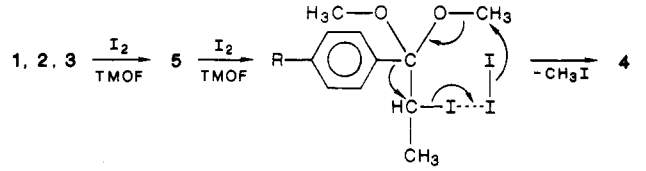
$ICl > I_2$ and the reagent ICl_3 is especially useful for the rearrangement of **1** (R = Br, F), (3) treatment of **1** (R = H, Br, F), or **2** (R = H) with ICl_3 afforded **4** with the formation of **7**, and (**4**) the reactivity of the substrate is in the order of R = CH_3O > Bu^i > H > Br > F as expected. The formation of **6** (R = H) and **6** (R = Br) from the corresponding **1** with 2 equiv of I_2 and the formation of **5** (R = Bu^i) from **1** (R = Bu^i) with 1.2 equiv of I_2 suggest that **4** was formed via these compounds. In fact, we confirmed separately that the ketal **5** (R = Bu^i) is converted to **4** (R = Bu^i) quantitatively by treatment with 1 equiv of I_2 in TMOF at 23 °C for 24 h, while **6** (R = Bu^i) scarcely afforded **4** (R = Bu^i) under similar conditions. Thus the ester **4** seems to be formed via **5** as shown below, methyl iodide being trapped and identified spectroscopically.



Experimental Section

^1H NMR spectra were recorded with a JEOL FX-40 Q (90 MHz) instrument in $CDCl_3$ with Me_4Si as an internal standard. GLC analysis was carried out with a Shimadzu GC-7AS apparatus using 10% DC-200 on a Chromosorb W (AW-DMCS) column (3 mm × 3 m).

Propiophenones **1** (R = H, CH_3O, Br, F), solvent, and inorganic materials were commercial products of the purest standard. Compounds **1** (R = Bu^i)[4] and **2**[9] were prepared by the reported methods. The yield and boiling point of **2** prepared from **1** are as follows: **2** (R = H) 71%, bp 75–77 °C/10 Torr; **2** (R = Bu^i) 94%, bp 92–97 °C/1 Torr; **2** (R = CH_3O) 68%, bp 90–93 °C/1 Torr; **2** (R = Br) 98%, bp 93–96 °C/2 Torr.

Preparation of 3 (R = Bu^i) and 3 (R = CH_3O). A mixture of **2** (R = Bu^i) (11.8 g, 50 mmol) and methanesulfonic acid (0.1 g, 1 mmol) was heated at 100–105 °C for 2 h. The resulting mixture was distilled in vacuo to give an isomeric mixture of (*E*)- and (*Z*)-1-(4-isobutylphenyl)-1-methoxy-1-propene (**3**, R = Bu^i) as a colorless oil (8.1 g, 79.3%), *E*/*Z* = 27/73, by ^1H NMR:[10] bp 92–96.5 °C/1 Torr; *Z* isomer δ 0.93 (6 H, d), 1.81 (3 H, d), 1.84 (1 H, m), 2.49 (2 H, d), 3.55 (3 H, s), 5.35 (1 H, q), 7.2–7.4 (4 H, m); *E* isomer δ 0.93 (6 H, d), 1.72 (3 H, d), 1.84 (1 H, m), 2.49 (2 H, d), 3.63 (3 H, s), 4.78 (1 H, q), 7.2–7.4 (4 H, m). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.35; H, 9.82. Similarly, an isomeric mixture of (*E*)- and (*Z*)-1-methoxy-1-(4-methoxyphenyl)-1-propene (**3**, R = CH_3O) was prepared in 88% yield at bp 90–93 °C/0.8 Torr, *E*/*Z* = 34/66, by ^1H NMR:[10] *Z* isomer δ 1.76 (3 H, d), 3.49 (3 H, s), 3.77 (3 H, s), 5.20 (1 H, q), 6.75–8.4 (4 H, m); *E* isomer δ 1.65 (3 H, d), 3.58 (3 H, s), 3.77 (3 H, s), 4.72 (1 H, q), 6.75–8.40 (4 H, m). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.97; H, 8.08.

Treatment of 1, 2, or 3 with Iodine Compound for the Preparation of 4, 5, and/or 6. A typical experimental procedure is as follows. Iodine (3.05 g, 12 mmol) was added to a solution of **1** (R = Bu^i) (1.90 g, 10 mmol) in TMOF (5.3 g) at 23 °C and the mixture was stirred for 24 h. Aqueous sodium thiosulfate (10%, 20 mL) was added and the resulting brown solution was extracted with $CHCl_3$ (2 × 30 mL). The extract was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. An oily residue was purified by column chromatography on SiO_2 [hexane–EtOAc (30:1–20:1) as eluent] to give methyl 2-(4-isobutylphenyl)propanoate (**4**, R = Bu^i)[5] (0.5 g, 23% yield) and 1,1-dimethoxy-1-(4-isobutylphenyl)-2-iodopropane (**5**, R = Bu^i) (2.50 g, 69% yield) together with a small amount of **6** (R = Bu^i) (2% yield) as a colorless oil, respectively. **5** (R = Bu^i): δ 0.90 (6 H, d), 1.73 (3 H, d), 1.6–2.1 (1 H, m), 2.48 (2 H, d), 3.19 (3 H, s), 3.32 (3 H, s), 4.58 (1 H, q), 7.0–7.5 (4 H, m). Anal. Calcd for $C_{15}H_{23}O_2I$: C, 49.73; H, 6.40. Found: C, 49.80; H, 6.33. Similar treatment of **1** (R = Bu^i) with I_2 (5.04 g, 20 mmol) afforded 2.13 g (98% isolated yield) of **4** (R = Bu^i). For identification of the produced methyl iodide, the reaction mixture was distilled directly under reduced pressure, the vapor was trapped by a cold trap at −78 °C, and the trapped liquid substance (a mixture of CH_3I and TMOF) was analyzed by ^1H NMR and GLC.

The treatment of **1** (R = Br) (2.13 g, 10 mmol) with iodine (5.04 g, 20 mmol) in TMOF (5.3 g) at 23 °C for 24 h afforded 1-(4-bromophenyl)-1,1-dimethoxy-2-iodopropane (**5**, R = Br) (47 mg, 0.12 mmol, 1.2% yield) and 4-bromophenyl 1-iodoethyl ketone (**6**, R = Br) (1.62 g, 4.8 mmol, 48% yield). **5** (R = Br) δ 1.70 (3 H, d), 3.16 (3 H, s), 3.27 (3 H, s), 4.52 (1 H, q), 7.3–7.5 (4 H, m). Anal. Calcd for $C_{11}H_{14}O_2BrI$: C, 34.31; H, 3.66. Found: C, 34.02; H, 3.53. **6** (R = Br): δ 2.03 (3 H, d), 5.38 (1 H, q), 7.4–7.9 (4 H, m). Anal. Calcd for C_9H_8OBrI: C, 31.89; H, 2.18. Found: C, 29.67; H, 2.20.

The compounds **5** and **6** were also prepared separately as follows and used as authentic samples for ^1H NMR and GLC. The ketal **2** (R = Bu^i) was treated with 1.2 equiv of I_2 in TMOF at 23 °C for 24 h and a normal workup procedure of the mixture afforded **5** (R = Bu^i) in 64% yield. A mixture of methanol (20 mL), 2 N sulfuric acid (1 mL), and **5** (R = Bu^i) (1.60 g, 4.4 mmol) was stirred at 60 °C for 1 h. After it had been cooled down, the solvent was evaporated under reduced pressure to leave an oily residue which was added to $CHCl_3$ (20 mL) and 2% aqueous sodiudm thiosulfate (10 mL). An organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to leave **6** (R = Bu^i) (1.36 g, 97% yield) as a light yellow oil: **6** (R = Bu^i) δ 0.90 (6 H, d), 1.88 (1 H, m), 2.04 (3 H, d), 2.52 (2 H, d), 5.45 (1 H, q), 7.18 (2 H, d), 7.89 (2 H, d). Anal. Calcd for $C_{13}H_{17}OI$: C, 49.38; H, 5.42. Found: C, 49.68; H, 5.64.

Acknowledgment. We thank Dr. Sakae Uemura of Kyoto University for useful discussion and reading the manuscript.

Registry No. **1** (R = H), 93-55-0; **1** (R = Bui), 59771-24-3; **1** (R = CH_3O), 121-97-1; **1** (R = Br), 10342-83-3; **1** (R = F), 456-03-1; **2** (R = H), 25310-92-3; **2** (R = Bui), 66202-89-9; **2** (R = CH_3O), 115943-56-1; **2** (R = Br), 115943-57-2; (*E*)-**3** (R = Bui), 115943-58-3; (*Z*)-**3** (R = Bui), 115943-59-4; (*E*)-**3** (R = CH_3O), 58889-88-6; (*Z*)-**3** (R = CH_3O), 58889-89-7; **4** (R = H), 31508-44-8; **4** (R = Bui), 61566-34-5; **4** (R = CH_3O), 50415-73-1; **4** (R = Br), 83636-46-8; **4** (R = F), 50415-71-9; **5** (R = Bui), 87498-05-3; **5** (R = Br), 115943-60-7; **6** (R = H), 6084-15-7; **6** (R = Br), 115943-61-8; **6** (R = Bui), 115943-62-9; **7** (R = H), 6084-17-9; **7** (R = Br), 87010-95-5; **7** (R = F), 81112-09-6; I_2, 7553-56-2; ICl_3, 865-44-1; ICl, 7790-99-0.

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A Versatile and Convenient Multigram Synthesis of Methylidenemalonic Acid Diesters[1]

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Owing to their multifunctionality, dialkyl methylidenemalonates **3** are useful synthetic intermediates in Michael, Diels–Alder, cyclopropanation, and epoxidation reactions[2–4] and in polymer synthesis.[5]

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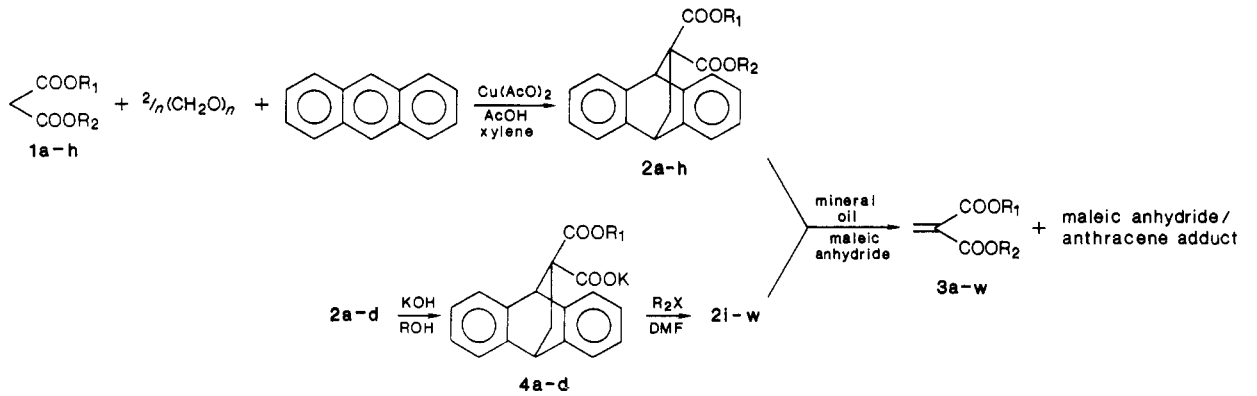
(2) Baum, K.; Guest, A. M. U. S. Patent 4 291 171, 1981.

(3) Raucher, S.; Lawrence, R. F. *Tetrahedron Lett.* **1983**, *24*, 2927.

0022-3263/88/1953-4859$01.50/0

Scheme I

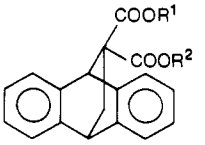


The major drawbacks in their synthesis are their high instability toward anionic polymerization and their purification. The preparation of these compounds is well documented in the patent and primary literature. Among the methods described, the most frequently used is the Knoevenagel condensation of paraformaldehyde with malonic acid esters 1 in the presence of various catalysts[6-12] (copper(II) and potassium acetate, secondary amines, potassium fluoride). The dialkyl methylidenemalonate dienophiles can be trapped in a Diels–Alder process by various substituted butadienes to avoid polymerization in the reaction mixture.[12] The olefinic product is recovered by pyrolysis of the distillation-purified adduct. 5-Carbalkoxy-2-norbornene can be used as starting material to afford the 5,5-dicarbalkoxy-2-norbornene, which undergoes a retro-Diels–Alder reaction under flash-pyrolysis conditions to yield the olefin.[13] Methods involving thermolytic elimination of an alcohol from dialkyl ethoxymethylmalonate[14] or dialkyl methoxymethylmalonate[15] are also reported in the literature.

The purpose of this paper is to describe a new easy multigram-scale synthesis of highly pure methylidenemalonic acid esters. This method has the advantage of offering ready access to a useful starting material at low cost and without requiring troublesome adjustments and purification.

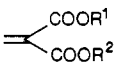
The only approach meeting our requirements was that of Ballesteros et al.,[8] which is a Knoevenagel condensation of paraformaldehyde and di-*tert*-butyl malonate in acetic acid in the presence of copper(II) and potassium acetate. This method, however, gives access only to the stable di-*tert*-butyl ester and does not work with simpler analogues due to the rapid anionic polymerization of the olefin in the reaction medium.

Table I.
9,10-Endoethano-9,10-dihydroanthracene-11-dicarboxylic Acid Diester 2



entry	R^1	R^2	yield, %	mp, °C
2a	CH_3	CH_3	53	161–162
2b	C_2H_5	C_2H_5	75	130–131
2c	n-C_3H_7	n-C_3H_7	72	104–106
2d	n-C_4H_9	n-C_4H_9	55	91–92
2e	i-C_3H_7	i-C_3H_7	72	136–137
2f	i-C_4H_9	i-C_4H_9	52	94–95
2g	n-C_5H_{11}	n-C_5H_{11}	45	75–79
2h	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	41	85–86
2i	CH_3	n-C_4H_9	51	80–82
2j	CH_3	n-C_6H_{13}	53	74–75
2k	C_2H_5	n-C_3H_7	82	107–108
2l	C_2H_5	n-C_4H_9	46	91–92
2m	C_2H_5	$CH_2CH{=}CH_2$	84	88–89
2n	C_2H_5	$CH_2C{\equiv}CH$	62	60–61
2o	C_2H_5	$C_2H_4OC_2H_5$	47	42–46
2p	c_2H_5	$CH_2CO_2C_2H_5$	42	76–77
2q	C_2H_5	$(CH_2)_3CO_2C_2H_5$	67	83–84
2r	n-C_3H_7	n-C_4H_9	47	91–92
2s	n-C_4H_9	n-C_5H_{11}	53	77–79
2t	CH_3	$CH_2C_6H_5$	42	109–112
2v	C_2H_5	CH_2OCH_3	75	106–107
2w	C_2H_5	$CH_2\overline{CHCH_2O}$	66	114–115

Table II. Methylidenemalonic Acid Diesters 3



entry	yield, %	bp, °C (Torr)	$M^+ + 1$
3a	54	80–82 (6)	145
3b	67	60–61 (0.25)	173
3c	81	77–81 (0.2)	201
3d	68	76–80 (0.01)	229
3e	64	40–42 (0.1)	201
3f	61	64–65 (0.02)	229
3g	46	99–101 (0.05)	
3h	48	67–68 (0.3)	
3i	75	65–68 (0.4)	
3j	77	80–85 (0.1)	
3k	63	52–55 (0.3)	
3l	71	62–63 (0.2)	
3m	48	52–55 (0.25)	185
3n	20	65–67 (0.3)	
3o	43	82–84 (0.2)	
3p	62	98–99 (0.1)	
3q	32	86–89 (0.06)	
3r	53	78–80 (0.1)	
3s	78	95–96 (0.1)	

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Similar to the approach used with alkyl cyanoacrylates,[16] heating of 1 with paraformaldehyde, copper(II) acetate, and anthracene in a mixture of xylene and acetic acid and further distillation of the acetic acid from the reaction mixture afforded **2a–h** (Table I), the Diels–Alder adducts of **3**, after in vacuo distillation of xylene (Scheme I). These adducts are crystalline materials easily purified by recrystallization, and which regenerate the olefinic material **3** in 50–81% yield by thermolysis at rather low temperature (200–250 °C) (Scheme I). The thermolytic step of the procedure can be best performed in the presence of maleic anhydride[17] to avoid further contamination of the olefin **3** by anthracene.

This approach proved to be efficient for the synthesis of both symmetric **3a–h** and nonsymmetric compounds **3i–s** (Table II) via hemihydrolysis of the symmetric adducts **2a–d** with potassium hydroxide in the corresponding alcohol, subsequent alkylation of the resulting monoacid potassium salt **4a–d** with an alkyl halide in DMF,[17] and subsequent retro-Diels–Alder thermolysis (Scheme I). Moreover, as exemplified by compounds **2m–q**, this approach allows extension toward functionalized **3m–q** by reacting **4b** with allyl bromide, propargyl chloride, chloroethyl ethyl ether, ethyl chloroacetate, and ethyl 4-bromobutyrate respectively.

Unfortunately, the general procedure described for the thermolytic step is not successful for compounds **2t–w**: instead of yielding pure olefinic material, the reaction yields a mixture of **3t–w** with several unidentified products.

However, it is noteworthy that the methylidenemalonic acid diesters synthesized by this method show improved stability compared to the material obtained by other methods,[14,15] probably due to their higher purity, and can be stored in the refrigerator for months without any special precaution.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured on a Reichert micro hot stage. Infrared data were obtained on a Perkin-Elmer Model 457 spectrophotometer using KBr disks. ^{13}C and ^{1}H NMR spectra were recorded in deuteriated chloroform on JEOL FX 60, Varian XL 200, and Bruker WM 250 spectrometers. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. GLC was performed on a Hewlett-Packard Model 5710A gas chromatograph (column; OV 17, 3%; detector; FID; carrier gas; nitrogen; temperature; 100 °C for 2 min, 10 °C/min up to 300 °C). Analytical HPLC was performed by using a Gilson Model 302 pump and a Pye Unicam LC-UV detector. Mass spectra were recorded on a MAT 44S spectrometer. Elemental analysis was performed by Continental Pharma Inc. (Mont Saint Guibert, Belgium). Satisfactory elemental analyses and IR and NMR spectra were obtained for all compounds.

11,11-Bis(methoxycarbonyl)-9,10-endoethano-9,10-dihydroanthracene (2a). This procedure is a general method for **2a–h**. A three-necked, 1-L, round-bottomed flask was fitted with a distilling apparatus, a thermometer, and a mechanical stirrer. The flask was charged with 132 g (1 mol) of dimethyl malonate (**1a**), 178 g (1 mol) of anthracene, 60 g (2 mol) of paraformaldehyde, 10 g (50 mmol) of copper(II) acetate monohydrate, 225 mL of acetic acid, and 225 mL of xylene. The reaction mixture was heated, with stirring, with a heating mantle at 100 °C for 2 h. The temperature was then increased in order to distill the acetic acid (atmospheric pressure). After essentially all acetic acid had been removed, the copper acetate precipitated and the reaction mixture was cooled to room temperature. The mixture was then filtered to separate the unreacted anthracene and the copper acetate. The filtrate was evaporated under reduced pressure, and the oily residue crystallized on standing. The crystalline material was recrystallized from ethanol to afford colorless crystals of **2a–h** contaminated by anthracene as shown by TLC (silica gel/benzene). Yields and melting points of compounds **2a–h** are presented in Table I. At this stage, the adduct **2** was suitable for the thermolytic step of the procedure. To determine the physicochemical data, we purified the recrystallized **2** on a silica gel column with hexane/2-propanol (100/2) as eluent. The purity of **2** was confirmed by HPLC using an analytical Zorbax CN^R column (Du Pont de Nemours, Dreieich, FDR) with hexane/2-propanol as eluent (100/2).

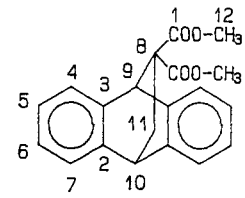

Figure 1.

Spectral data for 2a: ^{13}C NMR ($CDCl_3$, 62.9 MHz, assignments as shown in Figure 1) (C1) 170.28, (C2,3) 144.11, 139.91, (C4–7) 126.44, 125.74, 125.68, 123.27, (C8) 59.98, (C9,10) 49.81, 44.05, (C11) 36.52, (C12) 52.62; ^{1}H NMR ($CDCl_3$, 200 MHz, assignments as shown in Figure 1)(H_{4-7}) 7.3–7.07 (m, 8 H), (H_9) 4.98 (s, 1 H), (H_{10}) 4.33 (t, 1 H, ^3J = 2.69 Hz), (H_{12}) 3.58 (s, 6 H), (H_{11}) 2.49 (d, 2 H, ^3J = 2.69 Hz); IR (KBr disk) 3025 (w), 2960 (w), 2955 (w), 1730 (s), 1460 (w), 1450 (w), 1265 (m), 1240 (m), 1220 (m), 765 (m), 755 (m), 580 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.51; H, 5.62. Found: C, 74.47; H, 5.68.

Potassium (*R*,*S*)-11-(Ethoxycarbonyl)-9,10-endoethano-9,10-dihydroanthracene-11-carboxylate (4b). A three-necked, 2-L, round-bottomed flask was fitted with a reflux condenser attached to a drying tube (KOH), a mechanical stirrer, and a dropping funnel. The flask was charged with 100 g (286 mmol) of **2b** and 400 mL of anhydrous ethanol. The flask was heated at 65 °C with stirring until the starting material dissolved. A solution of 18.6 g (324 mmol) of potassium hydroxide in 400 mL of anhydrous ethanol was then added dropwise through the dropping funnel. During the course of the reaction, the potassium salt **4b** precipitated, and after 4 h, the reaction mixture was allowed to cool at room temperature. The crude precipitate was vacuum-filtered and extensively washed with diethyl ether to eliminate unreacted **2b**. The precipitate was vacuum-dried to yield 92 g (90%) of **4b** as a colorless powderlike material: IR (KBr disk) 3430 (br), 3080 (w), 3020 (w), 2975 (w), 1720 (s), 1695 (m), 1600 (s), 1460 (m), 1370 (s), 1360 (s), 1215 (s), 1180 (m), 1050 (m), 770 (m), 750 (m), 580 (m) cm^{-1}. This method is general for compounds **4a–d** except that ethanol is replaced by the alcohol corresponding to the alkyl chain to be hydrolyzed.

(*R*,*S*)-11-(Ethoxycarbonyl)-9,10-endoethano-9,10-dihydroanthracene-11-carboxylic Acid (5). HCl gas was bubbled for 15 in a suspension of 5 g (13.8 mmol) of potassium salt **4b** in 100 mL of dry diethyl ether cooled in an ice bath, after which time the only remaining precipitate was KCl. The solution was filtered and evaporated under reduced pressure to afford 4.47 g (13.8 mmol, 100%) of **5**: ^{13}C NMR ($CDCl_3$, 15.03 MHz) 175, 169.7, 144.2, 143.9, 139.5, 126.5, 125.7, 123.2, 61.9, 60.1, 49.9, 44.0, 36.3, 13.9; IR (KBr disk) 3080 (w), 3020 (w), 3000 (br), 2990 (w), 2980 (w), 1745 (s), 1710 (s), 1470 (m), 1460 (m), 1410 (w), 1370 (w), 1285 (s), 1270 (s), 1225 (s), 1190 (s), 1175 (w), 775 (m), 760 (m), 630 (m), 585 (m) cm^{-1}; mp 185–186 °C dec.

(*R*,*S*)-11-(Ethoxycarbonyl)-11-[(propyloxy)carbonyl]-9,10-endoethano-9,10-dihydroanthracene (2k). This procedure is the general method used throughout this work to synthesize nonsymmetric **2i–w**. A one-necked, round-bottomed flask fitted with a reflux condenser attached to a drying tube (KOH) was charged with 30 g (83.3 mmol) of **4b**, 11.07 g (90 mmol) of 1-bromopropane, and 250 mL of DMF redistilled from phosphorus pentoxide. The flask was heated with stirring in an oil bath at 80 °C for 2 h. After that time, all the insoluble **4b** had disappeared. The only remaining precipitate was KBr. The reaction mixture was poured while hot into a large excess of water, and

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the crude **2k** precipitated. The white precipitate was filtered and extensively washed with water. The dried material was recrystallized from ethanol and afforded 24.56 g (81%) of **2k**. For compounds **2m,n,v,w**, the reaction was carried out at room temperature overnight.

Spectral data for 2k: ^{13}C NMR ($CDCl_3$, 62.9 MHz) 170.28, 144.09, 139.94, 126.44, 125.71, 123.26, 67.25, 61.61, 59.99, 49.87, 44.07, 36.55, 21.88, 14.0, 10.29; IR (KBr disk) 3030 (w), 2970 (m), 2940 (w), 2880 (w), 1735 (s), 1470 (m), 1460 (m), 1450 (m), 1265 (s), 1230 (s), 1220 (s), 1180 (s), 755 (m), 625 (w), 585 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 76.07; H, 6.74.

Methylidenemalonic Acid Diesters 3. The following generalized procedure was utilized for synthesis of the methylidenemalonic acid diesters **3** reported in Table II. The glassware was washed with HCl and flame-dried under vacuum. A two-necked, 200-mL, round-bottomed flask fitted with a thermometer, a magnetic stirrer, and a distilling apparatus was charged under nitrogen with 50 mmol of **2**, 50 mmol of powdered maleic anhydride, and 80 mL of high-boiling mineral oil (bp >190 °C under 0.2 Torr). The mixture was heated with stirring at 225 °C for 45 min and allowed to cool to room temperature. While the mixture was cooling, the maleic anhydride/anthracene adduct precipitated as a white crystalline material. Distillation of the reaction mixture under reduced pressure (see Table II) yielded **3** contaminated with a small amount of maleic anhydride (<1%), as shown by GLC analysis. Redistilled **3** was free of maleic anhydride. This procedure did not prove effective for **3v,w**.

Spectral data for 3e: ^{13}C NMR ($CDDl_3$, 62.9 MHz) 163.73, 136.57, 132.41, 69.13, 21.70; ^1H NMR ($CDCl_3$, 200 MHz) 6.42 (s, 2 H), 5.14 (heptuplet, 1 H, ^3J = 6.3 Hz), 1.30 (d, 6 H, ^3J = 6.22 Hz); IR (neat film) 2980 (m), 2940 (w), 2880 (w), 1725 (s), 1630 (w), 1470 (w), 1455 (w), 1400 (w), 1390 (m), 1375 (m), 1315 (m), 1245 (s), 1145 (m), 1100 (s) cm^{-1}; GC-MS; $M^+ + 1 = 201$.

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Synthetic Applications of Organotellurium Compounds. 1. A Facile Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles

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With the development of organosulfur and organoselenium compounds, there has recently been remarkable interest in the synthetic application of organotellurium compounds.[1-3] However, little attention has been paid to telluronium ylides[6,7] in comparison with sulfonium and selenonium ylides.[4,5] The nonstabilized sulfonium and selenonium ylides can react with carbonyl compounds to yield epoxides in high yields,[4,8] but the stabilized sulfonium ylides are inert to carbonyl compounds. It is significant to study the reactivity of stabilized telluronium ylides, since telluronium ylides ought to be more active than their sulfur and selenium counterparts.

Osuka and his co-workers[6] have reported the synthesis of a stabilized telluronium ylide dibutyltelluronium carbethoxymethylide, but so far there are no reports concerning dialkyltelluronium cyanomethylide (**2a**) and phenacylide (**2b**). In this paper, we shall study the synthesis and the application of these two new telluronium ylides.

Cyanomethyldibutyltelluronium chloride (**1a**) and phenacyldibutyltelluronium bromide (**1b**) can be obtained from the reaction of dibutyl telluride with chloroacetonitrile and phenacyl bromide, respectively. Compounds 1a and 1b are treated with potassium *tert*-butoxide to yield the corresponding telluronium ylides (**2a,b**), which condense easily with a variety of carbonyl compounds to yield α,β-unsaturated nitriles and ketones in moderate yields (Table I).

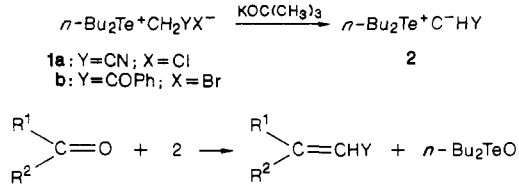

Table I. Synthesis of α,β-Unsaturated Nitriles and Ketones with Corresponding Telluronium Ylides.[a] Method A

products	% yield[b]	E/Z[c]
$C_6H_5CH{=}CHCN$	78	12/1
p-$ClC_6H_4CH{=}CHCN$	83	16/1
p-$CH_3OC_6H_4CH{=}CHCN$	60	70/1
p-$NO_2C_6H_4CH{=}CHCN$	80	18/1
p-$BrC_6H_4CH{=}CHCN$	71	25/1
o-$ClC_6H_4CH{=}CHCN$	61	124/1
p-$CH_3C_6H_4CH{=}CHCN$	78	16/1
$(CH_3)_2C{=}CHCN$	36	
c-$C_6H_{10}{=}CHCN$	49	
p-$ClC_6H_4CH{=}CHCOPh$	81	
p-$BrC_6H_4CH{=}CHCOPh$	74	

[a] All reactions were performed as described in detail in the text. [b] For isolated product. [c] Determined by ^1H NMR spectroscopy.

Table II. Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles with Corresponding Telluronium Salts.[a] Method B

	telluronium salt		
R	X	Y	% yield[b]
p-NO_2	Br	$COOCH_3$	95
m-NO_2	Br	$COOCH_3$	97
m-NO_2	Br	COPh	97
p-NO_2	Br	COPh	95
p-Cl	Br	COPh	97
p-Br	Br	COPh	96
p-NO_2	Cl	CN	88

[a] All reactions were performed as described in detail in the text. All products were found to be the *E* isomers by their melting points and IR and NMR spectra. [b] Isolated yields.

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