1.72 g (49%) of the monohydrochloride salt (the dihydrochloride salt was found to be a noncrystallizable, hygroscopic, amorphous solid): mp 203–204 °C; $[\alpha]^{22}$ +5.7°; NMR ($CDCl_3$) δ 1.38 (d, J = 6 Hz, 3 H), 3.09 (d, J = 7 Hz, 2 H), 3.5–3.8 (m) and 3.73 (s) (total = 4 H), 4.0–4.3 (m, 1 H), 6.40 (b s, 4 H), 6.7–6.9 (m, 2 H), 7.0–7.4 (m, 7 H).

Anal. Calcd for $C_{17}H_{22}N_2O$·HCl: C 66.55; H, 7.56; N, 9.13. Found: C, 66.74; H, 7.51; N, 9.18.

(*R*,*S*)-(+)-β-[(1-Phenylethyl)amino]-4-methoxyphenethylamine (24). The compound was prepared in the same manner as **21**: mp 222–224 °C; $[\alpha]^{22}$ +165.7°; NMR ($CDCl_3$) δ 1.43 (d, J = 6 Hz, 3 H), 3.20 (d, J = 7 Hz, 2 H), 3.4–3.9 (m) and 3.80 (s) (total = 5 H), 5.90 (b s, 5 H), 6.7–7.0 (m, 2 H), 7.1–7.4 (m, 7 H).

Anal. Calcd for $C_{17}H_{22}N_2O$·HCl·0.5H_2O: C, 64.44; H, 7.95; N, 8.84. Found: C, 64.47; H, 7.81; N, 8.78.

(*R*)-(+)-2-Amino-2-(4-methoxyphenyl)ethylamine (22). A solution of 25 g (0.082 mol) of **21**·2HCl in 800 mL of methanol was added to a suspension of 5.0 g of 10% Pd/C in 400 mL of methanol at 0 °C. The mixture was then shaken under an atmosphere of hydrogen at 50 psi and 45 °C for 48 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Crystallization from methanol/ethyl ether afforded 18 g (94%) of white crystals: mp 158–159 °C; $[\alpha]^{22}$ +35.6°; NMR (CD_3OD) δ 3.6–3.8 (m, 3 H), 3.88 (s, 3 H), 7.13 (d, J = 9 Hz, 2 H), 7.67 (d, J = 9 Hz, 2 H).

Anal. Calcd for $C_9H_{14}N_2O$·2HCl: C, 45.20; H, 6.74; N, 11.71. Found: C, 44.82; H., 6.76; N, 11.55.

Acknowledgment. We thank Professor A. I. Meyers of Colorado State University for a helpful discussion.

Registry No. **1**, 87712-72-9; **2**, 87712-73-0; **3**, 87712-74-1; **4**, 87712-75-2; **5**, 87712-76-3; **6**, 87712-77-4; **7**, 87712-78-5; **8**, 87712-79-6; **9**, 87712-80-9; **10**, 87712-81-0; **11**, 87712-82-1; **12**, 87712-83-2; **13**, 87712-84-3; **13** free base, 87712-85-4; **14**, 87712-86-5; **15**, 87712-87-6; **16**, 87712-88-7; **17**, 87712-89-8; **18**, 87712-90-1; **19**, 87712-91-2; **20**, 87712-92-3; **21**·HCl, 87712-93-4; **21**·2HCl, 87712-94-5; **22**·2HCl, 87712-95-6; **24**·HCl, 87712-96-7; NaCN, 143-33-9; (*R*)-(+)-α-methylbenzylamine hydrochloride, 10277-86-8; *p*-anisaldehyde, 123-11-5.

Polycyclic Hydroxyquinones. 13.[1] A Novel Synthesis of Islandicin and Digitopurpone

Pilar Cano, Antonio Echavarren, and Pilar Prados

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Canto Blanco, Madrid-34, Spain

Francisco Fariña*

Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, Madrid-6, Spain

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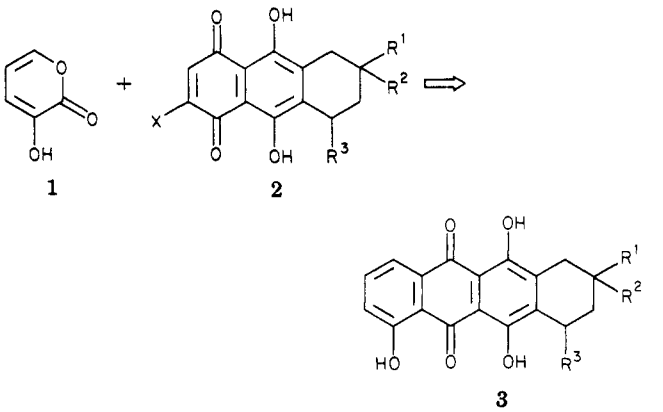
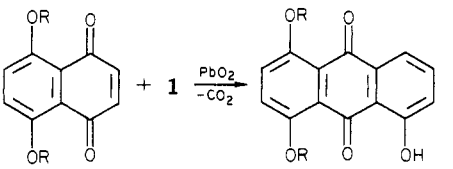
Recent interest in anthracyclines[2] is due to the useful antitumor activity which they possess and has stimulated the development of new routes to related systems and regiospecific synthesis of unsymmetrically substituted anthraquinones, which could be used as intermediates or synthetic models for anthracyclinones.

The use of 3-hydroxy-2-pyrone (1) as a diene in the Diels–Alder reaction, reported by Corey et al.,[3] could be of potential utility for the construction of the OH-substituted ring D of anthracyclinones. Thus, in view of the fact that the regiochemistry of the Diels–Alder reaction of 1 is controlled by the 3-OH group,[3] it seemed likely that the cycloaddition to an appropriate synthon of type 2 would afford tetracyclic precursors of anthracyclinones 3 in a simple and regiospecific way (Scheme I).

Scheme I



Scheme II



4, R = H
5, R = Ac

6, R = H
8, R = Ac

In the present paper we report on the Diels–Alder reaction of 3-hydroxy-2-pyrone (1) with naphthazarin (4), its diacetate (5), and adequately substituted derivatives, in order to gain more information on the reactivity of diene 1. We have also carried out a novel synthesis of the unsymmetrically substituted anthraquinones islandicin (15)[4] and digitopurpone (16)[5] which have served as models for the eventual construction of anthracyclinones.[6]

In a preliminary experiment, naphthazarin (4) and the diene 1 were refluxed in acetonitrile, affording in poor yields the known 1,4,5-trihydroxy-9,10-anthraquinone (6)[7] and 5,8-dihydroxy-2,3-dihydro-1,4-naphthoquinone (7).[8] The formation of 6 may be rationalized as a Diels–Alder reaction followed by extrusion of carbon dioxide and aromatization in the presence of the starting naphthazarin, which, in turn, is reduced to 7. In order to enhance the yield of the cyclization and to avoid the consumption of naphthazarin as an oxidant, we have conducted the reac-

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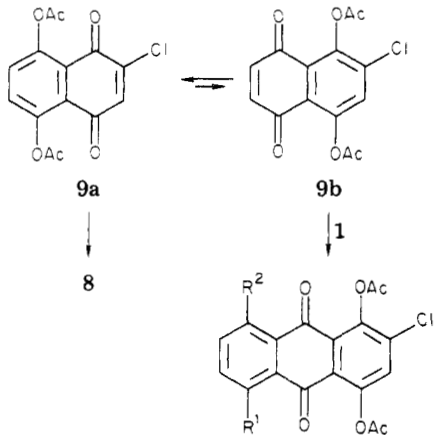
Scheme III



10, R^1 = OH; R^2 = H
11, R^1 = H; R^2 = OH

tion in the presence of an oxidizing agent such as PbO_2. Under these conditions, **4** is transformed into **6** in 27% yield, and when one starts with naphthazarin diacetate (**5**), higher yields of **8** (52%) are obtained (Scheme II).

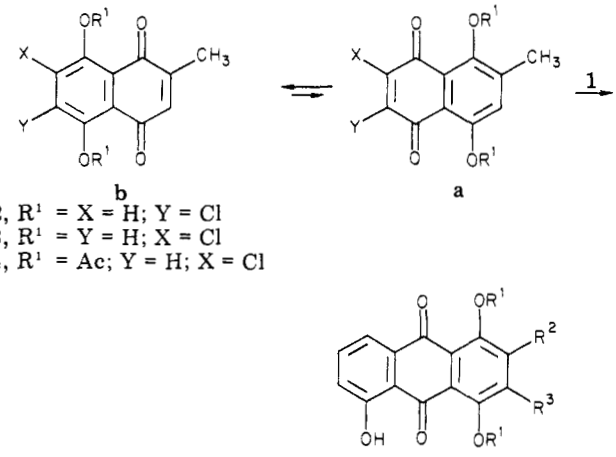
We have also attempted the introduction of a chloro-substituent attached to the quinonoid double bond, so that it could ultimately be eliminated as hydrogen chloride, yielding directly the aromatized system. The presence of the halogen in naphthazarin could also exercise an important directing effect on the adduct formation, thus allowing the preparation of regioisomers if the substituent bears a fixed relationship to other groups attached to naphthazarin nucleus.

The Diels–Alder cycloaddition of **1** with chloronaphthazarin diacetate **9** could, in principle, afford four different adducts. In fact, we have shown in a previous paper[9] that acyl migration takes place easily in diacetates of naphthazarins, thus allowing the equilibration of the two isomers **9a** and **9b**. ^{1}H NMR analysis indicates that **9a** is the predominant isomer in solution, and Diels–Alder reaction with 2,3-dimethyl-1,3-butadiene[10] or with cyclopentadiene[11] proceeds exclusively through the chlorine-containing double bond of this isomer **9a**.

However, we have now found that Diels–Alder cycloaddition of the diene **1** with chloronaphthazarin diacetate **9** proceeds through both isomers **9a** and **9b** to give ultimately a mixture of the three compounds **8**, **10**, and **11** in an approximate ratio of 1:1:1 (Scheme III). Chromatographic separation afforded compound **8**, which was shown to be identical with an authentic sample, and a mixture of the regioisomers **10** and **11**. Examination of the ^{1}H NMR spectrum of this mixture revealed the presence of both regioisomers, as indicated by two low-field singlets corresponding to chelated OH-protons at δ 12.19 and 12.16 in the ratio of 1:1. Therefore, the cycloaddition had also taken place through the unsubstituted double bond of **9b**, in contrast to our previous observations using simple dienes. The expected regioselectivity in the initial cycloaddition of **1** with **9a** was not observed because the subsequent CO_2 extrusion and HCl elimination of the initial adducts destroyed the regiochemistry, yielding **8** as the sole product.

In order to demonstrate the regioselectivity of the Diels–Alder reaction of **1** with halogenated naphthazarins,

Scheme IV



12, R^1 = X = H; Y = Cl
13, R^1 = Y = H; X = Cl
14, R^1 = Ac; Y = H; X = Cl

15, R^1 = R^3 = H; R^2 = CH_3
16, R^1 = R^2 = H; R^3 = CH_3
17, R^1 = Ac; R^2 = H; R^3 = CH_3

we have investigated the cycloaddition with 6(and 7)-chloro-2-methylnaphthazarins. In both compounds,[12] the presence of the chloro and methyl substituents could reverse the tautomer selectivity[13] of the initial cycloaddition reaction. As expected, the presence of the electron-donor methyl group at C-2 in **12b** and **13b** diminishes the reactivity of the quinonoid double bond, so that the reaction is now tautomer specific and proceeds only through the chlorine-substituted double bond of **12a** and **13a** (Scheme IV). Furthermore, the cycloaddition with **12a** and **13a** is presumably regiospecific, and the initial adducts, after extrusion of carbon dioxide and dehydrochlorination, afforded islandicin (**15**) and digitopurpone (**16**) in 20% and 16% yields, respectively. The properties of these compounds were identical with those previously reported.[4,5]

Better results were obtained by using diacetate **14** as the starting material. In fact, the reaction of hydroxypyrone **1** proceeded only with the less stable isomer **14a** obtained by transacylation from **14b**[12] and, under similar experimental conditions, afforded digitopurpone diacetate **17** in 52% yield. The ^{1}H NMR spectrum of **17** was consistent with this structure and showed one chelated HO proton at δ 12.40. Hydrolysis of **17** was accomplished by treatment with aqueous sodium hydroxyde and afforded digitopurpone (**16**) in 96% yield.

The observed regiochemistry in the above cycloadditions is consistent with previous results. In fact, Corey suggested[3] that the orientation of Diels–Alder reaction with hydroxypyrone **1** is controlled by the electron-donating 3-OH group with C-6 being the nucleophilic terminus of the diene. This terminus, with the larger HOMO coefficient, becomes attached to the unsubstituted quinonoid carbon of **12a–14a**, which presumably is the site having the largest LUMO coefficient. Similar regiospecific reactions have been observed in other halogenated quinones.[14]

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(12) The presence in the ^{1}H NMR spectra of **12** and **13** of broad signals at δ 6.98 and 6.83 for the quinonoid protons coupled with the methyl protons suggests that the predominant tautomers are **12b** and **13b**, respectively. Structure **14b** is also evidenced by a quartet at δ 6.63, the chemical shift of which is essentially the same as that for the C-3 proton in 2-methylnaphthazarin diacetate.
(13) We use the term "tautomer selective" (or "tautomer specific") to describe a reaction which proceeds predominantly (or exclusively) through one of the possible tautomers.
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Attempts to apply the cycloaddition of **1** to the synthesis of tetracyclic systems of type **3** failed to provide the desired adducts, either giving no reaction with 6-chloro-5,8-dihydroxy-1,2,3,4-tetrahydro-9,10-anthraquinone (**2**, $R^1 = R^2 = R^3 = H$; X = Cl)[15] or leading to 1,4,6-trihydroxy-9,10-anthraquinone when **2** ($R^1,R^2 = OCH_2CH_2O$; R^3 = OMe; X = H)[16] was used as the dienophile.

Nevertheless, the results reported here provide an extremely brief synthesis of islandicin and digitopurpone. Moreover, these new examples of Diels–Alder reactions with halogenated quinones prove the general utility of this methodology to control the orientation of remote substituents in the synthesis of unsymmetrical anthraquinones.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24A (60 MHz) spectrometer. Chemical shifts for $CDCl_3$ solutions are reported in parts per million (δ) downfield from Me_4Si. IR spectra were obtained on a Unicam SP-1100 spectrophotometer for Nujol mulls, unless otherwise stated. UV–vis spectra were determined on a Perkin-Elmer 124 instrument for ethanol solutions. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6MG spectrometer. Preparative and analytical thin-layer chromatography (TLC) were carried out on deactivated silica gel (DSG) plates prepared with 0.05 M KH_2PO_4 instead of water.[17] The 3-hydroxy-2-pyrone (**1**) was prepared by dehydration ($KHSO_4$ as catalyst) of mucic acid.[18]

1,4,5-Trihydroxy-9,10-anthraquinone (6). Method A. A solution of 5,8-dihydroxy-1,4-naphthoquinone (**4**; 270 mg, 1.4 mmol) and hydroxypyrone **1** (420 mg, 3.7 mmol) in dry acetonitrile (50 mL) was refluxed for 4 days and evaporated. The residue showed two spots by analytical TLC (DSG, benzene). Preparative TLC of the mixture gave quinone **6** (26 mg, 7%) as an orange solid [mp 274–275 °C (from pyridine) (lit.[7] mp 271 °C)] and 5,8-dihydroxy-2,3-dihydro-1,4-naphthoquinone (**7**; 20 mg, 7%) as a colorless solid, mp 151–154 °C (lit.[8] mp 154 °C). This compound was identified by comparison with an authentic sample prepared by reduction of naphthazarin (**4**).[8]

Triacetate of 6. Compound **6** (26 mg, 0.1 mmol) was acetylated by treatment with Ac_2O (2.5 mL) and 1 drop of sulfuric acid at room temperature for 10 min. The mixture was poured into water–ice, and the resulting precipitate was filtered off to yield 1,4,5-triacetoxy-9,10-anthraquinone: 30 mg (80%); mp 226–227 °C (from methanol) (lit.[7] mp 225 °C).

Tetraacetate of 7. 5,8-Dihydroxy-2,3-dihydro-1,4-naphthoquinone (**7**; 20 mg, 0.1 mmol) was acetylated (2.5 mL of Ac_2O, 1 drop of sulfuric acid, room temperature, 10 min) and after the usual workup gave the 1,4,5,8-tetraacetoxynaphthalene: 37 mg (100%); mp 276–277 °C (from ethanol) (lit.[19] mp 277–278 °C).

Method B. To a solution of quinone **4** (440 mg, 2.3 mmol) and hydroxypyrone **1** (300 mg, 3 mmol) in dry acetonitrile (50 mL) was added PbO_2 (500 mg, 2 mmol), and the mixture was refluxed until the starting quinone disappeared (4 days). The progress of the reaction was monitored by TLC on DSG with benzene as the eluant. The reaction mixture was concentrated on a rotatory evaporator, the residue was extracted in a Soxhlet apparatus with benzene, and the solvent was removed. The crude reaction product was purified by column chromatography (DSG, benzene) and recrystallized from pyridine to afford the pure quinone **6** (160 mg, 27%) as orange-red crystals, mp 274–275 °C (lit.[7] mp 271 °C), identical with the compound prepared above.

1,4-Diacetoxy-5-hydroxy-9,10-anthraquinone (8). The compound was obtained by starting with 670 mg (2.5 mmol) of quinone **5** and 500 mg (4.5 mmol) of **1** and using method B (reaction time 21 h; analytical TLC, benzene–ethyl acetate, 2:1). Purification of the crude reaction product by recrystallization from carbon tetrachloride afforded pure **8**: 440 mg (52%); mp 202–203 °C; IR ν_{max} 1770, 1676, 1647, 1600, 1585, 1250, 1200 cm^{-1}; ^1H NMR δ 2.42 (s, 3 H), 2.43 (s, 3 H), 7.23 (m, 1 H), 7.37 (br s, 2 H), 7.57 (m, 1 H), 7.65 (m, 1 H), 12.42 (s, 1 H); MS, *m/e* 340 (M^+, 1.5) 298, 256 (100), 220 (m*), 261 (m*). Anal. Calcd for $C_{18}H_{12}O_7$: C, 63.5; H, 3.6. Found: C, 63.4; H, 3.6.

The compound **8** prepared above (72 mg, 0.2 mmol) was acetylated (3 mL of Ac_2O, 1 drop of sulfuric acid, room temperature, 10 min) and after the usual workup gave 1,4,5-triacetoxy-9,10-anthraquinone: 81 mg (100%); mp 226–227 °C (from methanol) (lit.[7] mp 225 °C).

Diels–Alder Reaction of 3-Hydroxy-2-pyrone with Chloronaphthazarin Diacetate. Method B was followed by starting with quinone **9** (370 mg, 1.2 mmol) and hydroxypyrone **1** (370 mg, 3.3 mmol) (reaction time 48 h; analytical TLC, benzene–ethyl acetate, 9:1). Separation of the crude reaction mixture by column chromatography (using DSG for TLC; toluene–ethyl acetate, 10:1) afforded, in the order of elution, a 1:1 mixture (evaluated by ^1H NMR) of **10** + **11** (120 mg, 27%) as a yellow solid [mp 202–204 °C (from carbon tetrachloride)] and pure 1,4-diacetoxy-5-hydroxy-9,10-anthraquinone [**8**: 55 mg (13%); mp 202–203 °C (from carbon tetrachloride)], identical with the compound prepared above. Spectral data for **10** + **11**: IR ν_{max} 1769, 1760, 1639, 1577, 1188–1167 cm^{-1}; ^1H NMR δ 2.44 (s, 3 H), 2.45 (s, 3 H), 2.49 (s, 3 H), 2.50 (s, 3 H), 7.31 (s, 1 H), 7.60 (m, 3 H), 12.16 (s, 1 H), 12.19 (s, 1 H); MS, *m/e* 374 (M^+,1), 376 (0.4), 332, 290 (100), 255, 253 (m*). Anal. Calcd for $C_{18}H_{11}O_7Cl$: C, 57.7; H, 3.0; Cl, 9.5. Found: C, 56.9; H, 3.0; Cl, 9.5).

1,4,5-Trihydroxy-2-methyl-9,10-anthraquinone (Islandicin) (15). The compound was prepared by using method B and starting with 400 mg (1.7 mmol) of 6-chloro-5,8-dihydroxy-2-methyl-1,4-naphthoquinone (**12**)[20] and 330 mg (3 mmol) of hydroxypyrone **1** (reaction time 8 days; analytical TLC, benzene–hexane, 2:3). Purification of the crude product by column chromatography (DSG, benzene–hexane, 2:3) and recrystallization from chloroform–hexane afforded pure islandicin (**15**): 85 mg (20%); bright red crystals; mp 219–220 °C (lit.[4] mp 218 °C); IR ν_{max} 1610 cm^{-1}; UV–vis λ_{max} 232, 252, 287, 460 (sh), 480 (sh), 492, 513, 527 nm; MS, *m/e* 270 (M^+, 100).

1,4,5-Trihydroxy-3-methyl-9,10-anthraquinone (Digitopurpone, 16). The compound was obtained by using method B and starting with 500 mg (2.1 mmol) of 7-chloro-5,8-dihydroxy-2-methyl-1,4-naphthoquinone (**13**)[20] and 415 mg (3.7 mmol) of hydroxypyrone **1** (reaction time 12 days; analytical TLC, benzene–hexane, 1:1). Purification of the crude product by column chromatography (DSG, benzene–hexane, 2:3) and recrystallization from chloroform–hexane afforded pure digitopurpone (**16**): 90 mg (16%); red crystals; mp 209–210 °C (lit.[5] mp 209 °C); IR ν_{max} 1610 cm^{-1}; UV–vis λ_{max} 233, 254, 289, 468 (sh), 482 (sh), 493, 514, 528 nm; MS, *m/e* 270 (M^+, 100).

5,8-Diacetoxy-7-chloro-2-methyl-1,4-naphthoquinone (14). A solution of quinone **13** (500 mg, 1.5 mmol) in acetic anhydride (10 mL) containing 2 drops of sulfuric acid was stirred at room temperature for 1.5 h; the yellow solid which formed was filtered, and the solution was poured into water–ice. The resulting precipitate and the solid were combined, washed, and dried to give 630 mg (92%) of diacetate **14**: mp 165–167 °C (from methanol); IR ν_{max} 1780, 1670, 1580, 1260–1160 cm^{-1}; ^1H NMR δ 2.1 (br s, 3 H), 2.47 (s, 6 H), 6.63 (q, 1 H), 7.43 (s, 1 H); MS, *m/e* 280 (M^+ – 42, 12), 238 (100), 203. Anal. Calcd for $C_{15}H_{11}O_6Cl$: C, 55.8; H, 3.4; Cl, 11.0. Found: C, 55.3; H, 3.4; Cl, 11.1.

1,4-Diacetoxy-5-hydroxy-3-methyl-9,10-anthraquinone (17). Method B was followed by starting with 500 mg (1.5 mmol) of quinone **14** and 346 mg (3.1 mmol) of hydroxypyrone **1** (reaction time 9 days; analytical TLC, benzene–ethyl acetate, 9:1). Purification by crystallization from methanol afforded pure quinone **17** [182 mg (52%); yellow solid; mp 185–186 °C] and recovered starting quinone **14**: 190 mg; IR (KBr) ν_{max} 1770, 1675, 1650, 1220–1170 cm^{-1}; UV–vis λ_{max} 253, 281 (sh), 379 (sh), 399 (sh), 409, 419 (sh), 432 (sh) nm; ^1H NMR δ 2.35 (s, 3 H), 2.50 (s, 6 H), 7.35 (s, 1 H), 7.55–7.80 (m, 3 H), 12.40 (s, 1 H); MS, *m/e* 312 (M^+ –

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42, 10), 270 (100), 234 (m*). Anal. Calcd for $C_{19}H_{14}O_7$: C, 64.4; H, 4.0. Found: C, 64.2; H, 4.0.

The above compound **17** (16 mg, 0.04 mmol) was treated with 2 mL of 3% aqueous sodium hydroxide, and the mixture was stirred at room temperature for 45 min. The mixture was acidified with 3% hydrochloric acid; the resulting red precipitate was collected and, after recrystallization from chloroform–hexane (2:3), afforded 11 mg (96%) of digitopurpone (**16**), mp 210 °C, identical with a sample of the compound prepared above.

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Registry No. **1**, 496-64-0; **4**, 475-38-7; **5**, 14569-45-0; **6**, 2961-04-8; **6** triacetate, 75314-06-6; **7**, 4988-51-6; **7** tetraacetate, 6047-49-0; **8**, 87712-25-2; **8** acetate, 75314-06-6; **9a**, 78226-68-3; **9b**, 87712-26-3; **10**, 87712-27-4; **11**, 87712-28-5; **12b**, 14554-10-0; **13b**, 13720-75-7; **14b**, 87712-29-6; **15**, 476-56-2; **16**, 34425-57-5; **17**, 87728-26-5.

Regioselective Synthesis of Trimethylsilyl-Substituted α-Allenic Alcohols via Propargylic Organoboranes

Kung K. Wang,* Sham S. Nikam, and Chihmei D. Ho

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

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The chemistry of propargylic anions of 1-(trimethylsilyl)-1-alkynes has received considerable attention in recent years.[1] Various organometallic reagents (M = Li, Mg, Al, Si, Ti, Cu, Zn, Sn) have been used to control the regio- and stereoselectivity of the condensation reactions with aldehydes and ketones. We now report that the propargylic organoborane intermediates[2] derived from the corresponding lithium reagents react with aldehydes and certain ketones with high regioselectivity to form the corresponding trimethylsilyl-substituted α-allenic alcohols.

A general reaction sequence is outlined in Scheme I. Metalation of 1-(trimethylsilyl)propyne with *tert*-butyllithium by the procedure described previously (THF, 0 °C, 1 h)[1a] afforded the lithium reagent **1**. Treatment of **1** with 1 equiv of *B*-methoxy-9-borabicyclo[3.3.1]nonane (0 °C, 35 min) followed by the addition of $^4/_3$ equiv of $BF_3{\cdot}OEt_2$ (0 °C, 15 min)[3] provided the corresponding propargylic organoborane **3**. To the reaction mixture were then added aldehydes or ketones (room temperature, 1.5 h), which on oxidative workup gave the corresponding trimethylsilyl-substituted α-allenic alcohols **5** in excellent isolated yields (Table I). None of the corresponding β-acetylenic alcohols were detected.[4] The reactions of aldehydes and ketones with **3** to form α-allenic alcohols were assumed to proceed through a six-center electronic transfer with propargylic–allenic rearrangement as proposed previously.[2f] The reactions with **4** under similar conditions at room temperature were much less regioselective. For example, the reaction of hexanal with **4** gave a 35:65 mixture of α-allenic alcohol and β-acetylenic alcohol, whereas a 50:50 mixture was observed for acetone. However, the regioselectivity of the reaction was found to be dramatically affected by the reaction temperature. Thus, when the reaction with **4** was carried out at −78 °C and slowly warmed to room temperature, α-allenic alcohols were predominantly obtained as the products with all the aldehydes used and certain ketones (Table I).[4]

It is interesting to note from Table I that **3** and **4** exhibited some unusual characteristics. Both aldehydes and ketones reacted with **3** to form the corresponding α-allenic alcohols. This is in sharp contrast with the fact that the condensations of ketones with the propargylic titanium reagent derived from 1-(trimethylsilyl)propyne were unsuccessful.[1a] It was also indicated that the propargylic organoboranes derived from lithium chloropropagylide and trialkylboranes reacted with ketones to give mixtures of α-allenic and β-acetylenic alcohols.[2a,5] The high regioselectivity for the formation of α-allenic alcohols from **4** at low temperature is also markedly different from that of the titanium reagent derived from 1-(trimethylsilyl)-1-

Scheme I

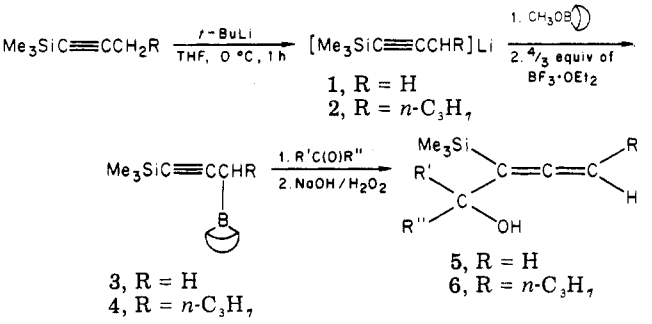

Table I. Reactions of Representative Aldehydes and Ketones with 3 and 4

R	R′	R″	isolated yield of 5 or 6,[a-c] %
H	n-C_5H_{11}	H	82
	i-C_3H_7	H	82
	t-C_4H_9	H	85
	C_6H_5	H	88
	(E)-CH_3CH=CH	H	79
	CH_3	CH_3	86
	C_2H_5	C_2H_5	91
	-$(CH_2)_5$-		91
	CH_3	C_6H_5	93
n-C_3H_7	n-C_5H_{11}	H	78 (88:12)
	i-C_3H_7	H	74 (88:12)
	C_6H_5	H	72 (87:13)
	CH_3	CH_3	71 (91:9)
	C_2H_5	C_2H_5	75 (83:17)
	-$(CH_2)_5$-		76 (91:9)
	CH_3	C_6H_5	88 (54:46)

[a] Isolated pure materials by vacuum distillation of 10-mmol reactions. [b] Combined yields of α-allenic alcohols and β-acetylanic alcohols in **6**. [c] The numbers in parentheses are ratios of α-allenic alcohols:β-acetylenic alcohols determined by GLC.

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