of guanosine and DMBA 5,6-oxide.[4b,8b]

DMBA 5,6-Oxide with Aniline in Diethyl Ether. To a solution of DMBA 5,6-oxide (0.0120 g, 0.0440 mmol) in diethyl ether (1 mL) containing methylene chloride (0.5 mL) was added a solution of aniline (0.0204 g, 0.219 mmol; 5 equiv) in diethyl ether (1 mL). After 2 h, the mixture was concentrated in vacuo at room temperature. Preparative TLC (diethyl ether) of the residue and isolation of the material with R_f 0.62 gave 0.0140 g (88%) of a mixture of adducts 1 and 2 in a ratio of 80:20 (^{1}H NMR).

DMBA 5,6-Oxide on *n*-Butylamine-Doped Alumina. DMBA 5,6-oxide (0.0071 g, 0.026 mmol) was allowed to react in diethyl ether with 0.1516 g of W-200-B alumina doped with *n*-butylamine (0.0114 g, 0.155 mmol; 6 equiv) for 2 h at ambient temperature. Workup afforded 0.0079 g (88%) of a spectroscopically clean (^{1}H NMR) mixture of regioisomeric adducts in a ratio of 3:1; mass spectrum, *m/e* 345 (parent, molecular ion). The major isomer was assigned, in a manner similar to that previously discussed for the anilino derivatives, as *trans*-5-(*n*-butylamino)-5,6-dihydro-6-hydroxy-7,12-dimethylbenz[*a*]-anthracene: ^{1}H NMR ($CDCl_3$) δ 0.75–1.50 (m, 7 H; $(CH_2)_2CH_3$), 1.50–1.75 (b, 2 H; NH, OH), 2.30–2.80 (m, 2 H; CH_2N), 2.81 (s, 3 H; 7-Me), 2.94 (s, 3 H; 12-Me), 4.48 (d, J = 3.3 Hz, 1 H; H_5), 4.93 (d, J = 3.3 Hz, 2 H; H_6), 7.25–8.25 (m, 8 H; Ar H). The minor isomer was assigned as *trans*-6-(*n*-butylamino)-5,6-dihydro-5-hydroxy-7,12-dimethylbenz[*a*]anthracene: ^{1}H NMR ($CDCl_3$) as described above with the exception of δ 3.94 (d, J = 3.2 Hz, 1 H; H_5) and 5.33 (d, J = 3.2 Hz, 1 H; H_6).

DMBA 5,6-Oxide on Methanol-Doped Alumina. DMBA 5,6-oxide (0.0385 g, 0.141 mmol) was allowed to react in diethyl ether for 2 h at ambient temperature with 1.4323 g of Woelm-200-Basic Super I activity alumina which had been doped with triethylamine (0.0200 g, 1.5%) and methanol (0.0627 g, 1.959 mmol; 14 equiv). The usual workup was effected with absolute ethanol and afforded, after filtration of the alumina and concentration of the ethanol in vacuo, 0.0417 g (97%) of a 78:22 mixture of regioisomeric methanolysis products as determined by ^{1}H NMR spectroscopy.[16] Preparative TLC (benzene/diethyl ether; 1:1) gave 0.0301 g (70%) of the mixture (R_f 0.49) in the same ratio as before chromatography. The major regioisomer **3** displayed signals (^{1}H NMR, $CDCl_3$; 300 MHz) at δ 2.8359 (s, 3 H; 7-Me) 2.9576 (s, 3 H; 12-Me), 3.3504 (s, 3 H; OMe), 5.002 (d, J = 3.38, 1 H; 5-H), 5.063 (dd, J = 3.38 and 1.36 Hz, 1 H; 6-H) and those of the minor isomer **4** were δ 2.8212 (s, 3 H; 7-Me), 2.9429 (s, 3 H; 12-Me), 3.3086 (s, 3 H; OMe), 4.428 (d, J = 2.79, 1 H; 5-H), 5.3629 (d, J = 2.79, 1 H; H-6). The remainder of the spectral information for the two isomers was indistinguishable: δ 1.88 (b s, 1 H; OH), 7.32–7.75, 8.10–8.25 (m, 8 H; Ar H).

The regiochemistry of these adducts was assigned on the basis of multiple NOE measurements as follows. Simultaneous irradiation of the 7-Me signals for both **3** and **4** resulted in enhancement of the downfield methine resonances of **3** (ca. 20%) and **4** (ca. 12%), thus establishing these as the 6-H resonance of **3** at 5.063 ppm and the 6-H resonance of **4** at 5.364 ppm. Further, simultaneous irradiation of the methoxy signals of both **3** and **4** caused enhancement of the benzylic protons at C-5 (5%) and C-6 (8%) of **3** while only the higher field methine proton at C-5 of **4** suffered enhancement (8%). Inspection of molecular models revealed that the methine proton of closer proximity to the methoxyl protons for both **3** and **4** is that which resides on that carbon that is adjacent to the methoxy-bearing carbon. Thus, the major isomer **3** is assigned as the 5-methoxy adduct while **4** is assigned as the 6-methoxy isomer in consideration of the magnitudes of the various NOE measurements. That no NOE is associated with the 6-H of **4** may be attributed to the steric congestion which would rise from interaction of the methoxy group with the 7-methyl upon close approach to the 6-H. For the major isomer **3** this type of interaction is not present and as a result both methines are enhanced but to differing extents.

Also, analysis of the chemical shifts of these adducts as described earlier for the adducts of guanosine and DMBA 5,6-oxide[4b,8b] supports these assignments in that the carbon bearing the methoxyl is shifted downfield by 0.26 ppm in **3** and 0.16 ppm in **4** relative to the dihydrodiol while the methines on adjacent benzylic positions in **3** and **4** are shifted *up*field by 0.14 and 0.31 ppm, respectively.

DMBA 5,6-Oxide with Methanol in Diethyl Ether. To a solution of DMBA 5,6-oxide (0.0050 g, 0.0183 mmol) in diethyl ether (1 mL) was added a solution of methanol (0.0121 g, 0.378 mmol; 21 equiv), and triethylamine (0.0011 g) in diethyl ether (1 mL). After 2 h, the volatiles were removed in vacuo. The residue was examined by ^{1}H NMR spectroscopy and consisted of unchanged arene oxide. A virtually quantitative recovery was obtained.

DMBA 5,6-Oxide on Water-Doped Alumina. DMBA 5,6-oxide (0.0076 g, 0.028 mmol) was allowed to react in diethyl ether with 0.5822 g of W-200-B alumina doped with distilled water (10 μL, 0.55 mmol; 20 equiv) for 2 h at ambient temperature. Workup followed by preparative TLC (diethyl ether) afforded 0.0048 g (59%) of *trans*-5,6-dihydroxy-5,6-dihydro-7,12-dimethylbenz-[*a*]anthracene:[19] ^{1}H NMR ($CDCl_3$) δ 1.50–1.80 (b s, 2 H, OH), 2.83 (s, 3 H; 7-Me), 2.93 (s, 3 H; 12-Me), 4.88 (d, J = 3,5 Hz, 1 H; H_5), 5.29 (d, J = 3.5 Hz, 1 H; H_5), 5.29 (d, J = 3.5 Hz, 1 H; H_6), 7.31–8.21 (m, 8 H; Ar H); mass spectrum, *m/e* 290 (parent, molecular ion). Treatment of this diol with acetic anhydride in pyridine at ambient temperature for 24 h followed by conventional workup afforded the trans diacetate derivative, which was recrystallized from ether/hexane (mp 199–200 °C, trans diacetate lit.[19] mp 210–211 °C, *cis* diacetate lit.[19] mp 154–156 °C) and exhibited spectral characteristics in accord with literature[19] values.

DMBA 5,6-Oxide on 2-Methyl-2-propanethiol-Doped Alumina. DMBA 5,6-oxide (0.0126 g, 0.0462 mmol) was allowed to react in diethyl ether with 0.7582 g of W-200-B alumina doped with 2-methyl-2-propanethiol (0.0208 g, 0.231 mmol) for 2 h at ambient temperature. Workup followed by preparative TLC afforded 0.0045 g (33%) of *trans*-5,6-dihydroxy-5,6-dihydro-7,12-dimethylbenz[*a*]anthracene as well as 0.0065 g (39%) of two regioisomeric addition products in a 3:1 ratio by ^{1}H NMR analysis. The predominant isomer was assigned as *trans*-5-hydroxy-6-[(2-methyl-2-propyl)thio]-5,6-dihydro-7,12-dimethylbenz[*a*]-anthracene and the minor isomer was asigned as the *trans*-6-hydroxy-5-[(2-methyl-2-propyl)thio]-5,6-dihydro derivative on the basis of ^{1}H NMR (300 MHz) data in accord with that previously noted.[19]

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Registry No. 1, 89690-57-3; 2, 89690-58-4; 3 (ZR = $PhCH_2NH$), 89690-59-5; 3 (ZR = BuNH), 89690-60-8; 3 (ZR = MeO), 89690-61-9; 3 (ZR = OH), 16644-15-8; 3 (ZR = *t*-BuS), 60731-00-2; 4 (ZR = $PhCH_2NH$), 89690-62-0; 4 (ZR = BuNH), 89690-63-1; 4 (ZR = MeO), 89690-64-2; 4 (ZR = *t*-BuS), 60731-01-3; $PhNH_2$, 62-53-3; $PhCHNH_2$, 100-46-9; $BuNH_2$, 109-73-9; MeOH, 67-56-1; H_2O, 7732-18-5; *t*-BuSH, 75-66-1; DMBA 5,6-oxide, 39834-38-3; alumina, 1344-28-1.

Preparation of Acetylenic Diethyl Acetals from the Ortho Ester $HC(OC_2H_5)_2OC_6H_5$

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The general method of reacting a monosubstituted acetylene with an ortho ester, in the presence of a zinc halide catalyst, has become routinely used for the preparation of acetylenic diethyl acetals in good to excellent yields.[1,2] However, there are some acetals that are either

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Table I. Characteristics of Acetylenic Diethyl Acetals

RMgBr, R =	solvent[a]	$RCH(OC_2H_5)_2$,[b] R =	yield (%)	bp/mmHg	n^{20}_D	NMR (δ) $HC(OC_2H_5)_2$
n-$C_4H_9C{\equiv}C$	a	n-$C_4H_9C{\equiv}C$	80	97/12	1.4370	5.05 t
$C_6H_5C{\equiv}C$	a	$C_6H_5C{\equiv}C$	90	108/4	1.5170	5.33 s
$CH_3OCH_2C{\equiv}C$	a/b	$CH_3OCH_2C{\equiv}C$	70[c]	93/11	1.4335	5.15 t
$(CH_3)_2NCH_2C{\equiv}C$	a/b	$(CH_3)_2NCH_2C{\equiv}C$	80[c]	100/10	1.4410	5.15 t
$(CH_3)_2C(OMgBr)C{\equiv}C$	a/b	$(CH_3)_2C(OH)C{\equiv}C$	85[c]	117/12	1.4415	5.10 s

[a] a = ether; b = dichloromethane. [b] All compounds gave satisfactory elemental analyses.[4] [c] In ether only complex polymeric material formed.[7]

temperature sensitive to distillation or just difficult to separate in good yields from the decomposition products that accompany such reactions, especially during prolonged distillation.[3,4] As an example, the preparation of n-butylpropiolaldehyde diethyl acetal[3] is prepared by heating an equimolar mixture of 1-hexyne and triethyl orthoformate, containing catalytic amounts of zinc chloride–zinc iodide, under autogenous pressure at 190 °C for 3 h. Under such conditions a product yield of 32% was obtained. Using the method reported here, the author has obtained n-butylpropiolaldehyde diethyl acetal in yields greater than 80%.[4,5]

The modified procedure for the general synthesis of acetylenic diethyl acetals is as follows. The commonly used ortho ester, triethyl orthoformate, is replaced by the mixed ortho ester, phenyl diethyl orthoformate [$HC(OC_2H_5)_2OC_6H_5$] and reacted at room temperature with the appropriate alkynyl Grignard reagent ($RC{\equiv}CMgBr$) in ether. This modification eliminates both the necessity for using a zinc halide catalyst and the harsh reaction conditions of distillation.

To illustrate the method, the preparation of phenylpropargylaldehyde diethyl acetal is given (yield > 90%). The optimum yield for this acetal, using ZnI_2 catalyst, is 72–78%.[3]

It is found[4-6] that polymerization occurs in the preparation of some acetylenic diethyl acetals in ether. This can be eliminated, and the appropriate diethyl acetal obtained in excellent yield (Table I), when the solvent is dichloromethane.[7]

Experimental Section

General Methods. All organometallic reactions were carried out under dry nitrogen. Reagent preparation and instrumentation have previously been reported.[5,7] Product isolation was by distillation under reduced pressure.[5] The NMR results are expressed in parts per million (δ) downfield from internal tetramethylsilane, followed by the signal shape: s, singlet, and t, triplet.

General Procedure for Preparation of Acetylenic Diethyl Acetals—Preparation of Phenylpropargylaldehyde Diethyl Acetal. To an ether solution (50 mL) of ethylmagnesium bromide (0.1 mol),[8] in a 250 mL three-necked round-bottom flask was added dropwise with stirring an ether solution (25 mL) of phenylacetylene (5.6 g, 0.055 mol). The contents were heated under reflux until evolution of ethane had ceased[5] and then left to attain room temperature.[9] To this stirred alkynyl Grignard solution was added dropwise at room temperature in its volume of ether phenyl diethyl orthoformate (7.32 g, 0.03 mol). The reaction was slightly exothermic. The contents were stirred for 4 h at room temperature and then hydrolyzed with a cold saturated aqueous solution of ammonium chloride (80 mL), followed by extraction with ether (3 × 150 mL). The organic phase was washed with 20% sodium hydroxide (2 × 10 mL) and water (100 mL) and dried over potassium carbonate. The solvent was removed under reduced pressure and the acetal isolated by vacuum distillation (5.4 g, 88%): bp 108 °C (4 mmHg); n^{20}_D 1.5170 (lit.[3] n^{25}_D 1.5153–1.5158); IR (neat) 2970 (s), 2240 (m), 2490 and 2440 (m), 1120–1000 (br, s) 755 and 690 (s); NMR (CCl_4) δ 7.53–7.06 (m, 5 H), 5.36 (s, 1 H), 4.06–3.26 (m, 4 H), 1.23 (t, 6 H).

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Registry No. n-$C_4H_9C{\equiv}CMgBr$, 32359-01-6; $C_6H_5C{\equiv}CMgBr$, 6738-06-3; $CH_3OCH_2C{\equiv}CMgBr$, 32666-87-8; $(CH_3)_2NCH_2C{\equiv}CMgBr$, 86111-72-0; $(CH_3)_2C(OMgBr)C{\equiv}CMgBr$, 920-01-4; n-$C_4H_9C{\equiv}CCH(OC_2H_5)_2$, 18232-30-9; $C_6H_5C{\equiv}CCH(OC_2H_5)_2$, 6142-95-6; $CH_3OCH_2C{\equiv}CCH(OC_2H_5)_2$, 53281-61-1; $(CH_3)_2NCH_2C{\equiv}CCH(OC_2H_5)_2$, 5799-77-9; $(CH_3)_2C(OH)C{\equiv}CCH(OC_2H_5)_2$, 25938-06-1; ethylmagnesium bromide, 925-90-6; phenylacetylene, 536-74-3; phenyl diethyl orthoformate, 14444-77-0.

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Preparation of α-Chloro Ketones from Enol Silyl Ethers with Sulfuryl Chloride Fluoride and Sulfuryl Chloride[1]

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α-Chloro ketones are versatile synthetic intermediates. They have been prepared by the reaction of the parent ketone with chlorine, N-chlorosuccinimide, copper(II) chloride, sulfuryl chloride, selenium oxychloride, or *tert*-butyl hypochlorite.[2] Chloro ketones have also been obtained by treating epoxides and enamines with a variety of electrophilic chlorinating agents such as chlorine,[3a] N-chlorosuccinimide,[3g] *tert*-butyl hypochlorite,[3a] chlorodimethylsulfonium chloride,[4] or hexachloroacetone.[5] Enol

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