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Reinvestigation of the synthetic and mechanistic aspects of Mn(III) acetate mediated oxidation of enones

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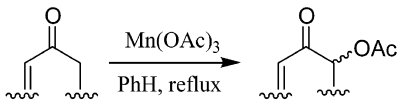
Abstract—$Mn(OAc)_3$ mediated α′-acetoxylation of α,β-unsaturated enones is reinvestigated from a synthetic and mechanistic point of view and an improved procedure based on the use of acetic acid as a co-solvent is presented. Excellent results were obtained for a variety of structurally diverse and synthetically important enones under the optimized conditions.

1. Introduction

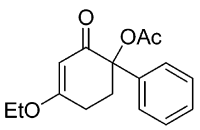
Selective α′-acetoxylation of α,β-unsaturated ketones **1** provides key precursors for pharmaceutically important compounds and useful chiral ligands.[1] As Williams and Hunter reported that the $Mn(OAc)_3$ oxidation of enones in AcOH produces α′-acetoxy enones, with low yields when compared to more commonly used lead(IV) acetate, the utility of this reagent was diminished.[2] Watt and co-workers greatly improved the yields by using excess dried $Mn(OAc)_3$ in refluxing benzene.[3] Today, $Mn(OAc)_3$ mediated acetoxylation is one of the most useful methods for the synthesis of α′-acetoxy α,β-unsaturated ketones **2** (Scheme 1).



1 **2**

Scheme 1.

Although successful α′-acetoxylation of a great variety of substrates have been reported so far by us and others (Table 1), there are some problems associated with the use of $Mn(OAc)_3$. A brief list of them is as follows: (1) excess $Mn(OAc)_3$ (4–6 equiv.) is generally used for acceptable yields and reaction times; (2) many contradictory results can be seen when literature reports are closely inspected. These include, the amount of $Mn(OAc)_3$ which was employed to carry out the desired conversion, and irreproducible yields/reaction times were observed under the same set of conditions. A representative example of this is the α′-acetoxylation of 1-indanone (**1a**) to 2-acetoxy-1-indanone (**2a**) that is a key precursor of the HIV protease inhibitor indinavir. Hiyama[4] reported a 53% yield as compared to the 82% previously reported by Demir.[5a] Possibly, the most striking contradictory observation is the different chemoselectivity observed for the same substrate under seemingly identical reaction conditions. For example, $Mn(OAc)_3$ mediated oxidation of β-ethoxy cyclohexenone **1c** was recently reported to be giving tandem α′-acetoxylation, and α′-phenylation product **3** in a 56% yield together with a 35% acetoxylation product **2c**. This observation was shown to be general for a variety of β-alkoxy cyclohexenone and cyclopentenone derivatives.[6] The presence of the arylation product was explained on the basis of fast trapping of the α′-keto radical by the solvent benzene. We reported the acetoxylation of β-methoxy cyclohexenone in a 79–83% yield and only a trace amount of unidentified arylated products were detected in crude ^1H NMR spectra.[7]



3

These inconsistencies and the use of an undesirable amount of $Mn(OAc)_3$ reduced the value of the method. This indirectly indicates that the mechanism and the factors governing the outcome of this reaction are not so clear. Considering that there are not many simple methods for the direct acetoxylation of enones, optimization of $Mn(OAc)_3$

Keywords: Enones; Oxidation; $Mn(OAc)_3$; Alkenes.
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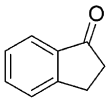
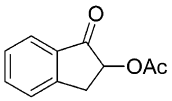
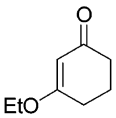
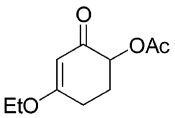
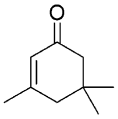
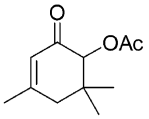
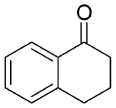
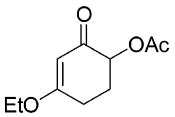
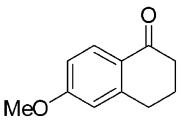
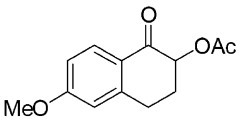
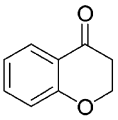
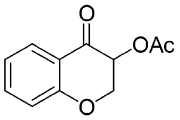
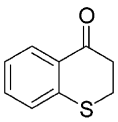
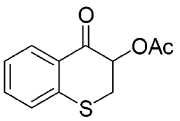
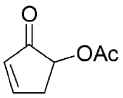
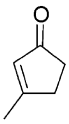
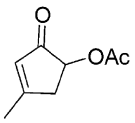
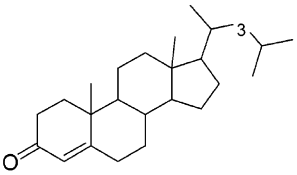
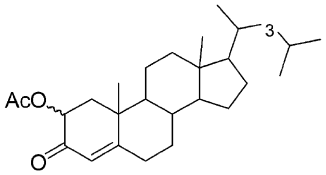
Table 1. Yields and structures of α′-acetoxy α,β-unsaturated ketones[a]

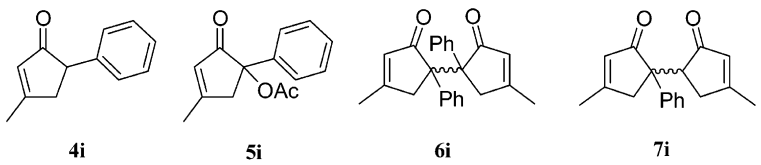
Entry	Enone **1**	Acetoxy enone **2**	Yield (%)[b]	Time (h)	Yield (%)[c]
1		**1a** 	98	1	53, A[4] 82, A[5a]
2		**1b** 	97	7	81,[d] A[7] 35, A[6]
3		**1c** 	99	7	78, B[10]
4		**1d** 	98	5	59, B[11] 86, A[5a]
5		**1e** 	97	5	82, A[5b]
6		**1f** 	96	5	82[12]
7		**1g** 	96	5	89[12]
8		**1h** 	75	2	65, A[13]
9		**1i** 	83	2	81, A[13]
10[e]		**1j** 	98	11	20, B[14]

[a] 1 mmol enone and 1.25 mmol $Mn(OAc)_3$ in 11 mL benzene–AcOH (10:1) was stirred under reflux; although 1.25 equiv. of $Mn(OAc)_3$ was used for full conversion, the addition of 0.25 equiv. of $Mn(OAc)_3$ towards the end of the reaction greatly shortens the reaction times.
[b] Isolated yields.
[c] Yields of previously reported acetoxylations mediated by Mn(III) acetate (Method A) or lead(IV) acetate (Method B).
[d] For methoxy derivative.
[e] 1:6 mixture of easily separable isomers was obtained.

mediated α′-acetoxylation of enones and reaching its maximum potential has a great importance from a synthetic and economical point of view. Herein we report our investigation towards understanding the nature of this reaction together with increasing its efficiency and reproducibility.

2. Results and discussion

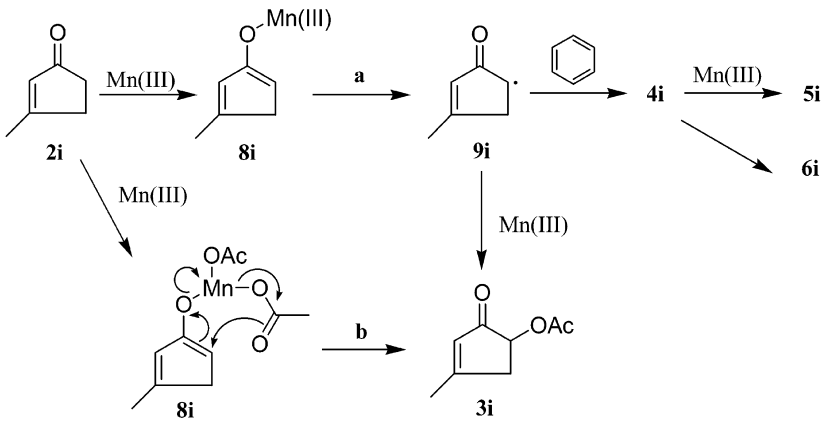
We started our investigations with the synthesis of $Mn(OAc)_3{\cdot}2H_2O$ from $Mn(OAc)_2{\cdot}4H_2O$ and $KMnO_4$ according to well established methods[8] in order to provide consistency for the source of $Mn(OAc)_3$ because Bush and



Scheme 2.

Finkbeiner[9] showed that the reactivity of $Mn(OAc)_3$ may change with the way it is synthesized. Next, we chose 1-indanone **1a** as the model substrate for our experiments and investigated its reaction with 4 equiv. $Mn(OAc)_3$. We first directed our attention to the reactivity of $Mn(OAc)_3$ and conversion times. According to the optimized procedure by Watt,[3] $Mn(OAc)_3$ was dried over P_2O_5 under high vacuum to remove water and was then reacted with **1a** in refluxing benzene monitored by TLC and GC–MS. Although a smooth reaction was observed, conversion was slow, therefore $Mn(OAc)_3$ was further dried in a heating gun (refluxing xylene) under high vacuum to obtain a dark brown colored $Mn(OAc)_3$. Reaction with this extensively dried $Mn(OAc)_3$ provided only a trace amount of product. An interesting property of this dry $Mn(OAc)_3$ was the lack of AcOH odor that is typical for any $Mn(OAc)_3$ either from a commercial source or synthesized from $Mn(OAc)_2{\cdot}4H_2O$ and $KMnO_4$. Considering that the absence of AcOH might be responsible for the slow conversions, we carried out the reaction in a AcOH–benzene (1:100) mixture. Reaction under this condition was quite successful with increased conversion rates. A careful monitoring revealed that increasing the AcOH content shortened the reaction time and full conversion was observed after 15 min at 1:10 AcOH–benzene affording **2a** in >99% yield (GC–MS). This is quite an improvement when compared to previous reports in terms of its yield, reaction time and reproducibility. $Mn(OAc)_3$ from a commercial source provided similar results as long as it was extensively dried. Although benzene is the most frequently used solvent after the report by Watt, we found that cyclohexane and MeCN can also be used instead of benzene and α'-acetoxylation was the only detectable product in a GC–MS analysis despite slower conversion rates. Reactions in THF and DMF were too slow to be useful for α'-acetoxylation. It is worth mentioning that acetic anhydride as a co-solvent instead of acetic acid shows a similar rate enhancement whereas the latter is more effective. Another optimization was made for the determination of the amount of $Mn(OAc)_3$ required for full conversion. Based on the largely accepted radical mechanism, a minimum 2 equiv. of $Mn(OAc)_3$ was necessary. After a series of reactions, we have found that 1 equiv. of $Mn(OAc)_3$ is sufficient for this conversion. A slight excess (1.25 equiv.) of the $Mn(OAc)_3$ was used to ensure complete conversion. Several structurally diverse enones were tested under optimized conditions for **1a** and where possible a comparison was made with previously reported results as shown in Table 1.

Although conditions were not optimized for any particular enone type, excellent results were obtained for a variety of enones. As can be seen in Table 1, these are the best available yields for the specified conversion except the fact that highly toxic reagent thallium(III) triflate (not shown in table) provides **2a** in a 99% yield.[15] Considering many high yield (>90%) hydrolysis methods for α-acetoxy groups that were developed thus far, this optimized protocol can also be considered as one of the most useful ways to obtain α'-hydroxy α,β-unsaturated ketones.[16] Generally, no product other than acetoxylation was detected in the ^1H NMR spectrum of crude products and they were pure enough for further synthetic manipulations. An apparent exception was observed for the cyclopentenones **1h** and **1i** in which a small amount of side products were detected in crude mixtures by NMR and GC–MS. These products were identified for **1i** and found to be an α'-phenylation product **4i**, α'-phenylation and α'-acetoxylation product **5i** and a dimerization product **6i**. Products **4i**, **5i** and **6i** (two isomers were separated providing a 1:2.5 ratio) were isolated in an approximate ratio of 1:2.5:2 accounting for ~15% of the starting material. These seem to be pointing out the intermediacy of **4i**, which is acetoxylated at the benzylic position or dimerized in an alternative pathway (Scheme 2). Thus, phenylation instead of acetoxylation is a minor alternative route, resulting in aromatic signals in NMR spectra of crude products of $Mn(OAc)_3$ mediated



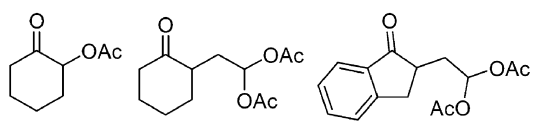
Scheme 3.

acetoxylation reactions. In a previous report, the formation of products **6i** and **7i** was reported, but not **4i** and **5i**.[13] Although these products do not have any importance from a synthetic point of view, they would be useful towards understanding the nature of the reaction as discussed below.

It is hard to justify the role of acetic acid, but it could be related to an increased solubility of $Mn(OAc)_3$ in the reaction mixture. Although the structure of $Mn(OAc)_3$ has been shown to be an oxo-centered triangle of Mn(III) with bridging acetates,[17] the prevalent form in benzene and a benzene–acetic acid mixture can be quite different resulting in different conversion rates and isolated yields.

For the mechanism of the reaction, both radical mechanism (route **a**) and ligand transfer via metal-enolate intermediate (route **b**, proposed based on $Pb(OAc)_4$ mediated acetoxylation of carbonyl compounds) have been proposed (Scheme 3).[2] Since $Mn(OAc)_3$ is a single electron oxidant and a vast majority of the reactions mediated by it have been shown to be taking place via a radical mechanism, route **a** is widely accepted.[17]

Although discrimination between the mechanisms is not a trivial question at this stage, we wish to underline a few points and address the questions to be clarified to improve our understanding of these types of processes. First, we carried out preliminary reactions to compare the behavior of enones with saturated ketones in the presence or absence of vinyl acetate. Oxidation of cyclohexanone afforded acetoxylation product **10**[18] together with side products in an unoptimized reaction (GC–MS). Same reaction in the presence of vinyl acetate mainly afforded product **11** along with little acetoxylation. Oxidation of **1a** in the presence of vinyl acetate afforded acetoxylation together with small amount (~15%) of alkene addition product **12** in benzene (Scheme 4). Different behavior of enones and saturated ketones might be the indication of different mechanisms (routes **a** and **b** in Scheme 3) depending on the types of substrates and solvents.[19] The structure and the amount of $Mn(OAc)_3$ employed in this study, possible presence of homolysis labile organomanganese[20] or manganese bound radical[21] intermediates should be clarified to elucidate the preferred mechanistic pathways and widen the scope of the reaction, a subject already under investigation.



10 **11** **12**

Scheme 4.

In conclusion, we have presented an improved procedure based on the use of acetic acid as a co-solvent. From a synthetic point of view, excellent results were obtained for a variety of structurally diverse and synthetically important enones under optimized conditions. From an economical point of view, as low as 1.25 equiv. $Mn(OAc)_3$ can be used as compared to the previously used 4–6 equiv. Moreover, MeCN and cyclohexane can also be used instead of benzene and acetic anhydride instead of acetic acid even though the presented conditions seem to be the best choice. However, combinations of these possibilities may prove to be more useful for different substrates and applications. We have also shown in unoptimized reactions that saturated ketones can be substrates of the $Mn(OAc)_3$ mediated acetoxylation.[18] Besides, these optimized conditions can be useful for the intermolecular addition of ketones to alkenes previously reported to be a low yield process that generally requires the use of an excess amount of carbonyl compound. Applicability and generality of these reactions together with the kinetic and mechanistic investigations in this context will be reported in due course. As a result, this report will be helpful by providing not only reliable and reproducible results for the $Mn(OAc)_3$ mediated acetoxylation of enones, but also a better understanding of the reaction for other applications utilizing $Mn(OAc)_3$.

3. Experimental

NMR spectra were recorded on a Bruker DPX 400. Chemical shifts δ are reported in ppm relative to $CHCl_3$ (^1H: δ=7.26) and $CDCl_3$ (^{13}C: δ=77.0) as an internal standard. Column chromatography was conducted on silica gel 60 (mesh size 40–63 μm). IR spectra were obtained from a Perkin–Elmer Model 1600 series FT-IR spectrometer and are reported in cm^{-1}. TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Merck), and the spots were visualized with UV light (λ=254 nm). GC–MS spectra were determined using a ThermoQuest (TSP) TraceGC-2000 Series equipped with Phenomenex Zebron ZB-5 capillary column. All known compounds have data in agreement with the previously published values; **2a**, **d**,[5a] **2b**,[6] **2c**,[10] **2e**,[5b] **2f**, **g**,[12] **2h**, **i**,[13] **4i**,[22] **6i**, **7i**,[13] **10**,[18] $Mn(OAc)_3.2H_2O$ was prepared as reported previously (Ref. 8, p 308). As reported by Bush and Finkbeiner,[9] increasing the amount of water at the end of the reaction yields $Mn(OAc)_3$ that results in much slower conversions and slightly reduced yields, possibly related to longer reaction times.

3.1. General procedure for the α′-acetoxylation of α,β-unsaturated ketones

A solution of 1 mmol α,β-unsaturated ketone and 1.25 mmol $Mn(OAc)_3$ in 11 mL benzene–AcOH (10:1) was stirred under reflux (Dean–Stark apparatus) during which the dark brown color of $Mn(OAc)_3$ disappeared by time which was also monitored by GC–MS and TLC. After all starting material was consumed, the reaction mixture was diluted with ether and washed with brine. Resulting organic phase was dried over $MgSO_4$ and concentrated under vacuum. If necessary, crude products were purified by column chromatography using EtOAc–hexane as eluent. In some cases, direct filtering of the reaction mixture through a pad of silica provided pure acetoxy enones. Reactions with 5–10 mmol substrates worked equally well.

For the oxidation of cyclohexanone and alkene addition reactions, the same procedure was applied according to the following points; 2 equiv. of alkene with respect to carbonyl compound was used for addition reactions. Due to the high volatility of vinyl acetate, Dean–Stark apparatus was

removed after refluxing the $Mn(OAc)_3$ solution for 15 min and substrates were added on to the resulting mixture.

3.1.1. 2-Acetoxy-4-cholesten-3-one (2j).[14] *Major isomer*. White solid, mp 102–104 °C (EtOAc–hexane); IR ($CHCl_3$, cm^{-1}) 1683, 1739, 2867, 2948; ^1H NMR ($CDCl_3$) δ 0.63 (3H, s), 0.79 (6H, d, J=5.5 Hz), 0.83 (3H, d, J=6.5 Hz), 0.9–1.1 (9H, m), 1.12 (3H, s), 1.15–1.6 (10H, m), 1.7–2.0 (4H, m), 2.07 (3H, s), 2.14–2.23 (2H, m), 2.37–2.47 (1H, m), 5.25 (1H, dd, J=12.5, 4.9 Hz), 5.7 (1H, s); ^{13}C NMR ($CDCl_3$) δ 12.4, 18.9, 21.3, 22.6, 22.9, 23.2, 24.2, 24.5, 28.3, 28.6, 33.3, 35.0, 36.1, 36.4, 37.8, 39.8, 39.9, 41.4, 43.2, 51.0, 56.1, 56.4, 70.9, 120.8, 129.4, 170.6, 173.8, 194.0. Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.68; H 10.47 found C, 78.85; H, 10.66

Minor isomer. White solid, mp 121–123 °C (EtOAc–hexane); IR ($CHCl_3$, cm^{-1}) 1686, 1742, 2868, 2944; ^1H NMR ($CDCl_3$) 0.63 (3H, s), 0.79 (6H, d, J=6.5 Hz), 0.84 (3H, d, J=6.4 Hz), 0.85–2.35 [22H(1.24, CH_3 and 2.10, CH_3), m], 5.38 (1H, dd, J=15, 5.3 Hz); 5.67 (1H, s); ^{13}C NMR ($CDCl_3$) δ 12.3, 18.5, 19.0, 21.2, 21.3, 22.9, 23.2, 24.1, 24.4, 28.4, 28.5, 32.3, 32.9, 35.4, 36.1, 36.5, 39.84, 39.88, 41.0, 41.8, 42.7, 54.7, 56.1, 56.4, 71.7, 122.0, 170.7, 171.6, 194.1. Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.68; H 10.47 found C, 78.75; H, 10.57.

3.1.2. 5-Acetoxy-3-methyl-5-phenyl-2-cyclopentenone (5i). Colorless oil, IR ($CHCl_3$, cm^{-1}) 1624, 1719, 3020; ^1H NMR ($CDCl_3$) δ 2.09 (3H, s), 2.16 (3H, d, J=1 Hz), 3.05 (1H, d, J=18.3 Hz), 3.24 (1H, d, J=18.3 Hz), 5.99 (1H, d, J=1 Hz), 7.2–7.3 (5H, m); ^{13}C NMR ($CDCl_3$) δ 19.9, 21.5, 47.2, 84.9, 124.9, 128.51, 128.54, 128.7, 138.2, 170.1, 174.2, 202.4; MS (EI), m/z 230 ($M^{+\cdot}$, 7), 187 (33), 170 (15), 141 (10), 128 (9), 105 (100), 76 (29). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H 6.13 found C, 73.15; H, 6.24.

3.1.3. 4,4′-Dimethyl-1,1′-diphenyl-bicyclopentyl-3,3′-diene-2,2′-dione (6i).[13] Separation of isomers provided a 2.5:1 ratio.

Major isomer. White solid, mp >165 °C (decompose); IR ($CHCl_3$, cm^{-1}) 1629, 1683; ^1H NMR ($CDCl_3$) δ 1.71 (6H, s), 2.94 (2H, d, J=19.6 Hz), 3.95 (2H, d, J=19.6 Hz), 5.47 (2H, s), 7.05–7.2 (6H, m), 7.57 (4H, d, J=7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.1, 45.9, 60.7, 127.4, 128.1, 129.9, 130.6, 138.9, 177.8, 209.7

Minor isomer. White semi-solid; IR ($CHCl_3$, cm^{-1}) 1630, 1689; ^1H NMR ($CDCl_3$) δ 2.0 (6H, s), 2.51 (2H, d, J=18 Hz), 3.9 (2H, d, J=18 Hz), 5.74 (2H, s), 7.05 (4H, m), 7.1–7.2 (6H, m); ^{13}C NMR ($CDCl_3$) δ 19.7, 46.0, 60.1, 127.6, 127.7, 129.1, 129.7, 139.7, 177.0, 209.3.

3.1.4. 2-(2,2-Diacetoxy-1-ethyl) cyclohexanone (11). Colorless liquid, IR ($CHCl_3$, cm^{-1}) 1709, 1757, 2863, 2938; ^1H NMR ($CDCl_3$) δ; 1.34 (1H, m), 1.47 (1H, m), 1.60 (1H, m), 1.81 (1H, m), 1.98 (3H, s), 2.0 (3H, s), 2.16–2.38 (6H, m); 6.70 (1H, dd, J=5.7, 5.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.0, 25.5, 28.3, 33.3, 34.8, 42.1, 46.0, 89.7, 168.7, 168.8, 210.3. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H 7.49 found C, 59.65; H, 7.54.

3.1.5. 2-(2,2-Diacetoxy-1-ethyl) indanone (12). Colorless viscous oil, IR ($CHCl_3$, cm^{-1}) 1712, 1759; ^1H NMR ($CDCl_3$) δ 1.78 (1H, m), 1.97 (3H, s), 2.03 (3H, s), 2.48 (1H, m), 2.66 (1H, m), 2.89 (1H, dd, J=17.1, 4.5 Hz), 3.35 (1H, dd, J=8.1, 17.1 Hz), 6.88 (1H, dd, J=4.6, 6.6 Hz), 7.3 (1H, m), 7.6 (1H, d, J=7.3 Hz), 7.52 (1H, m), 7.6 (1H, d, J=7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1, 33.4, 35.0, 43.2, 89.7, 124.4, 126.7, 127.8, 135.1, 136.6, 153.4, 168.6, 168.7, 206.1. Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H 5.84 found C, 65.31; H, 5.97.

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