vacuo, dissolved in H_2O, and made alkaline with NaOH solution. The product was extracted into EtOAc, the extract was dried over $MgSO_4$ and solvent was evaporated. The HCl salts were formed in ether with HCl gas dissolved in ether to give **9a** in 48% yield, mp 286–287 °C (EtOH), and **9b** in 90% yield, mp >290 °C dec (CH_3CN/CH_3OH). Compound **9a**: IR (KBr) 4.32, 5.92, 6.80, 6.92, 7.10, 7.78, 13.60 μm; NMR (D_2O) δ 2.5–5.0 (7 H, m), 3.17 (3 H, s), 7.70 (4 H, s); mass spectrum, *m/e* 202 (100), 159, 130. Anal. Calcd for $C_{12}H_{14}N_2O$·HCl: C, 60.37; H, 6.33; N, 11.73. Found: C, 60.24; H, 6.43; N, 11.77. Compound **9b**: IR (KBr) 3.77, 5.88, 6.86, 7.17, 7.25, 7.37, 7.77, 13.15 μm; NMR (Me_2SO-d_6/D_2O, 1:1) δ 1.73 (3 H, s), 2.5–4.7 (6 H, m), 2.95 (3 H, s), 7.73 (4 H, m); mass spectrum, *m/e* 216, 173, 158, 104, 58 (100). Anal. Calcd for $C_{13}H_{16}N_2O$·HCl: C61.79; H, 6.81; N, 11.08. Found: C, 61.70; H, 6.72; N, 11.14.

Acknowledgment. I gratefully acknowledge the expert technical assistance of Mr. W. H. Kappeler and thank Dr. E. B. Whipple of Pfizer Central Research for obtaining and interpreting the 250-MHz NMR spectra.

Registry No. 4a, 16859-59-9; **4b**, 1828-76-8; **5**, 80262-84-6; **6a**, 80262-85-7; **6b**, 80262-86-8; **7a**, 79016-59-4; **7a**·HCl, 80262-87-9; **7b**, 80262-88-0; **7b**·HCl, 80262-89-1; **8**, 80262-90-4; **9a**·HCl, 80262-91-5; **9b**·HCl, 80262-92-6; aminoacetonitrile hydrochloride, 6011-14-9; (benzyloxycarbonyl)ethylenediamine hydrochloride, 18807-71-1.

Stereoselective Protonation of Stable Carbanions Derived from 9,10-Dihydrophenanthrenes

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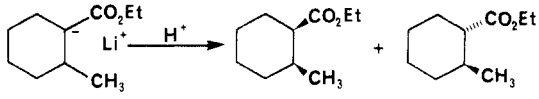
The stereochemistry of alkylation and protonation of stable carbanions remains a subject of current interest by virtue of its importance in organic synthesis.[1] Thermodynamic and kinetic control of protonation of cycloalkyl carbanions can yield products of different stereochemistry.[2,3] For example, Krapcho and Weimaster[2] report that protonation of **1** under equilibrating conditions favors the trans stereochemistry while kinetic control of protonation favors cis stereochemistry (eq 1). In cyclohexane ring



(1)

1	thermodynamic	24%	76%
	kinetic	72%	28%

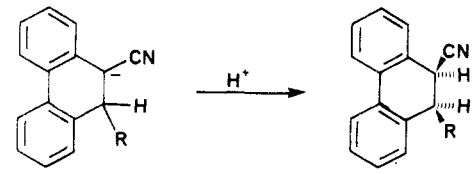
systems equatorial protonation is normally favored under kinetic control.[2] In contrast, kinetic control of protonation or methylation of carbanions derived from 9,10-dihydrophenanthrenes is reported to occur highly selectively from the axial direction.[4] Since the reactions of stable carbanions derived from 9,10-dihydrophenanthrenes have not previously been investigated, no comparisons of thermodynamic and kinetic product ratios have been reported for these systems. The 9,10-dihydrophenanthrenes represent a class of compounds with the unusual conformational property that substituents in the 9- and 10-positions preferentially occupy the pseudoaxial positions.[5,6] This preference leads to the prediction that thermodynamic and kinetic control of protonation should yield different stereoisomers.

Table I. Vicinal Coupling Constants for 9,10-Disubstituted 9,10-Dihydrophenanthrenes

compd	$J_{9,10}^{cis}$, Hz	$J_{9,10}^{trans}$, Hz
2	5.2	2.8
3	4.7	7.0
6[a]	4.5	
7[a]	4.9	
9,10-diphenyl-9,10-dihydrophenanthrene[b]	4.5	
9-acetoxy-10-chloro-9,10-dihydrophenanthrene[c]	4.0	3.2
10-methyl-9-phenyl-9,10-dihydrophenanthrene[d]	5.9	3.5

[a] From ref 7. [b] From ref 8a. [c] From ref 6d. [d] From ref 8b.

We report here our investigations of the carbanions derived from methyl 9,10-dihydro-10-methyl-9-phenthrenecarboxylate (**2c,t**) and 9,10-dihydro-10-methyl-9-phenanthrenecarbonitrile (**3c,t**). Our interest in the study of these carbanions was prompted by the observation that protonation of carbanions **4** and **5**, putative intermediates in the photochemical addition of 9-phenanthrenecarbonitrile and 2,3-dimethyl-2-butene in polar solvent, yields predominantly (>90%) a single isomer, **6** and **7** (eq 2).[7]



(2)

4 R = $CH_2C(CH_3)C(CH_3)_2$ 6

5 R = $C(CH_3)_2C(CH_3)_2OCH_3$ 7

Results

The dihydrophenanthrenes **2** and **3** were synthesized by Li/NH_3 reduction of the corresponding 9,10-disubstituted phenanthrenes (eq 3 and 4). The reduction yields a mixture of cis and trans isomers which are separable by chromatography. For both the ester and nitrile, the cis stereochemistry (**2c**, **3c**) predominates. Stereochemical assignments are made on the basis of comparison of the vicinal coupling constants for the benzylic hydrogens $J_{9,10}$, with literature values for 9,10-disubstituted 9,10-dihydrophenanthrenes (Table I).[6,8] The abnormally large trans coupling constant for **3t** reflects the unusual preference of the nitrile group for the pseudoequatorial position (see Discussion).

Base equilibration of **2c,t** and **3c,t** in 0.1 M sodium methoxide in refluxing methanol yields primarily the trans

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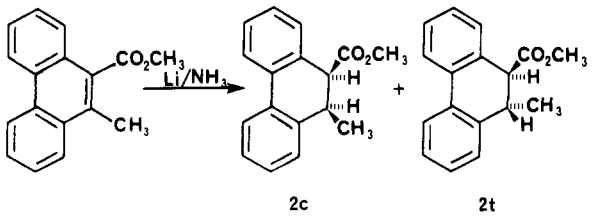
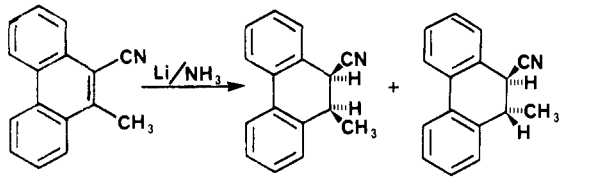


(3)

2c 2t

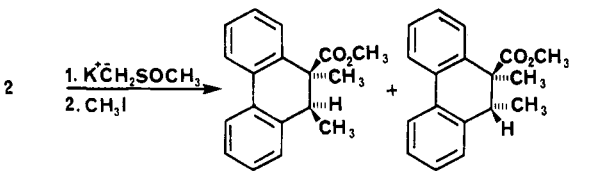


(4)

3c 3t

ester (**2t**) and cis nitrile (**3c**, Table II). The rate of isomerization of the cis and trans isomers is identical. However, **3c** and **3t** isomerize at a rate 30 times greater than that for **2c** and **2t**, consistent with the lower pK_a of **3c,t** vs. **2c,t** as measured in dimethyl sulfoxide solution (Table II).

The carbanions of **2c,t** and **3c,t** were generated quantitatively by the method of Bordwell and Hughes[9] using $K^+{}^-CH_2SOCH_3$ in dimethyl sulfoxide solution. When the carbanions are quenched with aqueous ammonium chloride, the predominant isomer is cis for both the ester (**2c**) and nitrile (**3c**, Table II). A somewhat higher cis/trans ratio (**2c**/**2t** ratio of 5.3) was obtained in their synthesis (eq 3). Quenching the carbanion of **2c** or **2t** with methyl iodide yields the alkylation product **8**, as a mixture of trans (74%) and cis (26%) isomers (eq 5, Table II). The ster-



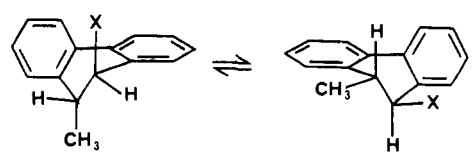
(5)

8t 8c

eochemistry was assigned by comparison of the chemical shifts of the benzylic hydrogen (H_{10}) in **8t** (3.00 ppm) and **8c** (3.40 ppm) with those for **2c** (3.27 ppm) and **2t** (3.45 ppm) and comparison of the 9-methyl chemical shift in **8t** (1.40 ppm) and **8c** (1.23 ppm) with benzylic hydrogen (H_9) chemical shifts for **2c** (3.81 ppm) and **2t** (3.58 ppm). Note that **2c** and **8t** have the 10-methyl group cis to carbomethoxy.

Discussion

Base equilibration of esters **2c** and **2t** favors the trans isomer while the cis isomer is favored with nitriles **3c** and **3t** (Table II). Analysis of the coupling constants for the benzylic hydrogens shows that the preferred conformation in both **2t** and **3t** is the one with both substituents occupying pseudoaxial positions (**9a**) as previously reported by



9a 9e

Harvey, Fu, and Rabideau[8a] for 9-monosubstituted 9,10-dihydrophenanthrenes (Table III). The pseudoaxial preference has been attributed to an unfavorable steric interaction between pseudoequatorial substituents and the peri hydrogens.[8a] The excellent agreement of the conformational populations calculated from the coupling constants for **2t** and **3t** (Table III) with those calculated by using the sum of the $\Delta G°$ values measured by Harvey et al.[8a] for monosubstituted dihydrophenanthrenes shows that the predominant factor in determining the conformational populations in **2t** and **3t** is the X–peri hydrogen interaction. The X–methyl gauche interaction is evidently of minor importance.

Table II. Product Ratios for Alkylation and Thermodynamic and Kinetic Protonation of Carbanions

X	CO_2CH_3	CN
pK_a[a]	22.7	21.7
cis/trans, thermodynamic[b]	0.19 ± 0.01	1.47 ± 0.02
cis/trans, kinetic[c]	3.8 ± 0.1	3.2 ± 0.1
trans/cis, methylation[d]	2.8 ± 0.2	

[a] From ref 10. [b] In refluxing 0.1 M $NaOCH_3$ in CH_3OH solution with 10^{-2} M carbon acid. [c] In dimethyl sulfoxide, 2×10^{-2} M carbon acid with 4×10^{-2} M $K^+{}^-CH_2SOCH_3$; quenched with aqueous NH_4Cl. [d] In dimethyl sulfoxide with 2×10^{-2} M carbon acid and 4×10^{-2} M $K^+{}^-CH_2SOCH_3$; quenched with excess CH_3I.

Table III. Conformational Populations and Free Energy of Isomerization for 2c,t and 3c,t

X	CO_2CH_3	CN
% pa-pa (J)[a]	94 (**2t**)	64 (**3t**)
% pa-pa ($\Sigma\Delta G°$)[b]	95 (**2t**)	72 (**3t**)
$\Delta G°_{trans-cis}$, kcal/mol	1.11	−0.25
$\Delta G°(X)$,[b] kcal/mol	1.11	−0.15
$\Delta G°(X) + \Delta G°(CH_3)$,[b] kcal/mol	1.85	0.59

[a] Calculated by using the relationship $J_{obsd} = xJ_{ee} + (1-x)J_{aa}$ from ref 8a. [b] Calculated from data in ref 8a; $\Delta G°(X) = \Delta G(X_{pa} - X_{pe})$.

The measured free-energy differences between the cis and trans isomers of **2** and **3** correlate well with the $\Delta G°$ values for the carbomethoxy and nitrile groups calculated from the NMR data of Harvey et al. (Table III).[8a] The cis–trans ratio for the ester **2** shows the expected preference for trans stereochemistry. The cis stereochemistry is favored for nitrile **3** in accord with Harvey's[8a] report that the nitrile group shows a slight preference for occupying a pseudoequatorial position in 9,10-dihydro-9-phenanthrenecarbonitrile. It is interesting to note that the $\Delta G°$ values of CN for 9,10-dihydrophenanthrenes (−0.15 kcal/mol) and cyclohexane (−0.15 to −0.25 kcal/mol)[11] are similar, but values for other substituents, including alkyl and carbomethoxy, are of opposite sign. The cis–trans ratios obtained from base equilibration of **2c,t** and **3c,t** (Tables II and III) are determined primarily by the X–peri hydrogen interaction. As in the conformational populations of the trans isomers, the X–methyl gauche interaction has a minor influence upon the equilibrium isomer ratios.

Kinetic control of methylation or protonation in dimethyl sulfoxide solution yields ca. 80% trans isomer for **2** and **3** (Table II). In the absence of ion pairing, the carbanions derived from **2** and **3** should assume a planar geometry in order to allow maximum overlap with both aromatic and carbonyl or nitrile π orbitals.[12] Planar

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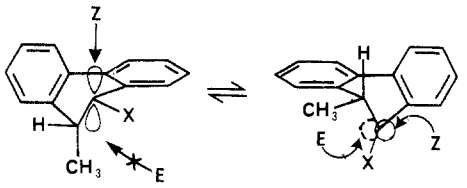
carbanions should exist as a mixture of two conformers (**10a,e**), the conformation with the methyl group pseudo-



10a 10e

axial (**10a**) being of lower energy. If **10a** were the only reactive conformer, stereoselective formation of **2c**, **3c**, and **8t** would be predicted ($Z > E$), with methylation being more selective than protonation,[2] a prediction contrary to the data in Table II. Reaction from **10e** should yield comparable amounts of cis and trans isomers upon methylation or protonation ($Z \approx E$). Assuming rapid conformational inversion on the reaction time scale and comparable reactivity for the two conformers, product mixtures which favor **2c**, **3c**, and **8t** to similar extents would be expected, as is observed.

From the results of base equilibration and kinetic protonation studies it is concluded that conformational inversion of 9,10-dihydrophenanthrenes and their carbanions is more rapid than either protonation or deprotonation. This conclusion is seemingly incompatible with Harvey's observation of 100% cis stereoselectivity for the protonation of 9,10-dialkyl-9,10-dihydrophenanthrenes and 100% trans stereoselectivity for the alkylation of 9-alkyl-9,10-dihydrophenanthrenes.[4b,8a] The greater stereoselectivity in these reactions may be due to the differences in behavior between the stable carbanions in this study vs. unstable alkyl carbanions. Harvey proposed that electrophilic attack occurs exclusively from the pseudoaxial direction on a pyramidal carbanion,[4b] whereas the more stable carbanions in this study are most likely planar.[12] Extensive ion pairing may also contribute to the high selectivity observed by Harvey as well as the greater selectivity of formation of **2c** vs. **2t** upon quenching of the lithium salt in liquid ammonia vs. the potassium salt in dimethyl sulfoxide. Carbanions derived from dihydrophenanthrenes may prove to be an attractive system for detailed investigations of ion-pairing effects.

Experimental Section

General Methods. A stock solution of $K^+{}^-CH_2SOCH_3$ in CH_3SOCH_3 was prepared as previously described.[13] Methanol was distilled from $Mg(OCH_3)_2$ under nitrogen prior to use. Melting points were measured on a Fischer-Johns melting point apparatus and are uncorrected. NMR spectra were obtained on Varian CFT-20 and EM360-A NMR spectrometers. Mass spectra were obtained on a Hewlett-Packard 5985 GC/MS system. Analyses were carried out by NMR or GC with a Hewlett-Packard 5750 gas chromatograph equipped with dual flame-ionization detectors and a 6 ft × $^1/_8$ in. GC column of 3% OV-101 on Supelcoport.

10-Methyl-9-phenanthrenecarboxylic Acid. Treatment of 9-bromo-10-methylphenanthrene[4b] (6.67 g) with 0.91 g of Mg in 150 mL of anhydrous ether for 5 h with heating resulted in formation of the Grignard reagent.[14] The solution was bubbled with CO_2 gas for 4 h. Workup in the usual way yields 4.75 g (82%) of the carboxylic acid which was recrystallized from 5% acetic acid in toluene: mp 203–205 °C; IR (KBr) 3450, 1692, 1258, 755, 721 cm^{-1}.

Methyl 9-Methyl-10-phenanthrenecarboxylate. Esterification of 10-methyl-9-phenanthrenecarboxylic acid was accomplished by stirring 3.65 g of the acid with 9.0 mL of trifluoroacetic anhydride in 75 mL dry benzene with heating for 15 min.[15] Methanol (9.0 mL) was added and heating continued for an additional 10 min. The solvent was removed at reduced pressure, and the residue was taken up in ether and washed with 20% NaOH. The ether was dried ($MgSO_4$) and removed under reduced pressure to yield a light yellow oil, 2.38 g (73%). Attempted crystallization was unsuccessful: NMR ($CDCl_3$) δ 2.60 (s, 3 H), 4.00 (s, 3 H), 7.37–7.67, 7.87–8.03, 8.43–8.60 (m, 8 H); IR (thin film) 1730, 1449, 1432, 1245, 1210, 756, 723 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.85; H, 5.75.

Methyl *cis*-9,10-Dihydro-10-methyl-9-phenanthrenecarboxylate (2c). The aromatic ester from above (0.55 g) in 80 mL anhydrous ether was added to 160 mL distilled ammonia.[8a] Lithium wire (90 mg) was added and the reaction mixture stirred for 30 min, at which time 40 g of NH_4Cl, 100 mL of H_2O, and 50 mL of ether were added sequentially. The ether layer was separated, dried ($MgSO_4$), and evaporated to yield 0.55 g (99%) of a colorless oil which contained 84% **2c** and 16% **2t** and was otherwise free from impurities by GC and NMR. A pure sample of **2c** was obtained from preparative thick-layer chromatography by elution with 2% ethyl acetate in hexane: NMR ($CDCl_3$) δ 1.37 (d, J = 7.0 Hz, 3 H), 3.27 (m, J = 7.0, 5.2 Hz, 1 H), 3.53 (s, 3 H), 3.81 (d, J = 5.2 Hz, 1 H), 7.12–7.32 (m, 6 H), 7.52–7.77 (m, 2 H).

Methyl *trans*-9,10-Dihydro-10-methyl-9-phenanthrenecarboxylate (2t). A 62-mg sample of **2c** in a 15-mL solution of 0.1 M $NaOCH_3$ in methanol was refluxed for 1 h. Ether was added and the mixture washed with 10% HCl. The ether layer was separated, dried ($MgSO_4$), and evaporated to yield 62 mg (100%) of a colorless oil which contained 85% **2t** and 15% **2c**. A pure sample of **2t** was obtained by chromatography on a preparative thick-layer plate by elution with 2% ethyl acetate in hexane: NMR ($CDCl_3$) δ 1.12 (d, J = 7.0 Hz, 3 H); 3.45 (s, 3 H), 3.45 (m, 1 H), 3.58 (d, J = 2.8 Hz, 1 H), 7.12–7.35 (m, 6 H), 7.55–7.75 (m, 2 H).

10-Methyl-9-phenanthrenecarbonitrile. A mixture of 9-bromo-10-methylphenanthrene[4b] (4.99 g) and CuCN (17.6 g) was refluxed in dimethyl sulfoxide (275 mL) for 2.2 h.[16] The mixture was allowed to cool before being poured into 1000 mL of 50:50 NH_4OH/H_2O. The white precipitate was filtered and chromatographed on silica by elution with toluene to yield 2.67 g (67%) of the nitrile, which was recrystallized from ethanol: mp 178–179 °C; NMR ($CDCl_3$) δ 2.90 (s, 3 H), 7.45–7.70 (m, 4 H), 7.90–8.20 (m, 2 H), 8.40–8.65 (m, 2 H). Anal. Calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.83; H, 5.38; N, 6.16.

***cis*-9,10-Dihydro-10-methyl-9-phenanthrenecarbonitrile (3c) and *trans*-9,10-Dihydro-10-methyl-9-phenanthrenecarbonitrile (3t).** A 0.50-g sample of the aromatic nitrile from above in 25 mL of dry THF was added to 50 mL of distilled ammonia.[8a] Lithium wire (60 mg) was added to the refluxing ammonia solution. After 45 min the reaction was quenched with 5 g of NH_4Cl. Ether and water were added (50 mL each), the ether layer was separated, and the aqueous layer was washed with ether. The ether layers were combined, dried ($MgSO_4$), and evaporated to yield 0.42 g (82%) of a crude mixture of **3c** and **3t**. Chromatography on a silica gel column (4.8 cm × 12 cm) eluted with 2% ethyl acetate in hexane affords good separation. The first isomer to elute was **3t** (0.18 g, 34%) followed by **3c** (0.12 g, 24%), both colorless oils: NMR ($CDCl_3$) for **3c** δ 1.26 (d, J = 7.0 Hz, 3 H), 3.30 (m, 1 H), 4.20 (d, J = 4.7 Hz, 1 H), 7.24–8.23 (m, 8 H); for **3t** δ 1.37 (d, J = 6.9 Hz, 3 H), 3.29 (quintet, J = 7 Hz, 1 H), 3.77 (d, J = 7.0 Hz, 1 H), 7.24–7.51 (m, 6 H), 7.70–7.86 (m, 2 H).

Kinetics of Isomerization of 2c,t and 3c,t. To a 0.5 mL solution of 0.2 M carbon acid (>97% one isomer) in methanol was added 25 μL of a standard solution of 0.23 M $NaOCH_3$. The reaction was followed by monitoring the methyl doublets in the NMR spectra. Pseudo-first-order kinetics were observed at low conversion. The relative rate constants ($k_{3c,t}/k_{2c,t}$ = 30, $k_{2c} = k_{2t}$, and $k_{3c} = k_{3t}$; Table II) are obtained from standard treatment of the data at low conversion.

Kinetic Protonation Product Ratios for 2c,t and 3c,t. A 30-mg sample of the carbon acid was dissolved in 5 mL of dimethyl

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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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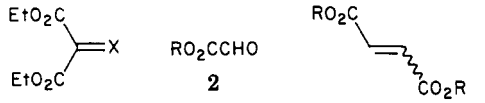
Diethyl oxomalonate (1) and ethyl, methyl, and benzyl glyoxylates (**2a,b,c**) are useful reagents in organic chemistry. The α-keto ester functionality of all of these compounds is quite reactive and participates in electrocyclic processes (Diels-Alder reaction,[2] ene reaction[3]) and various condensations (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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