lution of N_2 and gave a resinous product. The 0.5 equiv of triethylene glycol (0.39 g, 2.6 mmol) in benzene (10 mL) was added dropwise over 1 h to the reaction solution. After the solution was stirred for 1 h followed by treatment with a small amount of water, the precipitated $DDQH_2$ was filtered off and washed with benzene (20 mL × 3). The same workup technique as for method A was adopted to give a pale-brown viscous oil. The oily products were column chromatographed (alumina) with light petroleum–benzene (1:1) as an eluent to afford benzophenone and then with benzene–ether (1:3) to afford 1:1 macrocyclic **2b**, but possible **3b** and **4b** were not detectable when 0.5 equiv of glycol was used. However, 1 or 3 equiv of triethylene glycol brought about the formation of **3b** and **4b** in addition to **2b**.

Conversion of 4 into 3. This reaction was made by employing 0.5 equiv of **4** with respect to DDM and DDQ according to method B. The converted products **3** were isolated by column chromatography on alumina with ether or ether–methanol (20:1) as an eluent. The yields were respectively 65% (**3a**), 74% (**3b**), 58% (**3c**), and 73% (**3d**).

Acetylation of 4b. To a benzene solution (10 mL) of **4b** (300 mg, 0.47 mmol) was added all at once a benzene solution (10 mL) of acetyl chloride (100 mg, 1.27 mmol) and pyridine (150 mg, 1.9 mmol). After the solution stood for 1 h, precipitated salt was filtered off and washed with benzene (10 mL × 3). The washing and filtrate were combined, washed with 5% aqueous sodium carbonate (5 mL × 3) and then with NaCl saturated water (5 mL × 3), dried over anhydrous sodium sulfate, and evaporated in vacuo at 50 °C to give a pale-yellow viscous oil. The oily products were gel chromatographed (Sephadex LH-20, Pharmacia), with methanol as an eluent, to afford **7**: colorless oil; 80% yield; IR (neat) 2780, 1735, 1235, 1105 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, $COCH_3$, 6 H), 3.3–3.7 (m, OCH_2CH_2O, 28 H), 4.0–4.2 (m, CH_2OCO, 4 H), 7.1–7.5 (m, Ph, 10 H); MS *m/e* 401 (M – $(OCH_2CH_2)_4OCOCH_3$). Anal. Calcd for $C_{33}H_{48}O_{12}$: C, 62.24; H, 7.60. Found: C, 62.07; H, 7.60.

Reaction with Salicylic and Thiosalicylic Acids. To a stirred reaction solution of DDM (1.0 g, 5.2 mmol) and DDQ (1.18 g, 5.2 mmol) in benzene (20 mL) was added dropwise for 1 h a benzene solution (10 mL) of salicylic acid (0.72 g, 5.2 mmol) or thiosalicylic acid (0.80 g, 5.2 mmol). After the solution was stirred for 1 h, the precipitated $DDQH_2$ was filtered off and washed with benzene (20 mL × 3). The same workup technique as for method B was adopted to give a crude reaction mixture as a brown paste. **8a** and **8b** were isolated by alumina column chromatography with benzene–methanol (20:1) as an eluent.

8a: mp 104–106 °C (from benzene); 55% yield; IR (KBr) 1742, 1301, 765 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.6 (m, aromatic H). Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.72; H, 4.67.

8b: mp 178–180 °C (from benzene); 62% yield; IR (KBr) 1721, 1275, 748 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.8 (m, aromatic H). Anal. Calcd for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43. Found: C, 75.76; H, 4.63.

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Registry No. 1a, 111-46-6; **1b**, 112-27-6; **1c**, 112-60-7; **1d**, 4792-15-8; **1e**, 2615-15-8; **2a**, 77130-21-3; **2b**, 77130-22-4; **2c**, 81194-61-8; **2d**, 81194-62-9; **2e**, 81194-63-0; **3a**, 81194-64-1; **3b**, 81194-65-2; **3c**, 81194-66-3; **3d**, 81194-67-4; **4a**, 81205-68-7; **4b**, 81205-69-8; **4c**, 81194-68-5; **4d**, 81194-69-6; **5**, 119-61-9; **6a**, 81194-70-9; **6b**, 81194-71-0; **7**, 81194-72-1; **8a**, 1433-60-9; **8b**, 19185-81-0; DDQ, 84-58-2; DDM, 883-40-9; $DDQH_2$, 4640-41-9; salicyclic acid, 69-72-7; thiosalicylic acid, 147-93-3.

Palladium-Catalyzed Cross-Coupling of (2-Ethoxyvinyl)boranes with Aryl and Benzyl Halides. A New Method for Conversion of Organic Halides into Aldehydes with Two More Carbon Atoms

Norio Miyaura, Koji Maeda, and Hiroshi Suginome*

Organic Synthesis Division, Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Akira Suzuki

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

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Vinyl ethers **3** can be synthesized in high yields by the cross-coupling of an aryl or benzyl halide with tris(2-ethoxyvinyl)borane (**1**) or (2-ethoxyvinyl)-1,3,2-benzodioxaborole (**2**) in the presence of 1 mol % of a palladium complex such as $PdCl_2(PPh_3)_2$, $Pd(OAc)_2(PPh_3)_2$, or $Pd(PPh_3)_4$ and a base while retaining the original configuration of the double bond in (2-ethoxyvinyl)boranes. No noticeable quantities of biaryls or conjugated dienes were found in this reaction. The reaction did not proceed in the absence of a base. This new vinyl ether synthesis was found to be applicable to aryl halides substituted with a variety of functional groups such as halogen, methoxy, carboethoxy, and acetyl groups. Electron-attracting substituents facilitate the coupling. Since vinyl ethers **3** thus obtained can readily be hydrolyzed to give aldehydes (eq 4), the sequence (eq 1–4) provides an efficient new method for converting an aryl halide into an aldehyde with two more carbon atoms.

It is becoming increasingly apparent that palladium-catalyzed reactions of organoboranes are useful in organic synthesis. We have thus shown that alkenylboranes react with a variety of organic halides in the presence of a catalytic amount of a palladium complex and a base to give the conjugated alkadienes due to cross-coupling while retaining the configurations of the starting alkenylboranes and the alkenyl halides.[1-3] The usefulness of this coupling reaction in synthesis arises from the fact that the alkenylboranes are readily available via monohydroboration of alkynes and are quite inert toward functional groups and the couplings can be carried out without protecting these groups. Thus, this cross-coupling reaction provides a versatile method for the synthesis of the conjugated alkadienes.

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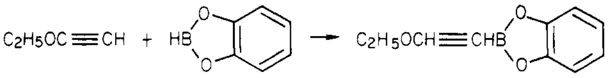
Table I. Effects of Catalyst and Base on Cross-Coupling of Tris(2-ethoxyvinyl)borane (1) or (2-Ethoxyvinyl)-1,3,2-benzodioxaborole (2) with Phenyl Halides[a]

entry	borane	PhX, X	catalyst (mol %)	base	% yield[b]
1	1	Br	$Pd(PPh_3)_4$ (1)	NaOH	34
2	1	Br	$Pd(PPh_3)_4$ (5)	NaOH	57
3	1	I	$Pd(PPh_3)_4$ (1)	NaOH	97
4	1	I	$PdCl_2$-$(PPh_3)_4$ (1)	NaOH	96
5	1	I	$Pd(OAc)_2$-$(PPh_3)_2$ (1)	NaOH	96
6	1	I	$Pd(PPh_3)_4$ (1)	NaOMe	82
7	1	I	$Pd(PPh_3)_4$ (1)	NaOAc	0
8	2	I	$Pd(PPh_3)_4$ (3)	NaOH	99

[a] All reactions were conducted in boiling THF containing 3 equiv of base and a palladium catalyst for 4 h under an atmosphere of nitrogen, using 7% excess of 1 or 10% excess of 2 against phenyl halides. [b] Yields of ethyl styryl ether were those determined by GLC and are based on phenyl halides.

This paper describes the synthesis of vinyl ethers[4] **3** by the cross-coupling between (2-ethoxyvinyl)boranes **1** or **2** and aryl or benzyl halides (eq 1–3). These vinyl ethers **3** can readily be hydrolyzed to give aldehydes (eq 4) and thus the sequence provides an efficient new method for converting an aryl halide into an aldehyde with two more carbon atoms.

$$3C_2H_5OC{\equiv}CH + BH_3 \rightarrow \underset{\textbf{1}}{(C_2H_5OCH{=}CH)_3B} \qquad (1)$$


(2)

2

$$\textbf{1} \text{ or } \textbf{2} + RX \xrightarrow[\text{base}]{\text{Pd catalyst}} \underset{\textbf{3},\ R\,=\,Ar,\ CH_2Ar}{RCH{=}CHOC_2H_5} \qquad (3)$$

$$\textbf{3} \xrightarrow{H_3O^+} RCH_2CHO \qquad (4)$$

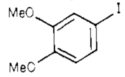
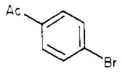
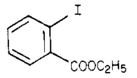
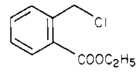
Results

The optimum conditions for carrying out the reaction of eq 3 were studied by using phenyl bromide or iodide as the organic halide and tris(2-ethoxyvinyl)borane (**1**) or (2-ethoxyvinyl)-1,3,2-benzodioxaborole (**2**) as (2-ethoxyvinyl)borane in the presence of different quantities of various palladium catalysts[5] and bases. The results are summarized in Table I. It has been found that the vinyl ethers **3** can be obtained in high yields by the reaction of phenyl iodide with (2-ethoxyvinyl)borane **1** in the presence of 1 mol % of a palladium complex as well as 3 equiv of sodium hydroxide or sodium methoxide without production of any noticeable quantities of byproducts such as biaryls and conjugated dienes. Fair yields of vinyl ethers could also be obtained from the reaction with phenyl bromide under the experimental conditions above.

Although $Pd(PPh_3)_4$ was used in the present work, $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2(PPh_3)_2$ are perhaps better palladium complexes for synthesis since $Pd(PPh_3)_4$ is unstable when it is exposed to air and is therefore less convenient to handle.

Vinylborane **1** rather than **2** is the reagent of choice since **1** can be prepared more easily and each of the three hydrogen atoms in BH_3 is used for the preparation of **1** and each of the three ethoxyvinyl groups in vinylborane **1** is available for transfer to aryl halides.

Table II. Yield of Vinylic Ethers 3 and 4 from the Reaction of Tris(2-ethoxyvinyl)borane (1) with Aryl Halides or Benzylic Halides[a]

aryl halide, aryl	X	rctn time, h	% yield[b]
phenyl	I	4	97
4-tolyl	I	4	97
4-anisyl	I	4	90
2-anisyl	I	4	78
		4	92
4-chlorophenyl	I	4	98
		2	96
		2	86[c,d]
naphthyl	I	4	96
benzyl	Cl	2	93[d]
2-bromobenzyl	Cl	2	68[d]
		2	48[c,d]

[a] All reactions were run at a refluxing temperature of THF by using three equivalents of powdered NaOH and 7% excess of 1 in the presence of 1 mole % of $Pd(PPh_3)_4$, unless otherwise stated. No unreacted halides were detected after the reaction time noted. [b] GLC yields based on ArX. No appreciable amount of by-products was detected in the products when they were analyzed by GLC. Analytically pure compounds can generally be obtained by distillation in yields lower than those by GLC by 5~10%.

The reaction did not proceed at a detectable rate in the absence of a base and the reaction also failed when weak bases such as sodium acetate were used. Three equivalents of sodium hydroxide was used in these experiments since the reaction was found to be accerelated when an excess of sodium hydroxide was used.

In Table II, the results of the reaction of a variety of aryl and benzylic halides with tris(2-ethoxyvinyl)borane (**1**) in the presence of sodium hydroxide and 1 mol % of $Pd(PPh_3)_4$ are summarized. Three equivalents of sodium hydroxide was used in most of these experiments. From these results it is apparent that this new vinyl ether synthesis is applicable to aryl iodides and bromides substituted with a variety of functional groups such as halogen, methoxy, carboethoxy, and acetyl groups. Organoboranes are inert to these functional groups under the conditions described above. It should be noted that high yields of vinyl ethers can be obtained even with an aryl halide carrying an alkoxycarbonyl groups such as 2-iodobenzoate when a lesser quantity of the base was used. Thus, when the coupling reaction of 2-iodobenzoate was carried out in THF in the presence of 1.5 equiv of NaOH, the formation of vinyl ether in a yield of 75% was observed, while the yield of the vinyl ether was only 39% when 3 equiv of the base was used. When the coupling was conducted in 1:1 benzene–THF by using 1.5 equiv of the base, even a higher yield (86%) of vinyl ether was obtained.

These results show that high yields of vinyl ether can be obtained in the present method even when an aryl halide carries a functional group which is base sensitive.

Although no quantitative study on the effects of nuclear substituents and the halogen of aryl halides was carried out, a brief study on the relative rate of the couplings

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(4) For other methods for synthesis of vinyl etheres by transition-metal-catalyzed cross-couplings, see (a) E. Negishi and D. E. V. Horn, *J. Am. Chem. Soc.*, **99**, 3168 (1977). (b) K. Tamao, M. Zembayashi, and M. Kumada, *Chem. Lett.*, 1237 (1976).

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indicated that amongst halogens the order of reactivities is ArI > ArBr > ArCl, electron-attacting substituents facilitate the reaction, and the order of the reactivities is *p*-acetyl > *p*-Cl > H > *p*-CH_3 > *p*-OCH_3. These results suggest that the slow step in this coupling may be the oxidation–addition of aryl halides to give ArPdX which reacts with (ethoxyvinyl)boranes.

The double bond in (2-ethoxyvinyl)boranes used in the present work should have an *E* configuration. The formation of only a single isomer of vinyl ethers **3** was proved by GLC analysis of the product in all the experiments and the *E* configuration of the double bond of **3** obtained was confirmed by the magnitude of the coupling constant (J = 13 Hz) of the olefinic protons in the ^1H NMR spectrum and by the characteristic band (1640 cm^{-1}) due to the trans CH=CH in the IR spectrum. The results indicate that the cross-coupling takes place while retaining the original configurations of the starting alkenylboranes as proved previously.[1b]

As shown in Table II, the present vinyl ether synthesis is applicable to the synthesis of arylated propenyl ethers by the reaction of (2-ethoxyvinyl)borane (**1**) with benzylic halide (eq 5). Thus, when the reaction of **1** with benzyl chloride was carried out in the presence of 3 equiv of sodium hydroxide, 3-phenylpropenyl ether (**4**) was obtained in 87% yield. The yield was improved to 93% when only 1.5 equiv of base was used as in the case of ethyl 2-iodobenzoate.

$$\mathbf{1} + ArCH_2X \xrightarrow[\text{base}]{\text{Pd catalyst}} \underset{\mathbf{4}}{ArCH_2CH{=}CHOC_2H_5} \quad (5)$$

An extension of this cross-coupling reaction for the synthesis of $ArCH{=}C(SC_2H_5)OC_2H_5$, which may readily be converted into arylacetic acids by hydrolysis, by the reaction of aryl halides with tris[2-(ethylthio)-2-ethoxyvinyl)borane,[8] is under investigation and the results will be reported at a later date.

Experimental Section

Reagents. Ethoxyethyne was prepared by following the method reported by Brandsma.[9] Phenyl iodide, 4-tolyl iodide, *p*-bromoacetophenone, ethyl 2-iodobenzoate, 1-iodonaphthalene, and benzylchloride were distilled before use. 4-Anisyl iodide,[10] 2-anisyl iodide,[10] 3-iodoveratrole,[11] 4-chlorophenyl iodide,[12] 2-bromobenzyl chloride,[13] and 2-(carboethoxy)benzyl bromide[14] were prepared following literature procedures. THF was distilled from benzophenone ketyl.[15]

Apparatus. Infrared spectra were recorded on a Hitachi Perkin-Elmer Model 125 spectrophotometer. ^1H NMR spectra were determined on a Hitachi R-22 spectrometer (90 MHz) and are reported in δ units downfield from Me_4Si as the internal standard. GLC analysis was performed on a Hitachi 163 instrument using 15% SE-30 or silicon OV-17 (1 m) on Uniport B. GLC yields were determined by using an appropriate hydrocarbon as the internal standard. Reactions were run under an atmosphere of nitrogen. Almost all specimens for analysis were prepared by distillation with Kugelrohr (Shibata GTO-250R). When necessary, a further purification was made by preparative GLC (15% Silicone OV-17 on Uniport B) with JEOL JGC-20K.

Palladium Catalyst. Tetrakis(triphenylphosphine)palladium(0),[16] dichlorobis(triphenylphosphine)palladium(II),[17] diacetoxybis(triphenylphosphine)palladium(II)[18] were prepared following literature procedures.

(2-Ethoxyvinyl)borane 1 and 2. Tris(2-ethoxyvinyl)borane (**1**) was prepared by following the method reported by Mikhaelov[6] from ethoxyethyne and diborane in THF and was used without further purification. *B*-(2-ethoxyvinyl)-1,3,2-benzodioxaborole (**2**) was prepared by the method reported by Brown with some modifications. A dry 25-mL flask equipped with a septum inlet and a magnetic stirring bar was flushed with dry nitrogen and was then charged with ethoxyethyne (8.3 g, 0.11 mol). 1,3,2-Benzodioxaborole (11 mL, 0.099 mol) then was added dropwise by a hypodermic syringe within 15 min at room temperature. The reaction mixture was stirred for 2 h at room temperature and was heated at 70 °C for 2 h. A Claisen head attached to a 10-cm Vigreaux column was connected to the flask and the flask was flushed with nitrogen. Distillation under reduced pressure gave *B*-(2-ethoxyvinyl)-1,3,2-benzodioxaborole (14.9 g, 66%), bp 72 °C (3 mm). (Ethoxyvinyl)benzodioxaborole was air sensitive, and when exposed to air, it turned immediately to deep brown.

2-Ethoxyvinylation of Aryl Halides. Typical Procedure. The general procedure for the preparation of vinyl ethers is illustrated by the preparation of 2-(3,4-dimethoxyphenyl)-1-ethoxyethene. A dry 100-mL flask equipped with a septum inlet, reflux condenser, magnetic stirring bar, and oil bubbler was flushed with nitrogen. To the flask charged with 0.11 g (0.1 mmol) of $Pd(PPh_3)_4$, 1.2 g (30 mmol) of powdered NaOH, and 30 mL of dry THF were added 2.54 g (10 mmol) of 3-iodoveratrole and tris(2-ethoxyvinyl)borane (**2**) in THF (12 mL, 4 mmol), at room temperature. The reaction mixture was heated gradually to reflux in the course of 15 min and the reflux was continued for 4 h. After the flask was cooled to room temperature, 5 mL of 3 N NaOH and 1 mL of 30% H_2O_2 were added to decompose the unreacted borane. The product was then extracted with 50 mL of 1:1 benzene–hexane, washed with a saturated aqueous NaCl solution, and dried over $MgSO_4$. GLC analysis using tetradecane as an internal standard indicated the formation of 9.2 mmol of 2-(3,4-dimethoxyphenyl)-1-ethoxyethene. After the usual workup, the product was distilled with Shibata GTO-250R Kugelrohr to give 1.79 g (86%) of analytically pure vinyl ether, bp 155–160 °C (oven temperature of Kugelrohr) (14 mm).

Physical Properties and Analytical and Spectral Data of Vinyl Ethers. Boiling points recorded are oven temperatures when it is distilled by Kugelrohr.

2-Phenyl-1-ethoxyethene: bp 102 °C (21 mm); $n^{29}{}_D$ = 1.5366; IR (neat) 3050, 3010, 1653, 1597 cm^{-1}; ^1H NMR δ 1.28 (t, 3 H), 3.25 (q, 2 H), 5.73 (d, 1 H, J = 13 Hz), 6.90 (d, 1 H, J = 13 Hz), 7.14 (s, 5 H); mass spectrum, m/e 148 (M^+); high-resolution mass spectrum calcd for $C_{10}H_{12}O$ 148.0887, found 148.0902.

2-(4-Tolyl)-1-ethoxyethene: bp 103 °C (0.3 mm); $n^{20}{}_N$ = 1.5445; IR (neat) 3020, 1655, 1635 cm^{-1}; ^1H NMR δ 1.29 (t, 3 H), 3.83 (q, 2 H), 2.23 (s, 3 H), 5.82 (d, 1 H, J = 13 Hz), 6.69 (d, 1 H, J = 13 Hz), 6.8–7.2 (m, 4 H); mass spectrum, m/e 162 (M^+); high-resolution mass spectrum calcd for $C_{11}H_{14}O$ 162.1043, found 162.1038.

2-(4-Anisyl)-1-ethoxyethene: $n^{20}{}_D$ = 1.5558; IR (neat) 3030, 1655, 1635, 1605, 1505 cm^{-1}; ^1H NMR δ 1.31 (t, 3 H), 3.75 (s, 3 H), 3.83 (q, 2 H), 5.70 (d, 1 H, J = 13 Hz), 6.79 (d, 1 H, J = 13 Hz), 6.72 (d, 2 H), 7.06 (d, 2 H); mass spectrum, m/e 178 (M^+); high-resolution mass spectrum calcd for $C_{11}H_{14}O_2$ 178.0983.

2-(2-Anisyl)-1-ethoxyethene: $n^{20}{}_D$ = 1.5573; IR (neat) 3070, 1650, 1653, 1595, 1575 cm^{-1}; ^1H NMR δ 1.31 (t, 3 H), 3.83 (s, 3 H), 3.88 (q, 2 H), 5.93 (d, 1 H, J = 13 Hz), 6.99 (d, 1 H, J = 13 Hz), 6.6–7.3 (m, 4 H); mass spectrum, m/e 178 (M^+); high-resolution mass spectrum calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0997.

2-(3,4-Dimethoxyphenyl)-1-ethoxyethene: bp 155–160 °C (14 mm); $n^{20}{}_D$ = 1.5593; IR (neat) 3040, 1655, 1640 cm^{-1}; ^1H NMR

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δ 1.13 (t, 3 H), 3.89 (s, 3 H), 3.91 (q, 2 H), 3.92 (s, 3 H), 5.85 (d, 1 H, J = 13 Hz), 6.83 (m, 3 H), 6.91 (d, 1 H, J = 13 Hz); mass spectrum, m/e 208 (M^+); high-resolution mass spectrum calcd for $C_{12}H_{16}O_3$ 208.1100, found 208.1116.

2-(4-Chlorophenyl)-1-ethoxyethene: bp 130 °C (13 mm); n^{20}_D = 1.5638; IR (neat) 3070, 3040, 1660, 1640 cm^{-1}; ^1H NMR δ 1.26 (t, 3 H), 3.86 (q, 2 H), 5.77 (d, 1 H, J = 13 Hz), 6.93 (d, 1 H, J = 13 Hz), 6.9–7.2 (m, 4 H); mass spectrum, m/e 182.184 (M^+); high-resolution mass spectrum calcd for $C_{10}H_{11}ClO$ 182.0499, 182.0470, found 182.0525, 184.0496.

2-(4-Acetylphenyl)-1-ethoxyethene: bp 180 °C (13 mm); mp 58 °C; IR (neat) 1675, 1635, 1595, 945 cm^{-1}; ^1H NMR δ 1.33 (t, 3 H), 2.57 (s, 3 H), 3.97 (q, 2 H), 5.89 (d, 1 H, J =13 Hz), 7.16 (d, 1 H, J = 13 Hz), 7.31 (d, 2 H), 7.88 (d, 2 H), mass spectrum, m/e 190 (M^+); high-resolution mass spectrum calcd for $C_{12}H_{14}O_2$ 190.0991, found 190.0988.

2-[2-(Carboethoxy)phenyl]-1-ethoxyethene: bp 105 °C (0.3 mm); n^{20}_D = 1.5444; IR (neat) 3060, 1715, 1635, 1600 cm^{-1}; ^1H NMR δ 1.38 (t, 3 H), 1.41 (t, 3 H), 3.99 (q, 2 H), 4.41 (q, 2 H), 6.78 (d, 1 H, J = 13 Hz), 7.03 (d, 1 H, J = 13 Hz), 7.1–7.55 (m, 3 H), 7.96 (d, 1 H); mass spectrum, m/e 220 (M^+); high-resolution mass spectrum calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1101.

2-Naphthyl-1-ethoxyethene: bp 80 °C (0.07 mm); n^{20}_D = 1.6248; IR (neat) 3060, 1655, 1640, 1595 cm^{-1}; ^1H NMR δ 1.30 (t, 3 H), 3.96 (q, 2 H), 6.48 (d, 1 H, J = 12 Hz), 6.92 (d, 1 H, J = 12 Hz), 7.2–8.2 (m, 7 H); mass spectrum, m/e 198 (M^+); high-resolution mass spectrum calcd for $C_{14}H_{14}O$ 198.1044, found 198.1084.

3-Phenyl-1-ethoxypropene: bp 100 °C (13 mm); n^{20}_D = 1.5109; IR (neat) 3060, 3030, 1675, 1655, 1605 cm^{-1}; ^1H NMR δ 1.21 (t, 3 H), 3.19 (d, 2 H, J = 7 Hz), 3.70 (q, 2 H), 4.89 (dt, 1 H, J = 13, 7 Hz), 6.31 (d, 1 H, J = 13 Hz), 7.22 (s, 5 H); mass spectrum; m/e 162 (M^+); high-resolution mass spectrum calcd for $C_{11}H_{14}O$ 162.1042, found m/e 162.1015.

3-(2-Bromophenyl)-1-ethoxypropene: n^{20}_D = 1.5422; IR (neat) 3060, 1670, 1650 cm^{-1}; ^1H NMR δ 1.27 (t, 3 H), 3.40 (d, 2 H, J = 7 Hz), 3.78 (q, 2 H), 4.97 (dt, 1 H, J = 7, 13 Hz), 6.41 (d, 1 H, J = 13 Hz), 7.0–7.4 (m, 3 H), 7.59 (d, 1 H); mass spectrum, m/e 240.242 (M^+); high-resolution mass spectrum calcd for $C_{11}H_{13}OBr$ 240.0150, 242.0131, found 240.0154, 242.0146.

3-[2-(Carboethoxy)phenyl]-1-ethoxyethene: bp 98 °C (0.07 mm); n^{20}_D = 1.5142; IR (neat) 3060, 1720, 1675, 1655 cm^{-1}; ^1H NMR δ 1.21 (t, 3 H), 1.36 (t, 3 H), 3.61 (d, 2 H, J = 7 Hz), 4.38 (q, 2 H), 4.48 (dt, 1 H, J = 7, 14 Hz), 6.37 d, 1 H, J = 14 Hz), 7.2–7.55 (m, 3 H), 7.90 (d, 1 H); mass spectrum, m/e 234 (M^+); high-resolution mass spectrum calcd for $C_{14}H_{18}O_3$ 234.1254, found 234.1237.

Registry No. 1, 32763-41-0; 2, 81206-43-1; 3 (Ar = Ph), 20565-86-0; 3 (Ar = 4-MeC_6H_4), 31026-84-3; 3 (Ar = 4-$MeOC_6H_4$), 31026-83-2; 3 (Ar = 2-$MeOC_6H_4$), 81206-44-2; 3 [Ar = 3,4-$(MeO)_2C_6H_3$], 81206-45-3; 3 (Ar = 4-ClC_6H_4), 31026-90-1; 3 (Ar = 4-AcC_6H_4), 81206-46-4; 3 (Ar = 2-$EtO_2CC_6H_4$), 81206-47-5; 3 (Ar = naphthyl), 81206-48-6; 4 (Ar = Ph), 16630-96-9; 4 (Ar = 2-BrC_6H_4), 81206-49-7; 4 (Ar = 2-$EtO_2CC_6H_4$), 81218-98-6; $EtOC{\equiv}CH$, 927-80-0; BH_3, 13283-31-3; 1,3,2-benzodioxaborole, 274-07-7; 3,4-$(MeO)_2C_6H_3I$, 5460-32-2; PhBr, 108-86-1; PhI, 591-50-4; 4-MeC_6H_4I, 591-50-4; 4-$MeOC_6H_4I$, 624-31-7; 2-$MeOC_6H_4I$, 529-28-2; 4-ClC_6H_4I, 637-87-6; 4-BrC_6H_4Ac, 99-90-1; 2-$EtO_2CC_6H_4I$, 1829-28-3; $C_{10}H_7I$, 90-14-2; $PhCH_2I$, 620-05-3; 2-$BrC_6H_4CH_2I$, 81206-50-0; 2-$EtO_2CC_6H_4Cl$, 7335-25-3.

Synthesis of Polycyclic Aromatic Hydrocarbons via a Novel Annelation Method

Ronald G. Harvey,* Cecilia Cortez, and Stephen A. Jacobs

Ben May Laboratory, University of Chicago, Chicago, Illinois 60637

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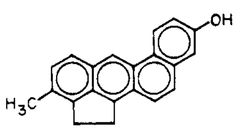
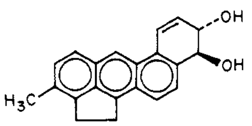
A new general synthetic approach to polycyclic aromatic hydrocarbons is described. The method is based on the convenient availability of *o*-lithioarylamides from regiospecific metalation of *N*,*N*-diethylarylamides with alkyllithium–amine reagents. Addition of the *o*-lithioarylamide to an aryl ketone or aldehyde affords a lactone. Reduction of the latter with zinc and alkali or HI generates the free acid which undergoes cyclization with $ZnCl_2$ and Ac_2O and reduction with zinc and alkali or HI to furnish the fully aromatic polyarene. Compounds synthesized via this route include 3-methylcholanthrene, benz[*a*]anthracene, dibenz[*a*,*h*]anthracene, dibenz[*a*,*j*]anthracene, benzo[*a*]pyrene, and their methyl derivatives. Overall yields are generally good. Competitive enolate anion formation depresses the yield in the initial step in the reactions of enolizable ketones. However, this pathway can be suppressed with substantial improvement in yield through deuterium exchange of the hydrogens α to the carbonyl. The last three steps of the general method can be condensed to only one step through reductive cyclization of the lactone intermediates with hydriodic acid in acetic acid. While tertiary lactones are resistant to HI under these conditions, the corresponding free acids undergo reductive cyclization under similar conditions.

Chemical and biological studies of polycyclic hydrocarbons are currently hampered by the relative complexity of existing synthetic methods, most of which were developed many years earlier.[1] We recently reported a novel synthesis of polycyclic arenes from *o*-quinones having one fewer ring.[2]

We now report a convenient new synthesis of polycyclic aromatic molecules utilizing a novel annelation method. This research was stimulated by the need for 9-hydroxy-3-methylcholanthrene (1), a potential synthetic precursor[3] of the 9,10-dihydrodiol of 3-methylcholanthrene (2), tentatively identified as the principal active carcinogenic metabolite of 3-methylcholanthrene (3-MC).[4,5] The es-



1



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[1] Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964; Vol. I, II.

[2] Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1981**, *46*, 2740.

[3] Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1980**, *45*, 4407.