sulfoxide (2×10^{-2} M) under argon, and a two-fold excess of a $K^+CH_2SOCH_3$ standard solution was added to generate the highly colored carbanion.[9] The solution was quenched by being poured into a separatory funnel containing 1 mL each of saturated aqueous NH_4Cl and ether. The ether layer was separated immediately and analyzed by GC using a 6 ft $\times$ $^1/_8$ in. GC column of 3% OV-101 on Supelcoport. The product ratios are reported in Table II.

Methyl *cis*-9,10-Dihydro-9,10-dimethyl-9-phenanthrenecarboxylate (8t) and Methyl *trans*-9,10-Dihydro-9,10-dimethyl-9-phenanthrenecarboxylate (8c). A 29-mg sample of **2c,t** was dissolved in 4 mL of dimethyl sulfoxide (2×10^{-1} M) under argon, and a twofold excess of a standard solution of $K^+CH_2SOCH_3$ was added.[9] The reaction was quenched by addition of 0.3 mL of CH_3I. After 15 min, 10 mL of saturated aqueous NH_4Cl was added and the mixture extracted with ether. The ether layer was washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated to yield 17 mg (56%) of a colorless oil, which contained 74% **8t** and 26% **8c** by NMR: NMR ($CDCl_3$, mixture of isomers) for **8c** δ 1.10 (d, J = 7.0 Hz, CH_3), 1.23 (s, CH_3), 3.40 (q, J = 7.0 Hz), 3.67 (s, OCH_3), 7.1-7.9 (m); for **8t** δ 1.10 (d, J = 7.0 Hz, CH_3), 1.40 (s, CH_3), 3.00 (q, J = 7.0 Hz), 3.67 (s, OCH_3), 7.1-7.9 (m); GC/MS (70 eV), m/e (relative intensity) 266 (M^+, 22.2), 207 (100), 192 (56).

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Registry No. 2c, 80360-58-3; **2t**, 80360-59-4; **3c**, 80360-60-7; **3t**, 80360-61-8; **8c**, 80360-62-9; **8t**, 80360-63-0; 10-methyl-9-phenanthrenecarboxylic acid, 65698-59-1; 9-bromo-10-methylphenanthrene, 52979-71-2; methyl 9-methyl-10-phenanthrenecarboxylate, 55042-80-3; 10-methyl-9-phenanthrenecarbonitrile, 17024-15-6.

Simple Syntheses of Diethyl Oxomalonate and Alkyl Glyoxylates

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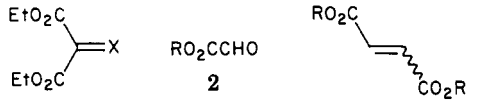
Diethyl oxomalonate (1) and ethyl, methyl, and benzyl glyoxylates (**2a,b,c**) are useful reagents in organic chemistry. The α-keto ester functionality of all of these compounds is quite reactive and participates in electrocyclic processes (Diels-Alder reaction,[2] ene reaction[3]) and various condensations (aldol,[4] carbinolamine formation,[5] Friedel-Crafts reaction,[6] and Wittig reaction[2e]). Recently several new methods have been developed for the preparation of 1[7] and **2ab**[8] which have significantly improved older methods.[9] We herein report a simple method for the preparation of these compounds on a reasonable scale from very readily available precursors. The technique involves essentially neutral conditions and thus should be useful for the preparation of acid- and base-sensitive oxo esters.

Condensation of diethyl malonate (3) with acetaldehyde and acetic anhydride gives a good yield (68-86%) of diethyl ethylidenemalonate (4).[10] Ozonolysis of 4 at -78 °C in dichloromethane followed by destruction of the ozonide with triphenylphosphine and distillation from phosphorus pentoxide produces diethyl oxomalonate 1 in 62% yield. The use of dimethyl sulfide as the reducing agent for the ozonide leads to the formation of dimethyl sulfoxide, which complicates somewhat the purification of 1. The overall yield of 1 from diethyl malonate 3 is approximately 45-50%, which compares well with most other methods.[7]



1, X = O
3, X = H_2
4, X = $CHCH_3$

RO_2CCHO
2

(*Z*)-5
(*E*)-6

a, R = Et; b, R = Me; c, R = CH_2Ph

By a similar procedure, the glyoxylates **2abc** can also be prepared in good yield.[11] Ozonolysis of diethyl and dimethyl maleate (**5a** and **5b**) at -78 °C in dichloromethane followed by reduction of the ozonide with dimethyl sulfide and distillation produces the glyoxylates **2a** and **2b** in yields of 65% and 53%, respectively. The corresponding fumarates **6a** and **6b** can also be used with little or no reduction in yield. An approximately 1:1 mixture of dibenzyl maleate (**5c**) and dibenzyl fumarate (**6c**), prepared from maleic acid and benzyl alcohol, could be converted into benzyl glyoxylate (**2c**) in 36% yield. Presumably this method could be extended to the preparation of any saturated alkyl glyoxylate. No attempts have yet been made to optimize any of the yields given. While perhaps not as convenient as other precedures for the production of large quantities of 1 and 2, this method permits the easy preparation of these materials on a 10-100-mmol scale.

Experimental Section

Diethyl Oxomalonate (1). Diethyl ethylidenemalonate (4; 10 g, 0.0537 mol), prepared from diethyl malonate (3) and acetaldehyde,[10] was dissolved in 100 mL of dried dichloromethane and ozonized at -78 °C for 2 h. After ozonization was complete and the solution had been purged of the blue color with an oxygen flow, triphenylphosphine (14.1 g, 0.0537 mol) in 50 mL of dichloromethane was added to destroy the ozonide. After evapo-

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ration of the solvent in vacuo, the residue was distilled [bp 63–65 °C (3–4 mm)] to give slightly impure diethyl oxomalonate (1). Redistillation of this material in the presence of a small amount of P_2O_5 afforded 5.8 g (62%) of pure diethyl oxomalonate (1), bp 80–3 °C (4 mm) [lit.[7a] bp 106–108 °C (17 mm); lit.[7b] bp 92–96 °C (11 mm)].

Ethyl Glyoxylate (2a). Diethyl maleate (**5a**; 20 g, 0.116 mol) in 200 mL of dichloromethane was ozonized for 2.25 h at −78 °C. After the blue color of ozone was purged for 15 min with an oxygen flow, the cold solution was added to excess dimethyl sulfide (8.0 g, 0.13 mol) via an addition funnel under nitrogen at 25 °C. The solution refluxed by itself and then was allowed to stir at 25 °C under nitrogen overnight. The solvents and excess dimethyl sulfide were distilled off at atmospheric pressure, and the residue was fractionally distilled through a 20-cm Vigreaux column to give 15.34 g (65%) of ethyl glyoxylate (**2a**) bp 49 °C (35 mm) [lit.[8] bp 40–45 °C (22 mm)]; phenylhydrazone mp 130–132 °C (lit.[12] mp 130.5 °C). When we began with 10 g of diethyl maleate and used 4 g of dimethyl sulfide with removal of solvent and excess dimethyl sulfide on a rotary evaporator, the yield varied from 57% to 65% (6.8–7.7 g). Diethyl fumarate (**6a**) (10 g, 0.058 mol) produced 7.0 g (59%) of ethyl glyoxylate (**2a**).

Methyl Glyoxylate (2b). Dimethyl maleate (**5b**; 10 g, 0.069 mol) in 100 mL of dichloromethane was ozonized and worked up under identical conditions, using 4.76 g of dimethyl sulfide with removal of solvent and excess dimethyl sulfide on a rotary evaporator. The yield of methyl glyoxylate (**2b**) varied from 5.5 to 6.5 g (48.8–53.5%), bp 45–50 °C (29 mm) [lit.[8] bp 55–65 °C (20 mm)]. Dimethyl fumarate (**6b**; 10 g, 0.069 mol) was ozonized and worked up under identical conditions to give 5.7 g (47%) of methyl glyoxylate (**2b**).

Benzyl Glyoxylate (2c). A mixture of dibenzyl maleate (**5c**) and dibenzyl fumarate (**6c**) (prepared from maleic acid and benzyl alcohol; 20 g, 0.0675 mol) in 200 mL of dichloromethane was ozonized at −78 °C for 2.25 h. Normal workup with excess dimethyl sulfide (4.66 g, 0.075 mol), rotary evaporation of solvent and excess dimethyl sulfide, and distillation produced 7.9 g (36%) of benzyl glyoxylate (**2c**), bp 130–132 °C (25 mm).

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Registry No. 1, 609-09-6; **2a**, 924-44-7; **2a** phenylhydrazone, 80447-71-8; **2b**, 922-68-9; **2c**, 52709-42-9; **4**, 1462-12-0; **5a**, 141-05-9; **5b**, 624-48-6; **5c**, 622-06-0; **6a**, 623-91-6; **6b**, 624-49-7; **6c**, 538-64-7.

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Conversion of Acyclic Amines to Amides by Chlorine Dioxide

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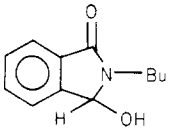
Chlorine dioxide (ClO_2) is well-known to react with aliphatic amines to give products of oxidative dealkylation or, in the presence of a β-hetero atom, oxidative fragmentation.[1] In most cases a single mechanism, involving rate-determining formation of an aminium cation radical, is operative.[1] Meta- and para-substituted benzyldimethylamines are unexceptional;[2] however, with benzyl-*tert*-butylamine and dibenzylamine, α-hydrogen abstraction competes with electron abstraction, and with benzylamine it is the predominant rate-determining process.[3] Kinetic studies had been carried out under pseudo-first-order conditions with a large excess of amine at controlled pHs (range 6–9), and product analyses were done following reaction of ClO_2 with excess or stoichiometric equivalents of the amine. Under these conditions only cleavage products were found.[1-3]

We here report that, for certain amines having an active α-methylene group, reaction with excess ClO_2 leads to a significant amount of amide formation in competition with oxidative dealkylation. An example is dibenzylamine (**1**, Table I). To determine the extent of competition between two different α-methylene groups in amide formation, we studied the reaction of ethyl *N*,*N*-dibenzylglycinate (**2**)[4] under different conditions of pH and solvent. Over the pH range 4–7 in the optimum medium, 1:1 acetonitrile–water, product composition did not greatly vary, and amides constituted 20–30% of the products. Of the two isomeric amides derived directly from **2**, **4** predominated by a factor of 3–5. Table I summarizes the results of a typical run. Below pH 4 (pH 2.5–3), **2** was consumed less readily, and the yields of amides were lower, with **4** still predominant.

While amide formation by ClO_2 has not been previously reported, the extent of competitive cleavage reactions under the above conditions precluded synthetic utility in these cases. However, treatment of **2** with ClO_2 generated in situ[5] from the reaction of chlorite and HOCl at pH 2.5–3 gave amides **4** and **5** in a combined yield of 80%, with **5** predominating (Scheme I). These amides were readily separated by preparative TLC. At higher pH the in situ reaction was slower, and the yields of amides were lower. It should be emphasized that HOCl alone at pH 2.8 gave only cleavage products, while chlorite alone was inert.

Previously reported conversions of amine α-methylene groups to carbonyls have been generally limited to cyclic amines. For example, ruthenium tetraoxide was useful for the oxidation of N-substituted pyrrolidines to amides, and in some cases further to imides.[6] *N*-Arylpyrrolidones were obtained on ozonation of *N*-arylpyrrolidines,[7] and air oxidation of *N*-butylisoindoline gave predominantly *N*-butylphthalimidine and *N*-butylphthalimide.[8] Some years prior to initiation of this work, *N*-butyl-3-hydroxyphthalimidine (**6**) had been observed in our laboratory as



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the major product of ClO_2 treatment of *N*-butylisoindoline.[9] We now anticipate that ClO_2 may be of general utility in the oxidation of active α-methylene groups in acyclic amines as well.

In addition to this practical aspect, the observed predominance of amide **4** over **5** except in the in situ reaction at low pH may be of some mechanistic significance. In the

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