# 14. A New Method for the Preparation of (*E*)-3-Acylprop-2-enoic Acids[1])

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Dedicated to Prof. *R. E. Ireland* on the occasion of his 60th birthday

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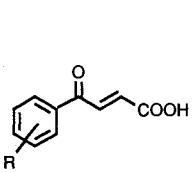
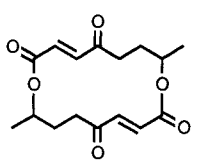
A new method for the preparation of (*E*)-3-acylprop-2-enoic acids ( = (*E*)-3-acylacrylic acids) of type **II** *via* acid-catalyzed isomerization of the corresponding 3-acylprop-2-ynal acetals of type **I** *(Scheme 1)* has been found. The described reaction gives a rapid and quite general access to these compouds known to exhibit a number of interesting biological activities. Some studies toward the elucidation of the reaction mechanism have been made, and a hypothetical mechanism is proposed.

**1. Introduction.** – In recent years, there has been a growing interest in (*E*)-3-acylprop-2-enoic acids. The 3-acylprop-2-enoic-acid moiety is thought to be the important part in many biologically active natural products, for instance such as pyrenophorin (**1**) [1] [2]. Recently, (*E*)-3-aroylprop-2-enoic acids have been synthesized as antiulcer compounds [3a–d], and several new synthetic methods have been developed.



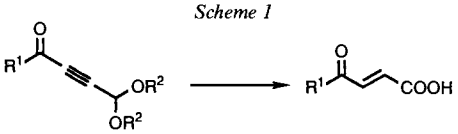

3-Aroylacrylic acids




Pyrenophorin (**1**)

Since there is still a lack of generally applicable methods for the synthesis of (*E*)-3-acylprop-2-enoic acids in good yields, we have been looking for a simple and new approach to this kind of compounds. Our new method is based on the finding that 3-acyl-prop-2-ynal acetals of type **I** can be isomerized into the corresponding (*E*)-3-acyl-prop-2-enoic acids of type **II** under acidic conditions *(Scheme 1)*.

*Scheme 1*




**I** ($R^2$ = Et) **II**

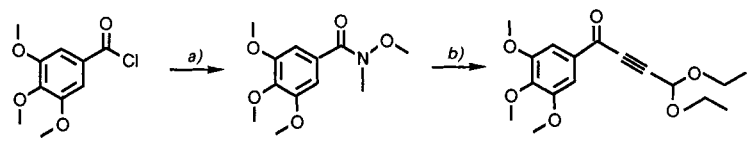
[1]) Presented in part at the autumn meeting of the Swiss Chemical Society in Bern on October 21, 1988.

**2. 3-Acylprop-2-ynal Diethyl Acetals I.** – The required acetals of type **I**, *i.e.* **7**–**10** (see *Table 1*), were easily accessible starting from either the *N*-methoxy-*N*-methylamide **12** [8] (**11**→**12**→**8**, *Scheme 2*) or from the corresponding aldehydes of type **III**, *i.e.* **3**–**6** (**III**→**IV**→**I**, *Scheme 3*). They reacted smoothly with the acetylide prepared from the commercially available 3,3-diethoxyprop-1-yne (**2**) and BuLi in THF at −78° [9]. In cases where the aldehyde **III** was available, we preferred the two-step procedure *via* the acetylenic alcohols **IV** because of slightly better overall yields.

Table 1. *Synthesis of the 3-Acylprop-2-ynal Acetal* **I**

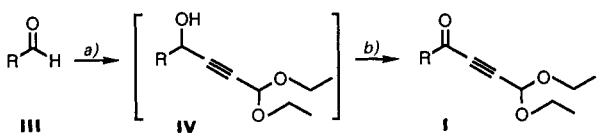
| $R^1$ | Aldehyde **III** | Acetal **I** | Yield [%] |
|---|---|---|---|
| Ph | **3** | **7** | 89 |
| 3,4,5-$(MeO)_3C_6H_2$ | **4** | **8** | 89 |
| $CH_3(CH_2)_4$ | **5** | **9** | 87 |
| (*E*)-PhCH=CH | **6** | **10** | 91 |

*Scheme 2*




*a)* $CH_3(CH_3O)NH \cdot HCl$, $(i\text{-}Pr)_2EtN$, $CH_2Cl_2$ (82%). *b)* BuLi, THF, $CH{\equiv}CCH(OEt)_2$ (**2**), −78°→0° (90%).

*Scheme 3*




*a)* BuLi, THF, $CH{\equiv}CCH(OEt)_2$ (**2**). *b)* $MnO_2$, $CH_2Cl_2$, 0°→r.t.

**3. (*E*)-3-Acylprop-2-enoic Acids II.** – The desired acids of type **II** were obtained by treatment of the corresponding acetals of type **I** with either 2N aq. HBr or 4N aq. HCl in dioxane (*Scheme 1*). The optimum conditions in our hands turned out to be 2N aq. HBr/dioxane 1:3 at temperatures ranging from 30 to 80° (*Table 2*). It is worth noting that only the (*E*)-isomers were formed.

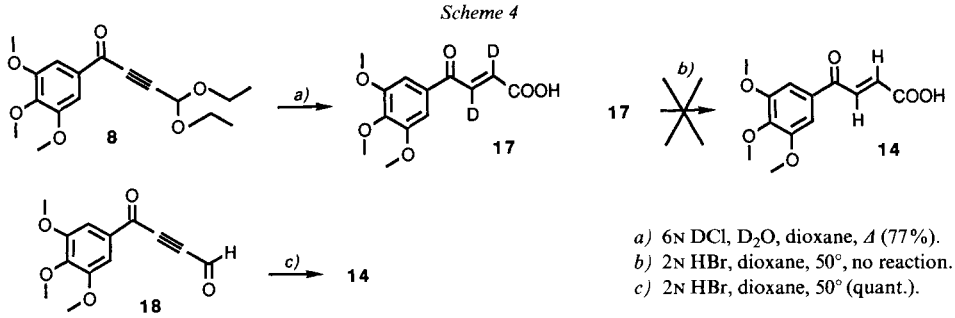
Table 2. *Isomerization of the 3-Acylprop-2-ynal Diethyl Acetals* **I**

| Acetal **I** | $R^1$ | Solvent | Time [h] | Temp. [°] | Acid **II** | Yield [%] |
|---|---|---|---|---|---|---|
| **7** | Ph | 2N aq. HBr/dioxane 1:3 | 12 | 50 | **13** | 79[a]) |
| **8** | 3,4,5-$(MeO)_3C_6H_2$ | 2N aq. HBr/dioxane 1:3 | 2.5 | 50 | **14** | 91[a]) |
| **8** | 3,4,5-$(MeO)_3C_6H_2$ | 4N aq. HCl/dioxane 1:3 | 7 | 50 | **14** | 80[a]) |
| **9** | $CH_3(CH_2)_4$ | 2N aq. HBr/dioxane 1:3 | 30 | 80 | **15** | 82[a]) |
| **10** | (*E*)-PhCH=CH | 2N aq. HBr/dioxane 1:3 | 30 | 30 | **16** | 78[b]), 41[c]) |

[a]) Isolated yield. [b]) Crude yield. [c]) Purified as the Na salt.

**4. Mechanistic Aspects.** – In order to elucidate the possible mechanism of the reaction **I**→**II**, we performed three experiments *(Scheme 4)*. When **8** was treated with 6N DCl/$D_2O$ in dioxane at 50°, the corresponding ($D_2$)acid **17** was obtained in 77% isolated yield (97% $D_2$ by $^1$H-NMR). When **17** was treated with 2N aq. HBr in dioxane at 50°, there was no loss of D observable, which indicated that the D-incorporation is not reversible. The quantitative transformation of the aldehyde **18**[2]) into the corresponding acid **14** using 2N aq. HBr in dioxane at 50° showed that hydrolysis of the acetal is most probably the first step of the transformation.

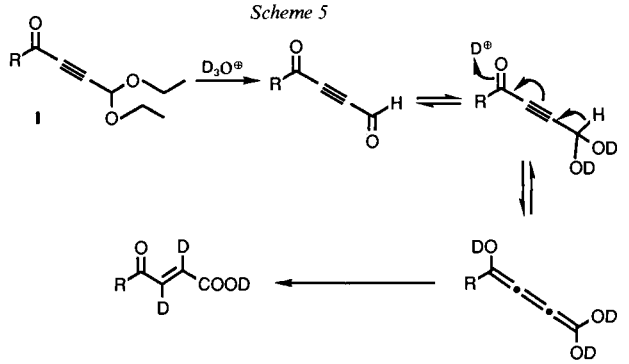
*Scheme 4*




*a)* 6N DCl, $D_2O$, dioxane, Δ (77%).
*b)* 2N HBr, dioxane, 50°, no reaction.
*c)* 2N HBr, dioxane, 50° (quant.).

Based on the experiments, we believe that the acetal **8** is first hydrolyzed to the aldehyde **18** which probably exists to a great extent in the hydrated form under the acidic reaction conditions. Then, **18** or its hydrated form isomerizes *via* vinylogous enolization and $H^+$ ($D^+$) transfers to the corresponding acid **14** (**17**). The incorporation of 2 D-atoms at C(2) and C(3) of **17** *(Scheme 4)* clearly rules out a mechanism involving a [1,2]-H shift from C(1) to C(2). The overall mechanism in DCl in $D_2O$/dioxane is given in *Scheme 5*.

*Scheme 5*




**5. Conclusions.** – Our new method of preparing (*E*)-3-acylprop-2-enoic acids **II** *(Scheme 1)* is especially well suited for molecules which tolerate dilute-acid conditions. It is worth mentioning that the method gives high yields in preparing various (*E*)-3-aroylprop-2-enoic acids, compounds which exhibit interesting antisecretory and cytoprotective activities [3a–d].

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[2]) Prepared in 45% yield by oxidation of the corresponding alcohol using $MnO_2$ in $CH_2Cl_2$.

We wish to thank our colleagues from the Central Research Units, *F. Hoffmann-La Roche & Co. AG*, for IR spectra (Mr. *A. Bubendorf*), NMR spectra (Dr. *W. Arnold*), MS (Dr. *W. Vetter* and Mr. *W. Meister*), and elemental analyses (Dr. *A. Dirscherl*). We thank also Dr. *R. Schmid*, Prof. Dr. *H.-J. Hansen* (ZFE); Dr. *E.-M. Gutknecht*, and Prof. Dr. *A. Fischli* (PF/GM) for fruitful discussions concerning mechanistic and pharmacological aspects.

## Experimental Part

(The authors wish to thank Mr. *O. Heitzelmann* for his excellent experimental work)

*General.* All reactions with air- and moisture-sensitive reactants and solvents were carried out in oven- or flame-dried glassware under a positive pressure of dry Ar. Reaction solvents and liquid reagents were purified by destillation shortly before use: THF was destilled under Ar from Na with benzophenone ketyl as indicator. $CH_2Cl_2$ and $(i\text{-}Pr)_2EtN$ (*Hünig's* base) were destilled from powdered $CaH_2$. All other reactants were 'reagent grade' unless described otherwise. Anal. TLC: 2.5 × 10 cm precoated TLC plates, $SiO_2$ *60F-254*, layer thickness 0.25 mm (*E. Merck & Co.*, Darmstadt, FRG). Flash chromatography: *E. Merck* $SiO_2$ *60* (230–400 mesh ASTM), according to [11]. M.p.: *Büchi SMP-20* apparatus; uncorrected. IR: *Nicolet 7199 FT-IR* spectrometer; solids in KBr pellets, liquids as thin films; indication of characteristic bands in $cm^{-1}$. $^1$H-NMR: at 250 MHz *(Bruker 250)*, TMS as internal standard; chemical shifts $\delta$ of signal centres or ranges in ppm, $J$ in Hz.

**1. General Procedures.** – 1.1. *Acetals of Type* **I**, *Method A.* To a stirred soln. of 1.43 ml (10.0 mmol) of 3,3-diethoxyprop-1-yne (**2**) in THF (30 ml), BuLi (6.25 ml, 10.0 mmol; 1.6M in hexane) was slowly added at −78° and stirred for 30 min at −78°. Then, aldehyde **III** (10.0 mmol) in THF (10 ml) was added and stirred for 30 min at −78°. The mixture was allowed to warm up to r.t. and quenched with sat. $HN_4Cl$ soln. (50 ml), ice (20 g), and $Et_2O$ (100 ml), the aq. phase extracted twice with $Et_2O$ (100 ml), and the combined org. phase extracted with brine (50 ml), dried ($MgSO_4$), and evaporated. The remaining oil in $CH_2Cl_2$ (30 ml) was slowly added to a mechanically stirred suspension of $MnO_2$ (26 g) in $CH_2Cl_2$ (50 ml) at 0°, vigorously stirred at 0° for 1 h, and slowly warmed up to r.t. until the reaction was completed (1–2 h). The suspension was filtered, the filtrate evaporated, and the residue chromatographed on $SiO_2$ (200 g) with AcOEt/hexane 1:3 to 1:5 or crystallized as indicated to give **I**.

1.2. *Acids of Type* **II**, *Method B.* To a stirred soln. of 1.0 mmol of **I** in dioxane (3 ml), 2N aq. HBr (1 ml) was added at r.t. The mixture was heated to 30–80° for 7–18 h (see *Table 2*), then quenched at 0° by addition of sat. $NaHCO_3$ soln. (10 ml) and $Et_2O$ (10 ml). The org. layer was extracted with sat. $NaHCO_3$ soln. (2 × 5 ml), the combined aq. phase carefully acidified to pH 2 with 4N aq. HCl and extracted with AcOEt (3 × 10 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the product **II** crystallized and dried.

**2. Acetals of Type I.** – 2.1. *N,3,4,5-Tetramethoxy-*N*-methylbenzamide* (**12**). To a stirred soln. of 5.0 g (21.7 mmol) of 3,4,5-trimethoxybenzoyl chloride (**11**) *(Fluka)* and 2.12 g (21.7 mmol) of *N,O*-dimethylhydroxylamine·HCl *(Fluka)* in dry $CH_2Cl_2$ (70 ml), 3.36 g (26.04 mmol) of $(i\text{-}Pr)_2EtN$ were slowly added at 0°. The mixture was stirred at 0° for 1 h and allowed to warm up to r.t. After addition of ice/$H_2O$, the org. phase was dried ($MgSO_4$) and evaporated. The remaining solid was crystallized from AcOEt/hexane yielding 4.54 g (82%) of **12** as a pale yellow solid. M.p. 61–62°. IR (KBr): 2940*m*, 1660*s*, 1585*s*, 1510*m*, 1420*s*, 1375*s*, 1245*s*, 1135*s*, 1010*s*. $^1$H-NMR (250 MHz, $CDCl_3$): 6.98 (*s*, 2 arom. H); 3.89, 3.60, 3.37 (3*s*, 4 $CH_3O$, $CH_3N$). MS: 255 (6, $M^+$), 195 (100). Anal. calc. for $C_{12}H_{17}NO_5$: C 56.46, H 6.71, N 5.49; found: C 56.34, H 6.77, N 5.47.

2.2. *4,4-Diethoxybut-2-ynophenone* (**7**) [10]. A soln. of 6.54 g (51.0 mmol) of **2** was treated following *Method A* with 5.95 g (56.06 mmol) of benzaldehyde (**3**) to yield 10.56 g (89.1%) of **7** as a colourless oil. IR (film): 2978*m*, 2932*w*, 2887*w*, 2150*w*, 1649*s*, 1559*w*, 1448*w*, 1261*s*, 1175*w*, 1119*m*, 1055*s*, 702*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 8.15–8.1 (*m*, 2 arom. H); 7.65–7.6, 7.55–7.45 (2*m*, 3 arom. H); 5.52 (*s*, $CH(OCH_2CH_3)_2$); 3.85–3.65 (*m*, $CH(CH_2CH_3)_2$); 1.29 (*t*, $J$ = 7.2, $CH(CH_2CH_3)_2$). MS: 231 (1, $M^+ - H$), 187 (96), 159 (100), 105 (46), 77 (43). Anal. calc. for $C_{14}H_{16}O_3$: C 72.39, H 6.94; found: C 72.17, H 7.05.

2.3. *4,4-Diethoxy-3',4',5'-trimethoxybut-2-ynophenone* (**8**). 2.3.1. *From* **12**: To a stirred soln. of 1.0 ml (6.98 mmol) of **2** in dry THF (15 ml), 4.6 ml of BuLi (1.6M in hexane) were added at −78° and stirred for 30 min at −78°. After addition of a soln. of 1.62 g (6.35 mmol) of **12** in THF (10 ml), the mixture was stirred for 30 min at −78°, slowly warmed up to 0°, and quenched with 5% HCl soln. in EtOH and ice. After addition of AcOEt (20 ml), the aq. phase was extracted with AcOEt (2 × 10 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue chromatographed on $SiO_2$ (60 g) with $Et_2O$/hexane 1:2 yielding 1.85 g (90%) of **8** as white crystals after recrystallization from isooctane. M.p. 54°. IR (KBr): 2960*m*, 2930*w*, 2230*w*, 1645*s*, 1505*m*, 1460*m*, 1412*m*, 1335*s*, 1215*m*, 1128*s*, 1065*m*, 740*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.42 (*s*, 2 arom. H); 5.51 (*s*, $CH(CH_2CH_3)_2$); 3.95, 3.93

(2*s*, 3 $CH_3O$); 3.85–3.65 (*m*, $CH(CH_2CH_3)_2$); 1.29 (*t*, *J* = 7.9, $CH(CH_2CH_3)_2$). MS: 322 (100, $M^+$), 277 (45), 249 (62), 195 (28), 168 (22). Anal. calc. for $C_{17}H_{22}O_6$: C 63.34, H 6.88; found: C 63.27, H 6.92.

2.3.2. *From 3,4,5-Trimethoxybenzaldehyde* (**4**). A soln. of 1.43 ml (10.0 mmol) of **2** was treated following *Method A* with 1.96 g (10.0 mmol) of **4** yielding 2.87 g (88.9%) **8** after recrystallization from isooctane. M.p. 54°. Spectra: identical to *2.3.1*.

2.4. *1,1-Diethoxynon-2-yn-4-one* (**9**). A soln. of 1.43 ml (10.0 mmol) of **2** was treated following *Method A* with 1.0 g (10.0 mmol) of hexanal (**5**) yielding 1.98 g (86.7%) of **9** as a colourless oil. IR (film): 2930*m*, 2870*m*, 2225*w*, 1685*s*, 1460*w*, 1405*w*, 1355*m*, 1330*m*, 1230*m*, 1155*s*, 1120*s*, 1060*s*. $^1$H-NMR (250 MHz, $CDCl_3$): 5.39 (*s*, $CH(CH_2CH_3)_2$); 3.8–3.6 (*m*, $CH(CH_2CH_3)_2$); 2.59 (*t*, *J* = 7.3, $CH_2CO$); 1.75–1.6 (*m*, 2 H–C(6)); 1.4–1.15 (*m*, 2 H–C(7), 2 H–C(8)); 1.25 (*t*, *J* = 7.1, $CH(CH_2CH_3)_2$); 0.9–0.85 (*m*, 3 H–C(9)). MS: 225 (1, $M^+ - H$), 181 (83), 111 (68), 83 (100), 55 (41). Anal. calc. for $C_{13}H_{22}O_3$: C 68.99, H 9.80; found: C 68.91, H 9.69.

2.5. *(E)-6,6-Diethoxy-1-phenylhex-1-en-4-yn-3-one* (**10**). A soln. of 1.43 ml (10.0 mmol) of **2** was treated following *Method A* with 1.40 g (10.59 mmol) of cinnamaldehyde (**6**) yielding 2.36 g (91.6%) of **10** as a pale yellow oil. IR (film): 2980*m*, 2930*w*, 2880*w*, 2225*w*, 1638*s*, 1600*m*, 1450*w*, 1330*w*, 1255*s*, 1120*m*, 960*s*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.74, 6.80 (2*d*, *J* = 16.2, H–C(1), H–C(2)); 7.6–7.55, 7.5–7.4 (2*m*, 5 arom. H); 5.49 (*s*, $CH(CH_2CH_3)_2$); 3.9–3.65 (*m*, $CH(CH_2CH_3)_2$); 1.29 (*t*, *J* = 7.2, $CH(CH_2CH_3)_2$). MS: 258 (13, $M^+$), 213 (100), 185 (82), 129 (78), 103 (50), 787 (51). Anal. calc. for $C_{16}H_{18}O_3$: C 74.40, H 7.02; found: C 74.59, H 7.39.

**3. Acids of Type II.** – 3.1. *(E)-4-Oxo-4-phenylbut-2-enoic Acid* (**13**) [3d]. A soln. of 3.0 g (12.9 mmol) of **7** was treated following *Method B* for 12 h at 50° to yield 1.78 g (79%) of **13** after recrystallization from AcOEt/hexane. M.p. 94–95°. IR (KBr): 3430*w*, 3070*m*, 2822*m*, 2675*w*, 2581*w*, 1704*s*, 1671*s*, 1501*m*, 1440*m*, 1408*m*, 1301*s*, 1130*m*, 1008*m*, 929*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 11.50 (br. *s*, COOH); 8.02, 6.91 (2*d*, *J* = 15.6, H–C(2), H–C(3)); 8.05–8.0, 7.7–7.65, 7.55–7.5 (3*m*, 5 arom. H). MS: 176 (20, $M^+$), 105 (100), 77 (53). Anal. calc. for $C_{10}H_8O_3$: C 68.18, H 4.58; found: C 67.97, H 4.58.

3.2. *(E)-4-Oxo-4-(trimethoxyphenyl)but-2-enoic Acid* (**14**) [3b]. A soln. of 500 mg (1.55 mmol) of **8** was treated following *Method B* for 2.5 h at 50° to yield 375 mg (90.8%) of **14** after recrystallization from AcOEt/hexane. M.p. 144° ([3b]: 144°). IR (KBr): 3075*w*, 2965*m*, 2580*m*, 1700*s*, 1670*s*, 1585*s*, 1415*s*, 1340*s*, 1230*m*, 1165*s*, 1130*s*, 1000*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.98, 6.92 (2*d*, *J* = 15.5, H–C(2), H–C(3)); 7.26 (*s*, 2 arom. H); 3.96, 3.95 (2*s*, 3 $CH_3O$). MS: 266 (100, $M^+$), 251 (24), 220 (25), 195 (42), 163 (11), 99 (16). Anal. calc. for $C_{13}H_{14}O_6$: C 58.65, H 5.30; found: C 58.53, H 5.53.

3.3. *(E)-4-Oxonon-2-enoic Acid* (**15**). A soln. of 1.0 g (4.42 mmol) of **9** was treated following *Method B* for 30 h at 80° to yield 617 mg (82%) of **15** after recrystallization from AcOEt/hexane. M.p. 105–106°. IR (KBr): 3440*w*, 2950*s*, 2925*s*, 1720*s*, 1680*s*, 1660*s*, 1625*w*, 1415*w*, 1290*w*, 1180*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 9.0 (br.*s*, COOH); 7.15, 6.68 (2*d*, *J* = 15.9, H–C(2), H–C(3)); 2.66 (*t*, *J* = 7.25, 2H–C(5)); 1.75–1.6, 1.45–1.25, 0.95–0.85 (3*m*, 9 aliph. H). MS: 171 (5, $M^+ + 1$), 152 (10), 123 (36), 114 (100), 99 (87), 96 (36), 71 (37), 43 (70). Anal. calc. for $C_9H_{14}O_3$: C 63.51, H 8.29; found: C 63.07, H 8.29.

3.4. *Sodium (all-E)-4-Oxo-6-phenylhexa-2,5-dienoate* (Na Salt of **16**). A soln. of 3.24 g (12.7 mmol) of **10** was heated following *Method B*, for 30 h at 30°, to afford 2.02 g (78.5%) of crude **16** as an oil. This material was dissolved in THF (5 ml) and solid $Na_2CO_3$ added at 0° until $CO_2$ formation ceased. After addition of $Et_2O$ (15 ml), the precipitate was filtered, washed with $Et_2O$, and dried: 1.17 g (41%) of Na salt of **16** as a pale yellow solid. M.p. 200° (dec.). IR (KBr): 3440*w* (br.), 3060*w*, 3030*w*, 1662*m*, 1605*s*, 1570*s*, 1500*w*, 1425*s*, 1345*m*, 1200*m*, 990*m*, 785*m*, 695*m*. $^1$H-NMR (250 MHz, $(D_6)$DMSO): 7.9–7.7 (*m*, 2 arom. H); 7.63, 7.34 (2*d*, *J* = 16.8, H–C(2), H–C(3)); 7.55–7.2 (*m*, 3 arom. H); 6.90, 6.82 (2*d*, *J* = 15.8, H–C(5), H–C(6)).

3.5. *(E)-4-Oxo-4-(trimethoxyphenyl)(2,3-$D_2$)but-2-enoic Acid* (**17**). A soln. of 500 mg (1.55 mmol) of **8** in dioxane (5 ml) and 6N DCl in $D_2O$ (1.5 ml) was stirred for 12 h at 30° following *Method B* to yield 380 mg (91.4%) of crude **17** as an oil which crystallized from AcOEt/hexane: 320 mg (77%) of **17**. M.p. 137–139°. IR (KBr): 3430*w* (br.), 2990*w*, 2945*w*, 2660*w*, 2555*w*, 1700*s*, 1660*s*, 1585*s*, 1508*m*, 1470*m*, 1420*s*, 1340*s*, 1295*m*, 1218*m*, 1133*s*, 1005*m*, 780*m*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.26 (*s*, 2 arom. H); 3.96, 3.95 (2*s*, 3 $CH_3O$) (97% $D_2$). MS: 268 (100, $M^+$), 195 (41).

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