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Potassium Permanganate-Mediated Radical Reactions: Chemoselective Addition of Acetone to Olefins

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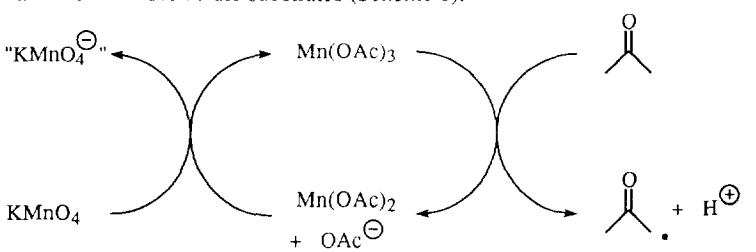
Abstract: A practical and efficient protocol for the radical addition of acetone (1) to olefins **2a-d**, mediated by potassium permanganate, has been developed. The *in situ* generation of manganese(III) allows the chemoselective synthesis of saturated C-C bond formation products **4a-d** in 39-58% yield. Furthermore, the required amount of manganese is reduced drastically in account of the catalytic reaction cycle.

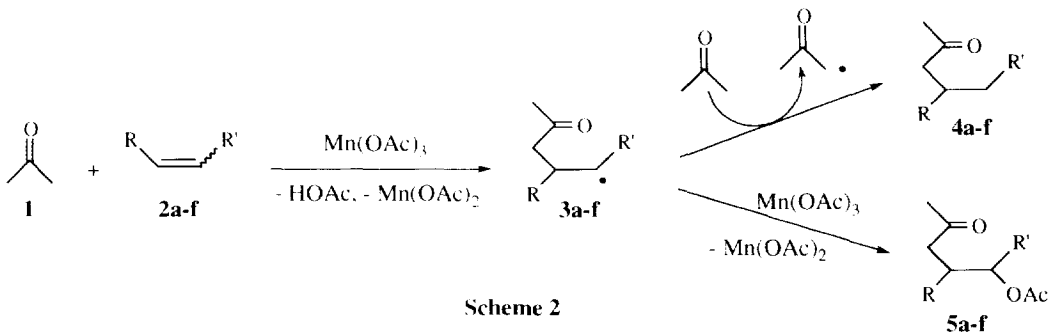
The addition of radicals to alkenes is an important methodology for carbon-carbon bond formation.[1] Alkyl halides represent widespread radical precursors and are used for inter- and intramolecular transformations in the presence of tributyltin hydride. Despite the broad applicability of these reactions, the toxicity of tin compounds and the requirement of precursor synthesis are disadvantageous. Therefore, radical additions of easily accessible CH-acidic substrates to unsaturated systems mediated by manganese(III) acetate have become increasingly attractive over the last decade and were recently comprehensively reviewed.[2] This methodology was mainly limited to the synthesis of γ-lactones[3] and olefins,[4] since overoxidation of the adduct radicals by $Mn(OAc)_3$ cannot be suppressed completely.

Herein we present a practical and efficient protocol for potassium permanganate-mediated radical additions to double bonds, which allow the chemoselective synthesis of saturated products. Our approach is based on the *in situ* generation of manganese(III) by a redox reaction of $Mn(OAc)_2$ and $KMnO_4$, resulting in the formation of radicals from CH-acidic substrates (Scheme 1).



Scheme 1

The advantage of this *in situ* method consists in the opportunity of keeping the $Mn(OAc)_3$ concentration low, by slowly adding the potassium permanganate. Furthermore, the required amount of manganese is reduced drastically, since one equivalent of potassium permanganate can generate five equivalents of radicals. Other approachs to achieve low manganese(III) concentrations were reported in literature,[5] but no detailed studies on the influence of the oxidant concentration on the product distribution were performed. Therefore, we compared radical additions of acetone (**1**) to various alkyl- and aryl-substituted olefins **2a-f** induced by the conventional manganese(III) acetate procedure (method A) with those mediated by the new potassium permanganate protocol (method B) (Scheme 2, Table 1).



Scheme 2

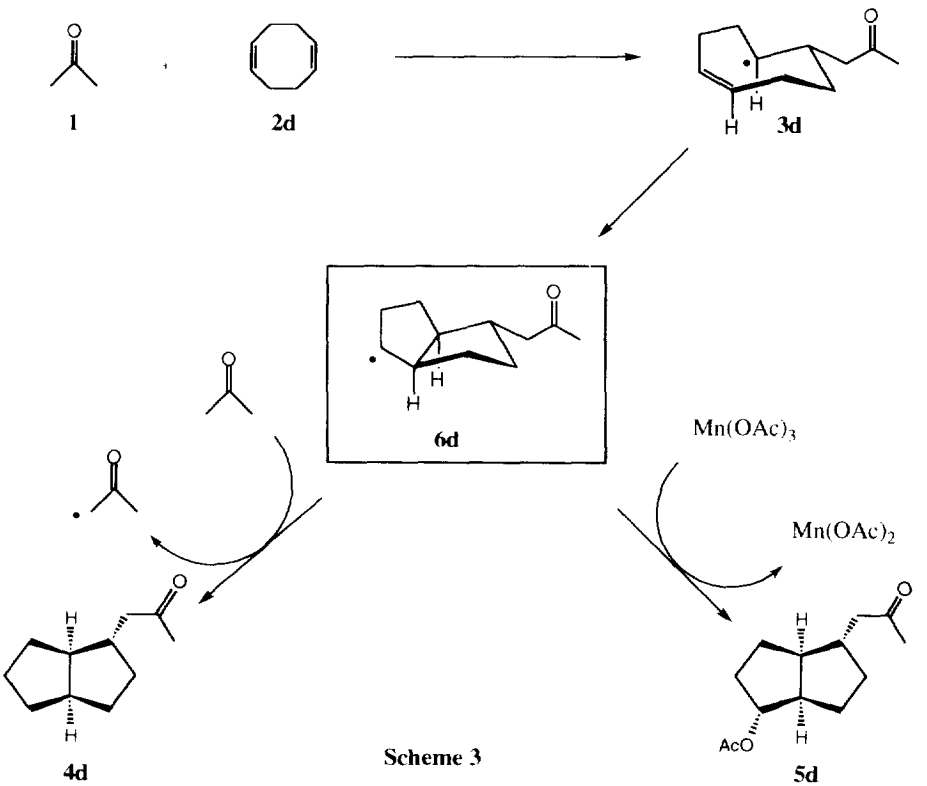
Table 1. Radical Additions of Acetone (**1**) to Different Olefins **2a-f**

entry	olefin **2**	method[a]	ketone **4** (%)[b]	keto acetate **5** (%)[b]
1	1-octene (**2a**)	A	31	15
2	1-octene (**2a**)	B	49	-
3	cyclohexene (**2b**)	A	25	19[c]
4	cyclohexene (**2b**)	B	56	-
5	cyclooctene (**2c**)	A	23	16
6	cyclooctene (**2c**)	B	39	-
7	1,5-cyclooctadiene (**2d**)	A	24	43
8	1,5-cyclooctadiene (**2d**)	B	58	-
9	styrene (**2e**)	A	-	81
10	styrene (**2e**)	B	-	-
11	*trans*-stilbene (**2f**)	A	-	61
12	*trans*-stilbene (**2f**)	B	-	-

[a] Method A: 2 equiv. $Mn(OAc)_3$, HOAc, 70 °C; method B: 0.01 equiv. $Mn(OAc)_2$, HOAc, 70 °C, slow addition of 0.3 - 0.4 equiv. $KMnO_4$. [b] Yield of isolated product after silica gel chromatography based on olefin **2**. [c] 3-Acetoxy-1-cyclohexene was formed as oxidation product.

As shown in Table 1, reactions with two equivalents of $Mn(OAc)_3$ (method A) afforded product mixtures or only the undesired acetates **5**. In contrast, radical additions of acetone to alkyl substituted olefins, mediated by potassium permanganate (method B), yielded chemoselectively the ketones **4a-d**, since over-oxidation was suppressed completely (entries 2, 4, 6, and 8). These results can be rationalized by the mechanism outlined in Scheme 2. In the first step of the reaction, adduct radicals **3** are generated which can abstract a hydrogen atom from acetone or the solvent to afford products **4** or are oxidized to the acetates **5**. Only the potassium permanganate-mediated *in situ* generation of manganese(III) (method B) permits a low concentration of $Mn(OAc)_3$, which results in the chemoselective formation of the desired saturated products **4a-d**.

1,5-Cyclooctadiene (**2d**) represents an interesting substrate for the radical addition of acetone (**1**). The initially formed adduct radical **3d** readily undergoes transannular cyclization to the intermediate **6d** which, depending on the reaction conditions, is transformed to the ketone **4d** or the keto acetate **5d** (Scheme 3). If the addition of acetone is mediated by manganese(III) acetate (entry 7), a mixture of both products results. On the other hand, potassium permanganate affords chemoselectively the ketone **4d** in good yield (entry 8).



Scheme 3

Furthermore, the reactions exhibit a high degree of diastereoselectivity, since the *exo,cis*-configurated isomers were formed as the sole products.[6] Thus, the manganese(III)-mediated addition of acetone to 1,5-cyclooctadiene provides a valuable route to bicyclo[3.3.0]octanes with control of up to four stereogenic centers. The stereochemical course of the reactions can be rationalized in terms of the prefered *pseudo* equatorial orientation of substituents in radical cyclizations [7] and is in accordance with literature examples.[8]

The limit of our *in situ* method was reached with styrene (**2e**) and stilbene (**2f**) (entries 10 and 12), for which no C-C bond formation to products **4e,f** was observed. This result is due to the fast oligomerization of aryl-substituted olefins and, thus, hydrogen atom abstraction cannot compete. On the other hand, with an excess of manganese(III) acetate (method A), the benzylic adduct radicals **3e,f** are readily oxidized to the cations and afford good yields of the acetates **5e,f** (entries 9 and 11). In none of the examined reactions was formation of diols from potassium permanganate and the olefins observed, which can be rationalized by the fast electron transfer from manganese(II) acetate to the oxidant. The only by-product was oligomeric material which was easily removed by column chromatography.

In conclusion, potassium permanganate-mediated radical additions of acetone to olefins exhibit several advantages over the conventional stoichiometric manganese(III) procedure. The *in situ* generation of $Mn(OAc)_3$ permits a low concentration of the oxidant and, thus, the saturated C-C bond formation products **4** were obtained chemoselectively in moderate to good yields. Additionally, cyclooctadiene (**2d**) has proved to be an attractive substrate for the manganese(III)-mediated addition of acetone, since the bicyclooctanes **4d** and **5d** were obtained in diastereomerically pure form. Finally, the required amount of manganese is reduced drastically employing the *in situ* method and, consequently, this procedure is environmentally more acceptable. Further investigations are currently underway to extend potassium permanganate-mediated radical reactions to other CH-acidic substrates and various functionalized olefins.

EXPERIMENTAL

Solvents and commercially available chemicals were purified by standard procedures or used as purchased. TLC was performed on Polygram Sil G UV (40 x 80 mm), Macherey & Nagel; products were observed by using UV light, potassium permanganate (to detect olefins) or phosphormolybdate spot tests. Silicagel gel (63-200 µm, Woelm, Erlangen) was used for column chromatography. Melting points were measured on a Büchi SMP 20 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were recorded on either a Bruker AC 200 or WM 400 with $CDCl_3$ as

solvent and TMS as internal standard. Combustion analyses were carried out at the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg, Germany. Manganese(III) acetate dihydrate was purchased from Heraeus, Karlsruhe.

General procedure for manganese(III) acetate-mediated reactions (method A):

A mixture of potassium acetate (1.75 g, 18 mmol), acetone (22 ml, 300 mmol) and glacial acetic acid (18 ml) was heated to 70 °C under argon atmosphere. The olefin (5.00 mmol) and manganese(III) acetate dihydrate (2.68 g, 10 mmol, 2 equiv.) were added in one portion and the solution was stirred at 70 °C until TLC indicated complete conversion of the olefin. The mixture was cooled to room temperature, diluted with water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic extracts were washed with saturated $NaHCO_3$ solution (2 x 100 ml), water (100 ml), dried (Na_2SO_4), and concentrated. The remaining oily residue was directly purified by column chromatography.

General procedure for potassium permanganate-mediated reactions (method B):

A mixture of potassium acetate (1.75 g, 18 mmol), manganese(II) acetate tetrahydrate (12.5 mg, 0.05 mmol), acetone (22 ml, 300 mmol) and glacial acetic acid (18 ml) was heated to 70 °C under argon atmosphere. After the addition of the olefin (5.00 mmol), solid potassium permanganate (0.3 - 0.4 equiv.) was added in very small portions at 70 °C over a period of 4 - 10 h until TLC indicated complete conversion of the olefin. The mixture was cooled to room temperature, diluted with water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic extracts were washed with saturated $NaHCO_3$ solution (2 x 100 ml), water (100 ml), dried (Na_2SO_4), and concentrated. The remaining oily residue was directly purified by column chromatography.

Manganese(III) acetate-mediated addition of acetone (1) to 1-octene (2a) (method A):

The reaction of 1-octene (**2a**) (560 mg, 5.00 mmol) afforded after silica gel column chromatography (hexane / EtOAc 98:2 » 90:10) 265 mg (31 %) of the ketone **4a** and 170 mg (15 %) of the keto acetate **5a** as viscous oils.

*2-Undecanone (**4a**)*:[9]

^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.20-1.34 (m, 12H), 1.57 (quint., J = 7.3 Hz, 2H), 2.13 (s, 3H), 2.42 (t, J = 7.3 Hz, 2H). ^{13}C NMR δ 14.0 (q), 22.5 (t), 23.8 (t), 24.2 (t), 29.3 (t), 29.4 (t), 29.8 (t), 30.4 (q), 31.8 (t), 43.7 (t), 209.2 (s).

IR (neat) ν 1719 cm^{-1}.

*5-Acetoxy-2-undecanone (**5a**):*[10]

^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.17-1.39 (m, 10H), 1.78 (q, *J* = 7.3 Hz, 2H), 2.04 (s, 3H), 2.15 (s, 3H), 2.46 (t, *J* = 7.3 Hz, 2H), 4.77-4.92 (m, 1H). ^{13}C NMR δ 14.2 (q), 22.7 (q), 21.4 (t), 22.8 (t), 25.4 (t), 25.5 (t), 30.4 (q), 31.9 (t), 34.5 (t), 35.8 (t), 39.7 (t), 73.8 (d), 171.2 (s), 209.2 (s).

IR (neat) ν 1777, 1716 cm^{-1}.

Potassium permanganate-mediated addition of acetone (1) to 1-octene (2a) (method B):

The reaction of 1-octene (**2a**) (560 mg, 5.00 mmol) afforded after silica gel column chromatography (hexane / EtOAc 98:2) 420 mg (49 %) of the ketone **4a** as a viscous oil. For spectroscopical data see method A.

Manganese(III) acetate-mediated addition of acetone (1) to cyclohexene (2b) (method A):

From the reaction of cyclohexene (**2b**) (410 mg, 5.00 mmol) were obtained 175 mg (25 %) of the ketone **4b** and 130 mg (19 %) of the acetate **5b** as clear oils after silica gel column chromatography (hexane / EtOAc 95:5 » 90:10).

*1-Cyclohexyl-2-propanone (**4b**):*[11]

^{1}H NMR δ 0.78-0.97 (m, 2H), 1.02-1.31 (m, 3H), 1.55-1.68 (m, 5H), 1.70-1.86 (m, 1H), 2.07 (s, 3H), 2.25 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR δ 26.0 (t), 26.1 (t), 30.4 (q), 33.1 (t), 33.8 (d), 51.4 (t), 208.9 (s).

IR (neat) ν 1716 cm^{-1}.

*3-Acetoxy-1-cyclohexene (**5b**):*[12]

^{1}H NMR δ 1.30-1.90 (m, 6H), 2.04 (s, 3H), 5.20-5.28 (m, 1H), 5.63-5.72 (m, 1H), 5.90-5.98 (m, 1H). ^{13}C NMR δ 20.4 (q), 21.4 (t), 22.6 (t), 24.8 (t), 28.2 (t), 68.1 (d), 125.6 (d), 132.7 (d), 170.8 (s).

IR (neat) ν 2924, 2854, 1735 cm^{-1}.

Potassium permanganate-mediated addition of acetone (1) to cyclohexene (2b) (method B):

The reaction of cyclohexene (**2b**) (410 mg, 5.00 mmol) afforded after silica gel column chromatography (hexane / EtOAc 95:5) 390 mg (56 %) of the ketone **4b** as a clear oil. For spectroscopical data see method A.

Manganese(III) acetate-mediated addition of acetone (1) to cyclooctene (2c) (method A):

From the reaction of cyclooctene (**2c**) (550 mg, 5.00 mmol) were obtained 195 mg (23 %) of the ketone **4c** and 180 mg (16 %) of the acetate **5c** as viscous oils after silica gel column chromatography (hexane / EtOAc 97:3 » 90:10). The acetate **5c** was isolated as a 65:35 mixture of *trans-cis* isomers which could be distinguished by NMR spectroscopy.

*1-Cyclooctyl-2-propanone (**4c**):*[11]

^{1}H NMR δ 1.18-1.28 (m, 2H), 1.30-1.55 (m, 12H), 2.10-2.20 (m, 1H), 2.12 (s, 3H), 2.33 (d, J = 6.9 Hz, 2H). ^{13}C NMR δ 25.0 (t), 25.9 (t), 26.9 (t), 30.1 (q), 32.0 (t), 33.3 (d), 52.0 (t), 208.9 (s).

IR (neat) ν 1713 cm^{-1}.

*1-(2-Acetoxycyclooctyl)-2-propanone (**5c**):*

major isomer: ^{1}H NMR δ 1.20-1.90 (m, 13H), 2.03 (s, 3H), 2.13 (s, 3H), 2.36 (d, J = 6.8 Hz, 2H), 4.81-4.98 (m, 1H). ^{13}C NMR δ 21.4 (q), 22.6 (t), 24.1 (t), 28.0 (t), 28.5 (t), 30.1 (q), 31.0 (t), 31.4 (t), 33.5 (d), 51.2 (t), 74.8 (d), 171.2 (s), 208.5 (s). minor isomer: ^{1}H NMR δ 1.20-1.90 (m, 13H), 2.01 (s, 3H), 2.14 (s, 3H), 2.41 (d, J = 6.4 Hz, 2H), 4.65-4.74 (m, 1H). ^{13}C NMR δ 21.7 (q), 23.5 (t), 25.4 (t), 26.1 (t), 29.5 (t), 30.5 (q), 30.8 (t), 31.2 (t), 33.8 (d), 51.8 (t), 74.3 (d), 172.3 (s), 208.8 (s).

IR (neat) ν 1777, 1716 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.83; H, 9.92.

Potassium permanganate-mediated addition of acetone (1) to cyclooctene (2c) (method B):

The reaction of cyclooctene (**2c**) (550 mg, 5.00 mmol) afforded after silica gel column chromatography (hexane / EtOAc 97:3) 330 mg (39 %) of the ketone **4c** as a clear oil. For spectroscopical data see method A.

Manganese(III) acetate-mediated addition of acetone (1) to 1,5-cyclooctadiene (2d) (method A):

From the reaction of 1,5-cyclooctadiene (**2d**) (540 mg, 5.00 mmol) were obtained 200 mg (24 %) of the ketone **4d** and 480 mg (43 %) of the acetate **5d** as viscous oils after silica gel column chromatography (hexane / EtOAc 95:5 » 80:20). Both products **4d** and **5d** were isolated in diastereomerically pure form. The relative configuration was established by NOE experiments.

exo-2-Acetonyl-cis-bicyclo[3.3.0]octane (**4d**):

^{1}H NMR δ 0.97-1.20 (m, 4H), 1.22-1.39 (m, 2H), 1.43-1.67 (m, 4H), 1.72-1.98 (m, 3H), 2.14 (s, 3H), 2.36 (dd, J = 15.5, 8.1 Hz, 1H), 2.53 (dd, J = 15.5, 5.3 Hz, 1H). ^{13}C NMR δ 25.5 (t), 25.7 (t), 30.2 (q), 32.4 (t), 33.1 (t), 33.6 (t), 42.9 (d), 43.2 (t), 49.5 (t), 49.9 (d), 209.3 (s).

IR (neat) ν 1714 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.36; H, 11.16.

exo-6-Acetonyl-exo-2-acetoxy-cis-bicyclo[3.3.0]octane (**5d**):

^{1}H NMR δ 0.98-1.27 (m, 4H), 1.39-1.50 (m, 2H), 1.67-1.90 (m, 5H), 2.01 (s, 3H), 2.15 (s, 3H), 2.40 (dd, J = 16.0, 7.9 Hz, 1H), 2.53 (dd, J = 16.0, 5.3 Hz, 1H), 4.78-4.84 (m, 1H). ^{13}C NMR δ 21.3 (q), 29.1 (t), 30.4 (q), 30.6 (t), 30.8 (t), 33.6 (t), 42.7 (d), 48.5 (d), 49.1 (t), 49.9 (d), 82.0 (d), 170.7 (s), 208.7 (s).

IR (neat) ν 1732, 1718 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.84; H, 9.26.

Potassium permanganate-mediated addition of acetone (1) to 1,5-cyclooctadiene (2d) (method B):

The reaction of 1,5-cyclooctadiene (**2d**) (540 mg, 5.00 mmol) afforded after silica gel column chromatography (hexane / EtOAc 95:5) 480 mg (58 %) of the diastereomerically pure ketone **4d** as a viscous oil. For spectroscopical data see method A.

Manganese(III) acetate-mediated addition of acetone (1) to styrene (2e) (method A):

From the reaction of styrene (**2e**) (520 mg, 5.00 mmol) was obtained 890 mg (81 %) of the acetate **5e** as a viscous oil after silica gel column chromatography (hexane / EtOAc 80:20). No ketone **4e** could be detected in the crude product.

5-Acetoxy-5-phenyl-2-pentanone (**5e**):[13]

^{1}H NMR δ 1.80-2.27 (m, 2H), 2.06 (s, 3H), 2.10 (s, 3H), 2.38-2.47 (m, 2H), 5.75 (t, J = 6.8 Hz, 1H), 7.03-7.39 (m, 5H). ^{13}C NMR δ 21.1 (q), 30.1 (q), 30.4 (t), 39.3 (t), 75.0 (d), 126.3 (d), 128.4 (d), 128.8 (d), 139.9 (s), 170.2 (s), 207.4 (s).

IR (neat) ν 3061, 3029, 1732, 1714 cm^{-1}.

Potassium permanganate-mediated addition of acetone (1) to styrene (2e) (method B):

The reaction of styrene (**2e**) (520 mg, 5.00 mmol) afforded only oligomeric material as indicated by NMR spectroscopy of the crude product.

Manganese(III) acetate-mediated addition of acetone (1) to *trans*-stilbene (2f) (method A):

The reaction of *trans*-stilbene (**2f**) (900 mg, 5.00 mmol) yielded after silica gel column chromatography (hexane / EtOAc 80:20) 900 mg (61 %) of the acetate **5f** as a white solid (m.p. 89-91 °C) in diastereomerically pure form. No ketone **4f** could be detected in the crude product.

5-Acetoxy-4,5-diphenyl-2-pentanone (5f):

^{1}H NMR δ 2.03 (s, 3H), 2.06 (s, 3H), 2.91 (d, J = 6.2 Hz, 2H), 3.72 (dt, J = 8.4, 6.2 Hz, 1H), 5.84 (d, J = 8.4 Hz, 1H), 6.97-7.37 (m, 10H). ^{13}C NMR δ 21.0 (q), 30.5 (q), 45.6 (t), 46.8 (d), 78.9 (d), 126.9 (d), 127.1 (d), 127.8 (d), 127.9 (d), 128.3 (d), 128.5 (d), 138.5 (s), 139.6 (s), 170.0 (s), 206.6 (s).

IR (KBr) ν 3087, 3062, 3031, 1740, 1716 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.04; H, 6.63.

Potassium permanganate-mediated addition of acetone (1) to *trans*-stilbene (2f) (method B):

The reaction of *trans*-stilbene (**2f**) (900 mg, 5.00 mmol) afforded only oligomeric material as indicated by NMR spectroscopy of the crude product.

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