Table I. Coupling Reactions of Allyl- and Acetonyltin Reagents[a]

ester	X	allyltin reagent	conditions T, °C	conditions time, h	solvent	isolated yield, %
	I	n-$Bu_3SnCH_2CH{=}CH_2$	30	20	THF	97
				45		0[b,c]
				45		54[d]
		n-$Bu_2Sn(CH_2CH{=}CH_2)_2$	30	1	THF	87
	Br	n-$Bu_3SnCH_2CO{-}CH_3$	50	12	THF	73
						35[b]
						0[d]
	I		50	12	THF	82
						72[b]
						81[d]
XCH_2CO_2Et	Br	n-$Bu_3SnCH_2CH{=}CH_2$	50	18	THF	0
			100	13	$C_6H_5CH_3$	36
		n-$Bu_2Sn(CH_2CH{=}CH_2)_2$	90	24	$C_6H_5CH_3$	38
			100	6		67
		n-$Bu_3SnCH_2CO{-}CH_3$	100	9	$C_6H_5CH_3$	41
			50	48	THF	21

[a] Reactions were catalyzed with 1 mol % bis(triphenylphosphino)dichloropalladium(II) based on the halo ester. [b] 1 mol % galvinoxyl based on the halo ester was added. [c] The same result was obtained when 1 mol % of 1,4-cyclohexadiene based on the halo ester was added. [d] The palladium catalyst was omitted.

noxyl. Thus, it appears to proceed primarily via a palladium-catalyzed mechanism.

This coupling reaction with the acetonyltin reagent represents a much improved procedure for the synthesis of α-acetonyl-γ-butyrolactone,[7] which had previously been obtained by the thiazolium salt catalyzed addition of acetaldehyde to α-methylene-γ-butyrolactone.

Experimental Section

α-Acetonyl-γ-butyrolactone. To a dry Schlenk tube under nitrogen was added 35.1 mg (0.0501 mmol) of dichlorobis(triphenylphosphine)palladium(II), 0.825 g (5.00 mmol) of α-bromo-γ-butyrolactone, and 5.0 mL of dry tetrahydrofuran (distilled from sodium/benzophenone). After mixture was stirred for 15 min at 50 °C, 2.87 g (7.50 mmol) of acetonyltributyltin[9] was added to the yellow suspension. The resulting homogeneous yellow solution was stirred for 12 h at 50 °C and cooled to room temperature, and the solvent was removed under reduced pressure. The resulting oil was dissolved in 25 mL of acetonitrile and washed with hexane (3 × 10 mL). Removal of the acetonitrile gave an oil which was further purified by radial chromatography (chromatotron,[10] 50% ethyl acetate/hexane). Bulb-to-bulb distillation (64–70 °C (0.1 mmHg) [lit.[8] 102 °C (0.25 mm Hg)] yielded 0.515 g (73%) of α-acetonyl-γ-butyrolactone: ^1H NMR (270 MHz, $CDCl_3$) δ 1.86–2.02 (m, 2 H), 2.21 (s, 3 H), 2.48–2.59 (m, 2 H), 2.69 (dd, J = 8, 18 Hz, 1 H), 2.90–2.98 (m, 1 H), 3.08 (dd, J = 3, 18 Hz, 1 H), 4.23 (dt, J = 7, 10 Hz, 1 H), 4.40 (dt, J = 2, 9 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) 28.6, 29.7, 34.9, 43.5, 66.4, 178.5, 205.1; IR (neat) 1760, 1705 cm^{-1}; mass spectrum, m/z (relative intensity) 142 (M^+, 0.7).

The same procedure was used for the reaction of α-iodo-γ-butyrolactone.[11]

α-Allyl-γ-butyrolactone. A similar reaction procedure was employed for the coupling of tributylallyltin[12] with the α-halo-γ-butyrolactones. After partitioning between acetonitrile and hexane, the resulting oil was further purified by radial chromatography using (40% ethyl acetate/hexane). Bulb-to-bulb distillation (20 °C (0.025 mmHg) [lit.[13] bp 90 °C (7 mmHg)] gave the desired product:[13] ^1H NMR (270 MHz, $CDCl_3$) δ 1.87–2.12 (m, 1 H), 2.12–2.51 (m, 2 H), 2.51–2.78 (m, 2 H), 4.15–4.39 (m, 2 H), 5.07–5.21 (m,2 H), 5.68–5.92 (m, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) 27.7, 34.2, 38.7, 66.3, 117.4, 134.4, 178.4; IR (neat) 3078, 1766, 1641 cm^{-1}.

Acknowledgment. This research was supported by Grant CHR-8305468 from the National Science Foundation. The palladium chloride was provided under the Johnson-Matthey Metal Loan Program.

Registry No. $Bu_3SnCH_2COCH_3$, 14583-98-3; $Bu_3SnCH_2CH{=}CH_2$, 24850-33-7; $Bu_3Sn(CH_2)_2Ph$, 14775-15-6; $Bu_3Sn(CH_2)CN$, 17729-59-8; $Ph(CH_2)_3CO_2Et$, 10031-93-3; $BrCH_2CO_2Et$, 105-36-2; $Bu_2Sn(CH_2CH{=}CH_2)_2$, 15336-98-8; $CH_2{=}CH(CH_2)_2CO_2Et$, 1968-40-7; $CH_3CO(CH_2)_2CO_2Et$, 539-88-8; Bu_3SnPh, 960-16-7; $Bu_3SnCH{=}CH_2$, 7486-35-3; $PhCH_2CO_2Et$, 101-97-3; $CH_2{=}CHCH_2CO_2Et$, 1617-18-1; $NC(CH_2)_2CO_2Et$, 10137-67-4; α-bromo-γ-butyrolactone, 5061-21-2; α-phenyl-γ-butyrolactone, 6836-98-2; galvinoxyl, 2370-18-5; 1,4-cyclohexadiene, 628-41-1; α-acetonyl-γ-butyrolactone, 71385-84-7; α-iodo-γ-butyrolactone, 31167-92-7; α-allyl-γ-butyrolactone, 10491-63-1; α-vinyl-γ-butyrolactone, 43142-60-5; α-(2-phenylethyl)-γ-butyrolactone, 3454-79-3; α-(cyanomethyl)-γ-butyrolactone, 932-48-9.

(7) (a) Lloyd, R. A.; Miller, C. W.; Roberts, D. L.; Giles, J. A.; Dickerson, J. P.; Nelson, N. H.; Rix, C. E.; Ayers, P. H. *Tob. Int.* **1976**, *20*, 125. (b) Sakuma, H.; Sugawara, S. *Agric. Biol. Chem.* **1979**, *43*, 1585.
(8) Stetter, H.; Basse, W.; Nienhaus, J. *Chem. Ber.* **1980**, *113*, 690.
(9) Pereyre, M.; Bellegarde, B.; Mendelsohn, J.; Valade, J. *J. Organomet. Chem.* **1968**, *11*, 97.
(10) Harrison Research, 840 Moana Ct., Palo Alto, CA.
(11) Daremon, C.; Rambaud, R. *Bull. Soc. Chim. Fr.* **1971**, 294.
(12) Daude, G.; Ereyre, M. *J. Organomet. Chem.* **1980**, *190*, 43.
(13) Meyers, A. I.; Yamamoto, Y.; Mihelich, E. D.; Bell, R. A. *J. Org. Chem.* **1980**, *45*, 2792.

Synthesis of Chrysene, 5-Substituted Chrysenes, and Chrysene Derivatives via Intramolecular Cycloaddition Reactions

Louis A. Levy* and V. P. Sashikumar

National Institute of Environmental Health Sciences, Laboratory of Molecular Biophysics, Research Triangle Park, North Carolina 27709

Received July 11, 1984

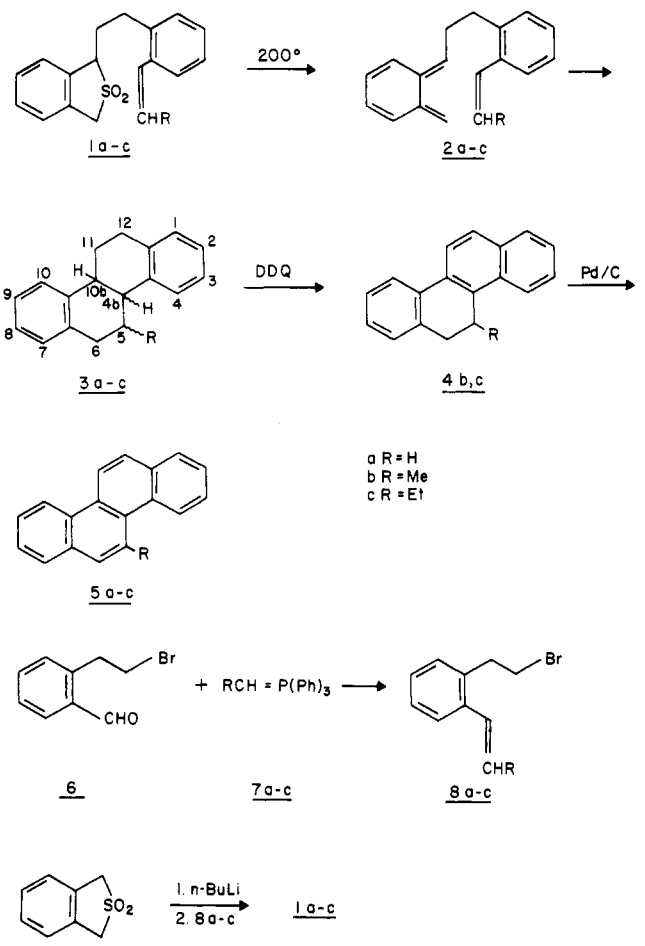
The chemistry of polynuclear aromatic hydrocarbons has been of continuing interest due to their widespread environmental distribution and the causal relationship between exposure and tumor production. An often-studied representative class of these compounds is the chrysene family. While chrysene is itself only weakly biologically active, 5-substituted chrysenes are much more potent in assays for mutagenic and carcinogenic activity.[1]

Several approaches to the synthesis of this class of compounds have been reported recently.[2] Our success

(1) Hecht, S. S.; Loy, M.; Hoffmann, D. "Carcinogenesis" Frendenthal, R., Jones, P. W., Eds.; Raven Press: New York, 1976; Vol. 1, pp 325–340.

0022-3263/85/1950-1760$01.50/0

Scheme I



with intermolecular Diels–Alder reactions of *o*-quinodimethanes to prepare benzanthracenes[3] and the considerable success by several groups of the use of this cycloaddition process in an intramolecular sense to synthesize complex polycyclic structures[4] suggested such a course for the synthesis of chrysene and chrysene derivatives (Scheme I). Alkylated *o*-quinodimethanes similar to **2** have been generated by a number of methods including cheletropic expulsion of SO_2 from an appropriately alkylated benzothiophene *S,S*-dioxide.[4]

For the application of this approach to the synthesis of the chrysene nucleus benzothiophene *S,S*-dioxide[5] (**9**) could be readily alkylated with intermediates of type **8** which are themselves prepared via Wittig condensation with 2-(2-bromoethyl)benzaldehyde[6] (**6**) as a mixture of *E* and *Z* isomers. The resultant alkylated sulfones **1** are smoothly converted to hexahydrochrysene derivatives **3** in boiling trichlorobenzene. In the case of the unsubstituted hexahydrochrysene **3a** (R = H) the product was isolated as a 2.1/1 mixture of two isomers corresponding to trans and cis stereochemistry at the ring junction. The known trans isomer[7a] could be isolated, but the structure of the minor isomer was assigned on the basis of its mass spectrum obtained by combined GLC/MS and the fact that dehydrogenation of the mixture to give chrysene proceeds in high yield. This mixture of stereoisomers occurs via the intervention of both exo and endo transition states in the cycloaddition, a phenomenon which has been observed in other examples of reactions of this type.[8] The partioning between the two possible transition states has been noted to be a sensitive function of the molecular geometry.[9] Transformation of the intermediates **1b** and **1c** to the substituted hexahydrochrysenes **3b** and **3c** occurred in a similarly smooth fashion, but here the product mixture was more complex since in addition to the production of stereoisomers arising from the newly created ring junction another stereocenter is created at the substituted C-5 position of chrysene since the olefinic moiety of the alkylated sulfone was itself a mixture of *E* and *Z* isomers. The stereoisomers could be observed by GLC/MS but no separation or further characterization was attempted since this complexity is eliminated in the next step. Dehydrogenation with Pd/C occurs smoothly and in high yield to produce the C-5 alkylated chrysenes.[5] Oxidation of hexahydrochrysene with DDQ in benzene yields the fully aromatic chrysene. However, with C-5 substituted hexahydrochrysenes oxidation with this reagent stops at the 4,5-dihydro-5-alkylchrysene **4b** and **4c**. 5-Methyl-5,6-dihydrochrysene (**4b**) was obtained crystalline[7b] and its ^1H NMR spectrum showed that it existed in a conformation with the methyl substituent at C-5 in a quasi-axial position. The values of 1.7 and 5.6 Hz found for the coupling between H-5 and the protons at C-6 are evidence for the proton at C-5 being in a quasi-equatorial orientation[10] with the substituent then occupying the quasi-axial orientation. The C-5 ethyl substituent in **4c** exists in a similar position. This conformational preference is due to the absence of steric interaction between the C-5 substituent and H-1 when the substituent is in a quasi-axial orientation.

Experimental Section

NMR spectra were obtained with either a Varian CFT-20 or a Nicolet 360 spectrometer in deuteriochloroform and are reported in ppm from Me_4Si. Mass spectra were obtained with a VG Model 7070 spectrometer. High-resolution measurements were obtained on purified samples, homogeneous by GLC and/or TLC, at 8–10K resolution by peak matching. Column chromatography was carried out with silica gel unless otherwise stated. Gas chromatography was performed on a Varian 2700 instrument equipped with a 6 ft × $^1/_8$ in OV-101 column.

***o*-(2-Bromoethyl)styrene (8a).** To a stirred suspension of 8.0 g of methyltriphenylphosphonium bromide (22 mmol) in 150 mL of tetrahydrofuran, at room temperature and maintained in an inert atmosphere, was added 2.24 g (20 mmol) of potassium *tert*-butoxide in several portions. After 0.5 h of stirring the resulting ylide was transferred to an addition funnel and added dropwise to a solution of 4.23 g (20 mmol) of *o*-(2-bromoethyl)-benzaldehyde[5] in 20 mL of THF. The bright yellow color of the ylide disappeared upon addition to the aldehyde and upon completion of the addition the solution had only a very faint color. After 2 h of stirring, the mixture was filtered and the solvent was removed on a rotary evaporator. The residue was dissolved in ether, washed with water and brine, and dried (Na_2SO_4). The solvent was removed and the crude product chromatographed (hexane) to yield 3.4 g (81%) of olefin as a colorless oil; homo-

(2) (a) Amin, S.; Camanzo, J.; Huie, K.; Hecht, S. S. *J. Org. Chem.* **1984**, *49*, 389. (b) LeHoullier, C. S.; Gribble, G. *J. Org. Chem.* **1983**, *48*, 1682. (c) Lee-Ruff, E.; Hopkinson, A. C.; Dao, L. H. *Can. J. Chem.* **1981**, *59*, 1675. (d) Lyle, T. A.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 4933. (e) Gore, P. H.; Kamonah, F. S. *Synthesis* **1978**, 773.

(3) (a) Levy, L. A.; Pruitt, L. *J. Chem. Soc., Chem. Commun.* **1980**, *227*. (b) Levy, L. A.; Kumar, S. *Tetrahedron Lett.* **1983**, *24*, 1221.

(4) (a) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 2017. (b) Nicolau, K. C.; Barnett, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463.

(5) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266.

(6) Rieche, A.; Schmitz, E. *Chem. Ber.* **1956**, *89*, 1254.

(7) (a) Harvey, R. G. *J. Org. Chem.* **1971**, *36*, 3306. (b) Neither a melting point nor a ^1H NMR spectrum was reported for this compound.

(8) Oppolzer, W.; Robiani, C. *Helv. Chim. Acta* **1983**, *66*, 1119.

(9) (a) Ito, Y.; Nakago, E.; Nakatsuka, M.; Saegusa, T. *Tetrahedron Lett.* **1983**, *24*, 2881. (b) Funk, R. L.; Vollhardt, K. P. C. *Chem. Rev.* **1980**, 41.

(10) Jerina, D. M. Selander, H.; Yagi, H.; Wells, M. C.; Davey, J. F.; Mahadevan, V.; Gibson, D. T. *J. Am. Chem. Soc.* **1976**, *98*, 5988.

geneous by GC and TLC: NMR (360 MHz) 3.23 and 3.49 (2 t, 7.9 and 8.2 Hz, 2 H each, $ArCH_2CH_2Br$), 5.35 (dd, J = 11 and 1.3 Hz, 1 H, $ArCH{=}CH_ZH_E$), 5.67 (dd, J = 17.3 and 1.3 Hz, 1 H, $ArCH{=}CH_ZH_E$), 6.96 (dd, J = 17 and 11 Hz, 1 H, $ArCH{=}CH_2$), 7.3 (m, 4 H, Ar); mass spectrum, m/e (relative intensity) 212 (20), 210 (20), 131 (100), 117 (65), 115 (65), 91 (60); calcd for $C_{10}H_{11}{}^{81}Br$ 212.0041, found 212.0052.

o-(2-Bromoethyl)propenylbenzene (8b). In a similar manner, using ethyltriphenylphosphonium bromide, there was obtained in 87% yield a 4.8/1 E/Z mixture of olefin product as a colorless liquid. The gas chromatogram, which displayed only two peaks, was consistent with this product ratio: NMR (360 MHz) 1.72 (dd, J = 7 and 1.8 Hz, 3 H, $CH{=}CHMe$), 1.92 (dd, J = 6.6 and 1.7 Hz, 3 H, $CH{=}CHMe$), 3.1–3.3 and 3.5–3.6 (2 m, 2 H each, $ArCH_2CH_2Br$), 5.88 (dq, J = 11.4 and 7 Hz, 1 H, $CH{=}CH_ZMe$), 6.14 (dq, J = 15.5 and 6.6 Hz, 1 H, $CH{=}CH_EMe$), 6.57 and 6.62 (m, 1 H, $CH{=}CHMe$), 7.2 (m, 4 H, Ar); mass specturm, m/e (relative intensity) 226 (25), 224 (25), 145 (100), 131 (65); calcd for $C_{11}H_{13}{}^{79}Br$ 224.0201, found 224.0210.

o-(2-Bromoethyl)butenylbenzene (8c). This material was likewise obtained as a clear liquid in 82% yield as a 3.3/1 mixture of E and Z isomers using propyltriphenylphosphonium bromide: NMR (360 MHz) 0.98 and 1.11 (2 t, J = 7.4 Hz, 3 H, CH_2Me), 2.13 and 2.27 (2 m, 2 H, $CH{=}CHCH_2Me$), 3.18 and 3.48 (m, 2 H each, $ArCH_2CH_2Br$), 5.70 (dt, J = 7.4 and 11.7 Hz, 1 H, $CH{=}CH_ZEt$), 6.18 (dt, J = 7.4 and 16 Hz, 1 H, $CH{=}CH_EEt$), 6.46 (d with further splitting, J = 11 Hz, 1 H, $ArCH_Z{=}CHEt$), 6.62 (d with further splitting, J = 16 Hz, 1 H, $ArCH_E{=}CHEt$), 7.18 (m, 4 H Ar); mass spectrum, m/e (relative intensity) 240 (30), 238 (30), 159 (30), 131 (70), 117 (100), 91 (40); calcd for $C_{12}H_{15}{}^{79}Br$ 238.0358, found 238.0344.

Alkylation of 1,3-Dihydrobenzo[c]thiophene S,S-Dioxide. General Procedure. A solution of n-butyllithium (11.4 mL, 1.6 M, 18.2 mmol) in hexane was added dropwise to a solution of 1,3-dihydrobenzo[c]thiophene S,S-dioxide[8] (2.51 g, 18 mmol) in 100 mL of THF at −78 °C and maintained below −40 °C during the course of the addition. After the addition was complete the solution was cooled to −78 °C and the appropriate alkyl bromide (17 mmol) was added all at once. The reaction mixture was allowed to warm to room temperature over a 2-h period. The THF was removed, 100 mL of water was added to the residue, and the mixture was neutralized with dilute HCl. The product was extracted with chloroform (3 × 50 mL), the organic phase was washed with water and dried, and the solvent was removed to obtain the crude product. This material was chromatrographed on silica gel and eluted, first with hexane to remove any unreacted bromide and then with methylene chloride to yield monoalkylated product.

o-[2-(1,3-Dihydrobenzo[c]thien-1-yl)ethyl]styrene S,S-Dioxide (1a). This compound is obtained in 85% yield as crystalline material: mp 119–121 °C ($CHCl_3$); NMR (80 MHz) 2.28 (m, 2 H, $ArCH_2CH_2$) 3.02 (m, 2 H, $ArCH_2CH_2$), 4.33 (br, 3 H, $CHSO_2CH_2$), 5.34 (dd, J = 11 and 1.6 Hz, 1 H, $ArCH{=}CH_EH_Z$) 5.67 (dd, J = 18 Hz and 1.4 Hz, 1 H, $ArCH{=}CH_EH_Z$), 7.02 (partially obscured dd, J = 11 and 18 Hz, 1 H, $ArCH{=}CH_2$), 7.24 (m, 8 H, Ar); mass spectrum, m/e (relative intensity) 298 (60), 233 (100), 129 (60), 117 (100), 115 (100), 105 (50), 91 (100); calcd 298.1026, found 298.1012.

o-[2-(1,3-Dihydrobenzo[c]thien-1-yl)ethyl]propenylbenzene S,S-Dioxide (1b). This compound was obtained as a noncrystalline solid in 65% yield as a mixture of monoalkylated sulfones isomeric at the olefinic center: NMR (360 MHz) 1.78 (dd, J = 7.3 and 2.2 Hz, 3 H, $CH{=}CHCH_3$), 1.93 (dd, J = 7.3 and 1.8 Hz), 2.35 (m, 2 H, $ArCH_2CH_2$), 3.0 (m, 2 H, $ArCH_2CH_2$), 4.23–4.41 (m, 3) H, $CHSO_2CH_2$), 5.90 (dq, J = 7 and 11 Hz, 1 H, $ArCH{=}CH_ZMe$), 6.17 (dq, J = 7 and 15 Hz, $ArCH{=}CH_EMe$), 6.59 (d with further splitting, J = 12 Hz, 1 H, $ArCH{=}CH_ZMe$), 6.68 (d with further splitting, J = 15 Hz, 1 H, $ArCH{=}CH_EMe$), 7.2–7.45 (m, 8 H, Ar); mass spectrum, m/e (relative intensity) 312 (40), 248 (50), 219 (40), 131 (100), 117 (80), 115 (50), 91 (90); calcd for $C_{19}H_{20}SO_2$ 312.1184, found 312.1184.

o-[2-(1,3-Dihydrobenzothien-1-yl)ethyl]butenylbenzene S,S-Dioxide (1c). This compound was obtained as a mixture of E and Z isomers in 64% yield as a noncrystalline solid: NMR (360 MHz) 1.05, 1.14 (2 t, J = 7 Hz, 3 H, CH_2CH_3), 2.22, 2.42, 3.01 (3 m, 2 H each), 4.25–4.45 (m, 3 H, $CHSO_2CH_2$), 5.79 (dt, J = 7.2 and 12 Hz, 1 H, $ArCH{=}CH_ZEt$), 6.21 (dt, J = 7.2 and 16 Hz, 1 H, $ArCH{=}CH_EEt$), 6.54, 6.68 (2 d with further splitting J = 12 and 16 Hz, 1 H, $ArCH{=}CHCHEt$), 7.2–7.4 (m, 8 H, Ar); mass spectrum, m/e (relative intensity) 326 (50), 219 (75), 145 (65), 131 (85), 117 (95), 91 (100); calcd for $C_{20}H_{22}SO_2$ 326.1335, found 326.1311.

Thermolysis of 1-Alkylated 1,3-Dihydrobenzo[c]thien-1-yl S,S-Dioxides to 4b,5,6,10b,11,12-Hexahydrochrysene Derivatives. General Procedure. A mixture of sulfone and 1,3,5-trichlorobenzene (approximately 1.5 g of solvent/g of sulfone) was heated in an oil bath at 230 °C. After 8 h the mixture was cooled, chromatographed on silica, and eluted with hexane to remove the solvent. After all of the trichlorobenzene had eluted, the product was eluted with 1:1 benzene–hexane.

4b,5,6,10b,11,12-Hexahydrochrysene (3a). This product was obtained in 78% yield as a 2.1/1 mixture of trans and cis isomers. Crystallization of the mixture from hexane gave the pure trans isomer, mp 114–115 °C (lit.[7] mp 114–115 °C). The mass spectrum of the minor cis isomer, obtained by GC/MS, was very similar to that of the pure trans isomer: mass spectrum cis isomer, m/e (relative intensity) 234 (60), 143 (100), 130 (30), 129 (70), 91 (40); calcd for $C_{18}H_{18}$ 234.1403, found 234.1409; trans isomer, m/e (relative intensity) 234 (50), 143 (100), 130 (40), 129 (70), 91 (35).

5-Methyl-4b,5,6,10b,11,12-hexahydrochrysene (3b). The product, a clear oil, was obtained in 88% yield as a mixture of stereoisomers. Both GC and combined GC/MS revealed three resolved peaks in the ratio 0.3:1:1. Each of these peaks yielded similar mass spectra. A typical spectrum exhibited m/e (relative intensity) 248 (100), 219 (55), 202 (30), 157 (40), 143 (75), 129 (80), 115 (70), 104 (60), 91 (90); calcd for $C_{19}H_{20}$ 248.1564, found 248.1554.

5-Ethyl-4b,5,6,10b,11,12-hexahydrochrysene (3c). This compound was obtained in 75% yield as a mixture of stereoisomers. Upon GC/MS analysis all four possible stereoisomers were observed in the ratio of 0.5:1.0:0.6:0.9. The spectra were all very similar: m/e (relative intensity) 262 (100), 219 (60), 205 (20), 171 (20), 157 (50), 129 (85), 117 (35), 105 (65), 91 (65).

Oxidation of Hexahydrochrysene Derivatives with DDQ. A mixture of 1.5 mmol of hydrocarbon, 5.2 mmol of DDQ, and 20 mL of benzene was refluxed for 1 h at which time product formation was complete. The mixture was concentrated and chromatographed on alumina; the product was eluted with benzene.

Chrysene (5a): 92% yield; mp 252–254 °C; chromatographically identical with an authentic sample.

5-Methyl-5,6-dihydrochrysene (4b): 79% yield; mp 125–126 °C (MeOH); NMR (360 MHz) 1.13 (d, J = 7.2 Hz, 3 H, $CHCMe$), 2.82 (dd, J = 1.7 and 15.3 Hz, 1 H, H_6), 3.23 (dd, J = 5.8 and 15.3 Hz, 1 H, H_6), 3.86 (m, 1 H, H_5), 7.2–8.1 (m, 10 H, Ar); mass spectrum, m/e (relative intensity) 244 (50), 229 (100), 226 (15), 114 (25); calcd for $C_{19}H_{16}$ 244.1251, found 244.1248.

5-Ethyl-5,6-dihydrochrysene (4c): 68% yield as a clear colorless oil, which did not crystallize; NMR (360 MHz) 0.95 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.45 (m, 2 H, $-CH_2CH_3$), 3.05 (AB system with each component split further into a doublet, J = 15.4, 2.2 and 5.3, Hz, 2 H, H_6,H_6), 3.56 (m, 1 H, H_5), 7.1–8.1 (m, 10 H, aromatic H); mass spectrum, m/e (relative intensity) 258 (30), 229 (100), 228 (50), 114 (20); calcd for $C_{20}H_{18}$ 258.1408, found 258.1416.

5-Methylchrysene (5b). A mixture of 200 mg of 5-methyl-4a,5,6,10a,11,12-hexahydrochrysene and 50 mg of 10% Pd/C was heated overnight in an oil bath at 260 °C. The cool reaction mixture was extracted with benzene, filtered, concentrated, and chromatographed on Florisil. Elution with benzene yielded 170 mg (85%) of pure 5-methylchrysene: mp 117–118 °C (lit.[2a] mp 115–117 °C).

5-Ethylchrysene (5c). In a similar manner 5-ethyl-4a,5,6,10a,11,12-hexahydrochrysene yielded (90%) 5-ethylchrysene: mp 75–76 °C (MeOH); NMR (80 MHz) 1.53 (t, J = 7 Hz, 3 H, CH_2CH_3, 3.55 (q, J = 7 Hz, 2 H, CH_2CH_3), 7.5–8.7 (m, 11 H, Ar H); mass spectrum, m/e (relative intensity) 256 (100), 241 (75), 240 (20), 239 (45), 226 (10), 207 (10); calcd for $C_{20}H_{16}$ 256.1251, found 256.1249.

Registry No. **1a**, 95798-55-3; (*E*)-**1b**, 95798-56-4; (*Z*)-**1b**, 95798-57-5; (*E*)-**1c**, 95798-58-6; (*Z*)-**1c**, 95798-59-7; *cis*-**3a**,

31579-69-8; *trans*-**3a**, 31579-70-1; **3b** (isomer 1), 95798-60-0; **3b** (isomer 2), 95909-01-6; **3b** (isomer 3), 95909-02-7; **3b** (isomer 4), 95909-03-8; **3c** (isomer 1), 95798-61-1; **3c** (isomer 2), 95909-04-9; **3c** (isomer 3), 95909-05-0; **3c** (isomer 4), 95909-06-1; **4b**, 34908-52-6; **4c**, 95798-62-2; **5a**, 218-01-9; **5b**, 3697-24-3; **5c**, 54986-62-8; **6**, 22901-09-3; **7a**, 3487-44-3; **7b**, 1754-88-7; **7c**, 16666-78-7; **8a**, 95798-50-8; (*E*)-**8b**, 95798-51-9; (*Z*)-**8b**, 95798-52-0; (*E*)-**8c**, 95798-53-1; (*Z*)-**8c**, 95798-54-2; methyltriphenylphosphonium bromide, 1779-49-3; ethyltriphenylphosphonium bromide, 1530-32-1; propyltriphenylphosphonium bromide, 6228-47-3; 1,3-dihydrobenzo[*c*]thiophene *S*,*S*-dioxide, 2471-91-2.

Synthesis of Arylacetylenes by the Sodium Hydride Catalyzed Cleavage of 4-Aryl-2-methyl-3-butyn-2-ols

Stephen J. Havens*

Kentron International Inc., Hampton, Virginia 23666

Paul M. Hergenrother

NASA Langley Research Center, Hampton, Virginia 23665

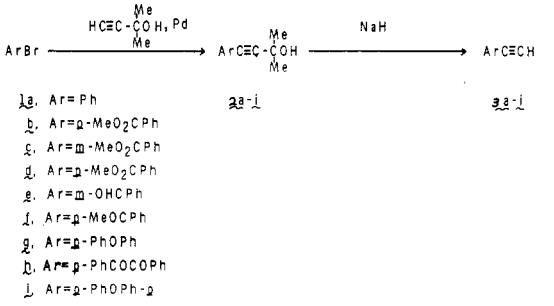
Received September 6, 1984

Recent advances in a two step synthesis of arylacetylenes have been reported.[1-4] The first step is displacement of an aromatic bromine or iodine atom by an acetylene adduct. The second step is removal of the protecting group to yield the arylacetylene.

Ethynyltrimethylsilane provides an excellent vehicle for the introduction of an acetylene group to an aromatic nucleus. Reaction of aryl halides (bromide or iodide) with ethynyltrimethylsilane in a secondary or tertiary amine solvent containing a small amount of palladium catalyst has given quantitative yields of (trimethylsilyl)ethynylaryls.[1,2a,b] The trimethylsilyl protecting group is easily removed by treatment with dilute potassium hydroxide[1] or under milder conditions by treatment with potassium carbonate.[2a,b] Yields of unpurified arylacetylenes are nearly quantitative. However, this method is expensive due to the high cost of ethynyltrimethylsilane.

The reaction of the relatively inexpensive reagent 2-methyl-3-butyn-2-ol with an aryl halide under conditions analogous with those employed with ethynyltrimethylsilane has given near quantitative yields of 4-aryl-2-methyl-3-butyn-2-ols (**2**).[3a,4a,b] Treatment with alkali-metal hydroxides at elevated temperatures is required for cleavage of the 2-hydroxypropyl group. In one case,[3a-d] **2** was heated at 120–140 °C under vacuum with powdered potassium hydroxide. Ester groups present were not affected under these conditions. In the other case,[4a,b] cleavage was effected by the slow distillation of a toluene solution of **2** containing a catalytic amount of sodium hydroxide. Acetone, the byproduct, must be removed by distillation to shift the equilibrium toward the arylacetylene (**3**).

Scheme I



We previously reported that the reaction of methyl 4-bromobenzoate with 2-methyl-3-butyn-2-ol at 90 °C in trimethylamine containing catalytic amounts of dichlorobis(triphenylphosphine)palladium, triphenylphosphine, and cuprous iodide provided 4-(4-(methoxycarbonyl)-phenyl)-2-methyl-3-butyn-2-ol (**2d**, Ar = MeO_2CPh-) in excellent yield.[5] Complete cleavage of the 2-hydroxypropyl group proved difficult. Treatment with sodium hydroxide in refluxing toluene combined with removal of acetone via distillation resulted in saponification of the ester. Only partial cleavage of the 2-hydroxypropyl group occurred even with distillation times of up to 10 h. Heating with a catalytic amount of potassium hydroxide at 120–140 °C under vacuum again resulted in only partial cleavage as both **2d** and the desired methyl 4-ethynylbenzoate sublimed from the reaction mixture under those conditions. No detectable saponification of the ester occurred. A weakly nucleophilic strong base may initiate the cleavage of the 2-hydroxypropyl group without affecting the ester group. This proved to be the case with sodium hydride. Distillation of a toluene solution of **2d** containing a catalytic amount of sodium hydride produced good yields of methyl 4-ethynylbenzoate. Herein, we report the results of the sodium hydride cleavage of various 4-aryl-2-methyl-3-butyn-2-ols, some containing base-sensitive groups (Scheme I).

Results and Discussion

Yields of arylacetylenes were generally good as shown in Table I, although some polymeric residue was a byproduct of the cleavage of the 2-hydroxypropyl group with sodium hydride. Removal of this group from **2a** was readily achieved but isolation of phenylacetylene (**3a**) from the toluene solution was not possible due to the tendency of phenylacetylene to codistill with toluene. HPLC analysis of the solution was used to determine yield in this case. Attempts to scale up the cleavage procedure met with some difficulty. Cleavage of the 2-hydroxypropyl group from **2d** on a larger scale (1.5 mol) required an extended distillation period (6–8 h) for an approximate 50% conversion. This prolonged heating was obviously leading to decomposition of the desired material. Several attempts to remove the 2-hydroxypropyl groups from **2e** and **2h**, compounds containing an aldehyde group and a 1,2-diketone group, respectively, failed. Only starting material was recovered. The precise reasons for these failures are unknown, but it has been reported that reaction of *p*-nitrobenzaldehyde with several equivalents of sodium hydride gives a mixture of *p*-nitrobenzoic acid and *p*-

(1) Takahashi, S.; Koroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(2) (a) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280. (b) Lau, K. S. Y., Kelleghan, W. J.; Boschan, R. H.; Bilow, N. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3009.

(3) (a) Shvartsberg, M. S.; Moroz, A. A.; Kotlyarevskii, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 981. (b) Shvartsberg, M. S.; Kotlyarevskii, I. L.; Kozhevikova, A. N.; Andrievskii, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1144. (c) Shvartsberg, M. S.; Moroz, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1582. (d) Shvartsberg, M. S.; Kozhevnikova, A. N.; Moroz, A. A.; Vasilevskii, S. F.; Bizhan, L. N.; Kotlyarevskii, I. L. *Dokl. Vses. Konf. Khim. Atsetilena, 4th* **1972**, (Pub. 1972), *2*, 52.

(4) (a) Sabourin, E. T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *24*, 233. (b) Sabourin, E. T.; Onopchenko, A. *J. Org. Chem.* **1983**, *48*, 5135.

(5) Havens, S. J.; Hergenrother, P. M. *J. Polym. Sci., Poly. Chem. Ed.* **1984**, *22*, 3011.

0022-3263/85/1950-1763$01.50/0