^{1}H NMR ($CDCl_3$) δ 1.9–2.8 (m, 2 H), 3.29 (m, 2 H), 3.68 (t, J = 8.6 Hz, 1H), 4.50 (q_{AB}, J_A = 14.8 Hz, J_B = 17.9 Hz, 2 H), 7.27 (br s, 10 H); ^{13}C NMR ($CDCl_3$) δ 27.74, 45.02, 47.29, 48.11, 125.25, 126.93, 127.64, 127.91, 128.34, 128.72, 136.95, 140.15, 174.55; IR (NaCl) 3060, 3040, 2930, 2880, 1690, 1604, 1500, 1460, 1430, 1360, 1290, 760, 710 cm^{-1}; GC/MS, m/e (rel abund) 251 (P, 27), 118 (30), 91 (100).

Preparation of 1-Benzyl-3-(3,4-dimethoxyphenyl)-2-pyrrolidinone. The usual procedure gave 1.8 g of crude product. Distillation gave veratrole as a first fraction, NBP as a second fraction, and the desired product (0.54 g, 35%) as a third fraction: bp 235–245 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.8–2.7 (m, 2 H), 3.2–3.7 (m, 3 H), 3.85 (s, 6 H), 4.52 (q_{AB}, J_A = 14.5 Hz, J_B = 18.0 Hz, 2 H), 4.52 (m, 2 H), 6.80 (br s, 3 H), 7.30 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.74, 44.91, 47.13, 47.62, 55.91, 56.02, 111.44, 111.65, 119.83, 127.64, 128.28, 128.72, 132.51, 136.63, 148.22, 149.25, 174.82; IR (NaCl) 2965, 1675, 1600, 1585, 1505, 1480, 1445, 1425, 1345, 1320, 1245, 1135, 1075, 1020, 930, 760, 730, 695 cm^{-1}; GC/MS, m/e (rel abund) 311 (P, 70), 164 (35), 151 (40), 91 (100).

Preparation of 1-Benzyl-3-[3,4-(methylenedioxy)-phenyl]-2-pyrrolidinone. The usual procedure gave a crude product, which was distilled. The first fraction was mainly unreacted NBP, while the desired product (0.21 g, 27%) was obtained as a second fraction: bp 230–240 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.8–2.6 (m, 2 H), 3.3 (m, 2 H), 3.64 (t, J = 8.8 Hz, 1 H), 4.51 (m, 2 H), 5.92 (s, 2 H), 6.74 (br s, 3 H), 7.30 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.95, 44.80, 47.13, 47.89, 100.98, 108.29, 108.40, 121.13, 127.64, 128.23, 128.72, 133.65, 136.57, 146.65, 148.00, 174.71; IR (NaCl) 2915, 1675, 1605, 1480, 1430, 1345, 1270, 1240, 1185, 1120, 1100, 1075, 1030, 930, 860, 810, 780, 740, 700 cm^{-1}; GC/MS, m/e (rel abund) 295 (P, 91), 204 (46), 162 (60), 148 (51), 135 (90), 91 (100).

Reaction of *p*-Bromoanisole with NMP. The usual procedure gave 0.85 g of dark oil. Chromatography on silica gel (2 × 20 cm) first gave nonpolar impurities followed by an aryl lactam fraction (0.53 g, 51%) as a yellow oil. Analysis by GC/MS showed two isomers in a 1:1 ratio having identical fragmentation patterns: GC/MS, m/e (rel abund) 205 (P, 100), 148 (60), 117 (30), 42 (60); ^{1}H NMR ($CDCl_3$) δ 1.8–2.7 (m, 2 H), 2.90 (s, 3 H), 3.2–3.65 (m, 3 H), 3.76 (s, $^3/_2$ H), 3.77 (s, $^3/_2$ H), 6.65–7.30 (m, 4 H); IR (NaCl) 2965, 2900, 1675, 1605, 1580, 1505, 1445, 1430, 1395, 1290, 1240, 1175, 1150, 1030, 780 cm^{-1}.

Acknowledgment. We thank Jim Spriggle and Robert Zimmermann for assistance with the GC/MS and NMR spectra.

Communications

Regiospecificity in the Alkylation of Ester Enolates: Synthesis of Sterically Hindered Diarylketene Acetals

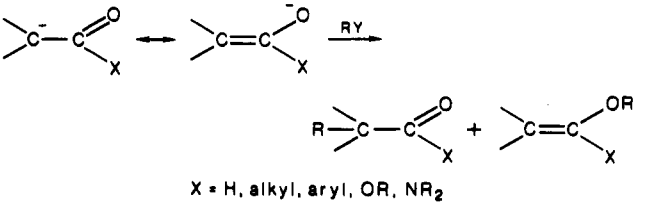
Summary: The alkylation of the enolates of methyl bis(pentamethylphenyl)acetate and of isopropyl bis(pentachlorophenyl)acetate occurs exclusively on oxygen to yield the diarylketene acetals; the extreme steric hindrance of these groups is also responsible for the stability of these ketene acetals in acid.

Sir: The alkylation of enolate anions (conjugate bases of aldehydes, ketones, esters, amides) may in principle occur on either carbon or oxygen (Scheme I).[1] The actual regiospecificity depends strongly on solvent, temperature, and counterion.[2]

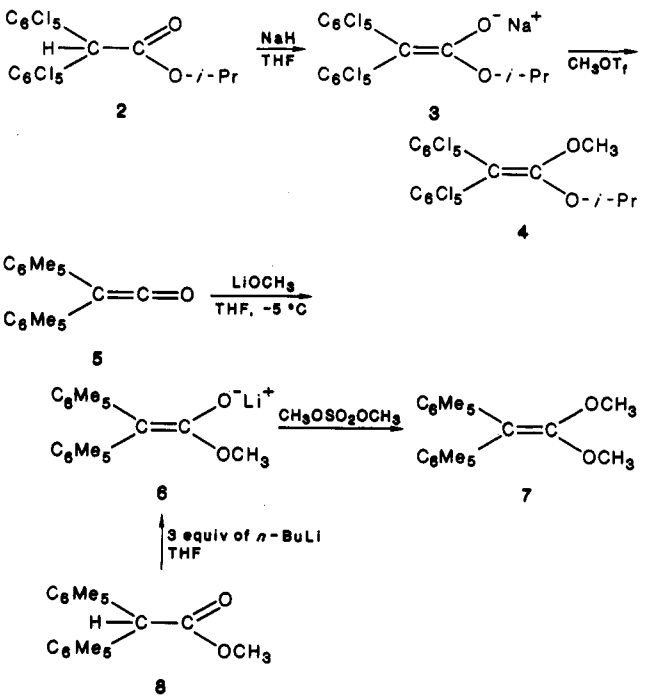
Alkylation of preformed enolates of aldehydes and ketones occurs exclusively on the carbon[3] in less polar solvents. The use of more polar solvents such as Me_2SO and HMPT increases the extent of O-alkylation.[4]

Tidwell[5] has investigated the alkylation of crowded Li enolates of aldehydes and ketones such as 1,1-di-*tert*-butylacetone and 1,1-di-*tert*-butyl-3,3,3-trimethylacetone and found C-alkylation only in the former and mixtures of O and C in the latter. It is interesting to note that in this case extreme steric hindrance with bulky alkyl groups does not afford regioselectivity; this may be related to the high strain energy resulting from interaction between adjacent *tert*-butyl groups.[6]

Scheme I



Scheme II



On the other hand, the alkylation of enolates of carboxylic acid derivatives is virtually always exclusively on

(1) For a review on factors affecting O vs. C alkylation of enolates, see: Barton, D.; Ollis, W. O. *Comprehensive Organic Chemistry*; Pergamon: New York, 1979; Vol. 1, p 1032 ff and references cited therein.
(2) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972.
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(5) Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 4987.

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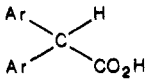
C. This is the basis of a highly versatile method for carboxylic acid homologation.[7]

Studies on alkylation of crowded enolates of carboxylic acid derivatives are not as prevalent as those of aldehydes and ketones, probably due to the difficulty in enolizing esters of di-*tert*-alkylacetic acids. The α-proton in these compounds is not removed by standard bases—again revealing the increase in strain energy that occurs on enolate formation. Dubois and McPhee[8] have studied the alkylation of enolates of α-isopropyl-*tert*-butylacetate esters and found them to undergo C-alkylation (except in the case of α-isopropyl-α-*tert*-butylacetate ester where predominant O-alkylation was observed).

We now wish to report exclusive O-alkylation of enolates of esters of diarylcarboxylic acids such as **1a,b**. These are among the most hindered diarylacetic acids synthesized to date because of the "buttressing effect" of the meta substituents in each ring.



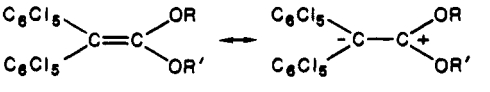
1a, Ar = C_6Me_5
b, Ar = C_6Cl_5

Enolates of esters of **1b** are easily formed due to the electron-withdrawing effect of the pentachlorophenyl groups. Thus treatment of the isopropyl ester **2** with sodium hydride in THF gives a yellow-orange air-stable solution of the sodium enolate **3**. This is not alkylated by methyl iodide or sulfate but is rapidly alkylated by methyl triflate at −5 °C. Quenching the solution followed by chromatography on silica affords (in 70% yield) bis(pentachlorophenyl)ketene methyl isopropyl acetal (**4**)[9] (Scheme II). No C-alkylated product was formed.

Enolates of esters of **1a** are more difficult to form but can be obtained in two ways. Reaction of bis(pentamethylphenyl)ketene (**5**) with lithium alkoxide in THF at 0 °C affords quantitative yields of the lithium ester enolates. Also treatment of esters of **1a** with 3 equiv of *n*-butyllithium in THF at ambient temperature affords the enolates. These anions are highly air-sensitive, and on exposure to oxygen, solutions change immediately from yellow to purple because of their oxidation to (α-alkoxycarbonyl) bis(pentamethylphenyl)methyl radicals.[10]

Thus, treatment of bis(pentamethylphenyl)ketene (**5**) with 1 equiv of lithium methoxide in THF at 0 °C, followed by addition of excess methyl sulfate, afforded 16% yields of bis(pentamethylphenyl)ketene dimethyl acetal (**7**)[9] after chromatography and recrystallization. The main product in this reaction was methyl bis(pentamethylphenyl)acetate. Again no C-alkylation was detected.

The two ketene acetals **4** and **7** show strong ν(C=C) absorptions in their IR spectra at 1610 and 1635 cm^{-1} and have characteristic UVs [308 (log ε = 3.92) and 260 nm (log ε = 4.17)]. The chloro compound **4** is considerably more polar than its precursor, isopropyl bis(pentachlorophenyl)acetate (**2**), while **7** is considerably *less* polar than its precursor methyl bis(pentamethylphenyl)acetate (**8**) (as judged from TLC). This is probably due to dipolar resonance **9** which is important in **4** but not in **7**.



9

The hydrolysis of **7** was surprisingly slow and followed in mixtures of concentrated aqueous HCl and methanol ranging in stoichiometric HCl concentrations from 1.96 to 3.92 M (Table I). The ketene acetal **4** could not be hydrolyzed at all, remaining unchanged in 6.23 M TFA in methanol (50% TFA) over 24 h at 25 °C.

Table I. Acid-Catalyzed Hydrolysis of Bis(pentamethylphenyl)ketene Dimethyl Acetal (7)[a]

[HCl], M[b]	$10^4 k_{obsd}$, s^{-1}	$t_{1/2}$, s
3.92	59.8	116
2.94	15.6	444
1.96	2.4	2900

[a] At 25 °C in methanol–water; the reactions were followed by UV spectroscopy. [b] In 1:1 MeOH–H_2O.

The extreme acid-resistance of these ketene acetals (many orders of magnitude less reactive than the previously least reactive species)[11] is ascribed to resistance to proton transfer from above or below the plane of the double bond by this very bulky aryl groups.

In summary, we have shown that introduction of pentasubstituted aryl groups into the α-carbon of an ester leads to exclusive O-alkylation of the ester enolate and that the resulting ketene acetals are highly acid-resistant. Studies are in hand at present with the novel pentamethylphenyl and pentachlorophenyl groups to determine stabilization of otherwise reactive species.

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(9) Both **4** and **7** give correct elemental analyses and the expected ^1H NMR spectra. The NMR spectrum of the methylated compound **7** is temperature dependent and shows coalescence below 0 °C, due to restricted rotation of the aryl groups. Also formed with **4** in this reaction was bis(pentachlorophenyl)ketene isopropyl 4-methoxybutyl acetal (formed by prior methylation of the solvent THF); starting material was also recovered in both cases.
(10) Hegarty, A. F.; O'Neill, P., unpublished results.
(11) Kresge, A. J.; Straub, T. S. *J. Am. Chem. Soc.* **1973**, *105*, 3957.

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A Novel Method for Direct Conversion of Carboxylic Acids to 1,3-Dithianes by 1,3,2-Dithiaborinane–Dimethyl Sulfide and Stannous Chloride

Summary: Reaction of carboxylic acids with 1,3,2-dithiaborinane–dimethyl sulfide in the presence of stannous chloride in tetrahydrofuran affords the corresponding 1,3-dithianes in high yields.

Sir: We wish to report the direct conversion of carboxylic acids into synthetically useful 1,3-dithianes[1] in high yields under mild conditions. The method for this facile conversion consists of a sequence of two steps, partial reduction of carboxylic acids into the aldehyde stage[2] and

(1) For reviews, see: (a) Seebach, D. *Synthesis* **1969**, 17. (b) Lever, O. W. *Tetrahedron* **1976**, *32*, 1943. (c) Gröbel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. (d) ApSimon, J.; Holmes, A. *Heterocycles* **1977**, *6*, 731.
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