2967, 1640, 1435, 1369 cm^{-1}; ^{1}H NMR 4.25 and 3.36 (heptets, J = 6 Hz, 1 H each), 2.57 (dd, J = 7.6, 5.2 Hz, 1 H), 1.56 (dd, J = 6.3, 5.2 Hz, 1 H), 1.45–1.25 (4 br d, 12 H), 1.40 (s, 3 H), 1.22 ppm (dd, J = 7.6, 6.3 Hz, 1 H); MS (EI) calcd for $C_{11}H_{20}NOI$, m/e 310, found 310.

(B) In Pyridine. Iodine (0.063 g, 0.12 mmol) was added to a solution of **3** (0.050 g, 0.12 mmol) in dry pyridine (0.5 mL) at room temperature. The mixture was stirred for 20 h open to the air and unprotected from light. Much of the iodine color disappeared. The mixture was diluted with CH_2Cl_2 (15 mL) and then washed with 10% aqueous Na_2SO_3, 3% aqueous HCl, and H_2O. The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo, leaving 0.038 g of a slightly orange oil. By ^{1}H NMR this contained approximately a 2:1 mixture of **4** and its trans isomer. These were separated by simple chromatography on silica gel, eluting with 15 vol % EtOAc in $CHCl_3$; the trans compound is the more mobile and was obtained as a slightly yellow oil that was not purified further: IR (CCl_4) ν 2968, 1645, 1436, 1370, 1338 cm^{-1}; ^{1}H NMR 4.16 (br 1 H), 3.29 (br, 1 H), 2.80 (dd, J = 8.5, 5.5 Hz, 1 H), 1.82 (dd, J = 8.5, 6.5 Hz, 1 H), 1.38 (s, 3 H), 1.4–1.1 (m, 12 H), 0.78 ppm (dd, J = 6.5, 5.5 Hz, 1 H); MS (EI) calcd for $C_{11}H_{20}NOI$, m/e 310, found 310.

Carboxylation of 1. (A) Via Cyclopropyllithium 2. Reverse transmetalation of **3** to **2** was accomplished by adding methyllithium in diethyl ether (Aldrich; 2.8 M, 0.70 mL, 2.0 mmol) to a stirred solution of **3** (0.30 g, 0.72 mmol) in dry THF (15 mL) at −70 °C under an argon atmosphere. The mixture was stirred for 30 min at this temperature, and then CO_2 was bubbled through for 10 min. The cooling bath was removed; CO_2 addition was continued for an additional 30 min as the solution warmed to room temperature. The mixture was acidified to pH 1 with 10% aqueous HCl and then treated with an excess of ethereal CH_2N_2. A crystal of iodine was added.[9] After 30 min, the solution was diluted with CH_2Cl_2 (50 mL) and then washed with aqueous Na_2HSO_3. The organic layer was dried ($MgSO_4$) and then evaporated in vacuo. The residue was chromatographed on silica gel, eluting with 1:2:8 $CHCl_3$/EtOAc/hexane to yield 0.158 g (90%) of **5** as an oil. This was not purified further: ^{1}H NMR 4.33 and 3.27 (heptets, J = 7 Hz, 1 H each), 3.64 (s, 3 H), 1.80–1.75 (m, 2 H), 1.38, 1.36, 1.22, 1.11 (d, J = 7 Hz, 3 H each), 1.34 (s, 3 H), 1.04 ppm (m, 1 H).

(B) Via the Cyclopropyl Grignard 6. Methyl Grignard in diethyl ether (Aldrich; 2.7 M, 0.45 mL, 1.2 mmol) was added dropwise to a magnetically stirred solution of **3** (0.20 g, 0.48 mmol) in dry THF (7 mL) at 0 °C under nitrogen. The mixture was stirred for 5 min, and then dry CO_2 was bubbled through for 30 min during which time the reaction temperature was held near 0 °C. The mixture was diluted with ether (20 mL) and then extracted with 5% aqueous NaOH (3 × 10 mL). The combined basic extract was acidified slowly with concentrated aqueous HCl to pH 1 and then extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried ($MgSO_4$) and the solvent removed in vacuo. The solid residue was crystallized from 2:1 hexane/benzene to afford 0.080 g (74%) of the fluffy, white solid **7**: mp 142.5–144 °C; IR (CCl_4) ν 2969, 1703, 1439, 1370, 1277, 1175, 1038 cm^{-1}; ^{1}H NMR 4.34 and 3.28 (heptets, J = 7 Hz, 1 H), 1.81 (dd, J = 8, 5 Hz, 1 H), 1.77 (dd, J = 5, 4.5 Hz, 1 H), 1.36, 1.34, 1.21, 1.16 (d, J = 7 Hz, 3 H each), 1.35 (s, 3 H), 1.10 ppm (dd, J = 8, 4.5 Hz, 1 H); ^{13}C NMR δ 176.5 (CO), 169.2 (CO), 48.6 (CH), 46.0 (CH), 32.9 (C), 27.9 (CH), 22.4 (CH_3), 21.9 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 20.2 (CH_3), 20.1 ppm (CH_3). Anal. Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31. Found: C, 63.26; H, 9.43.

X-ray Crystal Structure Analysis of 1-Methyl-1-(*N*,*N*-diisopropylcarbamoyl)-2-iodocyclopropane (4). A small, colorless crystal of **4** (0.1 × 0.1 × 0.1 mm) was cut from a larger crystal (larger samples did not show sharp diffraction spots). Preliminary Weissenberg photographs with Cu Kα radiation indicated that the crystals belong to the orthorhombic system. Systematic extinctions are $0kl$ ($k = 2n$), $h0l$ ($l = 2n$), and $hk0$ ($h = 2n$), thus defining the space group *Pbca*. Determination of the lattice parameters and intensity measurements were made with a Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. Twenty-two reflections determined with the Nonius peak-hunting procedure in the range $9° < 2\theta < 17°$ were carefully centered. Cell parameters were calculated by a least-squares procedure. All independent reflections in the range $2° \le 2\theta \le 50°$ were measured at $T = -85$ (2) °C by the ω–2θ scan technique. Every 100 reflections the orientation of the crystal was controlled, and every 3.3 h the intensity of the $\bar{1}42$ reflection was checked. During the experiment a loss of intensity of 8% was observed. A total of 2522 reflections was measured. After multiple measurements were averaged, 2192 independent reflections remained, of which 797 were unobserved with $I < 2.58\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied.

Crystal data (−85 °C; Mo K$\bar{\alpha}$, λ = 0.71069 Å, μ(Mo K$\bar{\alpha}$) = 24.382 cm^{-1}): orthorhombic *Pbca*; a = 12.617 (5), b = 12.713 (5), c = 16.016 (8) Å; V = 2569.0 Å^3; Z = 8; density = 1.60 g cm^{-3}; $C_{11}H_{20}NOI$, fw 309.2.

The structure was solved by Patterson methods. The light atoms were found with iodine-phased structure factors and successive Fourier calculations. The hydrogen atoms could not be seen. The structure was refined with block-diagonal least-squares calculations. In the last few cycles of refinement anisotropic temperature factors for the I, O, N, and C atoms were applied, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and w = 1. The atomic and anomalous scattering factors were taken from tables.[10] The final agreement index was R = 0.10 for observed reflections. All calculations and drawings were done on the program system KRIPROG.[11] Additional details of the structure are available in the supplementary material.

Acknowledgment. The National Institues of Health (GM) and the National Science Foundation provided support for this research. The departmental instrument facility was funded in part by the NSF Chemical Instrumentation Program and by the National Cancer Institute by way of the University of Chicago Cancer Research Center (Grant CA-14599). D.C. thanks EniChem Sintesi SpA, Milan, Italy, for a leave of absence and support of his stay at The University of Chicago.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters for non-hydrogen and hydrogen atoms and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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Flash Vacuum Thermolysis of Alkyl Dicyanoethanoates

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Flash vacuum thermolysis of organic compounds has been of great utility in the synthesis of thermally labile compounds, in the spectroscopic characterization of short-lived intermediates, and in the investigation of thermolysis reactions.[1] The thermolysis of esters has been reviewed by Depuy and King,[2] Maccoll,[3] and Smith and Kelly.[4] For over a century it has been known that many esters decompose into an olefin and carboxylic acid when heated at 300–550 °C.[5] Evidence, such as stereochemistry

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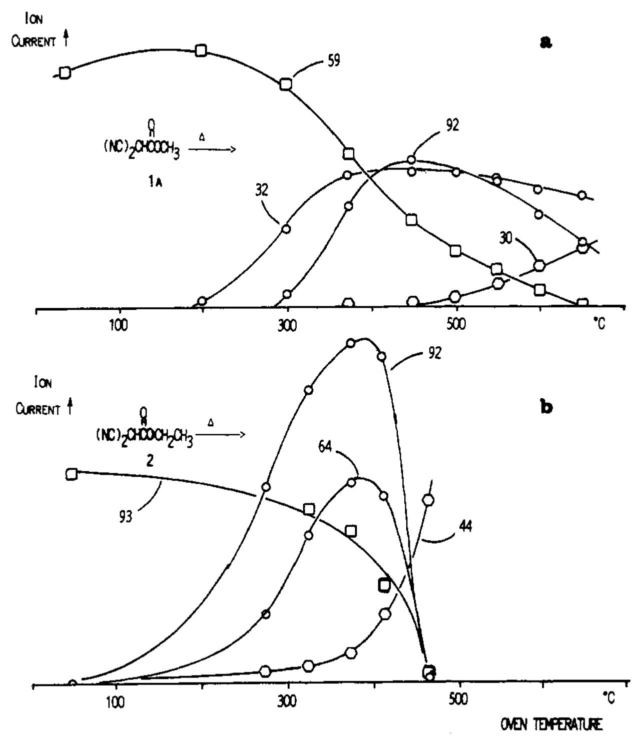


Figure 1. Variation of peak height (ion current) as oven temperature was increased in the thermolysis of (a) methyl dicyanoethanoate, and (b) ethyl dicyanoethanoate at low-ionization voltages (9 eV).

and structure–reactivity studies, supported a concerted β-elimination mechanism.[6] In 1938, Hurd and Blunck[6] first found the formation of ketene while investigating the gas-phase thermolysis of phenyl ethanoate at 625 °C. This result was exploited in these laboratories to devise a synthesis of dicyanoketene by the flash vacuum thermolysis of methyl dicyanoethanoate.[7] Unique features of the thermolysis suggested further investigation. The resulting structure–reactivity, thermolysis studies, which were distinctly different in low- and high-temperature regions, are described below.

Methyl (1) and ethyl dicyanoethanoate (2) were synthesized and characterized by IR, NMR, and MS techniques.[8] The esters were sublimed through an open quartz oven directly attached to a mass spectrometer or cryostat. Monitoring the mass spectrum signal intensities as the oven temperature increased gave the plots in Figure 1. At lower oven temperatures, the passage of the unreacted 1 (Figure 1a) and 2 (Figure 1b) through the oven was characterized by α-cleavage fragments at 59 or 93, respectively. Radical ions from 1 and 2 cleaved predominantly on the alkyl and alkoxy side of the carbonyl, respectively, as shown in eq 1. Even though low-ionizing voltages, ~9 eV, were used throughout, no molecular ion was observed in either case.

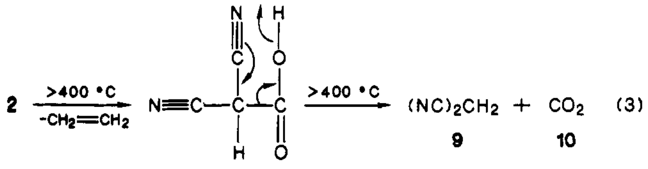
$$\underset{\mathbf{3}}{C({=}O)OR} \xleftarrow[R = CH_3^-]{e^-\ (9\ eV)} (NC)_2CHC({=}O)OR \xrightarrow[R = C_2H_5]{e^-\ (9\ eV)} \underset{\mathbf{4}}{(NC)_2CHC({=}O)} \quad (1)$$

As the oven temperature was increased, signals from the characteristic ester ions gradually gave way to the signals characteristic of dicyanoketene (m/z = 92, 64) and methanol (for 1) or ethanol (for 2)[7] (eq 2). Ethyl ester 2 was

$$\underset{\mathbf{6}}{CH_3OH} + \underset{\mathbf{5}}{O{=}C{=}C(CN)_2} \xleftarrow[R = CH_3]{300-400\ °C} (NC)_2CHC({=}O)OR \xrightarrow[R = C_2H_5]{100-350\ °C} \underset{\mathbf{5}}{O{=}C{=}C(CN)_2} + \underset{\mathbf{7}}{C_2H_5OH} \quad (2)$$

much more reactive toward dicyanoketene formation as indicated by onset of the reaction below 100 °C. No ketene signals were seen from 1 until 300 °C was attained. This was consistent with the difference in fragmentation of the molecular ions of 1 and 2 (vide supra).

As the oven temperature was raised, new reaction pathways became available which were different for 1 and 2. In the case of 2, the signals from dicyanoketene dropped off precipitously above 400 °C as a new peak grew in at m/z = 44 (Figure 1b), revealing the formation of carbon dioxide. Since dicyanoacetic acid was known to spontaneously decarboxylate even at room temperature,[9] this observation was explained by the intervention of the classic ester β-elimination reaction (eq 3). The identification of



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carbon dioxide was confirmed by appropriate absorptions in the infrared spectrum when the pyrolyzate was trapped on a cesium iodide window at 15 K.

The chemistry of 1 at higher temperatures clearly followed a different course. Above 480 °C, a new decomposition pathway began to gradually gain prominence. Clues to the nature of this unexpected pathway were provided by new peaks at m/z = 27, 29, 30, and 67, suggesting the formation of hydrogen cyanide, formaldehyde, and cyanoketene. The presence of formaldehyde was readily verified by detection of appropriate absorptions in the IR spectrum of the pyrolyzate at 15 K. Since HCN could not have come from dicyanoketene, a reaction of 1 giving both formaldehyde and HCN seemed likely.[10] A number of reasonable mechanistic possibilities, (eq 4–6, Scheme I) came to mind.[11a] Although chemically significant quantities of the enol must have been present,[11a] routes to the products through that species were not obvious.

Equation 4, through α-elimination of hydrogen cyanide to form a carbene intermediate, seemed a logical extension of the β-elimination which led to dicyanoketene at lower temperatures. Although there was ample precedent for the carbene insertion producing β-lactone 12, such β-lactones have been observed to thermally cleave by path 6, not observed here, rather than the necessary path a.[11b]

The distinction between the pathway in eq 4 and others (vida infra) was possible by thermolysis of trideuterio-

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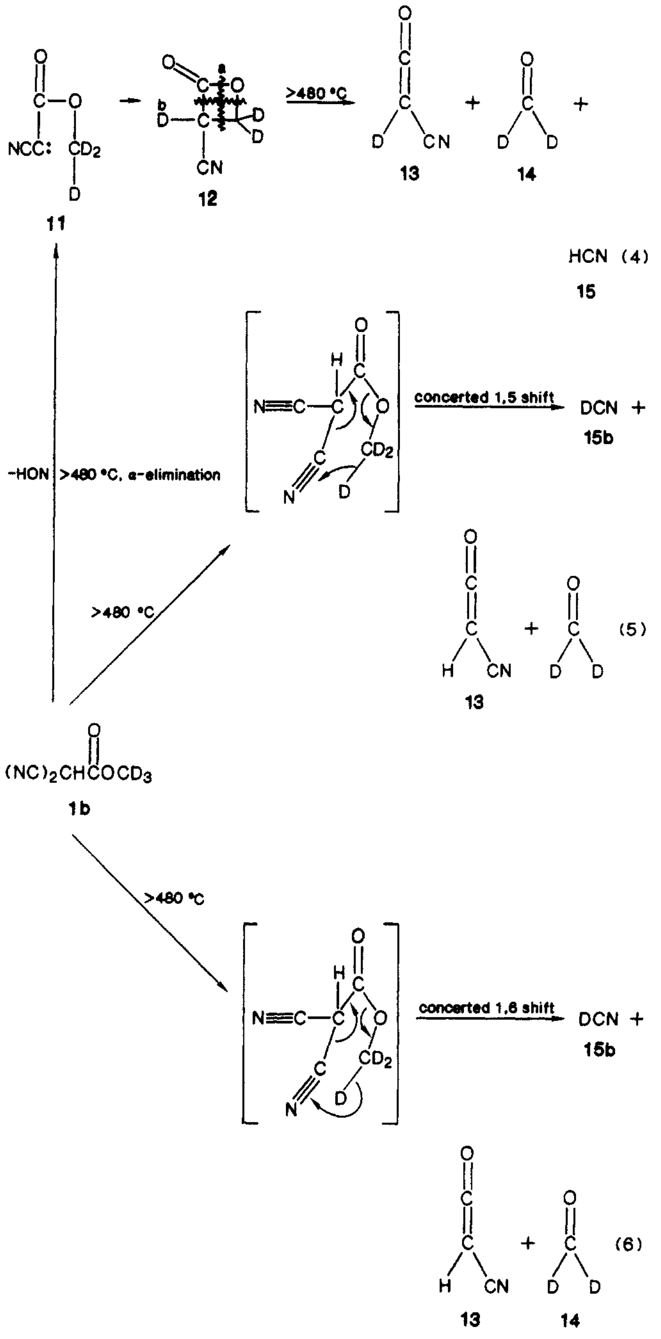
(10) Although formaldehyde can be formed upon the thermolysis of methanol, the formation of HCN required a proton source eliminating methanol formation as part of the new reaction sequence. Occam's razor suggested inclusion of formaldehyde formation in that sequence.

(11) (a) Broadening in the appropriate ^1H NMR and ^{13}C NMR (proton coupled) peaks of 1 indicated the α-hydrogens readily exchanged. This rapid exchange reaction probably involved the enol form, but the chemical shifts indicated the percentage of enol was very small, a result in contradiction to earlier reports based on titration measurements.[8] Whether theses reactions occurred in the gas phase or on the oven surface was not evident from the available data: (b) Richardson, C. D.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 3790.

Scheme I



methyl dicyanoethanoate (**1b**). The proton (deuteron) transfer necessitated in the carbene insertion step in eq 4 would have led to deuteriated cyanoketene in eq 4 but undeuteriated cyanoketene in eq 5 or 6. A sample of methyl dicyanoethanoate was prepared which was 65% perdeuteriated and 35% undeuteriated on the methyl position. Comparison of the mass spectra from thermolysis of the deuteriated and undeuteriated samples proved interesting. In the lower temperature region, the isotope substitution pattern was consistent with the formation of dicyanoketene and methanol. This result provided further evidence in support of ketene formation.[7] At higher temperatures, the peak positions and their intensity ratios confirmed the formation of hydrogen cyanide (CHN/CDN, 1:2) and methanol (CH_4O/CD_3HO, 1:2). Significantly, *the cyanoketene peak at 67 had no deuteriated counterpart at 68*. Thus, the mechanism in eq 4 was ruled out.

The distinction between the pathways in eq 5 and 6 was in the hydrogen-transfer step. Equation 5 involved a 1,5-shift, giving HCN, but eq 6 involved a 1,6-shift, giving HNC. Equation 5 had some precedent in a reported pyrolyses of nitriles.[12] Inspection of the low-temperature, matrix-isolated spectrum of the pyrolyzate from methyl dicyanoethanoate clearly showed the presence of HCN bands at 3310 and 720 cm^{-1} and the absence of HNC bands at 3620, 2029, and 477 cm^{-1}.[13] Thus, the pathway in eq 6 was ruled out.

In summary, the flash vacuum pyrolysis of alkyl dicyanoethanoates can be used to prepare dicyanoketene and an alcohol at low temperatures even when the alkyl group contains a β-hydrogen. At higher temperatures, methyl dicyanoethanoate rearranges thermally by the pathway in eq 5 whereas ethyl dicyanoethanoate reverts to the classic ester pyrolysis through β-elimination. The efficiency of the β-elimination step, observed at high temperatures in **2**, suggested the unusual elimination observed at high temperatures in **1** will only be observed in other esters that do not possess β-hydrogens on the alkoxy group.

Experimental Section

Thermolysis experiments were monitored with a Nuclide 12-90G mass spectrometer equipped with an electrically heated, 8 mm × 80 mm open quartz oven leading directly into the ionization chamber. The temperature was monitored by a thermocouple placed in the heating coil region of the vacuum insulated oven. The esters were sublimed at room temperature directly through the oven. The sample valve was closed, and a background spectrum was run between each sample spectrum. This background correction became important at higher oven temperatures. Thermolysis experiments on the cryostat were performed with a Displex CS-202 cryostat fitted with an 8 mm × 60 mm open, electrically heated, quartz oven. The 1-mm oven orifice was approximately 30 mm from the cesium iodide window cooled to approximately 14 K. Infrared spectra were obtained on Perkin Elmer 621 grating or Nicolet 60SX FTIR spectrometer. NMR spectra were obtained on a JEOL FX-90Q instrument in chloroform-*d*/1% Me_4Si unless otherwise noted.

Methyl Dicyanoethanoate (1a). This ester was prepared, as reported,[8] from the sodium salt of methyl dicyanoethanoate which was in turn prepared from the sodium salt of malononitrile and methyl chloroformate. Vacuum sublimation proved a useful means of purification during the subsequent experiments. Even if a freshly sublimed sample was resublimed, a significant fraction of the original material always remained behind as a reddish solid. Samples were stable indefinitely in the freezer, but they slowly decomposed to a red solid at room temperature. Since some difficulty was encountered in isolating this material and the high acidity of the α-hydrogen suggested the possibility of an usually high percentage of the enol form, **1a** was completely characterized.[11a] The crude product (0.9 g; 14%) recrystallized from chloroform to give **1a** (0.1 g; 1.5%): mp 59–60 °C (lit.[8] mp 65 °C); mass spectrum, *m/z* (relative intensity) at 9 eV) 59 (100); ^1H NMR δ 4.00 (s, CH_3, 3 H), 4.8 (br s, CH, 1 H); ^{13}C NMR δ 29.4 (CH, $J_{C,H}$ = 129 Hz), 55.9 (CH_3, $J_{C,H}$ = 150 Hz), 107.8 (C≡N), 157.8 (C=O); IR (film) 1753 (C=O) cm^{-1}.

Ethyl Dicyanoethanoate (2). The preparation was similar to that used for **1a**. The crude material, 17% yield, was distilled [microdistillation, 30–50 °C (0.2 mtorr)] to give **1a** (0.5 g; 4%), a pale yellow liquid which crystallized upon touch: mp 36–37 °C. Anal. Calcd for $C_6H_6N_2O_2$: C, 52.15; H, 4.39. Found: C, 51.84; H, 4.68; mass spectrum, *m/z* (relative intensity at 9 eV) 93 (95), 66 (100), 58 (40), 54 (27), 45 (35), 43 (30); ^1H NMR δ 1.40 (t, *J* = 7.3 Hz, CH_3, 3 H), 4.42 (q, *J* = 7.3 Hz, CH_2, 2H), 4.82 (br s, CH, 1 H); IR ($CHCl_3$) 1773 (s, $C{=}O_{str}$), 2400 (w, $C{\equiv}N_{str}$), 2895, 2995 (w, CH_{str}) cm^{-1}.

Trideuteriomethyl Dicyanoethanoate (1b). In an effort to avoid toxic, volatile phosgene, the preparation of **1b** employed

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J. Org. Chem. **1987**, *52*, 2105–2106 **2105**

a new reagent, diphosgene (Aldrich), methyl trichloromethyl carbonate, as follows. The sodium salt of malononitrile (0.92 g; 0.0104 mol) was mixed with 5 mL of dry THF under nitrogen. Diphosgene (1.01 g; 0.0052 mol) dissolved in an equal amount of ether, was added dropwise with cooling (ice bath). After being stirred at room temperature for 24 h, the mixture was refluxed for 1.5 h. After cooling, the mixture was filtered, and the precipitate was washed with ether, giving the sodium salt of trideuteriomethyl dicyanoethanoate, a hygroscopic solid, in 36% yield. Without further purification, the sodium salt of trideuteriomethyl dicyanoethanoate (0.29 g; 0.0022 mol) was dissolved in 9 mL of 2 N HCl. The solution was saturated with sodium chloride and filtered after treatment with activated charcoal. The filtrate was extracted 3× with methylene chloride. The combined organic layers were dried (MgSO$_4$) and concentrated to give the crude product (0.05 g; 17%). ^{1}H NMR and ^{13}C NMR were identical with those of **1a** except for splitting of each resonance by the deuterium substituents. The splitting patterns were consistent (vida infra) with approximately $^2/_3$ of the material being trideuteriomethyl and the remainder being methyl dicyanoethanoate. The mass spectrum [m/z (relative intensity at 9 eV) 15 (12), 16 (0), 17, (0), 18 (25), 59 (60), 60 (<2), 61 (<2), 62 (100)] confirmed the material contained a mixture of trideuteriated/undeuteriated product of 2:1.

Acknowledgment. Helpful discussions with M. Jones, Jr., technical assistance from G. Buenning and W. Opdycke, and financial support from the Research Corporation and the University of Toledo Faculty Research Awards and Fellowship Program are gratefully acknowledged.

Simple Synthesis of Biphenyls with the 2-Carbomethoxy-3,5-dihydroxyphenyl Moiety

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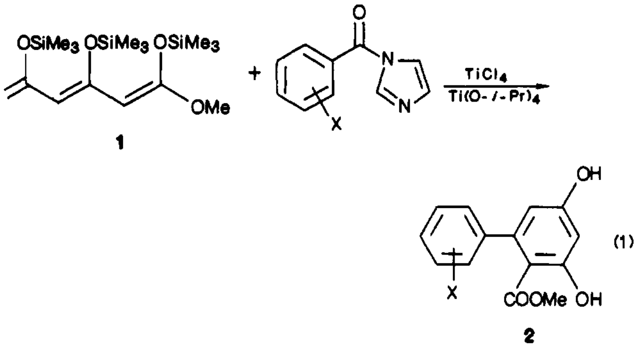
The Ullmann reaction and the Gomberg–Bachmann synthesis, extensively used for the preparation of biphenyl derivatives,[1] present some limitations:[2] the Ullmann synthesis does not give good yields unless one of the aryl halides has an activating group such as nitro, and it can be used for the preparation of unsymmetrical biaryls only if there is a difference in the reactivity of the two components; in the Gomberg–Bachmann reaction the yields are usually low, although recent examples[2] of biphenyl syntheses have improved the yields and used milder reaction conditions than the classical methods.[3-8]

We have recently reported[9] on the Ti^{IV}-promoted condensation of aliphatic imidazolides or equivalent active acylation reagents with 1,3,5-tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene (**1**) to provide methyl 2,4-dihydroxy-6-alkylbenzoates in yields of up to 75% in a 5C + 1C condensation.

Table I. Unsymmetrical Biaryls 2

2X	yield, %	mp, °C	formula	HRMS[a] found	HRMS[a] calcd
2′-Cl	trace				
3′-Cl	65	131–132	$C_{14}H_{11}O_4Cl$	280.030	280.031
4′-Cl	60	148–149	$C_{14}H_{11}O_4Cl$	280.032	280.031
3′,4′-diCl	58	144–145	$C_{14}H_{10}O_4Cl_2$	313.993	313.993
3′,5′-diCl	65	152–154	$C_{14}H_{10}O_4Cl_2$	313.995	313.993
4′-CH$_3$	10	141–143	$C_{15}H_{14}O_4$	258.090	258.089
H[b]	40	117–118[c]	$C_{14}H_{12}O_4$	244.070	244.074
2′-F	11	127–129	$C_{14}H_{11}O_4F$	262.066	262.064
3′-F	42	102–104	$C_{14}H_{11}O_4F$	262.062	262.064
4′-F	38	136–138	$C_{14}H_{11}O_4F$	262.064	262.064

[a] High-resolution mass spectra were obtained at 60 eV on a Du Pont 21-492B instrument at 65 °C. [b] Prepared from the condensation of trimethyl orthobenzoate and 1. [c] Lit.[11] mp 119–121 °C.



In contrast to aliphatic acid chlorides, the condensation of aromatic acid chlorides with **1** did not lead to detectable amount of product.

We have now found that the condensation of **1** did proceed with aromatic imidazolides, thus providing an easy route to unsymmetrical biphenyls **2** (eq 1). In the present case, it was necessary to use 4 equiv of silyl ether to obtain yields in the range of 40–65%. Trimethyl orthobenzoate also reacted with **1** to provide the corresponding biphenyl, showing that both aliphatic and aromatic ortho esters can undergo the 5C + 1C condensation. A range of functionalized biphenyls can be prepared by this method, as summarized in Table I. This method appears to be particularly useful for the synthesis of unsymmetrical biphenyls with halogen substitution in one phenyl ring, since the classical Ullmann reaction or its modifications may lead to the problem of selective halogen activation or polycondensation, and in the Carney–Harris method[11] the introduction of halogen substituents in the phenyl ring of the triketo ester used for the subsequent cyclization was not attempted.

In the condensation of (2-chlorobenzoyl)imidazoline with **1** only a small amount of the expected biaryl was detected by NMR, whereas in the reaction of (2,6-dichlorobenzoyl)imidazoline no biaryl was detected. Steric hindrance of the imidazolide is believed to be the major limiting factor since (2-fluorobenzoyl)imidazoline did give the corresponding biphenyl.

The interpretation of the ^{1}H NMR of biaryls **2** is straightforward as the two protons of the 2-carbomethoxy-3,5-dihydroxyphenyl moiety appear as an AB quartet in the 6.2–6.5 ppm region, and the aromatic protons of the second ring appear further downfield in all of the compounds studied. The ester carbonyl stretching frequency

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