fashion to that described above, to provide a hydrocarbon (0.32 g, 73%). On GLC analysis the mixture was found to contain two components with retention times of 18.91 and 19.55 min in the ratio 21.2:78.8 (column A; oven temperature 100 °C, 10 min–5°/min–250 °C), respectively. From GC/MS data and the ^{13}C NMR ($CDCl_3$) spectrum, the oil was found to contain the less symmetrical alkene as the minor component (15–20%) and the more symmetrical alkene as the major isomer. Tricyclo-[6.3.3.0^{1,8}]tetradec-4-ene: IR (FT, neat) 3016, 2901, 1467, 731, 639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37–1.95 (m, 16 H), 2.11–2.21 (q, 4 H), 5.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.97, 24.21, 40.55, 43.60, 54.30, 131.88; mass spectrum (CI, CH_4) *m/e* (relative intensity) 191 (M + 1, 100), 190 (26), 189 (83), 149 (17), 135 (28), 109 (46). Anal. Calcd for $C_{14}H_{22}$: C, 88.42; H, 11.58. Found: C, 88.30; H, 11.68. Tricyclo[6.3.3.0^{1,8}]tetradec-3-ene: ^{13}C NMR ($CDCl_3$) δ 23.27 (t), 24.34 (t), 26.15 (s), 27.92 (s), 29.72 (t), 35.49 (t), 39.60 (t), 40.47 (t), 42.36 (t), 43.24 (t), 55.50 (t), 55.70 (t), 130.63 (d), 131.32 (d); mass spectrum (CI, CH_4), *m/e* (relative intensity) 191 (M + 1, 100).

Tricyclo[6.3.3.0^{1,8}]tetradec-4-en-10-one (10). A mixture of monoketal (**25a**, 2.0 g, 6.5 mmol), potassium carbonate (3.0 g, 22 mmol), silver carbonate (1.5 g, 10 mmol), hydrazine hydrate (6 mL), and triethylene glycol (50 mL) was heated at reflux for 2 h under nitrogen. A small short-path distillation head was then placed on top of the flask in place of the condenser. The pot temperature was increased to 200 °C and the material was held at this temperature for 5 h, after which it was cooled and diluted with water. The mixture was heated with 100 mL of 2 N sulfuric acid for 6 h, cooled, and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were washed consecutively with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was removed under reduced pressure to provide **10** (1.1 g, 84%), which was further purified by column chromatography on activated alumina (basic) with ethyl acetate–hexane (20:80). The 4-ene (**10**) is a viscous oil: IR (FT, neat) 2957, 2929, 1734, 1286, 594 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 21.16, 24.60, 35.77, 42.21, 51.79, 52.21, 129.82, 219.39; mass spectrum (CI, CH_4), *m/e* (relative intensity) 205 (M + 1, 100), 187 (43), 149 (11), 135 (3). Anal. Calcd for $C_{14}H_{20}O$: C, 82.35; H, 9.80. Found: C, 82.15; H, 9.70.

***cis*-3-Oxobicyclo[3.3.0]octane-1,5-dipropanal Dimethyl Acetal (11).** Tricyclo[6.3.3.0^{1,8}]tetradec-4-en-10-one (**10**, 1.0 g, 4.8 mmol) was dissolved in a mixture of dry CH_3OH (40 mL) and CH_2Cl_2 (80 mL). The solution was cooled to −70 °C in a dry ice–acetone bath and ozone was passed through the mixture until a deep blue coloration developed. The solution was stirred for 5 min and the excess ozone was purged from the medium with a stream of nitrogen (15 min), after which the reaction mixture became colorless. The solution was allowed to warm to −10 °C, and dimethyl sulfide (6.2 g, 0.1 mmol) was added slowly. The solution was stirred first at −10 °C for 1 h and then at room temperature overnight. The solvent was removed under reduced pressure and the residue was dissolved in water (50 mL) and subsequently extracted with chloroform (3 × 50 mL). The dimethyl sulfoxide remained in the water layer. The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure to provide the bisacetal **11** (90%), accompanied by the corresponding dialdehyde. The bisacetal **11** was employed in the next step, although the same yield of **2** was obtained from the mixture of bisacetal **11** and dialdehyde as well as from the trisacetal **27**.[12]

Preparation of *trans,trans*-4,8-Diacetoxytetracyclo-[9.3.0.0.^{1,5}0^{7,11}]tetradecan-6-one (2). The *cis*-3-oxobicyclo-[3.3.0]octane-1,5-dipropanal dimethyl acetal (**11**) [or its hemiacetal (0.5 g)][12] was dissolved in glacial acetic acid (50 mL) and 3 drops of concentrated H_2SO_4 were added. The mixture was stirred under nitrogen for 10 days at 50 °C. The solution was cooled and brought to pH 4 with solid sodium carbonate, and the acetic acid was removed under reduced pressure. To the residue was added water (50 mL), and the solution was extracted with $CHCl_3$ (3 × 25 mL). The combined $CHCl_3$ extracts were washed consecutively with cold water, cold aqueous $NaHCO_3$ solution (5%, 30 mL), and brine. After drying ($MgSO_4$) the solvent was removed under reduced pressure to provide an oil (150 mg, 40% overall yield from the monoketone **10**). The crude **2** obtained in this fashion was purified by flash chromatography (2 times, ethyl acetate–hexane, 20:80) to provide white crystals of **2**: mp 98–99 °C; IR (FT, KBr) 2974, 2954, 1738, 1724, 1376, 1236, 1017 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.71 (m, 14 H), 2.05 (s, 6 H), 2.67 (m, 2 H), 5.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.93 (q), 24.20 (t), 33.34 (t), 33.74 (t), 42.80 (t), 56.03 (s), 66.23 (d), 76.25 (d), 170.06 (s), 213.10 (s); mass spectrum (EI, 15 ev), *m/e* (relative intensity) 320 (M$^+$, 3.4), 279 (23.8), 260 (22.3), 248 (14.1), 230 (15.3), 217 (32.7), 200 (100.0), 188 (31.1), 172 (55.7), 160 (18.5), 149 (34.3); high resolution mass spectrum calcd for $C_{18}H_{24}O_5$ − 60 (M$^+$ − CH_3COOH) 260.1412, found 260.1428; calcd for (M$^+$ − 2 × CH_3COOH) 200.1201, found 200.1230. Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.50; H, 7.50. Found: C, 67.25; H, 7.45.

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Registry No. **2**, 107784-79-2; **6**, 78046-17-0; **10**, 107784-85-0; **11**, 107802-95-9; **11**-(dialdehyde), 109307-54-2; **18**, 109307-55-3; **19a**, 109307-56-4; **19b**, 109307-57-5; **20a**, 107784-84-9; **21a**, 109307-58-6; **21b**, 109307-59-7; **22**, 107784-82-7; **23**, 109307-60-0; **24a**, 109307-61-1; **24b**, 109307-62-2; **25a**, 107784-81-6; **25b**, 107784-80-5; **26a**, 107784-83-8; **26b**, 107784-86-1; ethanedithiol, 540-63-6; butane-1,4-dithiol, 1191-08-8; propane-1,3-dithiol, 109-80-8; ethylene glycol, 107-21-1; 2,2-dimethylpropane-1,3-diol, 126-30-7; tricyclo[6.3.3.0^{1,8}]tetradec-4-ene, 109307-63-3; tricyclo-[6.3.3.0^{1,8}]tetradec-3-ene, 109307-64-4.

Polyvalent Iodine in Synthesis. 1. An Efficient Route to Isopropylidene Arylmalonates (5-Aryl-Substituted Meldrum's Acid)

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Meldrum's acid (**1**, isopropylidene malonate, 2,2-dimethyl-1,3-dioxane-4,6-dione) and its 5-substituted derivates are versatile reagents in organic synthesis[2] as well as valuable precursors in thermal decompositions.[3]

Several new methods have recently been reported[4–7] for the direct preparation of 5-alkyl-substituted derivatives from Meldrum's acid itself. However, few methods are available for the ready preparation of 5-aryl derivatives from **1** itself, as direct substitution with aryl halides by various salts of **1** via an S_NAr process requires highly activated aromatic substrates. The only known method of direct arylation employs aryllead triacetate as the arylating reagent to afford isopropylidene arylmalonates.[8] However, lead compounds are clearly toxic, and Meldrum's acid itself gave only a poor yield of the diarylated product.

Our recent interest[9] in tricoordinate iodine species and their renaissance in organic synthesis,[10] coupled with the ready availability and high reactivity[11] of diaryliodonium

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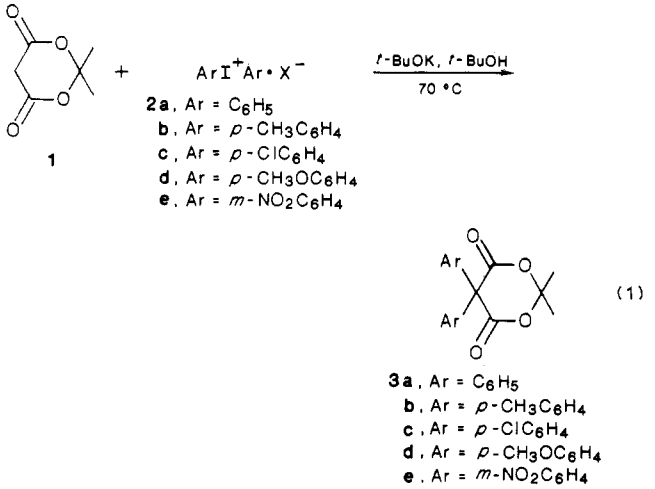
Table I. Physical and Spectral Data for Adducts 3 and 5

compd	X^- in 2	reactn time, h	yield,[a,b] %	mp, °C	IR (KBr), cm^{-1}	^1H NMR ($CDCl_3$), ppm
3a	Cl^-	16	73	161–162	1782, 1744, 1401, 1388, 1299, 759, 699	1.58 (s, 6 H), 7.23 (s, 10 H)
3b	Br^-	72	95	143–145	1784, 1748, 1396, 1382, 1295, 811	1.56 (s, 6 H), 2.34 (s, 6 H), 7.30 (m, 8 H)
3c	Cl^-	72	72	136–137	1789, 1748, 1401, 1386, 1305, 821, 746	1.60 (s, 6 H), 7.18 (m, 8 H)
3d	I^-	72	59	197–198	1785, 1747, 1400, 1385, 1301, 850, 839, 832	1.76 (s, 6 H), 3.59 (s, 6 H), 7.40 (q, 8 H)
3e	Cl^-	16	65	99–101	1785, 1745, 1540, 1400, 1386, 1371, 1280, 900, 838, 807, 730, 708	1.60 (s, 6 H), 7.32 (m, 8 H)
5a	Cl^-	18	88	84–86	1777, 1739, 1396, 1383, 1277, 753, 701	1.24 (s, 3 H), 1.42 (s, 3 H), 3.72 (s, 2 H), 7.25–7.65 (m, 10 H)
5b	Br^-	72	84	155–156	1786, 1753, 1399, 1385, 1275, 805, 745, 712	1.24 (s, 3 H), 1.41 (s, 3 H), 2.37 (s, 3 H), 3.70 (s, 2 H), 7.20–7.60 (m, 9 H)
5c	I^-	72	60	92–94	1785, 1745, 1398, 1383, 1285, 805, 745, 705	1.23 (s, 3 H), 1.40 (s, 3 H), 2.30 ns, 3 H), 3.57 (s, 2 H), 7.15–7.50 (m, 9 H)
5d	Cl^-	72	82	128–130	1781, 1749, 1398, 1384, 1280, 1037, 809, 769, 710	1.26 (s, 3 H), 1.43 (s, 3 H), 3.64 (s, 2 H), 7.16–7.56 (m, 9 H)
5e	Cl^-	8	79	110–112	1782, 1749, 1545, 1400, 1387, 1361, 1280, 807, 770, 709	1.17 (s, 3 H), 1.50 (s, 3 H), 3.66 (s, 2 H), 7.20–8.50 (m, 9 H)
5f	Cl^-	26	56	143–145	2960, 2895, 1780, 1750, 1403, 1392, 1290, 759, 701	1.01 (d, 6 H), 1.30 (s, 3 H), 1.69 (s, 3 H), 2.66–3.05 (m, 1 H), 7.34 (s, 5 H)
5g	Cl^-	20	55	160–162	2960, 2890, 1785, 1752, 1400, 1387, 1310, 871, 821, 730	1.02 (d, 6 H), 1.30 (s, 3 H), 1.68 (s, 3 H), 2.76–3.00 (m, 1 H), 7.36 (m, 4 H)
5h	Cl^-	12	95	132–133	3040, 1790, 1752, 1401, 1388, 1305, 1282, 957, 751, 699	1.33 (s, 3 H), 1.65 (s, 3 H), 3.15 (d, 2 H), 6.00–6.67 (m, 2 H), 7.20–7.45 (m, 10 H)
5i	Br^-	72	81	123–124	3040, 1788, 1750, 1397, 1387, 1304, 1285, 958, 810, 756, 689	1.30 (s, 3 H), 1.63 (s, 3 H), 2.34 (s, 3 H), 3.13 (d, 2 H), 6.15–6.30 (m, 2 H), 7.15–7.35 (m, 9 H)
5j	Cl^-	72	87	135–137	3045, 1795, 1750, 1403, 1392, 1313, 1288, 1020, 962, 829, 760, 745, 697	1.33 (s, 3 H), 1.64 (s, 3 H), 3.13 (d, 2 H), 6.00–6.60 (m, 2 H), 7.20–7.40 (m, 9 H)
5k	I^-	72	59	108–109	3050, 1790, 1753, 1400, 1385, 1310, 1295, 959, 810, 752, 698	1.30 (s, 3 H), 1.63 (3 H), 3.18 (d, 2 H), 6.40–6.46 (m, 2 H), 7.00–7.33 (m, 9 H)
5l	Cl^-	15	64	140–141	3050, 1787, 1750, 1543, 1401, 1387, 1370, 1307, 1287, 960, 807, 750, 740, 710	1.35 (s, 3 H), 1.65 (s, 3 H), 3.14 (d, 2 H), 6.15–6.45 (m, 2 H), 7.15–8.35 (m, 9 H)

[a] Isolated, recrystallized product. [b] Satisfactory analyses obtained for all products: C, ±0.33; H, ±0.03.

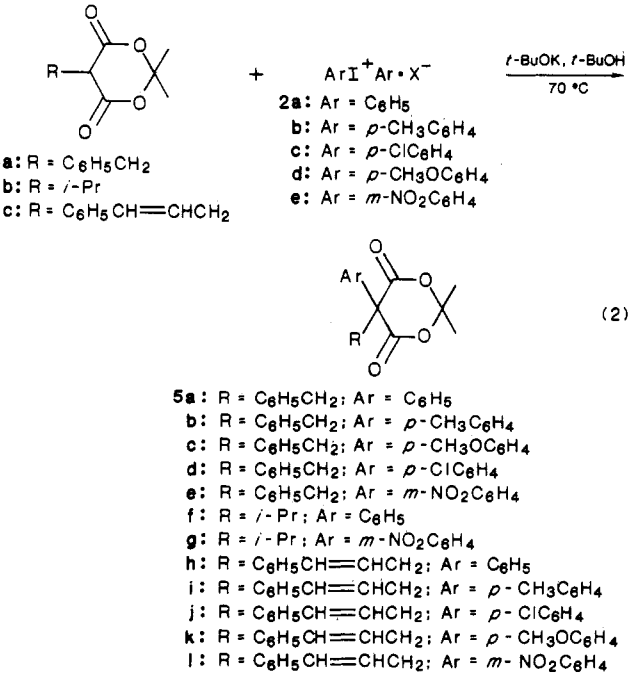
salts **2**, prompted us to examine their use as direct arylating agents in the formation of isopropylidene arylmalonates **3** and **5** from Meldrum's acid. Hence, in this paper we report an efficient, general synthesis of isopropylidene arylmalonates **3** and **5** via diaryliodonium salts.

Analogous to alkylation,[4] arylation of the potassium salt of Meldrum's acid (**1**) with diaryliodonium salts **2** readily occurred in a single step to afford diarylated products **3** (eq 1). Simple stirring of the potassium salt of **1** with the appropriate diaryliodonium salts **2** in *tert*-butyl alcohol at 70 °C gave after workup and isolation the desired diaryl products **3** in good to excellent yields as given in Table I.



(1)

Likewise, monosubstituted malonates **4** also readily underwent reaction with **2** to give **5** as in eq 2 (see Table I). The reaction may also be carried out with NaH in refluxing THF or in $CHCl_3$ with solid K_2CO_3 and 18-crown-6.



(2)

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The products were characterized by spectral and analytical means as summarized in the table. This reaction represents a general, simple, mild, and superior procedure for the direct synthesis of a variety of isopropylidene diarylmalonates **3** and isopropylidene alkylarylmalonates **5**. Furthermore, since substituted isopropylidene malonates are readily hydrolyzed to carboxylic acids[12] or converted to esters,[13] this method represents an indirect, efficient preparation of α-aryl carboxylic acids or their esters.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer with Me_4Si in $CDCl_3$ as the internal standard, and IR spectra were recorded on a PE-683 spectrometer.

Starting Materials. Meldrum's is commercially available or can be readily made by condensation of malonic acid with acetone. The necessary diaryliodonium salts **2** were prepared by standard procedures according to Beringer and co-workers.[14]

General Procedure for the Preparations of 3 and 5. Potassium metal (0.78 g, 20 mmol) was added to 20 mL of anhydrous *tert*-butyl alcohol. After reaction, 1.44 g (10 mmol) of Meldrum's acid (**1**) was added under nitrogen at 70 °C. To this solution was slowly added 20 mmol of the appropriate diaryliodonium salt **2**. (For reaction of **4** with **2** the molar ratio of K to **4** to **2** was 1:1:1.) The resulting solution was stirred at 70 °C for several hours (see Table I) until it turned clear. After cooling, the solvent was removed, and to the residue were added 30 mL of methylene chloride and 10 mL of water. The organic layer was separated, washed successively with 10 mL of water, 10 mL of 5% aqueous $NaHCO_3$, and 10 mL of water, and then dried over anhydrous $MgSO_4$. The methylene chloride was removed, to the residue was added 20 mL of petroleum ether, and the mixture was allowed to stand in a refrigerator overnight. The resulting crystals were collected by suction filtration and purified by recrystallization from benzene/hexane. All relevant data are summarized in the table.

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Polyvalent Iodine in Synthesis. 2. A New Method for the Preparation of Aryl Esters of Dithiocarbamic Acids

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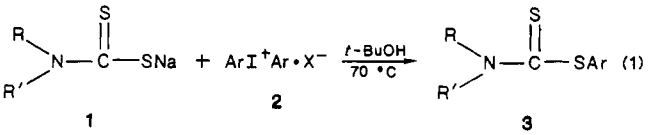
Esters of dithiocarbamic acids have received considerable interest because of their antimicrobial activity and application in organic synthesis.[2] Although a wide variety of methods have been reported for their synthesis, the most general and important one involves the alkylation of dithiocarbamic acid salts.[2,3] Since simple aryl halides cannot be used in alkylation reactions, this procedure only works for alkyl systems.

The current methods for the preparation of aryl esters of dithiocarbamic acids are essentially based upon the reactions of dithiochloroformates with amines,[4] or thioisocyanates with thiophenols,[5] and diazonium salts with salts of dithiocarbamic acid,[6] and certain organometallic reagents with tetramethylthiuran disulfide, $Me_2NC(S)SSC(S)NMe_2$.[7,8] These methods may be tedious and cumbersome, may employ some toxic and hazardous reagents, and generally give poor yields.

As indicated in the preceding paper,[9] the known[10] availability and reactivity of diaryliodonium salts **2** prompted us to examine their reaction with salts of dithiocarbamic acids for a general, efficient, new method of aryl ester synthesis.

Herein we report that salts of type **1** readily react with diaryliodonium salts **2** in either 2-methyl-2-propanol or acetonitrile at 70 °C to give aryl esters **3** (eq 1) in good isolated yields (Table I).



1 2 3

a: R = CH_3; R' = CH_3; Ar = C_6H_5
b: R = C_2H_5; R' = C_2H_5; Ar = C_6H_5
c: R, R' = $-(CH_2)_5-$; Ar = C_6H_5
d: R = $PhCH_2$; R' = CH_3; Ar = C_6H_5
e: R = Ph; R' = H; Ar = C_6H_5
f: R = CH_3; R' = CH_3; Ar = *p*-$CH_3C_6H_4$
g: R = C_2H_5; R' = C_2H_5; Ar = *p*-$CH_3C_6H_4$
h: R, R' = $-(CH_2)_5-$; Ar = *p*-$CH_3C_6H_4$
i: R = $PhCH_2$; R' = CH_3; Ar = *p*-$CH_3C_6H_4$
j: R = CH_3; R' = CH_3; Ar = *p*-$CH_3OC_6H_4$
k: R, R' = $-(CH_2)_5-$; Ar = *p*-$CH_3OC_6H_4$
l: R = CH_3; R' = CH_3; Ar = *p*-ClC_6H_4
m: R, R' = $-(CH_2)_5-$; Ar = *p*-ClC_6H_4
n: R = CH_3; R' = CH_3; Ar = *m*-$NO_2C_6H_4$
o: R = Ph; R' = H; Ar = *m*-$NO_2C_6H_4$

As in other arylations involving diaryliodonium salts **2** this reaction also exhibits a dependence[11,12] on the anion X^- associated with the iodonium salt **2** (Table I, entries 2–5). In particular, Cl^- and ^-OAc result in higher yields than Br^- and I^-. Moreover, isolated product yields are clearly superior to previous methods[6,7] (**3a–c,f–h**), and the procedure is applicable to a broad range of aryl systems.

Aryl esters of dithiocarbamic acid are easily hydrolyzed to the corresponding thiophenols.[8] For example, compound **31**, when heated under reflux in 20% aqueous KOH for 30 min, gave an 85% yield of pure *p*-chlorothiophenol. Hence, this procedure may also serve as an indirect method for the ready preparation of pure substituted thiophenols.

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