# Trifluoromethanesulfonic (Triflic) Acid Catalyzed Transformations of α-Hydroxy Carbonyl Compounds[1]

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Triflic acid catalyzed reaction of 2-hydroxy-2-adamantanecarboxylic acid results via ionizative decarbonylation in the formation of adamantanone. Under carbon monoxide pressure pinacol-type rearrangement gives 4,5-homoadamantanedione. Reaction of a series of α-hydroxy ketones result in fragmentation, deprotonation, and cyclization, respectively. The reactions and their suggested mechanism are discussed.

## Introduction

The interconversion of tertiary acylium ions into α-keto carbocations is still unknown.

$$R_1R_2R_3CCO^+ \rightleftarrows R_1R_2C^+C(O)R_3$$

The related acid-catalyzed reaction of pivaloyl chloride in hydrocarbon solution under carbon monoxide pressure gives 3-methyl-2-butanone.[2] However, the mechanism of this reaction was found to involve an aldehyde–ketone rearrangement pathway instead of the formation of an α-keto carbocation.[3]

It was long known that benzylic acid transforms into 9-fluorenecarboxylic acid under acidic conditions,[4] which suggests the initial formation of an α-carbonyl carbocation. Substantial stabilization of this carbocation by the phenyl rings involving electron delocalization and subsequent cyclization leads to the formation of 9-fluorenecarboxylic acid. Spectroscopic evidence was also obtained for the formation of the α-carbonyl carbocation.

Since the first report of protolytic ionization of α-hydroxy carbonyl compounds,[5] there was substantial interest in these reactions and their intermediates. Shudo and Ohwada studied the protolytic behavior of polyaromatic-substituted α-hydroxy carbonyl compounds (both ketones and carboxylic acids and their derivatives) and found initial protonation of the hydroxy group with subsequent ionization giving a labile α-carbonyl carbocation intermediate, which is stabilized by strong charge delocalization and leads to aromatic ring cyclization products.[6]

In our continued interest in carbocation chemistry, we found that without the assistance from stabilizing phenyl groups the formation of α-carbonyl carbocations is not favored and instead, in the case of α-hydroxy carboxylic acids, the formation of the more stable α-hydroxyacylium ions take place. In the case of α-hydroxy ketones, on the other hand, fragmentation results.

The study and chemistry of aliphatic α-hydroxyacylium ions have not yet been well established. This prompted us to report our results concerning their decarbonylation and pinacol-like rearrangement. Our studies centered on the trifluoromethanesulfonic (triflic) acid catalyzed transformation of α-hydroxy carbonyl compounds and their possible mechanism.

## Results and Discussion

2-Hydroxy-2-adamantanecarboxylic acid (1), prepared from 4,5-homoadamantananedione[7] (2) via benzilic acid-like rearrangement,[8] was used as a model compound in our initial studies.

To a Freon 113 solution of 2-hydroxy-2-adamantanecarboxylic acid was added under nitrogen atmosphere a catalytic amount of trifluoromethanesulfonic (triflic) acid, and the reaction mixture was stirred at ambient temperature for several hours. Upon workup 2-adamantanone was obtained in nearly quantitative yield. The reaction is suggested to involve the initial formation of a α-hydroxyacylium ion (3) with subsequent decarbonylation giving 2-adamantanone.

A referee suggested that the loss of carbon dioxide and proton from cation 4 can be reasonably expected to lead to the formation of adamantylidene carbene. It has been well documented that the adamantylidene carbene undergoes self-insertion to generate the corresponding 2,4-dehydroadamantane which protonates to give 2-adamantyl cation, which subsequently would intermolecularly rearrange to give the 1-adamantyl cation. The possible formation of cation 4 is, however, excluded as not even a trace of 1- or 2-adamantanol was detected from the reaction mixture upon aqueous workup. GC–MS analysis of gaseous byproduct showed the presence of only carbon monoxide. These data indicate that the tertiary acyl cation (3) formed by ionization of 1 immediately decarbonylates to adamantanone (5), as the protonated ketone 5 is a more stable than 3.

When 3 was generated from 1 under 600–800 psi of CO pressure no decarbonylation takes place and a pinacol type rearrangement gives 4,5-homoadamantanedione (2). The results indicate competition between decarbonylation and pinacol-like rearrangement of formed α-hydroxyacylium ion (3).

It should be noted that when 2-adamantanone was treated with triflic acid under carbon monooxide pressure no reaction takes place and 2-adamantanone was quantitatively recovered. This shows that no interchange of 2-adamantanone and 4,5-homoadamantanedione (2) is possible and the formation of 2 must come from α-hydroxyacylium ion (3), which is generated from 2-

(1) Synthetic Methods and Reactions. 158. For Part 157, see: Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.*, in press.
(2) Olah, G. A.; Farooq, O.; Marcelli, M., unpublished result.
(3) Oka, M.; Fry, A. *J. Org. Chem.* **1970**, *35*, 2801.
(4) (a) Vorlander, D.; Pritzsche, A. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1793. (b) Britrzycki, A.; Herbst, C. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 145. *Organic Syntheses*, Wiley: New York, 1963; Collect. Vol. IV, p 482. (c) Dobeneck, H. v.; Kiefer, R. *Justus Liebigs Ann. Chem.* **1965**, *684*, 115. (d) Arnold, R. T.; Parham, W. E.; Dodson, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 2439. (e) Hopkinson, A. C.; Khazanie, P. G.; Dao, L. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1395. (f) Delacre, M. *Bull. Soc. Chim. Fr.* **1918**, *23*, 229.
(5) (a) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (b) Pagni, R. M. *Tetrahedron* **1984**, *40*, 4161.
(6) Shudo, K.; Ohwada, T. *J. Am. Chem. Soc.* **1988**, *110*, 1862.
(7) Schlatmann, J. L. M. A.; Korsloot, J. G.; Schut, J. *Tetrahedron* **1970**, *26*, 949.
(8) Selman, S.; Eastham, J. F. *Q. Rev. Soc. Chem. (London)* **1960**, *14*, 221.

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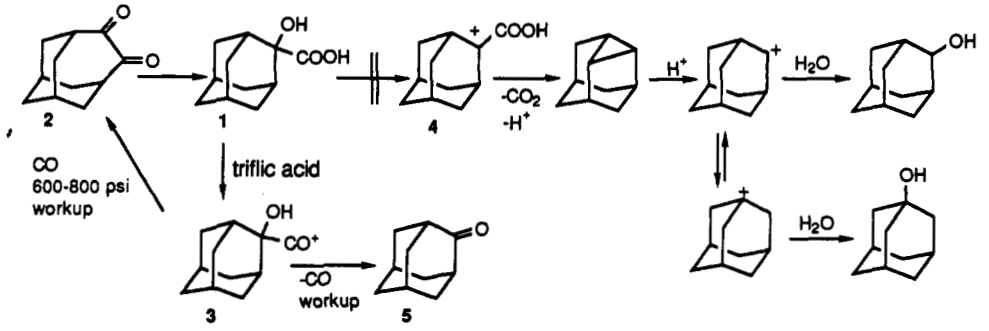
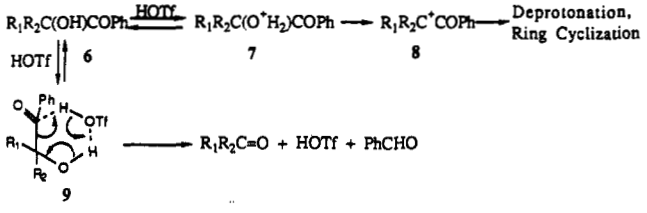
**Scheme I**

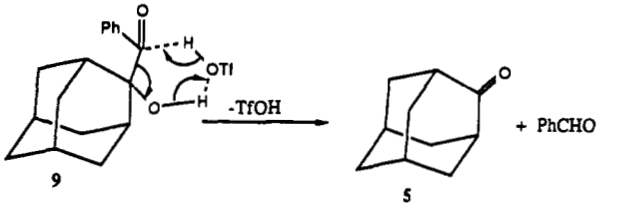



hydroxy-2-adamantanecarboxylic acid (1). A $^{13}C$ NMR study of 1 in "magic acid" ($FSO_3H/SbF_5$)$SO_2ClF$ solution at −60 °C showed only protonated 2-adamantanone. Neither an α-carbonyl carbocation nor a dication has been observed.

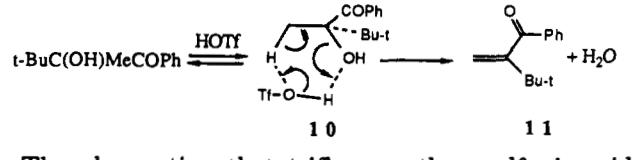
Subsequently we also studied a series of varied α-hydroxy ketones **6**, prepared via hydrolysis of the corresponding α-trimethylsiloxy ketones according to Zimmer's procedure,[9] in their reaction with triflic acid. We obtained related fragmentated ketones, α,β-unsaturated ketones and aromatic ring cyclized ketones, respectively (Table I). The general reaction scheme can be depicted as




Trifluoromethanesulfonic (triflic) acid catalyzed protolysis of α-hydroxy ketones (lacking β-hydrogen atoms) in methylene chloride solution at ambient temperature (for a reaction period of 24 h) gives the corresponding fragmented reaction products as shown in the case of 2-hydroxy-2-benzoyladamantane. Since formation of intermediate 2-benzoyl-2-adamatyl cation **8** is not favored in the absence of stabilizing groups, instead suggested intermediate **9** is formed which then fragments into adamantanone and benzaldehyde (detected from the reaction mixture by GC–MS).



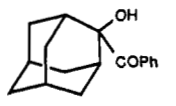
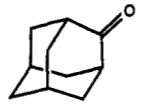
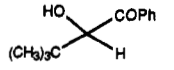
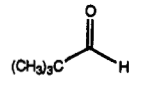
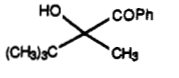
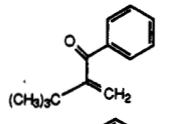
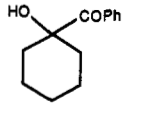
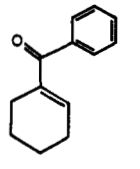
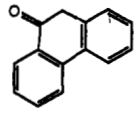
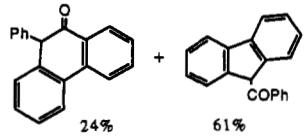

Trifluoromethanesulfonic (triflic) acid catalyzed protolysis of α-hydroxy ketones containing β-hydrogens was found under similar conditions to give the corresponding α,β-unsaturated ketones




The observation that trifluoromethanesulfonic acid catalyzed protolysis of these α-hydroxy ketones affords exclusively α,β-unsaturated ketones suggests that the reaction involves concerted elimination through suggested intermediate **10**, instead of the formation of α-carbonyl carbocation **8**. The formation of α,β-unsaturated ketones is irreversible as proven by the treatment of the corresponding α,β-unsaturated ketones with trifluoromethanesulfonic acid resulting in their complete recovery.

We reported the study of a variety of *tert*-butyl-substituted carbocations and their elimination and rearrangement reactions[10] which involved methyl group migration as the first step. However, no rearranged reaction products have been observed in the present triflic acid catalyzed protolytic fragmentations. Furthermore, study of α,β-unsaturated ketones in fluorosulfonic acid–antimony pentafluoride–$SO_2ClF$ solution at low temperature (−60 °C) failed to give C-protonated α-benzyl cations. Instead, only O-protonated α,β-unsaturated ketones were observed. Based on these observations formation of related α-car-

**Table I. Triflic Acid Catalyzed Transformation of α-Hydroxy Ketones**

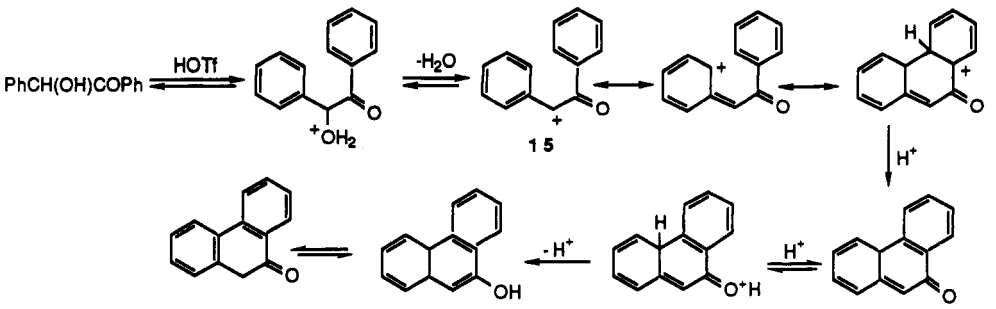
| α-hydroxy ketone | product | % yield[a] |
|---|---|---|
|  |  | 90 |
|  |  | 82 |
|  |  | 78 |
|  |  | 79 |
| PhCH(OH)COPh |  | 79 |
| $Ph_2C(OH)COPh$ |  24% +  61% | |

[a] Isolated yield.

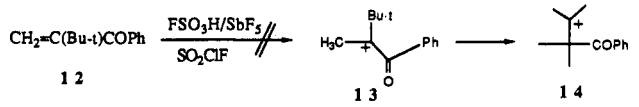
(9) Koenigkramer, R. E.; Zimmer, H. *Tetrahedron Lett.* **1980**, 1017.

(10) Olah, G. A.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Org. Chem.* **1990**, *55*, 1792.

**Scheme II**



bonyl carbocation does not occur under the reaction conditions.



In certain cases, however, aryl-substituted α-carbonyl carbocations are readily formed and are sufficiently stable to be observed under stable ion conditions.[11] In our studies ionization of α-hydroxy-1,1-diphenylmethyl phenyl ketone in fluorosulfonic acid–antimony pentafluoride–$SO_2ClF$ solution at low temperature (–60 °C) gave spectroscopic evidence for the related α-carbonyl carbocation showing significant delocalization of the carbocation center ($\delta(^{13}C)$ 217.3). This is in accordance with previous studies reported in $ClSO_3H$–$DC_2Cl_2$ solution for diaryl-substituted α-carbonyl cations.

Trifluoromethanesulfonic (triflic) acid catalyzed reaction of phenyl-substituted α-hydroxy ketones of the type PhCH(OH)COPh was also carried out and gave the corresponding ring cyclized ketones.

In case of the conjugated system α-carbonyl carbocation **15** can form because of stabilization provided by the aromatic ring delocalized resonance forms. Subsequent deprotonative cycloalkylation leads to the formation of the cyclic ketone product in good yield.

## Experimental Section

4,5-Homoadamantane (**2**) was prepared according to the literature procedure.[7] 1,1,2-Trifluorotrichloroethane (DuPont Freon 113) was distilled over $P_2O_5$. Trifluoromethanesulfonic acid (triflic acid, 3M Co.) was distilled prior to use. Gas chromatographic analyses were carried out using a quartz-silica capillary column coated with DB-1.

**Preparation of 2-Hydroxy-2-adamantanecarboxylic Acid (1).** A mixture of 4,5-homoadamantanedione (1.78 g, 10.0 mmol) potassium hydroxide (7.0 g, excess) in water (70 mL) was warmed at 60–70 °C for 14 h and then extracted with methylene chloride (30 mL × 3). The aqueous solution while stirred was slowly neutralized at 0 °C with 30% $H_2SO_4$ (external ice bath) and then extracted with methylene chloride (50 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to give 2-hydroxy-2-adamantanecarboxylic acid (1.72 g, 8.8 mmol): 88% yield as colorless crystals; mp 166 °C dec; IR (KBr) 1610 (s); $^{13}C$ NMR (50 MHz, acetone-$d_6$) 175.76 (s), 77.70 (s), 38.10 (t), 35.54 (t), 34.93 (d), 32.78 (t), 27.76 (d), 27.56 (d). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.35; H, 8.16. Found: C, 67.09; H, 8.24.

**Decarbonylation of 1.** To a well-stirred solution of 1 (1.96 g, 10.0 mmol) in dry Freon 113 (30 mL) was added a catalytic amount of fresh distilled trifluoromethanesulfonic acid (ca. 0.2 mL) at ambient temperature. The reaction mixture was then maintained stirring for another 6 h. Usual aqueous workup and extraction with methylene chloride (30 mL × 3) was carried out, and the combined extract was dried over anhydrous magnesium sulfate, filtered, and evaporated to afford 2-adamantanone (1.32 g, 8.8 mmol, 88% yield from 1).

**4,5-Homoadamantanedione (2).** A pressure vessel was charged with dry 1,1,2-trifluorotrichloroethane (Freon 113; 50 mL) and freshly distilled trifluoromethanesulfonic acid (ca. 0.5 mL) and cooled (external dry ice–acetone bath) to –78 °C under dry nitrogen atmosphere. To the solidified mixture then 2-hydroxy-2-adamantanecarboxylic acid (**2**; 1.96 g, 10.0 mmol) was added. The vessel was closed, pressurized with carbon monoxide to 600–800 psi, and while allowing to warm to room temperature it was stirred (magnetic stirrer) for 6 h. After usual workup and extraction with methylene chloride (50 mL × 3), the combined extract was dried, filtered, and evaporated to afford 4,5-homoadamantanedione (**2**; 1.08 g, 61% yield from 1) as a colorless solid, mp 228 °C (lit. mp 228 °C). All spectral data were consistent with those reported for **2** previously.[7]

**α-(Trimethylsiloxy)-2-adamantyl Phenyl Ketone.** To a stirred cold solution (dry ice–acetone) of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol) in tetrahydrofuran (THF; 10 mL) was added under dry nitrogen through a syringe lithium diisopropylamide (LDA; 2.0 M in cyclohexane; 5.0 mL, 10.0 mmol) over a period of 5 min. After the addition of LDA, the reaction mixture was stirred at –78 °C for 30 min. Consequently a solution of 2-adamantanone (1.5 g, 10.0 mmol) in dry THF (10 mL) was dropwise added during a period of 10 min. After the addition was completed, the stirred reaction mixture was allowed to stand for an additional 30 min. The dry ice–acetone could bath was then removed, and the reaction mixture was stirred at ambient temperature for overnight (ca. 16 h). After quenching with 10% aqueous hydrochloric acid (20 mL) the usual workup was carried out with ether extraction (30 mL × 3). The combined ethereal extract was dried over anhydrous magnesium sulfate, filtered, and vacuum evaporated to give the crude product, which was further purified via column chromatography on silica gel (20% ethyl acetate–hexane as eluent) giving α-(trimethylsiloxy)-2-adamantyl phenyl ketone (2.72 g, 8.2 mmol, 82% yield from 2-adamantanone) as colorless crystals: mp 85–87 °C; IR (KBr) 1760 (s) $cm^{-1}$; $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 202.38 (s), 145.21 (s), 129.33 (d), 129.01 (d), 128.64 (d), 61.45 (s), 42.36 (d), 38.49 (t), 36.32 (t), 36.04 (t), 29.82 (d), 28.35 (d), 0.21 (q); GC/MS (70 eV) $m/e$ 328 ($M^+$, 0.6), 313 (1.2), 223 (100.0), 135 (2.1), 105 (8.3), 73 (46.6). Anal. Calcd for $C_{20}H_{28}O_2Si$: C, 73.17; H, 8.54. Found: C, 73.29; H, 8.49.

**α-(Trimethylsiloxy)-1-neopentyl Phenyl Ketone.** Using the same procedure from the reaction of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol), lithium diisopropylamide (2 M in cyclohexane; 5 mL, 10.0 mmol) and trimethylacetaldehyde (0.86 g, 10.0 mmol) was obtained α-(trimethylsiloxy)-1-neopentyl ketone (2.32 g, 8.8 mmol, 88% yield from trimethylacetaldehyde). All spectral data were consistent with those given for α-(trimethylsiloxy)-1-neopentyl phenyl ketone in previous literature.[9]

**α-(Trimethylsiloxy)-3,3-dimethyl-2-butyl Phenyl Ketone.** Using the same procedure, from the reaction of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol), lithium diisopropylamide (2 M in cyclohexane; 5 mL, 10.0 mmol), and pinacolone (1.0 g, 10.0 mmol) was obtained α-(trimethylsiloxy)-3,3-dimethyl-2-butyl phenyl ketone (2.22 g, 8.0 mmol, 80% yield from pinacolone). All spectra data were consistent with those given for α-(trimethylsiloxy)-3,3-dimethyl-2-

(11) For a review, see: Creary, X.; Hopkins, A. C.; Lee-Ruff, E. In *Advances in Carbocation Chemistry*, Creary, X., Ed.; JAI Press: Greenich, 1989; Vol. I, pp 45–92 and references therein.

butyl phenyl ketone in previous literature.[9]

**α-(Trimethylsiloxy)-1-cyclohexyl Phenyl Ketone.** Using the same procedure, from the reaction of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol), lithium diisopropylamide (2 M in cyclohexane; 5 mL, 10.0 mmol), and cyclohexanone (0.98 g, 10.0 mmol) was obtained the corresponding α-(trimethylsiloxy)-1-cyclohexyl phenyl ketone (2.24 g, 8.1 mmol, 81% yield from pinacolone). All spectra data were consistent with those given for α-(trimethylsiloxy)-1-cyclohexyl phenyl ketone in previous literature.[9]

**α-(Trimethylsiloxy)-1-phenylmethyl Phenyl Ketone.** Using the same procedure, from the reaction of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol), lithium diisopropylamide (2 M in cyclohexane; 5 mL, 10.0 mmol), and benzaldehyde (1.06 g, 10.0 mmol) was obtained α-(trimethylsiloxy)-1-phenylmethyl phenyl ketone (2.67 g, 9.4 mmol, 94% yield from benzaldehyde). All spectral data were consistent with those given for the α-(trimethylsiloxy)-1-phenylmethyl phenyl ketone in previous literature.[9]

**α-(Trimethylsiloxy)-1,1-diphenylmethyl Phenyl Ketone.** Using the same procedure, from the reaction of diethyl 1-phenyl-1-(trimethylsiloxy)methanephosphonate (3.16 g, 10.0 mmol), lithium diisopropylamide (2 M in cyclohexane; 5 mL, 10.0 mmol), and benzophenone (1.82 g, 10.0 mmol) was obtained α-(trimethylsiloxy)-1,1-diphenylmethyl phenyl ketone (4.42 g, 8.2 mmol, 82% yield from benzophenone). All spectral data were consistent with those given for α-(trimethylsiloxy)-1,1-diphenylmethyl phenyl ketone in previous literature.[9]

**α-Hydroxy-2-adamantyl Phenyl Ketone.** A 10% aqueous solution (w/w; 50 mL) of sodium acetate and α-(trimethylsiloxy)-2-adamantyl phenyl ketone (3.28 g, 10.0 mmol) was stirred at ambient temperature for 2 h. After usual workup and extraction with ether the combined ethereal layer was dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to give α-hydroxy-2-adamantyl phenyl ketone (2.36 g, 9.2 mmol, 92% yield from α-(trimethylsiloxy)-2-adamantyl phenyl ketone) as colorless crystals: mp 95–96 °C; IR (KBr) 1760 (s) $cm^{-1}$; $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 201.98 (s), 144.29 (s), 129.94 (d), 129.30 (d), 128.89 (d), 61.82 (s), 42.91 (d), 38.81 (t), 36.92 (t), 36.27 (t), 30.26 (d), 28.61 (d); GC/MS (70 eV) *m/e* 256 ($M^+$, 1.7), 135 (2.7), 105 (54.9), 73 (100.0). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.69; H, 7.81. Found: C, 79.52; H, 7.92.

**α-Hydroxy-1-neopentyl Phenyl Ketone.** Using the previously described procedure, from the reaction of α-(trimethylsiloxy)-1-neopentyl phenyl ketone (2.64 g, 10.0 mmol) with aqueous sodium acetate solution was obtained α-hydroxy-1-neopentyl phenyl ketone (1.69 g, 8.8 mmol, 88% yield from α-(trimethylsiloxy)-1-neopentyl phenyl ketone). All spectra data were consistent with those given for α-hydroxy-1-neopentyl phenyl ketone in previous literature.[9]

**α-Hydroxy-3,3-dimethyl-2-butyl Phenyl Ketone.** Using the previously described procedure, from the reaction of α-(trimethylsiloxy)-3,3-dimethyl-2-butyl phenyl ketone (2.78 g, 10.0 mmol) with aqueous sodium acetate was obtained α-hydroxy-3,3-dimethyl-2-butyl phenyl ketone (1.87 g, 9.1 mmol, 91% yield from α-(trimethylsiloxy)-3,3-dimethyl-2-butyl phenyl ketone). All spectral data were consistent with those given for α-hydroxy-3,3-dimethyl-2-butyl phenyl ketone in previous literature.[9]

**α-Hydroxy-1-cyclohexyl Phenyl Ketone.** Using the same procedure, from the reaction of α-(trimethylsiloxy)-1-cyclohexyl phenyl ketone (2.76 g, 10.0 mmol) with aqueous sodium acetate was obtained α-hydroxy-1-cyclohexyl phenyl ketone (1.75 g, 8.6 mmol, 86% yield from α-(trimethylsiloxy)-1-cyclohexyl phenyl ketone). All spectral data were consistent with those given for α-hydroxy-1-cyclohexyl phenyl ketone in previous literature.[9]

**Benzoin.** Using the same procedure, from the reaction of α-(trimethylsiloxy)-1-phenylmethyl phenyl ketone (2.84 g, 10.0 mmol) with aqueous sodium acetate was obtained benzoin (1.89 g, 8.9 mmol, 89% yield from α-(trimethylsiloxy)-1-phenylmethyl phenyl ketone). All spectral data were consistent with those given for benzoin in previous literature.[9]

**α-Hydroxy-1,1-diphenylmethyl Phenyl Ketone.** Using the same procedure, from the reaction of α-(trimethylsiloxy)-1,1-diphenylmethyl phenyl ketone (3.60 g, 10.0 mmol) with aqueous sodium acetate was obtained α-hydroxy-1,1-diphenylmethyl phenyl ketone (2.36 g, 8.2 mmol, 82% yield from α-(trimethylsiloxy)-1,1-diphenylmethyl phenyl ketone). All spectral data were consistent with those given for α-hydroxy-1,1-diphenylmethyl phenyl ketone in previous literature.[9]

**General Procedure of Protolysis of α-Hydroxy Ketones with Triflic Acid.** To a solution of the corresponding α-hydroxy ketone (generally 10 mmol) in dry methylene chloride (50 mL) was slowly added a catalytic amount, ca. 0.1–0.2 mL, of freshly distilled trifluoromethanesulfonic acid (triflic acid) with stirring under nitrogen atmosphere at 0 °C (ice bath). The cooling bath was then removed, and the reaction mixture was stirred for an additional 16 h at ambient temperature. After quenching with 10% aqueous sodium bicarbonate (50 mL), the usual workup was carried out with extraction with methylene chloride (30 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and vacuum evaporated to give the crude material. Purification was usually carried out by column chromatography on silica gel (10% ether–petroleum ether as eluent) to give the pure reaction product (Table I). All physical and spectral data of the reaction products, including GC/MS and NMR, were consistent and in accordance with those reported previously.

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# Straightforward Synthesis of 1,2,3-Tricarbonyl Systems

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A simple two-step protocol for the preparation of α,β-diketo amides is described. The first step involves condensation of the anion of an α-phenylthio amide with an aldehyde. This is followed by oxidation of the resulting β-hydroxy α-sulfide with the Dess–Martin periodinane. The vicinal tricarbonyl system is obtained in good to excellent yields.

Two considerations have increased interest in the preparation of 1,2,3-tricarbonyl compounds (cf. 1, Scheme I). From the chemical standpoint, Wasserman and coworkers have identified fascinating applications of such

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