254; precise mass calcd for $C_{12}H_{14}O^{80}Se$ m/e 254.020 96, found 254.021 01.

***cis*- and *trans*-3-Methyl-2-(phenylselenenyl)-2-(2-pentynyl)cyclopentanone (7).** To a round-bottomed flask containing 1.15 g (11.4 mmol) of diisopropylamine and two crystals of α,α'-bipyridyl in 10 mL of anhydrous THF at -78 °C was added 6.70 mL of 1.5 M *n*-BuLi (10.05 mmol) in hexane via syringe. The resulting solution was allowed to stir for 15 min. A second round-bottomed flask containing 1.70 g (6.70 mmol) of **6** and in 25 mL of anhydrous THF was cooled to -78 °C, and to it was slowly added the LDA solution, prepared in the first flask, until the color remained pink. After the solution was allowed to stir for 15 min, 2.2 mL of HMPA and 3.50 g of 1-bromo-2-pentyne were added. The reaction mixture was then allowed to stir for 2 h at -78 °C and an additional 10 h at room temperature. The reaction was then quenched by the addition of 10 mL of 10% HCl. The bulk of the THF was removed in vacuo, and the residue was extracted with ether (3 × 40 mL). The combined ether layers were washed sequentially with 10% HCl solution (3 × 10 mL), saturated $NaHCO_3$ solution (2 × 10 mL), and water (2 × 10 mL). The solution was dried with $MgSO_4$, and the solvent was removed in vacuo, leaving 2.05 g of **7**. The small amounts of impurities present were separated from the mixture via silica gel chromatography, which gave 2.00 g (96.4% yield) of **7**: ^1H NMR ($CDCl_3$) 7.71–7.13 (m, 5), 2.93–1.50 (m, 9), 1.34–0.97 (overlapping pair of d and t, 6); IR ($CHCl_3$) 1724 cm^{-1}; mass spectrum, m/e 320.

3-Methyl-2-(pent-2-ynylidene)cyclopentanone (8). To 15 mL of a CH_2Cl_2 solution containing 0.40 g of at 0 °C were added three 0.20-mL portions of 30% H_2O_2 solution at 10-min intervals. Fifteen minutes after the final peroxide addition, the mxiture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with saturated $NaHCO_3$ solution (3 mL) and water (3 mL), dried ($MgSO_4$), and stripped of its solvent in vacuo to give 0.22 g (100% yield) of **10**. The sample obtained from this procedure was spectroscopically pure: ^1H NMR ($CDCl_3$) 6.35 ("q", J = 2.5 Hz, 1) 3.25–2.97 (m, 1), 2.60–1.45 (m, 6), 1.31–1.10 (overlapping pair of d and t, 6); IR ($CHCl_3$) 2205, 1700, 1610 cm^{-1}; mass spectrum, m/e 162; precise mass calcd for $C_{11}H_{14}O$ m/e 162.104 66, found 162.110 78.

3-Methyl-2-(2-oxo-1-pentyl)cyclopent-2-enone (10). A mixture of 30 μL of *n*-BuOH, 15 mL of 50% H_2SO_4, and 0.10 g of **8** (2.62 mmol) was heated at 90 %C for 25 min. The cooled reaction mixture was then poured onto solid $NaHCO_3$, and the resulting mixture was washed with pentane (5 × 5 mL). The combined pentane layers were washed with a small amount of water (3 × 1 mL) and dried ($MgSO_4$). After removed of the solvent in vacuo, 0.08 g (80% yield) of **12** remained. Further purification was achieved via silica gel chromatography: ^1H NMR ($CDCl_3$) 0.83 (t, J = 6 Hz, 3), 1.58 (Br q J = 6 Hz, 2), 1.99, (s, 3), 2.65–2.40 (m, 4), 3.24 (br s, 2); IR ($CHCl_3$) 1700, 1650 cm^{-1}; mass spectrum, m/e 180.

5-(Phenylselenenyl)-3-methyl-2-(pent-2-ynyl)cyclopentanone (14). To a 100-mL round-bottomed flask containing 0.25 g (2.5 mmol) of diisopropylamine in 20 mL of anhydrous THF at -78 °C was added 1.2 mL of 1.5 M *n*-BuLi (1.8 mmol) in hexane via syringe. The resulting solution was allowed to stir for 15 min, at which time 1.0 g (3.14 mmol) of **7** and 2 mL of HMPA were added. The reaction mixture was stirred at -78 °C for 30 min and then allowed to slowly warm to room temperature. After being stirred at room temperature for 1 h, the reaction mixture was quenched with 1 mL of a saturated ammonium chloride solution. The THF was removed via a rotary evaporator, and the resulting residue was partitioned between ether (50 mL) and water (15 mL). The aqueous layer was washed twice with ether (25 mL). The combined ether layers were dried with $MgSO_4$ and stripped of solvent to give 1.0 g of **13** (mixture of epimers, 100% yield). This material was used in the next step of the sequence without any additional purification: ^1H NMR ($CDCl_3$) 7.79–7.20 (m, 5), 3.97–3.51 (m, 1), 2.85–1.50 (m, 8), 1.33–0.85 (m, 6).

5-(Pent-2-ynyl)-4-methylcyclopent-2-en-1-one (15). To 25 mL of a methylene chloride solution containing 1.0 g (3.14 mmol) of **14** were added six 1-mL portions of 30% H_2O_2 at 10-min intervals. Five minutes after the final peroxide addition, the mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed sequentially with water (5 mL), saturated $NaHCO_3$ solution (5 mL), and again with water (5 mL). The solution was dried over $MgSO_4$ and evaporated to give 0.54 g of **15** which contained virtually no impurities. Complete purification was achieved via silica gel chromatography: (0.51 g (100% yeild); ^1H NMR ($CDCl_3$) 7.63–7.52 (dd, J = 7 Hz, J' = 2 Hz, 1), 6.17–6.05 (dd, J = 7 Hz, J' = 1.5 Hz, 1), 3.03–1.85 (m, 6), 1.27 (:, J = 7 Hz, 3), 1.08 (t, J = 6 Hz, 3); IR ($CHCl_3$) 1700, 1620, 1597 cm^{-1}; mass spectrum, m/e 162; precise mass calcd for $C_{11}H_{14}O$ m/e 162.104 66, found 162.107 66.

Dehydrojasmone (9).[8,9] A methanol solution (10 mL) containing 500 mg (3.10 mmol) of **15** and 100 mg (1.9 mmol) of sodium methoxide was allowed to stir at room temperature under nitrogen for 5 h. The reaction mixture was quenched with water (0.5 mL), and the bulk of the methanol was removed via a rotary evaporator. The residue was extracted with ether (3 × 20 mL). The combined organic layers were washed with water, dried with $MgSO_4$, and stripped of solvent in vacuo to give 0.5 g of crude **9**. Purification was achieved via silica gel chromatography: 440 mg (88% yield); ^1H NMR ($CDCl_3$) 3.06 (br s, 2), 2.60–1.93 (m with overlapping s at δ 2.20, 9), 1.05 (t, J = 6 Hz, 3); IR ($CHCl_3$) 1700, 1650 cm^{-1}.

***cis*-Jasmone (1).**[8,9] A 50-mg (3 mmol) sample of **9** in 1 mL of ethyl acetate was added to a mixture containing Lindlar catalyst in 2 mL of ethyl acetate under 1 atm of hydrogen. After a few minutes the hydrogen uptake ceased. After the catalyst was filtered off, the solution was stripped of its solvent to yield spectroscopically pure **1**: 47 mg (95% yield); ^1H NMR (CCl_4) 5.22 (td, J = 6 Hz, J' = 4 Hz, 2), 2.84 (d, J = 5 Hz 2), 2.20 (m, 6), 2.02 (s, 3), 0.97 (t, J = 7.5 Hz, 3).

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Registry No. **1**, 488-10-8; **2**, 1128-08-1; **3**, 71996-27-5; *cis*-**4**, 78763-71-0; *trans*-**4**, 78763-72-1; **5**, 78763-73-2; **6**, 78763-74-3; *cis*-**7**, 78763-75-4; *trans*-**7**, 78763-76-5; **8**, 78763-77-6; **9**, 7051-37-8; **10**, 78763-78-7; **14** (isomer 1), 78763-79-8; **14** (isomer 2), 78821-59-7; **15**, 78763-80-1; amyl iodide, 628-17-1; 1-bromo-2-pentyne, 16400-32-1.

Direct Amidation of Aromatic Compounds

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Comparatively few reports have appeared of direct aminations[1] or amidations (by NHCOR or NR'COR)[2] of aromatic rings. Wassmundt and Padegimas[3] reported in 1967 that an acylamido group could be directly introduced into the para position of anisole by heating with acetohydroxamic acid in polyphosphoric acid (PPA) as solvent (eq 1). The reported yield (57%) was obtained only when

$$ArH + CH_3C(O)NHOH \xrightarrow{PPA} ArNHC(O)CH_3 + H_2O$$

a large excess (10:1 molar ratio) of hydroxamic acid was used. The yield was sharply reduced when equimolar quantities of hydroxamic acid and the substrate were employed. The necessity for such a large molar ratio obviously diminishes the value of the method. Apart from an intramolecular example, anisole was the only substrate mentioned by Wassmundt and Padegimas. We have investigated this reaction in an effort to determine the optimum conditions and the scope.

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(2) For some other direct amidations, see: Cadogan, J. I. G.; Rowley, A. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1069. Abramovitch, R. A.; Singer, G. M. *J. Org. Chem.* **1974**, *39*, 1795. So, Y.-H.; Becker, J. Y.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1975**, 262.

(3) Wassmundt, F. W.; Padegimas, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 7131.

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(a) Optimum Conditions in PPA. A large number of runs were made to find the best conditions for the reaction between acetohydroxamic acid and anisole. In contrast to the report of Wassmundt and Padegimas,[3] we were able to get isolated yields as high as 59% with a molar ratio of only 1:1. Wassmundt and Padegimas gave few experimental details, but we believe that the improvement is the result of more efficient stirring (PPA is a viscous solvent). The optimum conditions consist of mixing the anisole (0.05–0.10 mol) and the hydroxamic acid (0.05–0.10 mol) in 45–46 g of PPA over a period of 2–3 min and then heating the well-stirred mixture at 110–115 °C for 90–120 min. The order of addition of the two reagents is not important.

(b) Other Substrates. The optimum conditions given below (in the Experimental Section) were used in extending the reaction to other substrates. We found the scope to be quite limited. Satisfactory yields were obtained with *o*-, *m*-, and *p*-methylanisole (63%, 46%, and 54% yields, respectively), 2,6-dimethylanisole (49%), and phenetole (49%). The product with phenetole is the important drug phenacetin [*N*-(4-ethoxyphenyl)acetamide], and this reaction provides a simple way to make it. *o*-Chloro- and *o*-iodoanisole and 1,2,3-trimethylbenzene gave much lower yields (25%, 8%, and 18%, respectively), while essentially no yields at all were obtained with 1,2- or 1,4-dimethoxybenzene, *o*-methoxyacetophenone, methyl *o*-methoxybenzoate, or a series of compounds PhX, where X = OH, $OCOCH_3$, $NHCOCH_3$, SCH_3, cyclohexyl, ethyl, Br, OPh, or NO_2. The scope is therefore essentially limited to alkyl aryl ethers whose aromatic group is either unsubstituted or substituted with alkyl groups. Where the reactions failed it was either because the PPA caused extensive decomposition of the aromatic substrate or because the aromatic ring was unreactive.

(c) Possible Substitutes for PPA. Because of the decomposition noted in the previous sentence, we attempted to replace PPA by other solvents. It has been reported[4] that a solution of P_2O_5 in methanesulfonic acid can substitute for PPA in other applications, but in this case, heating of anisole and acetohydroxamic acid in a 1:10 P_2O_5-methanesulfonic acid solution gave only sulfur-containing products[5] and no nitrogen-containing products. Also unsuccessful as solvents were polyphosphate ester,[6] a mixture of P_2O_5 and bromoform, and a mixture of trichloracetic acid and acetic anhydride.

Experimental Section

***N*-(4-Methoxyphenyl)acetamide.** The reaction was carried out in a 150-mL two-piece reaction flask, the upper piece of which had three necks fitted with a mechanical stirrer, a condenser, and a stopper. Polyphosphoric acid (45 g, obtained from the Research Organic/Inorganic Chemical Corp.) was placed in the lower portion of the flask, and the two pieces were clamped together. The contents of the flask were moderately stirred while being heated to 115 °C by an oil bath. Then, over a 2-min period was added 3.75 g (0.050 mol) of acetohydroxamic acid[7] and 5.41 g (0.050 mol) of anisole. The mixture was maintained at 115 °C, with vigorous stirring, for 2 h. It was then allowed to cool with moderate stirring. When room temperature was reached, the stopper was replaced by an addition funnel, and 50 mL of water was slowly added, followed by 50 mL of chloroform. The water layer was extracted several times with chloroform, the combined chloroform extracts were treated with anhydrous magnesium sulfate and activated charcoal, and the chloroform was removed by an aspirator. The resulting solid was sublimed at 130–140 °C, and the sublimed solid was recrystallized from water and then twice from *n*-butyl ether. The yield of *N*-(4-methoxyphenyl)acetamide (mp 123–123.5 °C) was 4.88 g (59%). IR spectra and VPC showed the absence of the ortho and meta isomers.

***N*-(4-Ethoxyphenyl)acetamide (Phenacetin).** The procedure was the same as above, except that 12.22 g (0.10 mol) of phenetole was used instead of anisole, 7.51 g (0.10 mol) of acetohydroxamic acid was used, and the product was recrystallized once from water and three times from *n*-butyl ether. The yield of phenacetin (mp 132.0–132.8 °C) was 8.7 g (49%). IR spectra and VPC showed the absence of the ortho and meta isomers.

Registry No. *N*-(4-Methoxyphenyl)acetamide, 51-66-1; acetohydroxamic acid, 546-88-3; anisole, 100-66-3; phenacetin, 62-44-2; phenetole, 103-73-1; *o*-methylanisole, 578-58-5; *m*-methylanisole, 100-84-5; *p*-methylanisole, 104-93-8; 2,6-dimethylanisole, 1004-66-6; *o*-chloroanisole, 766-51-8; *o*-iodoanisole, 615-37-2; 1,2,3-trimethylbenzene, 526-73-8.

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Oxyfunctionalization of Hydrocarbons. 11.[1] Hydroxylation of Benzene and Alkylbenzenes with Hydrogen Peroxide in Hydrogen Fluoride/Boron Trifluoride

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The utility of hydrogen peroxide as source of electrophilic oxygen has gained increasing importance. Various studies on electrophilic hydroxylation of aromatics have been reported, including the $AlCl_3$-catalyzed reaction with H_2O_2/urea adducts,[2] with anhydrous HF (in the presence of CO_2,[3,4] highly concentrated H_2O_2 in the presence of $AlCl_3$,[5] BF_3 etherate,[6] or strong acids[7] such as FSO_3H, FSO_3H, or FSO_3H–SbF_5/SO_2ClF), and with H_2O_2/HF_x/pyridine.[1] The major difficulty encountered was the ease of further oxidation of the initially formed hydroxyarenes to a wide range of byproducts. This was substantially decreased in superacidic FSO_3H or FSO_3H–SbF_5 systems which protonate the formed phenols.[8] However, these systems are not always easy to handle, and acid recovery is inconvenient.

We now report that 30% hydrogen peroxide with superacidic hydrogen fluoride/boron trifluoride smoothly converts benzene and alkylbenzenes into their monohydroxylated products at −78 to −60 °C in a clean reaction with a satisfactory to good yields (eq 1). No appreciable (<1%) amount of (poly)hydroxylated products are formed,

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