Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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To cite this Article Rangappa, Paramashivappa and Shine, Henry J.(2008) 'Reactions of thianthrene cation radical tetrafluoroborate with aldehydes: formation of α-(5-thianthreniumyl)aldehyde tetrafluoroborates - a facile synthesis of α-ketols through Lobry de Bruyn-van Ekenstein rearrangement', Journal of Sulfur Chemistry, 29: 1, 9 — 18
To link to this Article: DOI: 10.1080/17415990701753407
URL: http://dx.doi.org/10.1080/17415990701753407

Journal of Sulfur Chemistry
Vol. 29, No. 1, February 2008, 9–18

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RESEARCH ARTICLE

Reactions of thianthrene cation radical tetrafluoroborate with aldehydes: formation of α-(5-thianthreniumyl)aldehyde tetrafluoroborates – a facile synthesis of α-ketols through Lobry de Bruyn–van Ekenstein rearrangement

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(*Received 23 August 2007; final version received 23 October 2007*)

Reactions of thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) with aldehydes, namely, butanal, pentanal, hexanal, heptanal, octanal, nononal, decanal, undecanal, dodecanal, tridecanal, and 3-phenylpropanal, led to the formation of α-(5-thianthreniumyl)aldehyde tetrafluoroborates (**13a**–**k**). Adducts (**13a**–**k**) are unstable and are converted to the corresponding hydrates (**14a**–**k**) when exposed to moisture or by deliberate addition of water to their solutions. Adducts (**13a**–**k**) and their hydrates (**14a**–**k**) were characterized with ^1H, ^{13}C, and DEPT NMR spectroscopy. Interestingly, when solutions of adducts (**13a**–**k**) in acetonitrile were stirred with activated alumina, facile conversion to α-ketols (**15a**–**k**) occurred. It is proposed that the formation of α-ketols (**15a**–**k**) occurred through the Lobry de Bruyn–van Ekenstein rearrangement from the initially formed α-hydroxyaldehydes. α-Ketols **15a**–**j** were isolated in good yield and their identities were confirmed with NMR spectroscopy.

Keywords: aldehydes; thianthrene cation radical; α-ketols

1. Introduction

About 30 years ago, one of us reported that reactions of thianthrene- ($Th^{\bullet+}$), phenoxathiin-, N-methylphenothiazine-, and N-phenylphenothiazine cation radical perchlorates with ketones gave β-ketosulfonium salts **1**–**4** (Figure 1) (*1–4*). The reactions were described as probably beginning with the addition of the cation radical to the enolic form of the ketone (*3*), which has been supported in later work by Wayner (*5*).

Surprisingly, although the enolic content of simple aldehydes is higher than that of ketones (in aqueous solution) (*6*), suggesting that additions of organosulfur cation radicals to aldehydes should be facile, such reactions with aldehydes were not reported until 1994 (*7*). A series of adducts (**5a**–**h**) was prepared by the reaction of aldehydes with thianthrene cation radical

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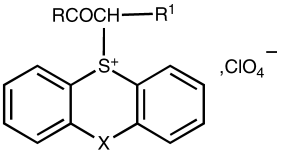
ISSN 1741-5993 print/ISSN 1741-6000 online

DOI: 10.1080/17415990701753407
http://www.informaworld.com

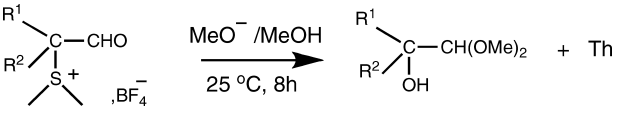


1-4

1	**2**	**3**	**4**
X = S	O	NMe	NPh

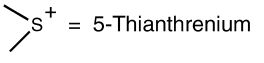
R, R^1 = alkyl, aryl, cycloalkyl

Figure 1. Compounds **1**–**4**.



5a-h **6a-h**

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
R^1	C_6H_{13}	$PhCH_2$	$-(CH_2)_5-$	Ph	Et	C_9H_{19}	tBu	Et
R^2	H	H	-	H	H	H	H	Et

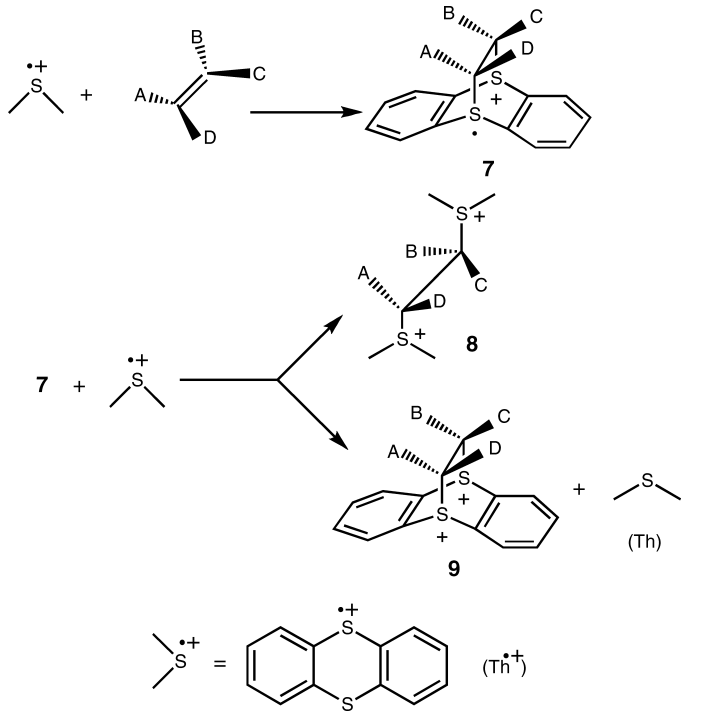


Scheme 1.

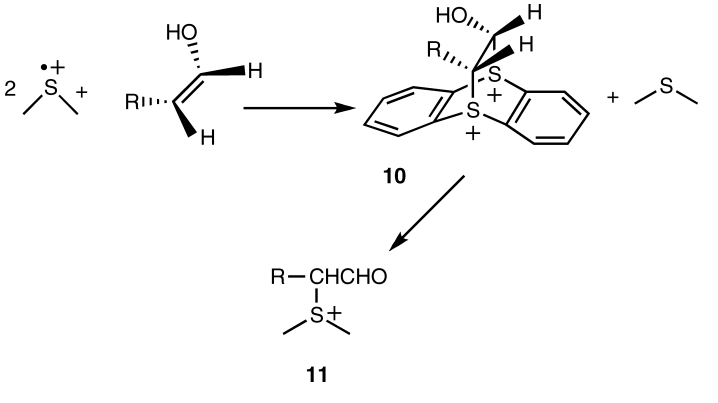
tetrafluoroborate ($Th^{\bullet+}BF_4^-$), among which only **5a**–**c** were stable enough to be isolated as pure crystalline compounds. The remainder (**5d**–**h**) decomposed on storage and, particularly, on contact with moisture. Nevertheless, all **5a**–**h** were reported to have given satisfactory ^{1}H NMR spectra and were converted by reaction with MeO^-/MeOH into stable α-hydroxyacetals **6** (Scheme 1).

Addition of $Th^{\bullet+}$ to alkenes has been shown to involve the formation of a cyclic intermediate **7** from which two types of dicatonic adducts (**8** and **9**) are formed (Scheme 2) (*8*). In that reactions of $Th^{\bullet+}$ with ketones and aldehydes are thought to begin with the enolic forms, we set out to search for the formation of an adduct (**10**, Scheme 3) of $Th^{\bullet+}$ and aldehydes because of the encouraging work of Schulz (*7*) and because aldehydes have a higher enolic content than ketones. We have proposed this scheme, recently, as a possible route to the adducts of aldehydes and also ketones (*9*). In the event, we have been unable to find evidence for the participation of **10** in reactions of $Th^{\bullet+}$ with butanal, even when conducting the reactions with an NMR search at low temperature – a technique that was successful in the reaction of $Th^{\bullet+}$ with 2,2-dimethyl-2-butene (*10*).

As a consequence of our taking up reactions with aldehydes, however, we were successful in preparing 11 adducts (**13a**–**k**) of $Th^{\bullet+}BF_4^-$ and aldehydes (**12a**–**k**) and have characterized them with ^{1}H and ^{13}C NMR spectroscopy. We have found that these adducts can be hydrated in solution to form the hydrates (**14a**–**k**) and that they (**13a**–**k**) are converted directly into isolable α-ketols (**15a**–**k**) by being stirred in MeCN solution with basic alumina. Bearing in mind how many preparations of hydroxy ketones can be found in the literature (*11*), the reactions on alumina serve as a convenient two-step conversion of α-methylene-aldehydes into the corresponding α-ketols.



Scheme 2.

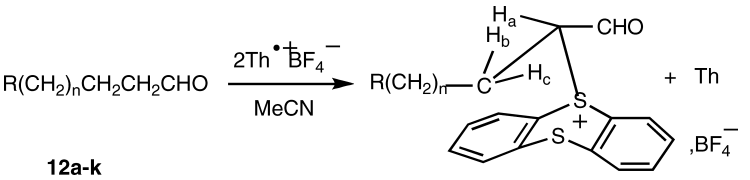


Scheme 3.

2. Results and discussion

2.1. *Preparations of adducts 13a–k*

A reaction of $Th^{\bullet+}BF_4^-$ with the aldehydes (**12a**–**k**) occurred readily in acetonitrile to give α-(5-thianthreniumyl)aldehyde adducts **13a**–**k** (Scheme 4), which were precipitated from the solution by the addition of dry ether. Only **13a, b,** and **k** were obtained as solids. The others (**13c**–**j**) were obtained as viscous oils. Nevertheless, all adducts were characterized with ^1H, ^{13}C, and DEPT NMR spectroscopy. In each of our ^1H NMR spectra, the aldehyde proton (9.44 ppm) was clearly visible and the coupling behavior of the C-2 and C-3 protons (shown as H_a, H_b, and



12a-k

13a-k

12a-j, R = Me; **12k**, R = Ph

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**
n =	0	1	2	3	4	5	6	7	8	9	0

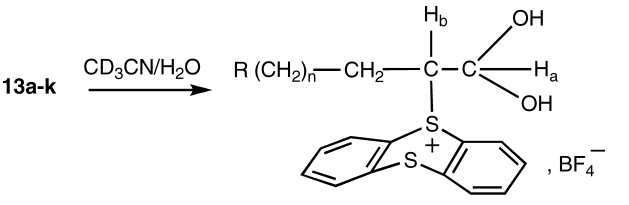
Scheme 4.

H_c in Scheme 4) was consistent throughout the series. It is notable that in every adduct, the NMR signal for the aldehyde proton was a singlet, with δ spanning the narrow range of 9.44–9.45 ppm; there was no indication of coupling with the α-proton, H_a. Correspondingly, in each of **13a**–**j** the signal from H_a was a doublet of doublets with δ spanning the narrow range of 5.58–5.60 ppm and J = approximately 7 and 4.5. Coupling with H_a, here, is attributed to H_b and H_c. Again, no indication of coupling between H_a and C*H*O was discernable. Coupling between an aldehyde and α-proton is ordinarily quite small; in the range of 1–3 Hz (*12*). In our adducts, it appears that the conformation around the C_1-C_2 bond is such as to make coupling between H_a and C*H*O even smaller, too small to be registered. Furthermore, rotation about the C_2-C_3 bond must also be restricted to give rise to the dd signal from H_a in all adducts except **13k,** where a triplet (J = 6.8 Hz) was obtained. The coupling patterns of the thianthrenium protons were also consistent, appearing as four sets of dd and four sets of td throughout the series. The ^{1}H NMR signals of the remaining CH_2 groups in **13c**–**j** were broad multiplets that overlapped and were not well integrated or decipherable. ^{1}H and ^{13}C NMR data for only the solid products **13a, b,** and **k** are given in Section 3. The data for **13c**–**j** were similar to those of **13a**, **b**, and **k** and are not therefore, reported. The ^{1}H NMR spectra of **13c**–**j** showed that small amounts of an impurity were present. This did not impede our deciphering parts of the spectra, however. The impurity was the hydrated adduct, which is described below. The ^{13}C NMR and DEPT data for all adducts (**13a**–**k**) were clear and in full agreement with their structures.

We have noted that **13c**–**j** were oils. Possibly, the lengthening of the alkyl chain and/or the presence of small amounts of hydrate was the cause of our obtaining oils rather than solid products.

2.2. *Hydrated adducts 14a–k*

Hydration of aldehydes occurs more easily than of ketones and is made all the more easy with aldehydes by the presence of an electron withdrawing group on the α-carbon atom (*6*). The classic example, often quoted in textbooks of organic chemistry, is the stable chloral hydrate (*6*). Thus, hydration of adducts such as **5** and **13** containing the electron-withdrawing Th^+ group should not be unexpected. Schulz *et al.* (*7*) noted that **5** decomposed on contact with water. We found that most of our adducts (**13**) also deteriorated on standing in the laboratory air and surmized that the deterioration was initiated by hydration (Scheme 5). We found, then, that the addition of a small amount of water to a solution of an adduct in CD_3CN initiated changes that could be followed with ^{1}H and ^{13}C NMR spectroscopy over a period of hours. The characteristic ^{1}H and ^{13}C NMR peaks of the CHO group diminished greatly, but remained visible in the ^{1}H NMR for some of the adducts. The characteristic ^{1}H peak at 9.4 ppm was replaced with a doublet at 5.2 ppm and the characteristic dd at 5.6 ppm was replaced with a dt at 4.3 ppm. In the ^{13}C spectra, the characteristic



14a-k

14a-j, R = Me; **14k**, R = Ph

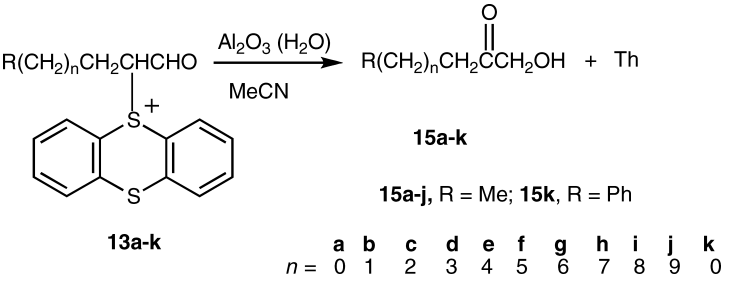
Scheme 5.

CHO peak at 196 ppm was replaced by a new peak at approximately 89 ppm, which we attribute to the $CH(OH)_2$ carbon atom, and a small change was observed in a quaternary C of the Th^+ group. We attribute these changes to the formation of an adduct's hydrate in the solution. Uniformity and consistency in the ^1H and ^{13}C portions of the thianthrenium unit and carbon atoms bearing H_a, H_b protons are concordant with the assigned structures of the hydrates. Again, ^1H and ^{13}C NMR spectral data for only **14a, b,** and **k** are reported in Section 3. The spectra of the other hydrates (**14c**–**j**) were similar to those of **14a, b,** and **k** except for the numbers of CH_2 groups and the resulting complexity of their ^1H signals.

The ^1H NMR spectrum of chloral hydrate in acetone shows a triplet at 5.04 ppm ($J = 6.6$ Hz) and a doublet at 6.02 ppm ($J = 6.7$ Hz) (*13*). These data mean that in the stable isolated hydrate and in acetone solution, the OH peaks can be detected along with their coupling to the protons on C-1 (H_a in Scheme 5). The OH peaks and their coupling with the C-1 proton were not seen in the spectra of **14a**–**k**. The reason for this may be that the spectra were recorded in CD_3CN containing added water, which facilitated exchange of the OH protons in the hydrates and the loss of their NMR signals and coupling phenomena. However, the peak at 5.04 ppm for the C-1 proton in chloral hydrate corresponds with the C-1 (H_a) proton peak at ~5.2 ppm in **14a**–**k**. Prolonged standing of solution of the hydrates and attempts to isolate hydrates caused decomposition with the formation of Th and products whose nature was not pursued.

2.3. *Synthesis of α-ketols 15a–k*

The α-ketols we refer to here are the 1-hydroxy-2-alkanones (**15a–k,** Scheme 6). Each was prepared in good yield by the simple procedure of stirring a solution of an adduct (**13a**–**k**) in MeCN with basic alumina and separating the α-ketol from Th. This method of preparing **15a**–**k** (Scheme 6) constitutes, therefore, a simple two-step procedure for converting an aldehyde (**12**)



13a-k

15a-k

15a-j, R = Me; **15k**, R = Ph

	a	b	c	d	e	f	g	h	i	j	k
n =	0	1	2	3	4	5	6	7	8	9	0

Scheme 6.

into an α-ketol (**15**) (Schemes 4 and 6). The aldehyde, therefore, must have a methylene group as its C-2 carbon atom.

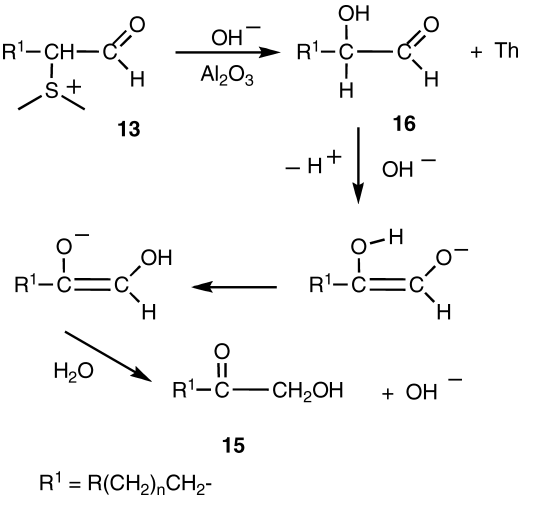
A variety of methods for preparing α-ketols can be found in the literature and among them are the following that have been used for earlier preparations of the α-ketols (**15a**–**h** and **k**): reaction of RMgBr with $HO(CH_2)CN$ for **15a–c, i,** and **k** (*14*); reaction of an α-bromoketone with NaOH for **15a** and **b** (*15*); acyloin condensation of HCHO with propanal or butanal catalyzed by a thiazolium salt for **15a** and **b** (*16*); oxidation of an alkane-1,2-diol with a peroxotungsten phosphate complex for **15a** and **c,** and **e** (*17*); oxidation of an alkane-1,2-diol with dimethyloxirane or H_2O_2 and a metal-doped zeolite for **15b** (*18*); oxidation of an alkene with oxone/$RuCl_3$ for **15e** (*19*); oxidation of an alkane-1,2-diol with $NaBrO_3/Ce(SO_4)_2$ for **15g** (*20*); oxidation of a terminal alkene with $OsCl_3$/peracetic acid for **15d** and **e** (*21*); oxidation of alkenes with RuO_4 in acetone-water at −70 °C for **15i** (*22*); reaction of an iodocyclic carbonate (obtained from an allylic alcohol) with fluoride ion for **15c** and **h** (*23*); oxidation of a ketone with dioxygen and a dipalladium catalyst for **15c** (*24*); and reaction of a silylated ketone acetal with an acid chloride for **15f** and **k** (*25*). Among these methods, only one begins with an aldehyde. That method calls for the catalytic condensation of formaldehyde (as paraformaldehyde) with another aldehyde; in essence, a chain extension [Equation (1)] (*16*). R does not have to have an α-methylene group, in which respect, the method has a wider scope than ours (Scheme 6). On the other hand, the method of chain extension requires heating the reactants and catalyst in the solution at 60 °C for 1–4 days in a sealed flask and has a selectivity of 73–100% for product formation from aldehydes comparable with ours. The product has to be separated by fractional distillation. In these respects, our two-step method is simpler, gives excellent yields, and appears to be useful. The recovered Th can be recycled.

$$\mathrm{RCHO} + \mathrm{HCHO} \longrightarrow \mathrm{R(CO)CH_2OH}. \quad (1)$$

We have characterized each of the α-ketols (**15a**–**k**) with ^{1}H and ^{13}C NMR spectroscopy. A number of them have already been characterized with ^{1}H NMR spectroscopy – namely, **15a** (*15*, *16*), **15b** (*15*), 1**5c** (*23*, *24*), **15e** (*19*), **15f** (*25*), **15g** (*20*), **15h** (*23*), **15i** (*22*), and **15k** (*25*). The ^{13}C NMR data for six of the α-ketols have also been reported – namely, for **15a** and **b** (*16*), **15c** (*24*), **15e** (*19*), **15g** (*20*), and **15i** (*22*). Insofar as ^{1}H NMR spectra are concerned, all of the α-ketols (**15a**–**k**) were found here and in the literature to have characteristic peaks at ∼4.2 ppm ($-CH_2OH$), 3.1–3.6 ppm (OH), 2.4 ppm ($CH_2-C{=}O$), and 0.9 ppm (CH_3). Signals from the remaining CH_2 groups were overlapping multiplets. NMR data for **15d** and **j** were not found in the literature and therefore are reported in Section 3. Our data for **15i** are better resolved in part than those in the literature (*22*) and are reported here, too.

We propose that the formation of **15** from **13** on basic alumina begins with the conversion of **13** into an α-hydroxyaldehyde (**16**), which then undergoes a base catalyzed rearrangement (Scheme 7) – first discovered by Lobry de Bruyn and van Ekenstein in the interconversion of aldoses and ketoses (*26*, *27*).

The rearrangement of α-hydroxyaldehydes into α-ketols has since been shown to be a general problem in attempts to prepare α-hydroxyaldehydes in both acidic (*28*) and basic media (*29*). Hassner *et al.* (*29*) noted that α-hydroxyaldehydes may not only rearrange to α-ketols but may also dimerize or polymerize. In that regard, Schulz and coworkers found that attempts to convert their thianthreniumyl adducts (**5**) into α-hydroxyaldehydes with bases such as NaOH, $NaHCO_3$, and Na_2CO_3 in aqueous solution failed, and only oligomeric and polymeric products were obtained. In contrast, they were able to convert **5a**–**h** into α-hydroxyaldehyde dimethylacetals by the reaction with methoxide ion in dry methanol (*7*). In our reactions of adducts **13** with basic alumina, it appears that the conversion into α-ketols (**15**) is clean and other deleterious reactions are avoided.



Scheme 7.

3. Experimental section

Solvent acetonitrile was dried by distillation from P_2O_5. Diethyl ether was dried over sodium. Aldehydes were from commercial sources. NMR spectra were recorded with a 500 MHz instrument; coupling constants (J) are averaged where necessary. DEPT was used in aiding identification of compounds.

3.1. *Preparation of adducts (13a–k)*

An example is given with **13b**. $Th^{\bullet+}BF_4^-$ (1.5 g, 4.9 mmol) was placed in a three-necked flask equipped with a magnetic stirrer, a three-way stopcock, rubber septa, and an argon bubbler. The flask was evacuated and flushed with argon, after which dry MeCN (10 mL) was added and was followed by an injection of pentanal (220 mg, 2.6 mmol) through a septum. The suspension was stirred and the color of the cation radical disappeared within 1 h. Dry ether (200 mL) was added to cause the precipitation of an off-white solid, which was separated by filtration and washing with ether (50 mL) to give 920 mg (2.4 mmol, 96%) of adduct **13b,** mp 135–136 °C (dec). All other products were made with the same procedure; % yield and mp °C (dec) for solids only: **13a,** 85, 142–143; **13c,** 97; **13d,** 98; **13e,** 98; **13f,** 93; **13g,** 94; **13h,** 95; **13i,** 95; **13j,** 96; **13k,** 93, 130–132.

3.2. *Elemental analysis*

13b, calcd for $C_{17}H_{17}S_2OBF_4$: C, 52.6, H, 4.15, S, 16.5. Found C, 52.4, H, 4.00, S, 16.4.

3.3. *^1H and ^{13}C NMR data (500 MHz, CD_3CN) for 13a, b, and k*

13a, ^{1}H NMR $\delta(J)$: 9.44, s, 1H; 8.20 (8.0, 1.5), dd, 1H; 8.10 (8.0, 1.0), dd, 1H; 7.98 (8.0, 1.0), dd, 1H; 7.92 (8.0, 1.0), dd, 1H; 7.85 (7.8, 1.5), td, 1H; 7.78 (7.8, 1.0), td, 1H; 7.72 (7.9, 1.2), td, 1H; 7.69 (7.8, 1.5), td, 1H; 5.60 (6.8, 4.3), dd, 1H (H_a); 2.02 (15.5, 7.7, 4.3), dqd, 1H (H_b); 1.57 (15.5, 7.4), dquint, 1H (H_c); 0.96 (7.5), t, 3H. ^{13}C NMR; 196.3, 138.5, 137.6, 136.3, 136.1, 135.9,

135.6, 131.7, 131.4, 130.9, 130.5, 117.9, 115.0, 64.5, 20.1, 10.0. **13b,** ^{1}H NMR $\delta(J)$: 9.45, s, 1H; 8.19 (8.0, 1.0), dd, 1H; 8.10 (8.0, 1.0), dd, 1H; 7.97 (7.0, 1.0), dd, 1H; 7.92 (8.0, 1.0), dd, 1H; 7.86 (7.8, 1.0), td, 1H; 7.78 (7.8, 1.5), td, 1H; 7.72 (7.8, 1.0), td, 1H; 7.69 (7.8, 1.5), td, 1H; 5.59 (7.0, 4.5), dd, 1H (H_a); 1.84 (15.3, 11.3, 5.5, 4.3), dddd, 1H (H_b); 1.53, m, 1H (H_c); 1.49–1.40, m, 1H; 1.32–1.19, m, 1H; 0.78 (7.5), t, 3H. ^{13}C NMR: 196.1, 138.5, 137.5, 136.3, 136.1, 135.9, 135.6, 131.6, 131.4, 130.9, 130.5, 118.1, 115.1, 63.3, 28.1, 19.7, 13.7. **13k,** ^{1}H NMR $\delta(J)$: 9.46, s, 1H; 8.19 (8.0, 1.5), dd, 1H; 7.98 (8.0, 1.0), dd, 1H; 7.91 (7.75, 1.5), dd, 1H; 7.78 (7.3, 1.5), dd, 1H; 7.74 (9.8, 1.5), td, 1H; 7.73 (7.5,1.5), td, 1H; 7.69 (7.4, 1.2), td, 1H; 7.65 (7.4, 1.3), td, 1H; 7.24–7.23, m, 3H (Ph); 7.00–6.98, m, 2H (Ph); 5.81 (6.8), t, 1H (H_a); 3.32 (15.8, 6.8), dd, 1H (H_b); 3.07 (16.0, 6.5), dd, 1H (H_c). ^{13}C NMR: 195.6, 138.7, 137.7, 136.3, 136.2, 136.1, 135.5, 134.3, 131.5 (2C) overlapped, 130.9, 130.5, 130.0 (2C) overlapped, 129.8 (2C) overlapped, 128.7, 118.7, 115.1, 62.9, 32.1.

3.4. *Identification of hydrated adducts (14a–k)*

Attempts to isolate hydrated adducts (**14a**–**k**) by precipitation with ether were unsuccessful. Each hydrate was made by the addition of small amount of water to the solution of the adduct in d_3-acetonitrile while it was in an NMR tube. The solution was allowed to stand for a period of 20–24 h, after which ^{1}H and ^{13}C NMR spectra were recorded. The spectra showed the conversion to the hydrated adduct with a small amount of unreacted adduct remaining.

3.5. *^{1}H and ^{13}C NMR data (500 MHz, CD_3CN with a small amount of added H_2O) for 14a, b, and k*

14a, ^{1}H NMR $\delta(J)$: 8.06 (8.3, 1.3), dd, 1H; 8.05 (8.3, 1.3), dd, 1H; 7.94 (7.8, 1.2), dd, 1H; 7.90 (7.5, 1.5), dd, 1H; 7.80 (7.8, 1.3), td, 1H; 7.74 (7.7, 1.5), td, 1H; 7.67 (5.9, 1.4), td, 1H; 7.62 (6.9, 1.4), td, 1H; 5.28 (3.3), d, 1H (H_a); 4.33 (9.0, 3.3), dt, 1H (H_b); 1.53 (15.3, 7.6), dquint, 1H; 1.31 (15.0, 7.4, 4.3), dqt, 1H; 0.84 (7.5), t, 3H. ^{13}C NMR: 138.8, 137.4, 135.9, 135.7, 135.3, 134.6, 131.2, 130.9, 130.3, 130.0, 121.5, 118.2, 88.7 (CHOH), 64.9 (CH), 21.8, 10.8. **14b,** ^{1}H NMR $\delta(J)$: 8.06 (8.0, 1.3), dd, 1H; 8.05 (7.8, 1.3), dd, 1H; 7.92 (8.0, 1.0), dd, 1H; 7.88 (8.0, 1.0), dd, 1H; 7.79 (7.8, 1.0), td, 1H; 7.72 (7.8, 1.0), td, 1H; 7.64 (7.8, 1.0), td, 1H; 7.62 (7.3, 1.0), td, 1H; 5.23 (3.0), d, 1H (H_a); 4.36 (9.0, 3.5), dt, 1H (H_b); 1.58–1.48, m, 1H; 1.36–1.25, m, 1H; 1.20–1.10, m, 2H; 0.64 (7.5), t, 3H. ^{13}C NMR: 138.9, 137.4, 136.1, 136.0, 135.5, 134.8, 131.4, 131.2, 130.6, 130.3, 121.6, 118.0, 89.2 (CHOH), 63.6 (CH), 30.2, 20.3, 13.7. **14k,** ^{1}H NMR $\delta(J)$: 8.08 (8.3, 1.3), dd, 1H; 7.96 (8.0, 1.0), dd, 1H; 7.89 (7.0 1.0), dd, 1H; 7.76 (7.3, 1.3), dd, 1H; 7.73 (7.9, 1.2), td, 1H; 7.67 (7.6, 1.2), td, 1H; 7.62 (7.8, 1.3), td, 1H; 7.58 (7.6, 1.3), td, 1H; 7.15–7.14, m, 3H (Ph); 6.92–6.91, m, 2H (Ph); 5.02 (3.0), d, 1H (H_a); 4.65 (8.0, 6.3, 2.8), ddd, 1H (H_b); 3.08 (15.0, 8.0), dd, 1H; 2.61 (14.5, 6.6), dd, 1H. ^{13}C NMR: 138.9, 137.8, 136.08, 136.07 (2C), 135.9, 135.4, 134.9, 131.29 (2C), 130.28 (2C), 130.6, 130.3, 128.2, 121.2, 117.9, 88.9 (CHOH), 64.5 (CH), 33.9.

3.6. *Synthesis of α-ketols (15a–j)*

An example is given with **15i**. In a 250-mL, flask, **13i** (1.5 g, 3.1 mmol), alumina (15 g), and acetonitrile (50 mL) were placed. The suspension was stirred for 2 h at room temperature and filtered. The alumina was washed with acetonitrile (10 mL) and the combined acetonitrile solution was concentrated under reduced pressure to a small volume. This solution was cooled to 0 °C to precipitate Th, which was removed by filtration. The solvent was then removed under reduced

pressure to give an off-white solid. The solid was purified with flash chromatography on silica gel by eluting with hexane to remove Th followed by ethyl acetate. Concentration of the ethyl acetate fraction gave 480 mg (2.3 mmol, 78%) of white solid, mp 49–50 °C; lit. mp 48 °C (*14*), 47–48 °C (*22*). All other α-ketols were synthesized by the same procedure; % yield and mp °C for solids only: **15a,** 84; **15b,** 96; **15c,** 96; **15d,** 88; **15e,** 71; **15f,** 77, 34–35 (oil (*25*)); **15g,** 82, 39–40 (oil (*20*); **15h,** 80, 44–45 (47 (*23*)); **15j,** 88, 54–55.

3.7. ^{1}H *and* ^{13}C *NMR data (*$CDCl_3$*, 500 MHz) for 15d, i, and j*

15d, ^{1}H NMR $\delta(J)$: 4.25, s, 2H; 2.41 (7.5), t, 2H; 1.64 (7.5), quint, 2H; 1.33–1.28, m, 4H; 0.90 (7.0), t, 3H. ^{13}C NMR: 209.9, 68.0, 38.4, 31.3, 23.4, 22.3, 13.8. **15i,** ^{1}H NMR: 4.24 (4.5), d, 2H; 3.13 (4.5), t, 1H, (OH); 2.41 (7.5), t, 2H; 1.63 (7.3), quint, 2H; 1.31–1.26, m, 14H; 0.88 (7.0), t, 3H. ^{13}C NMR: 209.9, 68.1, 38.4, 31.9, 29.5, 29.4, 29.3 (2C), 29.2, 23.7, 22.6, 14.1. **15j,** ^{1}H NMR: 4.24 (4.5), d, 2H; 3.11 (4.8), t, 1H (OH); 2.41 (7.8), t, 2H; 1.63 (7.4), quint, 2H; 1.28 and 1.26, bs, 16H; 0.88 (7.0), t, 3H. ^{13}C NMR: 209.9, 68.1, 38.4, 31.9, 29.57, 29.56, 29.4, 29.3, 29.27, 29.19, 23.7, 22.7, 14.1.

3.8. *HRMS*

HRMS (ESI-TOF) $[M + H]^+$: **15i,** calcd for $C_{12}H_{24}O_2$, 201.1849; found, 201.1843 (error 3 ppm). **15j,** calculated for $C_{13}H_{26}O_2$, 215.2005; found, 215.2002 (error 1.4 ppm).

Acknowledgements

We thank the Welch Foundation for support (Grant D-0028) and Mr David W. Purkiss for the 500-MHz NMR spectroscopy.

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