(11) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **90,** 347 (1968).
(12) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87,** 4520 (1965).
(13) P. Petersen, A. K. Carpenter, and R. F. Nelson, *J. Electroanal. Chem.*, **27,** 1 (1970).
(14) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88,** 143 (1966); N. Kornblum, S. D. Boyd, H. W. Finnick, and R. G. Smith, *J. Am. Chem. Soc.*, **93,** 4316 (1971).
(15) A. A. Abdullah, Y. Iskander, and Y. Riad, *J. Chem. Soc. B*, 1178 (1969).
(16) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66,** 918 (1962).
(17) It was observed that the dinitrostilbenes undergo isomerization in DMF, and, therefore, it was necessary to obtain the uv spectrum immediately after preparing the solutions.
(18) E. Bergmann and J. Hervey, *Ber.*, **62,** 893 (1929).
(19) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **89,** 300 (1967).
(20) P. Ruggi and F. Lang, *Helv. Chim. Acta*, **21,** 38 (1938).

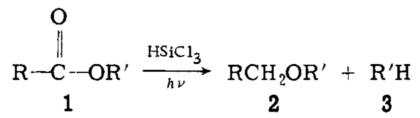
Reductive Deoxygenation of Esters with Trichlorosilane[1]

S. W. Baldwin* and S. A. Haut

Paul M. Gross Chemical Laboratory, Duke University,
Durham, North Carolina 27706

Received June 30, 1975

Trichlorosilane has been shown to be an efficient reagent for reducing simple aliphatic esters to the corresponding ethers under free-radical conditions.[2] We recently demonstrated the applicability of the reagent to the reduction of more complex bicyclic lactones and also the existence of significant selectivity when additional ester groupings were present.[3] We now wish to report that under the appropriate conditions trichlorosilane can be an effective reagent for the reductive deoxygenation of esters of nonprimary aliphatic alcohols.



$$\underset{1}{R-\overset{O}{\overset{\|}{C}}-OR'} \xrightarrow[h\nu]{HSiCl_3} \underset{2}{RCH_2OR'} + \underset{3}{R'H}$$

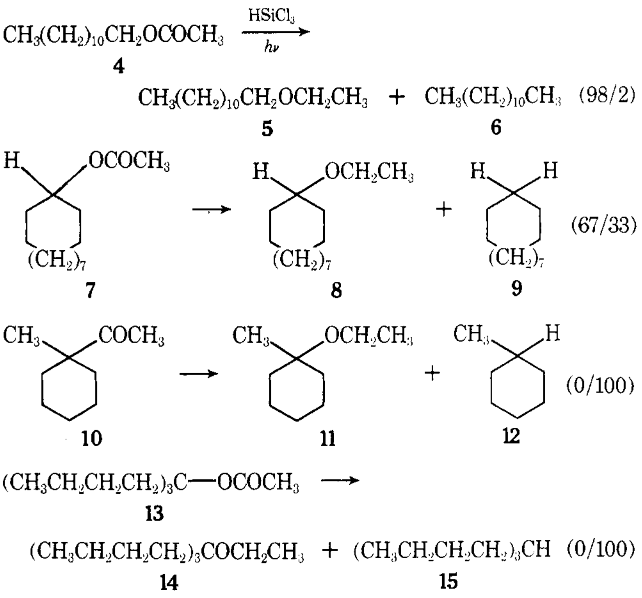
In general we find that for the reaction of a given ester **1** with trichlorosilane, two products, **2** and **3**, are formed competitively. Ether **2** is the result of a "normal" reaction with $HSiCl_3$ while **3** is the product of reductive deoxygenation. The relative amounts of **2** and **3** are most profoundly affected by the nature of R′. As shown in Scheme I for the acetates of several alcohols, irradiation with excess $HSiCl_3$ yields largely **2** for a primary acetate, exclusively **3** for a tertiary acetate, and a mixture of **2** and **3** for a secondary acetate.[4,5] These results are consistent with a reaction mechanism which involves radical **16** as a common intermediate for the formation of **2** and **3**, with the proportion of **16** which undergoes reductive deoxygenation being influenced by the stability of radical ·R′. Thus tertiary acetates give the highest proportion of reductive deoxygenation and primary acetates the lowest.

Table I
Reaction of 1-Adamantyl Esters with $HSiCl_3$

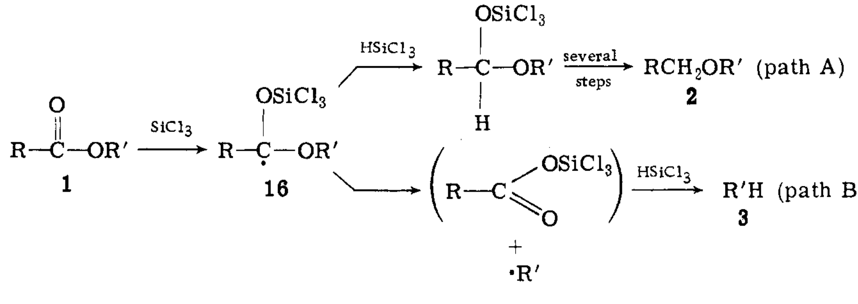
Ester	$HSiCl_3$/**17**[a]	THF/**17**[b]	% reaction	**18**/**19**[c]
17a[d]	8		100	42[f]/58[g]
17a	4		100	30/70
17a	4	24	100	18/82
17a	4	72	87	6/94
17a	2	72	58	2/98
17b[e]	8		100	12[h]/88
17b	4		100	3/97
17b	8	29	7	1/99

[a] Moles of $HSiCl_3$ per mole of ester. [b] Moles of THF per mole of ester. [c] Determined by GLC analysis. [d] Registry no., 19066-22-9. [e] Registry no., 56830-70-7. [f] Registry no., 6221-75-6. [g] Registry no., 281-23-2. [h] Registry no., 56830-71-8.

Scheme I



In an effort to determine if a judicious choice of reaction conditions would render the method preparatively useful in instances where ·R′ was of intermediate stability (i.e., secondary esters), several experiments were performed with esters of 1-adamantanol. The tertiary 1-adamantyl radical has been shown to be slightly more stable than a normal secondary radical,[6] and thus 1-adamantyl esters should provide a sensitive probe of the results of changes in reaction conditions. It was expected that one could most effectively maximize reductive deoxygenation by retarding the *bimolecular* second step of the ether-forming pathway (path A). For instance, a decrease in the $HSiCl_3$ concentration should retard path A to the benefit of path B. In addition, an increase in the steric bulk of the ester (pivalates vs. acetates) should have a similar effect. The results summarized in Table I are in general accord with these predictions. It is seen that either decreasing the amount of



$HSiCl_3$ or diluting the reaction medium with an inert solvent (THF) increases the proportion of reductive deoxygenation. A similar decrease is observed in going from 1-adamantyl acetate (**17a**) to 1-adamantyl pivalate (**17b**). At lower concentrations of $HSiCl_3$ the reaction does not go to completion, presumably because the radical chains become unproductively shortened.

$$\underset{\textbf{17a,b}}{\text{1-Ad-OCOCR}_3} \xrightarrow[h\nu]{HSiCl_3} \underset{\textbf{18a,b}}{\text{1-Ad-OCH}_2\text{CR}_3} + \underset{\textbf{19}}{\text{1-Ad-H}}$$

$$\textbf{a},\ R = H$$

$$\textbf{b},\ R = CH_3$$

It should be mentioned that the application of these trends to 1-dodecyl pivalate and cyclododecyl pivalate gives parallel results as compared to acetates **4** and **7**.[7]

In conclusion we have reported a new reaction of aliphatic esters with trichlorosilane, reductive deoxygenation. We have shown that the reaction is responsive to experimental changes in a predictable manner, and that it can be made to be preparatively useful for esters of secondary and tertiary alcohols. It should be pointed out that the high reactivity of $\cdot SiCl_3$ toward many functional groups[2] limits the generality of the method in some cases. We can see few examples where this reaction would be preparatively superior to other literature procedures for reductive deoxygenation,[8] except for the ease of preparation of the esters in question.

Experimental Section

The ir spectra were recorded on Perkin-Elmer 137 and 237 spectrophotometers. NMR spectra were determined on a Jeol MH-100 spectrometer and are reported in δ units downfield from Me_4Si. GLC analyses were performed on a Hewlett-Packard Model 700 laboratory gas chromatograph equipped with dual thermal conductivity detectors. A flow rate (He) of 55 ml/min through 6 ft × 0.25 in. columns (5% SE-30 on Chromosorb P) was employed. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

Preparation of Starting Materials. Dodecyl acetate (**4**),[9] cyclododecyl acetate (**7**),[10] 1-methylcyclohexyl acetate (**10**),[11] and 1-adamantyl acetate (**17a**)[12] were prepared by standard procedures.

5-*n*-Butyl-5-nonyl Acetate (13). A solution of 5.0 g (25 mmol) of 5-*n*-butyl-5-nonanol in 25 ml of anhydrous THF was added to a stirred suspension of 2.0 g (51 mmol) of KH (8.2 g of a 24.04% suspension) in 25 ml of dry THF under N_2. The mixture was stirred for 2 hr at room temperature and then cooled to 0°, whereupon 4.8 g (62 mmol) of acetyl chloride in 10 ml of dry THF was slowly added. The reaction mixture was stirred at 0° for 1 hr and at room temperature for 6 hr, and finally heated at reflux for 2 hr, whereupon it was poured into 500 ml of ice water and extracted with ether (3 × 100 ml). The combined organic extracts were washed with brine (2 × 50 ml), dried ($MgSO_4$), and concentrated. Two distillations gave 3.89 g (63%) of pure acetate, bp 67–76° (0.15 mm): ir (neat) 1749 cm^{-1} (C=O); NMR (CCl_4) δ 0.91 (t, *J* = 7 Hz, 9 H, $-CH_3$), 1.05–1.57 (broad, 12 H, $-CH_2-$), 1.57–1.88 (broad, 6 H, $-OCH_2-$), 1.91 (s, 3 H, $COCH_3$).

Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.47. Found: C, 74.49; H, 12.63.

1-Adamantyl Pivalate (17b). To a solution of 7.6 g (50 mmol) of 1-adamantanol in 75 ml of anhydrous THF under N_2 was slowly added 23 ml (55 mmol) of a 2.14 *M* hexane solution of *n*-butyllithium. After stirring the resulting suspension for 30 min at room temperature, a solution of 6.7 g (55 mmol) of pivaloyl chloride in 50 ml of anhydrous THF was added dropwise and the resulting red-orange mixture heated at reflux for 16 hr. To the cooled reaction mixture was added 100 ml of H_2O, the layers separated, and the aqueous phase extracted with ether (3 × 5 ml). The combined organic layers were washed with saturated $NaHCO_3$ (1 × 50 ml) and brine (1 × 50 ml), dried ($MgSO_4$), and concentrated. The crude product was chromatographed on silica gel, elution with benzene providing pure ester which was then distilled to give 7.3 g (62%) of viscous oil, bp 67–75° (0.05 mm). The oil solidified on standing: mp 25.5–27.0°; ir (neat) 1724 cm^{-1}; NMR (CCl_4) δ 1.10 [s, 9 H, $(CH_3)_3C-$], 1.61–1.79 (broad, 6 H, $-CH_2CO-$), 1.95–2.24 (broad, 9 H, $-CHCH_2-$).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.14; H, 10.21.

Reduction Products. Dodecane (**6**), cyclododecane (**9**), methylcyclohexane (**12**), 5-(*n*-butyl)nonane (**15**), and adamantane (**19**) were commercial samples. 1-Adamantyl ethyl ether (**18a**) was prepared according to the literature.[13] Dodecyl ethyl ether (**5**)[14] and cyclododecyl ethyl ether (**8**)[15] have been prepared previously but full characterization was not readily available in the literature. We have prepared them by standard (Williamson) methods and report pertinent physical data below.

Dodecyl Ethyl Ether (5): bp 97° (1.25 mm, Kugelrohr); NMR (CCl_4) δ 0.89 (t, *J* = 6 Hz, 3 H, $-CH_3$), 1.15 (t, *J* = 7.5 Hz, 3 H, $-CH_3$), 1.29 (broad s, 20 H, $-CH_2-$), 3.35 (q, *J* = 6 Hz, 2 H, $-CH_2O-$), 3.39 (q, *J* = 7.5 Hz, 2 H, $-OCH_2-$).

Anal. Calcd for $C_{14}H_{30}O$: C, 78.43; H, 14.10. Found: C, 78.15; H, 14.12.

Cyclodocecyl Ethyl Ether (8):[16] bp 95° (0.65 mm, Kugelrohr) [lit.[15] 117–119° (3 mm)]; NMR (CCl_4) δ 1.12 (t, *J* = 7 Hz, 3 H, $-CH_3$), 1.36 (broad s, 22 H, $-CH_2-$), 3.32 (m, unresolved, 1 H, $CHO-$), 3.36 (q, *J* = 7 Hz, 2 H, $-OCH_2-$).

Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.40; H, 13.48.

1-Adamantyl Neopentyl Ether (18b).[16] According to the general method of Pettit,[17] a solution of 0.375 g (0.01 mol) of $NaBH_4$ in 25 ml of anhydrous diglyme was placed in a three-neck 250-ml flask and cooled to 0° (ice bath) under a nitrogen atmosphere. To this was added over 20 min a solution of 1.19 g (0.005 mol) of 1-adamantyl pivalate and 21.25 g (0.15 mol) of freshly distilled boron trifluoride etherate in 50 ml of anhydrous THF. Stirring was continued for 1 hr at 0° and then an additional 1 hr at reflux whereupon the reaction mixture was cooled and quenched by the careful successive addition of 2 *N* HCl (25 ml) and water (50 ml). The layers were separated, the aqueous layer extracted with ether (3 × 50 ml), and the combined organic layers dried ($MgSO_4$) and concentrated. The residue (containing diglyme) was dissolved in 50 ml of petroleum ether and washed with water (3 × 25 ml), dried ($MgSO_4$), and again concentrated to give 0.843 g of crude product. GLC and NMR analysis showed the product to contain the desired ether, starting ester, and 1-adamantanol in the approximate ratio of 1:2:1. Chromatography (100 g of silica gel, benzene elution) afforded 0.212 g of ether (19%), homogeneous by GLC and TLC. The analytical sample was prepared by Kugelrohr distillation (85°, bath, 0.05 mmHg): NMR (CCl_4) δ 0.84 [s, 9 H, $-C(CH_3)_3$], 1.50–1.75 (broad, 12 H, $-CH_2-$), 2.00–2.50 (broad, 3 H, $-CH-$), 2.95 (s, 2 H, $-OCH_2-$).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.08; H, 11.94.

When this reaction was performed using $LiAlH_4$–boron trifluoride etherate,[17] the only observable product was 1-adamantanol plus a considerable amount of unreacted ester.

General Photolysis Procedure. The following experiment for the reaction of 1-adamantyl acetate with $HSiCl_3$ is typical. Other experiments were performed similarly with the molar ratios of $HSiCl_3$ and THF to starting ester being as indicated in Table I or ref 4.

A solution of 0.500 g (2.58 mmol) of 1-adamantyl acetate, 1.39 g (1.04 ml, 10.3 mmol) of $HSiCl_3$, 0.192 g (0.244 ml, 1.29 mmol) of di-*tert*-butyl peroxide, and 4.4 g (5.0 ml, 61.5 mmol) of anhydrous THF (doubly distilled from $LiAlH_4$) was placed in a Pyrex tube (ca. 14 mm i.d.) and degassed with three to eight freeze–pump–thaw cycles (0.01 mm). After sealing, the tube was irradiated for 5 hr at a distance of 12 mm from an Hanovia 450-W medium-pressure ultraviolet lamp. The resulting clear solution was diluted with 50 ml of CH_2Cl_2 and then the excess $HSiCl_3$ was destroyed by the careful addition (0°, stirring) of 10 ml of water and 2.5 ml of 10% NaOH solution. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 ml) and the combined organic layers washed with brine (50 ml) and dried ($MgSO_4$). Gas chromatographic (150°) analysis (standardized) of this dilute solution showed two peaks at 79 and 184 sec, respectively corresponding to adamantane (82%) and adamantyl ethyl ether (18%). Concentration of the organic material afforded 350 mg of crude product, which by NMR analysis was of the composition indicated above.

GLC data for the compounds from other experiments, which were conducted in a similar fashion, are as given: 1-dodecyl acetate (175°, 264 sec), 1-dodecyl ethyl ether (165 sec), dodecane (66 sec); cyclododecyl acetate (175°, 220 sec), cyclododecyl ethyl ether (171 sec), cyclododecane (97 sec); 1-methylcyclohexyl acetate (100°, 168 sec), 1-methylcyclohexane (74 sec); 5-butyl-5-nonyl acetate (150°, 209 sec), 5-butylnonane (88 sec); 1-adamantyl pivalate (180°, 261 sec), 1-adamantyl neopentyl ether (204 sec), adamantane (47 sec).

Registry No.—**4,** 112-66-3; **5,** 3482-63-1; **7,** 6221-92-7; **8,** 2986-53-0; **10,** 16737-30-7; **13,** 56830-72-9; **15,** 17312-63-9; trichlorosilane, 10025-78-2; 5-*n*-butyl-5-nonanol, 597-93-3; 1-adamantanol, 768-95-6; dodecane, 112-40-3; cyclododecane, 294-62-2; 1-methylcyclohexane, 108-87-2.

References and Notes

(1) Acknowledgment is made to the North Carolina Board of Science and Technology, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this work.

(2) Y. Nagata, T. Dohmaru, and J. Tsurugi, *J. Org. Chem.*, **38,** 795 (1973), and earlier papers in the series.

(3) S. W. Baldwin, R. J. Doll, and S. A. Haut, *J. Org. Chem.*, **39**, 2470 (1974).

(4) The reductions of acetates **4**, **7**, **10**, and **13** were performed using 8 equiv of $HSiCl_3$ (neat) and 0.5 equiv of di-*tert*-butyl peroxide as initiator and were irradiated as described in the Experimental Section.

(5) Another photochemical conversion of esters to alkanes has recently appeared: H. Deshayes, J.-P. Pete, C. Portella, and D. Scholler, *J. Chem. Soc., Chem. Commun.*, 439 (1975).

(6) I. Tabushi, Y. Aoyama, S. Kojo, J. Hamuro, and Z. Yoshida, *J. Am. Chem. Soc.*, **94,** 1177 (1972), and references cited therein.

(7) In addition the reduction of pivalate esters by the $HSiCl_3$ method provides a convenient route to otherwise difficulty prepared neopentyl alkyl ethers when performed at high $HSiCl_3$ concentrations.

(8) R. E. Ireland, D. C. Muchmore, and V. Hengartner, *J. Am. Chem. Soc.*, **94,** 5098 (1972).

(9) F. Krafft, *Chem. Ber.*, **16,** 1714 (1883).

(10) M. Kobelt, P. Barman, V. Prelog, and L. Ruzicka, *Helv. Chim. Acta*, **32,** 256 (1949).

(11) T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76,** 4124 (1954).

(12) W. H. W. Lunn, *J. Chem. Soc. C*, 2124 (1970).

(13) (a) J. MacMillan and R. J. Pryce, *J. Chem. Soc. B*, 337 (1970); (b) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92,** 7300 (1970).

(14) (a) G. Akazome, S. Sakai, and K. Murai, *Kogyo Kagaku Zasshi*, **63,** 592 (1960); *Chem. Abstr.*, **56,** 4924*g* (1962); (b) H. A. Schneiderman, A. Krishnakumaran, V. G. Kulkarni, and L. Friedman, *J. Insect Physiol.*, **11,** 1641 (1965).

(15) Haarmann and Reimer, Netherlands Patent Appl. 6,411,715 (1965); *Chem. Abstr.*, **63,** 8228*d* (1966).

(16) We thank Ms. S. C. Lottich for performing this preparation.

(17) G. R. Pettit and D. M. Piatak, *J. Org. Chem.*, **27,** 2127 (1962).

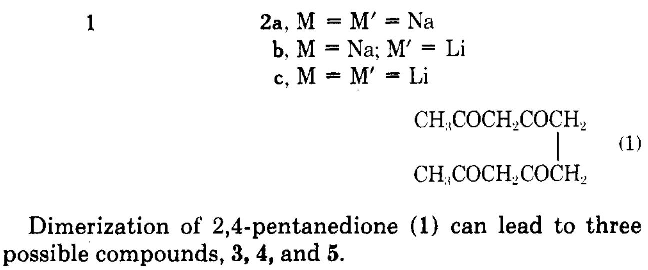
Cuprous Chloride Catalyzed Dimerizations of β-Dicarbonyl Compounds via Their Dicarbanions

K. Gerald Hampton* and J. Joseph Christie

Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39401

Received July 8, 1975

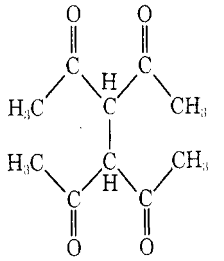
The use of dicarbanions from β-dicarbonyl compounds like β-diketones and β-keto esters in γ-alkylations and γ-acylations has become a common procedure.[1,2] The dicarbanions **2a–c** were investigated in an effort to dimerize them into bisacetylacetones (eq 1).



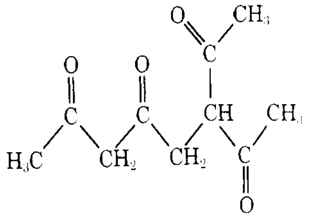
$$\underset{\mathbf{1}}{CH_3COCH_2COCH_3} \longrightarrow \underset{\substack{\mathbf{2a},\ M = M' = Na \\ \mathbf{b},\ M = Na;\ M' = Li \\ \mathbf{c},\ M = M' = Li}}{CH_3COCHMCOCH_2M'} \longrightarrow \begin{array}{c} CH_3COCH_2COCH_2 \\ | \\ CH_3COCH_2COCH_2 \end{array} \quad (1)$$

Dimerization of 2,4-pentanedione (**1**) can lead to three possible compounds, **3, 4,** and **5.**

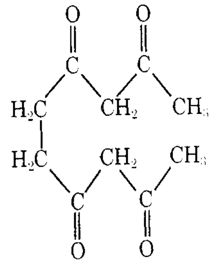
The 3,3′ dimer or symmetrical tetraacetylethane **3** has been made by the self-condensation of the monoanion of 2,4-pentanedione in an ether solution of iodine.[3,4] The unsymmetrical 1,3′ dimer or 3-acetyloctane-2,5,7-trione, **4,** was obtained by Gritter and Patmore from copper acetylacetonate by a free-radical process.[5a,b] As for the 1,1′ dimer or decane-2,4,7,9-tetrone **5**, there is no record of such a compound in the chemical literature.



3



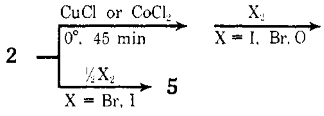
4



5

Table I provides a representative account of the attempts to obtain **5** by Scheme I. When cuprous chloride or cobaltous chloride was used as a catalyst in the reaction between **2b** and iodine, the reaction proceeded very efficiently (entries 1–5). That the tan solid, mp 62–63°, obtained from the reactions has structure **5** is supported by several pieces of data. For example, this compound is enolic to $FeCl_3$ solution (brown-red color), and its ir and uv spectra are similar to those of **1**. The ^1H NMR spectrum of this solid has four proton centers, namely, at τ 8.02 (singlet) and 7.84 (singlet), $-C(=O)CH_3$ (6 H), 7.45 (singlet), $C(=O)CH_2CH_2C(=O)$ (4 H), 4.64 (singlet), $C(=O)CH=C(=O)$ (2 H), and a broad peak at −4.86 due to enolic protons (2 H). The mass spectrum (70 eV) of this material showed *m/e* 198 (M^+ ion). Elemental analysis is consistent with the formula $C_{10}H_{14}O_4$ (see Experimental Section).

Scheme I



Dilithioacetylacetone (**2c**, entry 6) did not undergo oxidative dimerization under the same conditions. Since **2c** was generated in liquid ammonia, which was then replaced by THF, traces of ammonia could have interfered rather than **2c** being inherently unreactive. The use of pyridine to solublize the cuprous chloride reduced the reaction period markedly, in addition to rendering the work-up procedure less tedious (entry 5).

The importance of the cuprous chloride or cobaltous chloride catalyst in these reactions as well as the conditions of the reactions is illustrated by entries 6–15. In these cases where the catalyst was not used, the conditions were changed, or other reagents that have been successful in coupling monoanions[3,4,6–9] were used with the dianions, no coupled product **5** could be isolated.

This procedure can be applied to other β-dicarbonyl compounds. As Scheme II illustrates, the method was successfully applied to the syntheses of 1,1′ dimers of benzo-