivative. These conclusion are based on the



(V)

a n=3

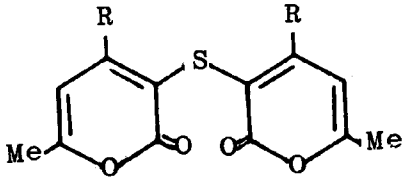
b n=4



(VI)

isolation of C-acylated product in the acylation reactions. In the present investigation as no O-acylation product of type (III) have been identified, it appears that bisacylation occurs directly at the 3-position of (l).

Treatment of triacetic lactone (l) with thionyl chloride at ambient temperature resulted in the formation of 3,3-bis(4-hydroxy-6-methyl-pyran-2-one) sulphide (VIIa). This formulation is supported by elemental analysis and spectral data (Table-I). Additional confirmation is provided by its conversion to methyl ether (VIIIb) using dimethyl sulphate. The same product was also obtained by the action of thionyl chloride on 4-methoxy-6-methyl-pyran-2-one[5] at room temperature. The identity of these products was established through mixed m.p. and superimposable spectral data.



(VII)

a R=OH

b R=OMe

Formylation of (1) did not give the anticipated product (i.e. 3-formyl-4-hydroxy-6-methyl-pyran-2-one) but 3-chloro-4-formyl-6-methyl-pyran-2-one (VIIIa).This formulation is supported by infrared absorptions (1750 $cm^{-1}$ C=O of ring, 1710 $cm^{-1}$ C=O of aldehyde) and nmr spectrum (Table-1) which shows the absence of enolic protons but confirms the presence of aldehydic proton at 10.15 ppm (3-position), allylic proton at 6.25 ppm (5-position) and of methyl at 2.3(6-position). It also forms 2,4-dinitrophenyl hydrazone m.p. 247°

Benzene diazonium chloride on addition to an aqueous solution of sodium carbonate containing tri-

Table 1. Spectral Data.

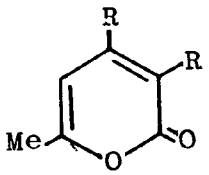
| Compound | S. ppm. | Assignmetn (Position). | ν max. * ($cm^{-}$) | λmax. nm (log ε) |
|---|---|---|---|---|
| IIa | 2.0 (M) | 1 $CH_2$ | 1710 (C=O ring)<br>1643 (C=O side chain) | 309 (3.41) |
| | 2.26 (S) | 2 $CH_3$ (6,6′) | | |
| | 3.1-3.3 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.91 (S) | 2 H (5,5′) | | |
| | 16.88 (S) | 2 H enolic (4,4′) | | |
| IIb | 1.6 | 2 $CH_2$ | 1707 (C=O ring)<br>1640 (C=O side chain) | 310 (4.30) |
| | 2.3 (S) | 2 $CH_3$ (6,6′) | | |
| | 3.1-3.2 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.9 (S) | 2 H (5,5′) | | |
| | 16.7 (S) | 2 H enolic (4,4′) | | |
| IIc | 1.5 | 3 $CH_2$ | 1710 (C=O ring)<br>1640 (C=O side chain) | 308 (4.4) |
| | 2.26 (S) | 2 $CH_3$ (6,6′) | | |
| | 2.95-3.19 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.9 (S) | 2 H (5,5′) | | |
| | 16.81 (S) | 2 H enolic (4,4′) | | |
| IId | 1.4 | 3 $CH_2$ | 1715 (C=O ring)<br>1640 (C=O side chain) | 310 (4.55) |
| | 2.36 (S) | 2 $CH_3$ (6,6′) | | |
| | 3-3.2 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.9 (S) | 2 H (5,5′) | | |
| | 16.85 (S) | 2 H enolic (4,4′) | | |
| IIe | 1.36 | 5 $CH_2$ | 1710 (C=O ring)<br>1640 (C=O side chain) | 310 (4.8) |
| | 2.28 (S) | 2 $CH_3$ (6,6′) | | |
| | 2.95-3 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.9 (S) | 2 H (5,5′) | | |
| | 16.8 (S) | 2 H enolic (4,4′) | | |
| IIf | 1.38 | 6 $CH_2$ | 1715 (C=O ring)<br>1640 (C=O side chain) | 308 (4.9) |
| | 2.26 | 2 $CH_3$ (6,6′) | | |
| | 2.9-3.2 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.9 (S) | 2 H (5,5′) | | |
| | 16.81 (S) | 2 H enolic (4,4′) | | |

| | | | | |
|---|---|---|---|---|
| IIg | 1.36 | 8 CH | 1710 (C=O fing) | 308 (4.47) ($CHCl_3$) |
| | 2.28 | 2 $CH_3$ (6,6′) | | |
| | 3-3.19 (T) | 2 $CH_2$ adj. to C=O | | |
| | 5.92 (S) | 2 H (5,5′) | | |
| | 16.88 (S) | 2 H enolic (4,4′) | | |
| VIIa | 2.2 (D) | 2 $CH_3$ (6,6) | 1700 (C=0 ring) | 300 (3.89) |
| | 6.61 (S) | 2 H (5.5) | | |
| | 16.4 (S) | 2 H enolic (4,4) | | |
| VIIb | 2.2 (D) | 2 Me (6,6′) | 1720, 1700 (C=O ring) | 300 (3.89) |
| | 3.95 (S) | $CH_3$ of Meo- (4,4′) | | |
| | 6.1 (S) | 2 H (5,5′) | | |
| VIIIa | 2.3 (D) | $CH_3$ (6) | 1750 (C=O ring) 1710 (C=O side chain) | 310 (4.15) |
| | 6.25 (S) | H (5) | | |
| | 10.15 (S) | H-Aldehyde (3) | | |
| VIIIb | 2.2 (D) | $CH_3$ (6) | 1735 (C=O ring) | 310 (4.15) |
| | 5.8 (Q) | 1 H (5) | | |
| | 7.5 (M) | 5 H Aromatic (3) | | |
| | 16.6 (S) | 1 H enolic (4) | | |
| VIIId | 2.2 (D) | $CH_3$ (6) | 3410, 3320 ($NH_2$) 1680 (C=O) | 320 (3.91) |
| | 3.6 (S) | 2 H of $NW_2$ (3) | | |
| | 6.1 (S) | 1 H (5) | | |
| | 16.5 (S) | 1 H enolic (4) | | |
| VIIIe | 2.2 (D) | 1 $CH_3$ (6) | 3410, 3320 ($NH_2$) 1680 (C=O) | 320 (3.91) |
| | 3.6 (S) | 2 H of $NH_2$ (3) | | |
| | 3.9 (S) | $CH_3$ of $CH_3O$ (4) | | |
| | 6.1 (S) | 1 H (5) | | |

* Infrared (K.Br) of compounds (IIa-g), (VIIa), (VIIIb,d) showed absorption band in the region 3400-3415 $cm^{-1}$ due to the OH group.

acetic lactone (I) at 5°C resulted in the formation of 3-azophenyl-4-hydroxy-6-methyl-pyran-2-one (VIIIb) as light yellow solid.

3-Nitro-derivative of triactic lactone[3] on reaction with tin and concentrated hydrochloric acid gave 3-aminohydro-chloride (VIIIc), and on reduction with steam and iron filings afforded 3-aminoderivative (VIIId). Methylation of (VIIId) gave (VIIIe). The same product was also obtained by the reduction of 4-methoxy-6-methyl-3-nitro-pyran-2-one[3] using iron filings and steam in benezene as solvent. 3-Amino derivatives (VIIId,e) were characterised by their infrared absorptions at 1685 $cm^{-1}$ (C=O of ring) and at 3410, 3320 $cm^{-1}$ (-$NH_2$).




(VIII)

| | R | R |
|---|---|---|
| a | CHO | Cl |
| b | N=N–Ph | OH |
| c | $^{+}NH_3Cl$ | OH |
| d | $NH_2$ | OH |
| e | $NH_2$ | OMe |

## Experimental

Ultraviolet spectra were recorded on the unicam SP 800 spectrophotometer in ethanol, infrared spectra (unicam SP 200) for mulls in Nujol and NMR spectra were measured with Perkin-Elmer R10 (60MHZ) spectrophotometer with $CDCl_3$ as solvent and tetramethyl silane as internal reference, unless otherwise stated. All melting points are uncorrected.

Triacetic lactone(4-Hydroxy-6-methyl-pyran-2-one) (1) was prepared by the deacetylation of dehydroacetic acid (Koch Light London) using Collie's method. m.p. 188°C.

*General method for the preparation of bispyran-2-ones (II):*

A mixture of tiracetic lactone (1) (0.05 mole) and appropriate dicarboxylic acid chloride (0.025 mole) in trifluoroacetic acid (15 ml) was refluxed on a steam bath for 2.5 hours. The resulting solid products of bispyrones (II) were filtered out from the reaction mixtures. Products (IIb,c,f,g) and (IIa,d,e) were crystallized from ethanol-chloroform mixture (1:1) and ethanol-pet. ehter (60-80°C) mixture (1:1) respectively. Experimental conditions and analytical data for individual compounds are given in Table-II.

**Bispyran-4-one (IVa):**

Compound (IIa) 1 g. ) was suspended in concentrated hydrochloric acid (20ml) and the mixture refluxed for 6 hours. After cooling the reaction mixture was neutralized which on crystallisation from benzene gave white solid m.p. 140°C. $\nu$max. 1680 $cm^{-1}$ (C=O 4-pyrone ring). Found: C, 69.10, H, 6.00; $C_{15}H_{16}O_4$ requires C, 69.23; H, 6.15%).

Bispyran-4-one (IVb) was also obtained by the above method m.p. 160

pet. ehter (60-80°C) mixture (1:1) respectively. Experimental conditions and analkytical data for individual compounds are given in Table-II.

*Bispyran-4-one (IVa):*

Compound (IIa, 1.0 g) was suspended in concentrated hydrochloric acid (20ml) and the mixture refluxed for 6 hours. After cooling the reaction mixture was neutralized. The products was filtered out which on crystallisation from benzene gave white solid m.p. 140°C. $\nu$ max. 1680 $cm^{-1}$ (C=O 4-pyrone ring). Found: C, 69.10, H, 6.00; $C_{15}H_{16}O_4$ requires C, 69,23; H, 6.15%).

Bispyran-4-one (IVb) was also obtained by the

Table II Reaction conditions for the preparation of Bispyran-2-ones (II) and their analytical data.

| Compound | $ClOC(CH_2)_n COCl$ | Yield % | M.P. (°C) |
|---|---|---|---|
| IIa | n=3 | 14 | 135 |
| IIb | n=4 | 27 | 183-184 |
| IIc | n=5 | 40 | 168-169 |
| IId | n=6 | 40 | 156-157 |
| IIe | n=7 | 50 | 180-181 |
| IIf | n=8 | 60 | 142-143 |
| IIg | n=10 | 61 | 142 |

| | | Analysis | | | |
|---|---|---|---|---|---|
| | | Found | | Calcd | |
| | Formula | C | H | C | H |
| IIa | $C_{17}H_{16}O_8$ | 59.01 | 4.68 | 58.62 | 4.59 |
| IIb | $C_{18}H18O_8$ | 59.24 | 4.98 | 59.66 | 4.97 |
| IIc | $C_{19}H_{20}O_8$ | 60.5 | 5.20 | 60.63 | 5.31 |
| IId | $C_{20}H_{22}O_8$ | 61.35 | 5.21 | 61.53 | 5.64 |
| IIe | $C_{21}H_{24}O_8$ | 62.2 | 5.8 | 62.37 | 5.94 |
| IIf | $C_{22}H_{26}O_8$ | 63.39 | 6.2 | 63.16 | 6.22 |
| IIg | $C_{24}H_{30}O_8$ | 64.69 | 6.68 | 64.57 | 6.73 |

above method m.p. 160°C $\nu$ max. 1680 $cm^{-1}$ (C=O of 4-pyrone ring). (Found: C, 70.20; H, 6.35; $C_{16}H_{18}O_4$ requires C, 70.07; H, 6.56%).

*Bispridone (Va):*

A mixture of bispyrone (IIa, 1.0g.) in 25% in aqueour methyl amine (25ml) was kept at ambient temperature for five days. Evaporation of the solution afforded viscous residue which on crystallisation from pet. ether (60-80°C)- ethanol mixture gave white solid m.p. 230°C $\nu$max. 1690 $cm^{-1}$ (C=O of 2-pyrone ring), 1640 $cm^{-1}$ (C=O of side chain). (Found: C, 61.2; H, 6.0; N,7.5; $C_{19}H_{22}O_6N_2$ requires C,60.96. H,5.88. N,7.48%).

Bispyridone (Vb) was also prepared by the action of methylamine (25%) with bispyrone (IIb) as given in the previous method. Product on crystallistaion from ethanol-pet. ether (60-80°C) gave white needles m.p. 210°C $\nu$ max. 1685 $cm^{-1}$ (C=O of 2-pyrone ring), 1640 $cm^{-1}$ (C=O side chain). (Found: C, 61.56; H, 5.9; N.7.4; $C_{20}H_{24}O_6N_2$ requires C,61.85; H,6.18; N, 7.21%).

Deacylation of bispyridones (Va, b):

A mixture of bispyridone (Va) or (Vb) (0.5 g.) and concentrated sulphuric acid (2 ml) was heated in anoil bath at 175-180°C for 5 minutes. After cooling the reaction mixture was poured into ice-water mixture and then neutralized with barium hydroxide. The solid was filtered out. Filtrate on evaporation yielded 4-hydroxy-1,6-dimethyl-2-pyridone (VI) m.p. 228°C (from ethanol). (Lit.[14] m.p. 230°C). The identity of the compound was established by the comparison of m.p., mixed m.p. and comparison of spectral data with an authentic sample.

*3,3-Bis-(4-hydroxy-6-methyl-pyran-2-one) sulphide (VIIa):*

Triacetic lactone (1) (4.5g.) was added gradually to thionyl chloride (15 ml). The reaction mixture was left at room temperature for 6 hours. The unreacted thionyl chloride was removed and residue on crystallisation from benzene gave off white needles. m.p. 260°C (Dec.) (Found: C, 51.08; H, 3.99, S, 11.41; $C_{12}H_{10}O_6S$ requires C, 51.06; H, 3.54; S, 11.34%).

*3,3-Bis-(4-methoxy-6-methyl-pyran-2-one) sulphide (VIIb):*

A mixture of (VIIa) (1 g.), dimethyl sulphate (1 ml) and anhydrous potassium carbonate (6.0 g.) in acetone (50 ml) was refluxed for 10 hours with stirring. After cooling the reaction mixture was filtered. Filtrate was evaporated and residue on recrystallisation from ethanol-pet. ether (60-80°C) gave light yellow solid m.p. 190 (Dec.) (Found: C, 54.1; H, 4.57; S, 9.87; $C_{14}H_{14}S\,O_6$ requires C, 54.19; H, 4.52; S, 10.32%).

The same product was also obtained when a mixture of 4-methoxy-6-methyl-pyran-2-one[5] (3.0 g.) and thionyl chloride (10.0 ml) was kept at room temperature for 24 hours and then evaporated to dryness under vacuum. The dark brown residue on crystallisation from ethanol-pet. ether (60-80°C) gave (VIIb). identified by m.p., mixed m.p. (190°C) and comparison of spectral data.

*4-Chloro-3-formyl-6-methyl-pyran-2-one (VIIIa):*

Finely powdered triacetic lactone (1) (5 g.) was added gradually with stirring to a mixture (1:1) (12 ml) of dimethylformamide and phosphorus oxychloride. The resulting thick viscous mass was allowed to stand at room temperature for 12. hours, then poured into ice-water mixture (100 ml). The lihgt yellow solid was filtered out which on crystallisation from ethylacetate-pet. ether (60-80°C) mixture (2:1) gave light yellow needles m.p. 125°C. (Found: C, 48.7; H, 2.65; Cl, 20.0, $C_7H_5O_3Cl$ requires C, 48.69; H, 2.89; Cl, 20.57%). The compound on treatment with 2,4-dinitrophenyl-hydrazine gave the hydrazone m.p. 247°C.

*3-Azophenyl-4-hydroxy-6-methyl-pyran-2-one (VIIIb):*

Benzenediazonium chloride was added to triacetic lactone (1.59) dissolved in 10% aqeuous solution of sodium carbonate (20 ml) at 5°C. After one hour the reaction mixture was acidified with acetic acid. The resulting yellow precipitate was filtered, dried, and crystallised from thanol as yellow solid m.p. 192-193°C. (Found: C, 62.45; H, 4.31; N, 12.15; $C_{12}H_{10}n_2O_3$ requires C, 62.62; H, 4.34; N, 12.17%).

*3-Amino-4-hydroxy-6-methyl-pyran-2-one hydrochloride (VIIIc):*

4-Hhdroxy-6-methyl-3-nitro-pyran-2-one[3] (5 g.) in concentrated hydrochloric acid (15 ml) was treated with tin metal (5 g.). The reaction mixture was diluted with water (50 ml) and hydrogen sulphide gas was passed to remove tin. The precipitate was filtered and the filtrated onevaporation gave white solid. m.p. 240°C (Dec.). $\nu$ max. 2250, 2450 ($NH_3$), 1700 (sh), 1685 $cm^{-1}$ (C=O of 2-pyrone ring).

*3-Amino-4-hydroxy-6-methyl-pyran-2-one (VIIId):*

A mixture of 4-hydroxy-6-methyl-3-nitro-pyran-2-one[3] (0.3 g.) and activated iron filings (3 g) in benzene (30 ml) was vigorously refluxed for half an hour. Water (4 ml) was added through a dropping funnel in 1.0 ml portion at half hourly intervals and evaporated. Residue on crystallisation fron benzene-pet. ehter (60-80°C)

mixture (2:1) gave white needles. m.p. 140°C. (Found: C, 51.2; H, 4.65; N, 9.91; $C_6H_7O_3N$ rquires C, 51.06; H, 4.96; N. 9.92%).

*3-Amino-4-methoxy-6-methyl-pyran-2-one (VIIe):*

This compound was obtained by the methylation of (VIIId) using dimethyl sulphate as described in the preparation of compound (VIIIb) m.p. 115°C. (Found: C. 54.10; H, 5.6; N, 9.03. $C_7H_9NO_3$ requires C, 54.19; H, 5.80; N, 9.03%).

The same product (VIIIe) was also obtained by the reduction of 4-methoxy-6-methyl-3-nitro-pyran-2-one[3]

using iron filing and steam. The identity of the product was established by m.p., mixed m.p. (115°C) and comparison of spectral data.

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