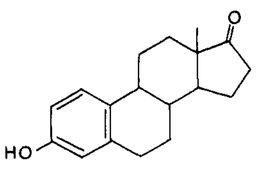
find a means to improve its recovery. Our procedure using "clayfen" has been applied to nitration of phenols in general with excellent results,[11] comparable to those of Kagan et al.[12] but requiring only ferric nitrate[11] as compared to the much more expensive lanthanum nitrate.[12]

Experimental Section

"Clayfen" was prepared as previously described[13] from a mixture of 45 g of iron(III) nitrate nonahydrate, 60 g of K-10 bentonite clay (Süd-Chemie, Munich), and 750 mL of acetone. Freshly prepared "clayfen" (2 g) was added to a mixture of 1 (2 mmol) and toluene (150 mL). The resulting suspension was stirred overnight at room temperature and filtered under vacuum. The crude yellow filtrate was then purified by column chromatography on silica gel (70–230 mesh) by using an 80:20 (v/v) mixture of *n*-hexane and ethyl acetate as the liquid phase. 2-Nitroestrone (**2**) was the sole eluted product, obtained as pure crystals by mere solvent evaporation: 0.347 g (55% isolated yield); mp 178–180 °C (lit. mp 176–178 °C,[9] 183.5–184 °C[8]). ^{1}H NMR (CDCl$_3$) δ 7.96 (s, 1 H$_1$), 6.82 (s, 1 H$_4$), 0.93 (s, 3 H$_{18}$); IR (KBr) 3300 (br, OH), 1738, 1525, 1310 cm^{-1} (lit.[14] 3315, 1736, 1525, 1310 cm^{-1}); MS, *m/e* 315 (M$^+$), 297, 279, 271. Anal. Calcd (^{12}C = 12.00): C, 68.57; H, 6.71; N, 4.44. Found: C, 69.00; H, 6.80; N, 4.33.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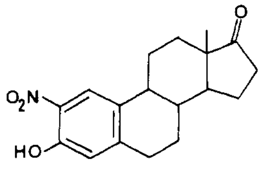

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Results

A likely mechanish involves NO$_2^+$ formation from ferric nitrate on the clay. We are now examining whether the observed regiospecificity is dictated by the steroid or by the clay structure.

Acknowledgment is made to Programmation de la Politique Scientifique, Brussels, for support of this research (Action Concertée 82/87-34) and to Fonds National de la Recherche Scientifique, Brussels, for help in purchasing the HPLC instrument used in this work.

Registry No. 1, 53-16-7; 2, 5976-73-8; ferric nitrate, 10421-48-4.

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Periodination of Benzene with Periodate/Iodide[1]

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Periodination of benzene was recently described in this journal by Levitt and Iglesias,[2] who added C$_6$H$_6$ to a chilled solution of H$_5$IO$_6$ in concentrated H$_2$SO$_4$ and reported a 48% yield of C$_6$I$_6$ upon crystallization of the resulting yellow-tan precipitate. I thought that this reaction might be of use in functionalizing some biaryls. The above procedure was unsuccessful in my hands, however: the reaction appeared to proceed according to the description but upon workup gave highly impure material in yields of only a few percent. I report here a modified procedure for this reaction that gives hexaiodobenzene in acceptable yield under vigorous conditions but gives *tetra*iodobenzene at room temperature.

Levitt and Iglesias propose the following stoichiometry for their reaction:

$$2C_6H_6 + 3\ IO_4^- + 9\ I^- + 12H_3O^+ \rightarrow 2C_6I_6 + 24H_2O \tag{1}$$

They suggest that the iodide is generated from periodate during oxidation of benzene to carbon dioxide. If this is true, much of the starting arene must be expended in creating iodide. The overall reaction equation would then be

$$11C_6H_6 + 30IO_4^- + 30H_3O^+ \rightarrow 5C_6I_6 + 36CO_2 + 78H_2O \tag{2}$$

For this reaction, only 45% of the starting C$_6$H$_6$ can be converted to C$_6$I$_6$.

The aromatic substrate might be conserved if iodide were added directly to the reaction mixture, instead of being generated in situ. Therefore, potassium iodide was added to a solution of periodic acid in concentrated sulfuric acid (making a deep brown solution suggestive of the formation of molecular iodine[3]), followed by addition of benzene, according to the stoichiometry of eq 1. Crystallization of the resulting precipitate gave a product whose melting point (249–252 °C) corresponded to Levitt and Iglesias's melting point of "~260 °C". However, this cannot be hexaiodobenzene. Although the melting point for C$_6$I$_6$ was once thought to be 248 °C,[4] it has, like the melting points of many of the polyiodoarenes, undergone repeated revision. A recent preparation of C$_6$I$_6$[5] resulted in orange crystals with a melting point of ">360 °C". The melting point obtained here suggested rather the literature value (253 °C) of another likely product: 1,2,4,5-tetraiodobenzene.[6] NMR spectra confirmed that C$_6$I$_4$H$_2$ was, in fact, the compound in hand: ^{1}H NMR showed a single aromatic signal; ^{13}C NMR showed two carbon signals, one coupled to H. (The preparation of C$_6$I$_4$H$_2$ was subsequently made more efficient by reducing the quantities of periodate and iodide to stoichiometric amounts.)

Only trace amounts of C$_6$I$_6$ were obtained at the reaction temperatures used by Levitt and Iglesias. C$_6$I$_6$ was finally prepared by heating the reaction mixture at 100 °C with a twofold excess of periodate/iodide. The orange product was crystallized in 45% yield, mp 430 °C (dec with loss of I$_2$ starting about 370 °C); NMR and mass spectra were consistent with C$_6$I$_6$. While the modified periodination procedure described here is not so elegant as the original report, it is still quite simple to perform and avoids the need for the fuming sulfuric acid used in more conventional iodinations.[7,8]

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[1] Dedicated to Dr. Kurt D. Kaufman of Kalamazoo College on the occasion of his designation as Emeritus Professor of Chemistry.

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Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Spectra were determined with JEOL JNM-FX60Q NMR, Hewlett-Packard 5985 GC/MS, and Beckman Acculab-1 IR spectrometers. Microanalyses were performed by Galbraith Laboratories.

1,2,4,5-Tetraiodobenzene. Periodic acid (2.56 g, 11.2 mmol) was dissolved in 60 mL of concentrated H_2SO_4 while the mixture was stirred on ice. Crushed potassium iodide (5.58 g, 33.6 mmol) was added in small portions, followed by dropwise addition of benzene (1.00 mL, 11.2 mmol) to the resulting dark solution. After stirring to room temperature overnight, the thick, lavendar mixture was poured onto ice, and the resulting brownish precipitate filtered, triturated with methanol to remove I_2, and refiltered. The crude pink product (5.46 g, 84% yield) was moderately soluble in carbon disulfide and tetrahydrofuran and was crystallized from pyridine/ethanol, giving a 60% yield of off-white needles: mp 249–252 °C (lit.[6] mp 253 °C); ^1H NMR (CS_2 + $CDCl_3$) δ 8.23 (s); ^{13}C NMR δ 108.5 (s, CI), 147.1 (d, CH); MS, *m/e* 581.5 (M^+); small signal at 707.5 suggests less than 2% contamination with C_6I_5H; IR 3057 (w, CH), 1425, 1397, 1272, 1107, 982 (s), 869 cm^{-1}.

Anal. Calcd for $C_6I_4H_2$: C, 12.39; H, 0.35; I. 87.26. Found: C, 12.60; H, 0.26; I, 87.22.

Hexaiodobenzene. Periodic acid (3.82 g, 16.7 mmol), potassium iodide (8.35 g, 50.2 mmol), and benzene (0.50 mL, 5.58 mmol) were combined in 40 mL of sulfuric acid as described above. After stirring[9] for 6 h, the mixture was heated to 100 °C. After 10 h, the mixture was poured onto ice, filtered, washed with methanol, and finally washed with hot tetrahydrofuran to remove incompletely iodinated arenes. The orange crude product (3.40 g, 73% yield) was moderately soluble in *N*-methylpyrrolidinone and hot Me_2SO. Crystallization from pyridine/ethanol gave orange needles (45% yield) in two crops: mp 430 °C (dec with loss of I_2 starting about 370 °C) (lit.[5] mp >360 °C); ^1H NMR (Me_2SO-d_6) no signal; ^{13}C NMR δ 121.4 (CI); MS, *m/e* 833.3 (M^+); IR 1237, 1205 cm^{-1}.

Anal. Calcd for C_6I_6: C, 8.65; I, 91.35. Found: C, 8.77; I, 91.25.

Acknowledgment. I thank Dr. J. F. Parcher for the mass spectral analyses. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Benzene, 71-43-2; periodic acid, 13444-71-8; potassium iodide, 7681-11-0; 1,2,4,5-tetraiodobenzene, 636-31-7; hexaiodobenzene, 608-74-2.

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(8) Presented in part at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983.

(9) **Note Added in Proof**: Prof. Robert Hutchins has informed me that vigorous mechanical stirring is required when this procedure is performed on a large scale.

Thioimidate Methylides by the Desilylation Method: An Improved Synthesis of Pyrrolines and Pyrroles

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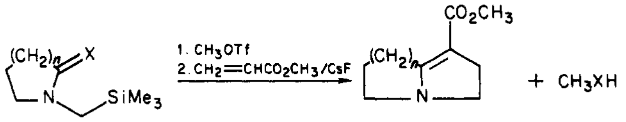
There are now several approaches to the generation of nonstabilized azomethine ylides by desilylation of α-trimethylsilyl iminium salts or equivalent species.[1-3] We had used an imidate methylide to assemble the retronecine nucleus in acceptable (51%) yield by trapping with methyl acrylate.[1b] However, other imidate ylide cycloadditions have proved inconsistent, and yields have often been low. For example, treatment of 1 with methyl triflate followed by $CsF/CH_2{=}CHCO_2CH_3$ affords a modest 37% yield of adduct 2. We now report a substantial yield improvement by using the analogous thiolactam 3. Under the usual conditions of ylide generation, enamine ester 2 is obtained in 66% yield.

Table I. Cycloadducts from Imidate or Thioimidate Ylides + Dipolarophiles[a]

entry	starting material	dipolarophile	product(s)[6] (yield,[b] %)
11	1[b]	$CH_2{=}CHCO_2CH_3$	2 (37)
22	3[c]	$CH_2{=}CHCO_2CH_3$	2 (66)
33	4[c]	$CH_2{=}CHCO_2CH_3$	5 (61)
4	4	$CH_3O_2CC{\equiv}CCO_2CH_3$	6 (66) 9 (>90)
5	4	$HC{\equiv}CCO_2CH_3$	7[e] (31) 8[e] (25) 10 (35)
6	11[d]	$CH_2{=}CHCO_2CH_3$	13 (34)
7	12[c]	$CH_2{=}CHCO_2CH_3$	13 (53)
8	12	$HC{\equiv}CCO_2CH_3$	14[e] (49) 15[e] (20) 10 (53)
9	16[d]	$CH_2{=}CHCO_2CH_3$	complex
10	17[c]	$CH_2{=}CHCO_2CH_3$	18 (56)

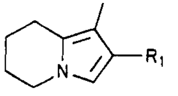
[a] Amide or thioamide + CH_3OTf/CH_2Cl_2; desilylation in situ, CsF/DME. [b] Yield of noncrystalline adduct, purified by preparative-layer chromatography. [c] From the amide + Lawesson's reagent,[8] >95% yield; see representative case in Experimental Section. [d] From the parent *N*-benzyl amide + NaH + Me_3SiCH_2I (see Experimental Section). [e] Isomers separated by preparative TLC, silica gel.



1, X = O; *n* = 1
3, X = S; *n* = 1
4, X = S; *n* = 2

2, *n* = 1
5, *n* = 2

As seen from Table I, an improved yield of adducts is obtained in all cases (entries 1 vs. 2; 6 vs. 7; 9 vs. 10) where the thioimidate ylides have been compared with their oxygen analogues. The reasons for improved yields are probably related to (1) the relative ease of thioamide alkylation, (2) the greater stability of thioimidate salts, and (3) the tendency of the dipolarophile to scavenge the methyl mercaptan that is eliminated from the initial adduct. With $CH_3O_2CC{\equiv}CCO_2CH_3$ as dipolarophile (entry 4), the corresponding mercaptan adduct 9 can be isolated in >90% yield in addition to the pyrrole 6 (66%). With methyl propiolate as dipolarophile, the mercaptide adduct 10 is obtained.



6, R = R$_1$ = CO_2CH_3
7, R = CO_2CH_3; R$_1$ = H
8, R = H; R$_1$ = CO_2CH_3

$CH_3O_2CC(SCH_3){=}CHCO_2CH_3$

9

$CH_3SCH{=}CHCO_2CH_3$

10

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