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Selective Cleavage of β-Keto Esters by 1,4-Diazabicyclo[2.2.2]octane (Dabco)

Bao-Shan Huang, Edward J. Parish, and D. Howard Miles*

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

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As a result of a continuing study utilizing nitrogenous bases,[1-4] we now wish to report that 1,4-diazabicyclo[2.2.2]octane (Dabco) is useful for the cleavage of β-keto esters.

β-Keto ester **1** was treated with 6 equiv of Dabco in 16 equiv of *o*-xylene at reflux (165°) for 6 hr to give ketone **10** as a white, crystalline solid in 84% yield. Ketone **10** was identical by ir, nmr, mass spectrum, glc retention time, and mixture melting point with an authentic sample prepared from **1** by a known procedure.[5]

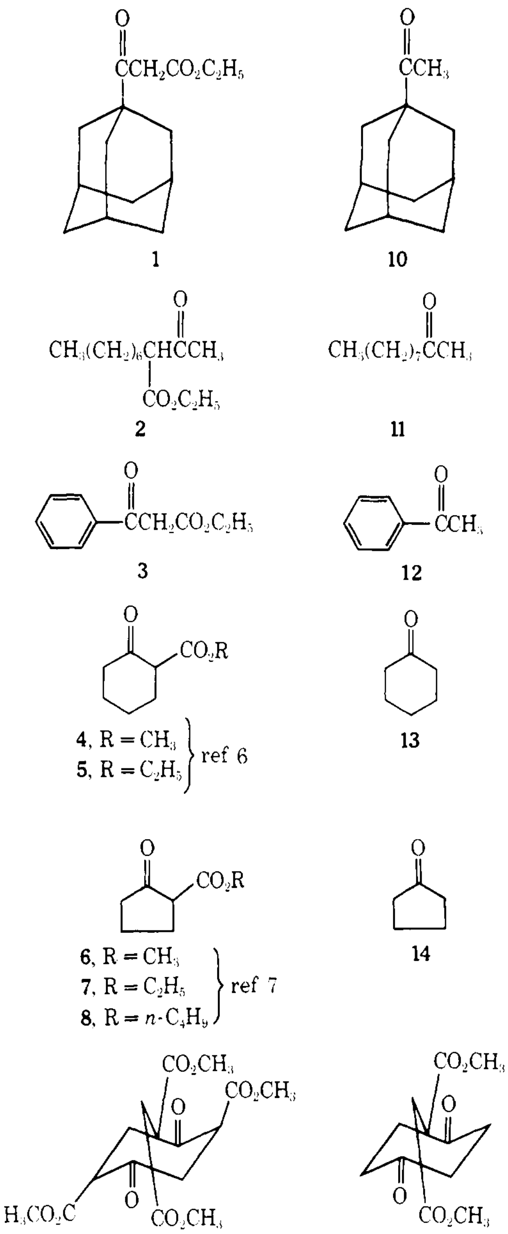
The generality of Dabco as a reagent for cleaving β-keto esters is demonstrated by the results illustrated in Scheme I. Typically, a mixture of 1 equiv of the appropriate β-keto ester and 10 equiv of Dabco in 15 equiv of *o*-xylene was heated to reflux for 4 hr.[11] The resulting ketones (**11-14**) were obtained in greater than 96% yield by glc analyses and were identical by mass spectral and glc retention time comparison with authentic samples.[5,8]

The selectivity of the cleavage reaction is demonstrated by the application of Dabco to the cleavage of substrate **9** to give compound **15**. This result shows that only the β-keto esters with at least one α hydrogen were cleaved. The report[4] that a variety of nonconjugated esters are stable under conditions similar to those which cleaved β-keto esters provides further evidence of selectivity.

The facile cleavage of methyl, ethyl, and *n*-butyl β-keto esters with a reagent (Dabco) that does not cleave saturated esters by either the *O*-alkyl cleavage or hydrolytic routes suggests that a mechanism similar to that reported by Krapcho and Lovey[5,12] for the cleavage of β-keto esters with sodium chloride and DMSO is probably operative.

A variety of reagents have been reported for achieving the cleavage of β-keto esters.[5,9] However, to our knowledge this is the first report involving the utilization of a nonionic reagent in a relatively nonpolar solvent system.

Scheme I



Experimental Section

Infrared spectra were obtained using a Perkin-Elmer Model 137G spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Jeolco Minimar spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were obtained using a Perkin-Elmer Model 270 mass spectrometer. Gas-liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 3 mm i.d.) packed with 5% SE-30 on 80/100 mesh Chromosorb W (programed from 70 or 100° to 200° at 5°/min) with a nitrogen flow rate of 11 ml/min was used for the glc analyses of most compounds. A metal column (6 ft × 2 mm i.d.) packed with 4% SE-30 and 6% QF-1 on 80/100 mesh Chromosorb W (programed from 100 to 200° at 5°/min) with a nitrogen flow rate of 10 ml/min was used for the glc analyses of compounds **3** and **12**. A glass column (6 ft × 3 mm i.d.) packed with 5% Apiezon L on 80/100 mesh Chromosorb W (programed from 62 to 200° at 5°/min) with a flow rate of 10 ml/min was used for the glc analyses of compounds **4**, **5**, and **13**. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Decarbethoxylation of β-Keto Ester 1. A mixture of β-keto ester **1** (2.239 g, 9.9 mmol) and Dabco (5.926 g, 52.9 mmol) in *o*-xylene (14.639 g, 138.1 mmol) was heated to reflux for 6 hr in an oil bath with constant stirring. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous MgSO$_4$, and evaporated *in vacuo*. The crude product was purified through a column packed with silica gel alumina and recrystallized from methanol to give 1.289 g (84%) of white, crystalline **10**: mp 55.5-56.5° (lit.[10] mp 53-54°); λ_{max} (KBr) 2780, 1670, 1430, 1330, 1240 cm^{-1}; nmr (CDCl$_3$) δ 1.77 (15 H, multiplet), 2.07 (3 H);

mass spectrum M+ *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 80.97; H, 9,95. Compound **10** was identical by ir, nmr, mass spectrum, glc retention time, and mixture melting point with an authentic sample prepared according to the procedure described by Krapcho and Lovey.[5]

General Procedure for the Decarbalkoxylation of β-Keto Esters 2–8. A mixture of 10 equiv of Dabco, 1 equiv of β-keto esters **2–8**, and 15 equiv of *o*-xylene was heated to reflux for 4 hr with constant stirring. The cooled prodct mixtures were analyzed by glc and mass spectral analysis. The corresponding ketones (**11–14**) were identical by comparison of mass spectra and glc retention time with those of authentic samples.[8]

Decarbomethoxylation of β-Keto Ester 9. A mixture of 1.158 g (3.0 mmol) of compound **9** and 3.371 g (30.1 mmol) of Dabco in 10.434 g (98.4 mmol) of *o*-xylene was heated at 85–92° for 1 hr with constant stirring. The chloroform extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous $MgSO_4$, and evaporated *in vacuo* to give 0.890 g of crude compound **15** in 72% yield by glc analysis. The crude product was purified through a column packed with silica gel and eluted with hexane–chloroform to give 0.541 g (67%) of crystalline compound **15**: mp 189–191°; λ_{max} (KBr) 2820, 1690, 1440, 1240, 1020 cm^{-1}; nmr ($CDCl_3$) δ 3.63 (6 H), 2.43 (10 H, multiplet); mass spectrum M+ *m/e* 268. *Anal.* Calcd for $C_{13}H_{16}O_6$: C, 58.21; H, 5.97. Found: C, 58.06; H, 5.95.

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Registry No.—**1**, 19386-06-2; **2**, 40778-30-1; **3**, 94-02-0; **4**, 41302-34-5; **5**, 1655-07-8; **6**, 10472-24-9; **7**, 611-10-9; **8**, 6627-69-6; **9**, 6966-22-9; **10**, 1660-04-4; **15**, 51869-06-8; Dabco, 280-57-9.

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New Synthetic Reactions. A Convenient Approach to Methyl 3-Oxo-4-pentenoate

Barry M. Trost* and Robert A. Kunz

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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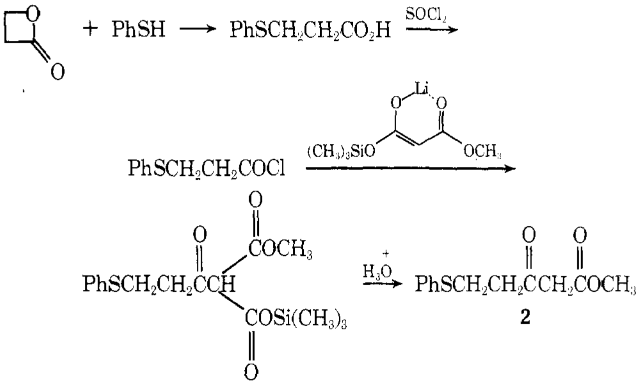
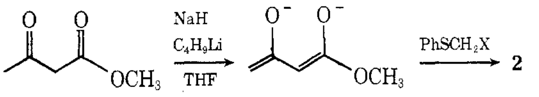
The utility of methyl 3-oxo-4-pentenoate (**1**) as an annelating agent in the synthesis of terpenes and alkaloids has been previously demonstrated.[1–4] Nevertheless, this reagent is not easily synthesized. The original method requires an acid-catalyzed elimination as the last step (eq 1) and proceeded in 7–12% overall yields from readily available starting materials. In our hands, this step never went to completion without substantial decomposition. An alternative approach based upon a retro Diels–Alder reaction to introduce the unsaturation proceeds in excellent yields (68% overall) but requires the availability of a special high-temperature pyrolysis apparatus.[5] The facility of dehydrosulfenylations as a method to introduce unsaturation conjugated to a carbonyl group suggested this reaction for the introduction of the double bond.[6] We wish to report utilization of this approach as a particularly convenient one for the preparatin of **1**. More generally, this methodology represents a novel approach to the introduction of a methylene group α to a carbonyl group.[7]

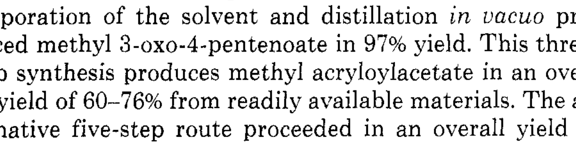
$$C_2H_5OCH_2CH_2COCH_2CO_2CH_3 \xrightarrow{TsOH} \underset{\mathbf{1}}{H_2C{=}CHCOCH_2CO_2CH_3} \qquad (1)$$

The synthesis of the requisite phenylthio derivative **2** initially paralleled a modified route for the formation of the ethoxy precursor.[8] While three steps are required, **2** was prepared in 62–76% overall yield. A more convenient one-step synthesis of **2** involved the alkylation of the dianion of methyl acetoacetate[9] with halomethyl phenyl sulfide. Alkylation proceeds in about 40% yield with chloromethyl phenyl sulfide, but in 63–80% yield with iodomethyl phenyl sulfide. Equally important to the increased yield with the latter reagent was the formation of fewer side products.





Oxidation to the sulfoxide proceeds nearly quantitatively with sodium metaperiodate at room temperature. Heating the sulfoxide in refluxing chloroform for 12 hr followed by evaporation of the solvent and distillation *in vacuo* produced methyl 3-oxo-4-pentenoate in 97% yield. This three-step synthesis produces methyl acryloylacetate in an overall yield of 60–76% from readily available materials. The alternative five-step route proceeded in an overall yield of 60–72%.



Experimental Section

Infrared spectra were determined on a Beckman IR-8 spectrophotometer. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer. Chemical shifts are given in δ units, parts per million relative to TMS as an internal standard. Mass spectra were taken on a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 eV.

All reactions were carried out under nitrogen. Thick layer chromatography was performed in 1.5-mm layers of silica gel PF-254 (E. Merck AG, Darmstadt). Removal of solvents from products normally involved rotary evaporation at water aspirator pressure followed by evacuation of the flask to approximately 1 mm to remove the last traces of the solvent.

3-Phenylthiopropionic Acid. A neat mexture of 19.41 g (269