mg (47%) of white crystals was collected. The melting point was 93–100 °C with decomposition and partial resolidification. The compound was recrystallized by dissolving it in CH_2Cl_2 (several minutes of warming required); the solution was filtered to clarify and then evaporated at reduced pressure to a solid which was rinsed with ether. This material decomposed with softening and slight darkening at 95–100 °C.

Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61. Found: C, 65.67; H, 6.42.

The 90 MHz FT proton NMR ($CDCl_3$) spectrum at 25 °C showed the following: δ 1.51 (s, 5-CH_3), 2.19 and 2.25 (two s, CH_3CO), 3.45 and 3.47 (two s, CH_3O) 4.86 and 4.94 (two s, H-7), 6.87 and 7.52 (two s, H-3), 7.26 and 7.28 (two s, C_6H_5). At 45 °C, the spectrum showed peaks due to **17a** at δ 1.50, 2.20, 3.45, 4.90, and 7.27 (the coalesced peaks due to H-3 were merged with the large C_6H_5 peak at δ 7.27) and peaks due to pyrrolinone **14a** at δ 2.10 (t, 3-CH_3), 2.61 (CH_3CO), 4.59 (CH_2), and 7.47 (s, C_6H_5) [lit.[3] δ 2.08 (t), 2.60 (s), 4.58 (q), 7.48 (s)]. After 20 min at 45 °C, integration of the CH_3 peaks indicated 23% of **14a**, after 30 min, 30% of **14a**, and after 1 h, 42% of **14a**.

Identification of Glycine from Reaction of 1b and KOH. A 30-mg (100-μmol) amount of the benzoyl bicyclic ketone **1b** was dissolved in 0.2 mL of 10% aqueous KOH containing a drop of methanol. After 2 h, the solution was diluted with water, and 10.5 mg of serine plus 11.7 mg of valine (100 μmol) were added as standards. The pH was adjusted to 6, causing a yellow gum to separate. After filtration through Darco, the solution was further diluted and analyzed on a Beckman 120C amino acid analyzer.[7] The ratio of standards/glycine was 4.15, indicating a 24% yield of glycine based on **1b**.

Registry No.—**1a**, 5109-37-5; **1b**, 5109-45-5; **7a** (R′ = Et), 67350-78-1; **7b** (R′ = Et), 67350-77-0; **13b**, 10137-10-7; **14a**, 10147-13-4; **14b**, 10137-11-8; **17a**, 67328-94-3; **17b**, 67328-95-4; **17b** *N*-acetyl derivative, 67328-96-5; **17b** 7-ethoxy analogue, 67328-97-6; **23b**, 67328-98-7; **25b**, 10137-17-4.

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(7) We thank Professor J. Wriston and Mrs. Jean Denis for this determination.

^{13}C-Labeled Benzo[a]pyrene and Derivatives. 1. Efficient Pathways to Labeling the 4, 5, 11, and 12 Positions[1,2]

Richard S. Bodine, Mark Hylarides, Guido H. Daub,* and David L. VanderJagt

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

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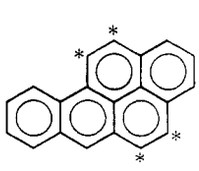
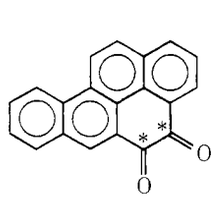
Efficient pathways leading to the synthesis of benzo[a]pyrene labeled with ^{13}C in the 4, 5, 11, or 12 positions are described. A method of synthesis of the benzo[a]pyrene-4,5- and -11, 12-quinones leading to labeling in the 4 or 5 and 11 or 12 positions, respectively, is also presented, allowing ready access to the labeled 4,5- and 11,12-oxides. The values of the ^{13}C NMR chemical shifts for C_4, C_5, C_{11}, and C_{12} of benzo[a]pyrene were determined using the labeled compounds.

Discussion

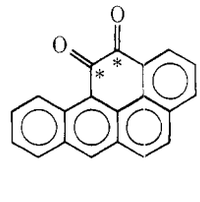
As part of a program to develop efficient syntheses of the potent carcinogen benzo[a]pyrene labeled with ^{13}C (90%) at each one of the peripheral carbon atoms of the ring system we have successfully developed such routes to the 4-, 5-, 11-, and 12-labeled benzo[a]pyrenes (**1a, 1b, 1c,** and **1d**). In addition, the benzo[a]pyrenequinones **2** and **3** have been prepared as intermediates for the synthesis of the corresponding arene oxides **4** and **5.**



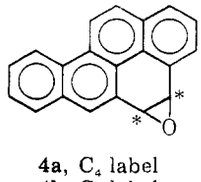
1a, label at C_4
1b, label at C_5
1c, label at C_{11}
1d, label at C_{12}



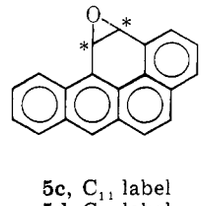
2a, C_4 label
2b, C_5 label



3c, C_{11} label
3d, C_{12} label



4a, C_4 label
4b, C_5 label

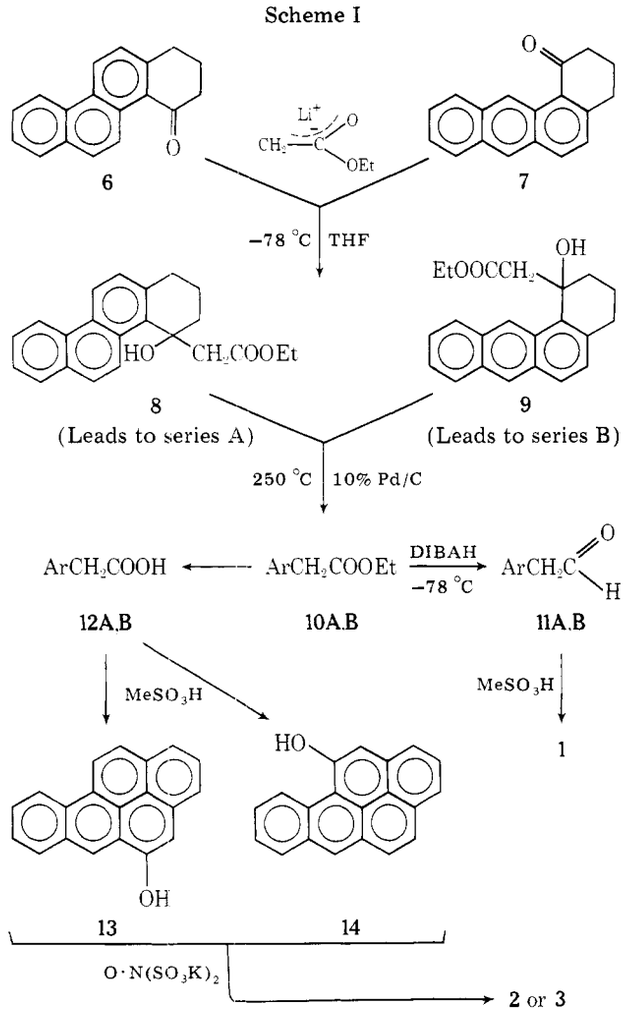


5c, C_{11} label
5d, C_{12} label

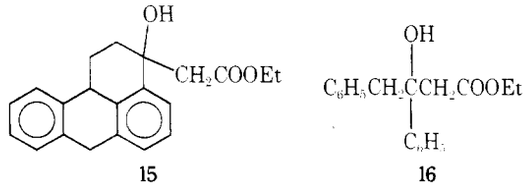
The synthesis of benzo[a]pyrene (1) from 1,2-dihydrochrysen-4(3*H*)-one (**6**)[3a] and from 3,4-dihydrobenz[a]anthracen-1(2*H*)-one (**7**)[4] was studied (Scheme I), since these ketones are relatively easily synthesized and have been shown previously to undergo the Reformatsky reaction[3b,4] in moderate yield. Furthermore, these two approaches would allow the introduction of the ^{13}C label at the 4 or 5 and the 11 or 12 positions, respectively, late in the synthesis depending on the position of the label in the starting ester. It was felt that the Reformatsky reaction as carried out earlier[3b,4a] would be unsuitable for labeling studies, since an excess of bromo ester was used, and in the case at hand this would contain the label. Attempts to prepare the hydroxy esters **8** and **9** via the Reformatsky reaction failed to give satisfactory yields using equimolar ratios of the ketones **6** or **7** and ethyl bromoacetate even under conditions reported to give excellent yields for selected ketones.[5-7] However, when the ketone **6** or **7** was allowed to react with the lithium enolate of ethyl acetate[8] in THF at −78 °C, the hydroxy ester **8** or **9** was obtained in 82% yield. The hydroxy esters **8** and **9** rapidly revert to the respective ketones if the reaction mixture is allowed to warm to room temperature before acidification; thus, acidification of the reaction mixtures had to be carried out at −78 °C in order for the hydroxy esters to survive.

0022-3263/78/1943-4025$01.00/0

Scheme I



Indeed, the esters **8, 9, 15,** and **16** undergo rapid retroaldol reactions when treated with lithium isopropylcyclohexylamide in THF at 15–25 °C, and we are currently studying the generality of this reaction.



Dehydration and dehydrogenation of the hydroxy esters **8** or **9** was accomplished by heating with Pd/C at 250 °C to afford the arylacetic esters **10A** or **10B** in 82 and 89% yields, respectively. Saponification of either ester with ethanolic potassium hydroxide gave the corresponding acid **12A** or **12B** in excellent yield. Reduction of the esters with DIBAH at −78 °C in toluene afforded the respective aldehydes **11A** and **11B,** which were directly cyclized to benzo[*a*]pyrene (**1**) by treatment with methanesulfonic acid in overall yields of 85 and 82%, respectively, from **10A** and **10B.**

Cyclization of either of the arylacetic acids, **12A** or **12B,** with methanesulfonic acid[9] gave the respective phenols, **13** or **14,** which were directly oxidized with Fremy's salt [10] in buffered aqueous acetone to the corresponding quinones, **2** and **3.**

The overall yield of benzo[*a*]pyrene from the ketone **6** was 52% and from the ketone **7** was 55–60%. The overall yields of the quinones **2** and **3** from the ketones **6** and **7** were 51 and 52–57%, respectively. These overall yields are sufficiently good to render these approaches to benzo[*a*]pyrene useful for the synthesis of the ^{13}C-labeled compounds **1a–d.** In addition, the route via the quinones **2** and **3** to the respective arene oxides **4a, b** and **5c, d** represent excellent paths for the synthesis of such labeled systems.[11-13]

We have utilized the sequences described above in synthesizing benzo[*a*]pyrene-*5*-^{13}C (**1b**) and -*11*-^{13}C (**1c**) using ethyl acetate-*1*-^{13}C (**17**) and benzo[*a*]pyrene-*4*-^{13}C (**1a**) and -*12*-^{13}C (**1d**) from ethyl acetate-*2*-^{13}C (**18**). Both labeled esters **17** and **18** were prepared in better than 90% yield by allowing labeled sodium acetate to react with triethyl phosphate at 180 °C.[14] The labeled quinones **2a, b** and **3c, d** have also been prepared.

Carbon-13 NMR spectra of the benzo[*a*]pyrenes **1a–d** have allowed us to identify the chemical shifts for the carbon atoms in the 4, 5, 11, and 12 positions of benzo[*a*]pyrene. Indeed, the correct chemical shifts for C_4, C_5, and C_{12} of benzo[*a*]pyrene are 127.63, 128.00, and 127.33 (δ_C from Me_4Si), respectively, and not 127.33, 127.66, and 128.00, respectively, as assigned by Buchanan and Ozubko[15] based on model compounds, empirical correlations, and deuterium substitution. The chemical shift for C_{11} was identified as 122.00, in agreement with the value assigned by these workers. The ^{13}C NMR spectra were measured by spiking a 0.24 M solution of benzo[*a*]pyrene in $CDCl_3$ successively with small amounts of the labeled products **1a, 1b, 1c,** and **1d,** and running the spectrum at 32 °C after each addition.

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected as are reported boiling points. Elemental analyses were performed by Mrs. Ruby Ju of the Department of Chemistry. IR measurements were obtained on a Perkin-Elmer Model 337 spectrophotometer. ^1H NMR spectra at 60 MHz were recorded on a Varian A-60 or Varian EM-360 instrument at ambient temperature. ^{13}C NMR spectra were obtained in a pulse Fourier transform Varian XL-100 or Varian CFT-20 spectrometer. Product purity and reaction progress were detected with analytical thin-layer chromatography using 2.5 × 10 cm Analtech plates coated with silica gel GF.

Ethyl 2-(1-Hydroxy-1,2,3,4-tetrahydrobenz[*a*]anthracen-1-yl)acetate (9). To a mixture of 2.33 g (16.5 mmol) of *N*-isopropylcyclohexylamine and 15 mL of anhydrous THF, cooled to −78 °C and under a N_2 atmosphere, was added 9.4 mL of 1.6 M *n*-butyllithium (15.0 mmol) in hexane. This mixture was cooled again to −78 °C, and 1.32 g (15.0 mmol) of ethyl acetate in 15 mL of anhydrous THF was added dropwise at a rate to maintain the temperature of the reaction mixture below −75 °C. After addition was complete, stirring was continued for 15 min, after which time 3.69 g (15.0 mmol) of 3,4-dihydrobenz[*a*]anthracen-1(2*H*)-one (**7**), mp 113.5–114.5 °C, dissolved in 45 mL of anhydrous THF was added at a rate which maintained the temperature below −75 °C. After the addition was complete, stirring at −78 °C was continued for 1 h. The orange complex was hydrolyzed by the dropwise addition of 2 mL of concentrated HCl in 10 mL of THF at such a rate as to maintain the reaction mixture at a temperature below −70 °C. The mixture was allowed to warm to room temperature, and 50 mL of water and 50 mL of ether were added. The layers were separated, and the ether layer was extracted with two 20-mL portions of 5% HCl. The aqueous layer was extracted with 25 mL of ether, and the combined ether extracts were dried over $MgSO_4$. Removal of the ether afforded an orange oil which solidified on trituration with ethanol. Crystallization of this solid from 95% ethanol gave 4.02 g (80% yield) of pale yellow crystals, mp 114.5–115.5 °C (reported mp 114–115 °C).[16] In subsequent runs it was found that trituration of the crude product with hexanes in the cold afforded good hydroxy ester, mp 114–116 °C, in 82% yield (4.12 g): IR (KBr) 3465 (OH), 1710 (C=O), 1295, 1195, 1165, 1090, 1050, 1000, 890, 740 cm^{-1}.

Ethyl 1-Benz[*a*]anthraceneacetate (10B). In a dehydrogenation tube fitted with a ground-glass cold finger condenser and gas inlet and outlet tubes was placed 2.00 g (6.0 mmol) of ethyl 2-(1-hydroxy-1,2,3,4-tetrahydrobenz[*a*]anthracen-1-yl)acetate (**9**), mp 114.5–115 °C, 0.20 g of 10% Pd/C, 1.20 g (6.6 mmol) of 1,1-diphenylethene, and 10 mL of 1-methylnaphthalene. The reaction mixture was placed in a preheated Woods metal bath and the temperature was maintained at 250–260 °C for 2 h while steam was passed through the condenser

and with maintenance of a slow flow of N_2. The cooled reaction mixture was diluted with benzene and filtered from the catalyst, which was washed with benzene. After removal of the benzene on a rotary evaporator, the 1-methylnapthalene, 1,1-diphenylethane, and unreacted 1,1-diphenylethene were removed under reduced pressure (0.025 Torr, 50–60 °C) on a Kugel-Rohr. The resultant orange oily residue was crystallized from 95% ethanol to afford 1.54–1.67 g (82–89% yield) of **10B** as beige colored needles, mp 107–109.5 °C. A sample recrystallized from 95% ethanol melted at 109–109.5 °C: IR (KBr) 1720 (C=O), 1250 (CO—O), 1192, 1097, 1024, 886, 770, 744 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.1 (3 H, t, J = 7 Hz), 4.1 (2 H, q, J = 7 Hz), 4.3 (2 H, s), 7.2–8.9 (11 H, m).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.24; H, 5.72.

Benzo[a]pyrene (1). A solution of 1.42 g (4.5 mmol) of ethyl 1-benz[a]anthraceneacetate (**10B**), mp 109–109.5 °C, in 45 mL of dry toluene was cooled to −75 °C under a N_2 atmosphere. To this solution was added 4.5 mL of 1 M diisobutylaluminum hydride (DIBAH) in hexane. The reaction mixture was stirred for 1 h at −75 °C, and the pale yellow complex was hydrolyzed by the addition of 1 mL of concentrated HCl in 9 mL of THF. After warming to room temperature, the reaction mixture was extracted with 5% aqueous NH_4Cl and the toluene layer was dried over $MgSO_4$. Removal of the toluene gave the aldehyde **11B** as a pale yellow oil which was directly dissolved in 65 mL of methanesulfonic acid and stirred under a N_2 atmosphere for 40 min while warming in a water bath. The deep red complex was hydrolyzed by pouring the reaction mixture into 100 mL of water and ice, which resulted in the precipitation of benzo[a]pyrene (1) as a yellow solid. This crude product was chromatographed on neutral alumina using benzene as the eluting solvent. The benzene eluate was concentrated and methanol was added to give 0.70 g of lemon yellow shiny platelets, mp 177.5–178 °C (reported[17] mp 176–177 °C). An additional 0.23 g (82% overall yield) of product, mp 176–177 °C, was obtained from the mother liquor.

1-Benz[a]anthraceneacetic Acid (12B). To a solution of 1.41 g (4.5 mmol) of ethyl 1-benz[a]anthraceneacetate (**10B**), mp 108.5–109.5 °C, in 50 mL of 95% ethanol was added 1.00 g (15.1 mmol) of 85% KOH, and the solution was refluxed for 3 h. The ethanol was removed and the residue was dissolved in water and acidified with concentrated HCl to give crude 1-benz[a]anthraceneacetic acid (**12B**) as an off-white solid. Recrystallization from benzene gave 1.22 g (95% yield) of off-white fibrous needles, mp 202–203 °C (reported mp 203.6–204.6 °C).[4a]

11,12-Dihydrobenzo[a]pyrene-11,12-dione (3). A solution of 286 mg (1.00 mmol) of 1-benz[a]anthraceneacetic acid (**12B**), mp 202.5–204 °C, in 10 mL of methanesulfonic acid under a N_2 atmosphere was stirred for 30 min. The deep red complex was hydrolyzed by pouring into 100 g of water and ice, and the green precipitate which was collected was directly dissolved in 50 mL of acetone and added to a solution of 1.07 g (4.0 mmol) of dipotassium nitrosodisulfonate (Fremy's salt) in 40 mL of water buffered with 10 mL of 0.167 M KH_2PO_4. The solution was shaken in a stoppered Pyrex hydrogenation bottle on a Parr shaker until it no longer exhibited fluroescence when illuminated with a short-wave UV lamp. The acetone was removed on a rotary evaporator; the red-brown precipitate was collected and dried under reduced pressure. This crude product was dissolved in CH_2Cl_2 and applied to a silica gel column, the quinone being eluted with 1:1 chloroform/ethyl acetate. After removal of the solvent, the dark red solid was dissolved in CH_2Cl_2 and reduced in volume, and ethyl acetate was added to facilitate crystallization to afford 230 mg (82% yield) of **3** as dark red needles, mp 253–254.5 °C. An analytical sample, mp 257.5–259 °C (evac), was prepared by recrystallization from CH_2Cl_2/ethyl acetate: IR (KBr) 1655 (COCO), 1283, 1177, 1115, 891, 820 cm^{-1}.

Anal. Calcd for $C_{20}H_{10}O_2$: C, 85.09; H, 3.57. Found: C, 84.73; H, 3.51.

Ethyl 4-Hydryoxy-1,2,3,4-tetrahydro-4-chryseneacetate (8). In like manner to that described above for the synthesis of **9**, 4.92 g (20.0 mmol) of 1,2-dihydrochrysen-4(3*H*)-one (**6**),[3] mp 124–125 °C, was allowed to react with the lithium enolate prepared from 1.78 g (20.0 mmol) of ethyl acetate. Workup provided a pale yellow oil which solidified on trituration with 95% ethanol. Crystallization of this oil from 95% ethanol gave 5.48 g (82%) of colorless **8**, mp 77–81 °C (reported[3] as an oil), which was shown by TLC to contain trace amounts of the ketone **6**. Further crystallization failed to improve the melting point or remove the traces of **6**: IR (KBr) 3470 (OH), 1710 (C=O), 1395, 1300, 1230, 1197, 1168, 1090, 1032, 753 cm^{-1}.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.04; H, 6.59. Found: C, 78.95; H, 6.51.

Ethyl 4-Chryseneacetate (10A) and 4-Chryseneacetic Acid (12A). Dehydration and dehydrogenation of 2.5 g (7.5 mmol) of the hydroxy ester **8**, mp 77–81 °C, was carried out as described above for **9**. Workup afforded a brown oil which was crystallized from 95% ethanol to give 1.75 g (74%) of the ester **10A** as colorless prisms: mp 63.5–65 °C; IR (KBr) 1735 (C=O), 1380, 1257, 1095, 1030, 833 cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.2 (3 H, t, J = 7 Hz), 4.1 (2 H, q, J = 7 Hz), 4.3 (2 H, s), 7.3–8.7 (11 H, m).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.20; H, 5.59.

The residue in the mother liquor from the crystallization of **10A** was heated with 0.1 g of KOH in 15 mL of 95% ethanol for 1.5 h. The ethanol was removed, the residue was dissolved in water, and the solution was filtered through filter-cel and acidified to give crude 4-chryseneacetic acid (**12A**). Recrystallization from toluene gave 0.17 g (8% yield) of **12A**, mp 203–205.5 °C (reported[3b] mp 206.5–207.5 °C). The total yield of dehydrogenated product thus amounted to 82%. Direct saponification of the crude oily ester in a similar run gave 1.59 g (74%) of the acid **12A**, mp 205.5–207 °C, after recrystallization from toluene: IR (KBr) 2700–3200 (br, COOH), 1700 (C=O), 1376, 1270, 1225, 1205, 836, 813 cm^{-1}.

Benzo[a]pyrene (1). Reduction of 0.94 g (3.0 mmol) of the ester **10A** was carried out as described above for **10B**. Workup provided the aldehyde **11A** as a pale yellow oil which solidified on standing: IR (KBr) 3050, 2830 (CHO), 2725 (CHO), 1715 (C=O), 1465, 1376, 1265, 1222, 1183, 1152, 1097 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (2 H, d, J = 3 Hz), 7–8.8 (11 H, m), 9.8 (1 H, t, J = 3 Hz). Cyclization of the crude aldehyde as described for **11B** gave benzo[a]pyrene as a pale green solid. Chromatography over neutral alumina followed by crystallization from benzene/methanol afforded 0.64 g (85%) of **1**, mp 176.5–178 °C.

4,5-Dihydrobenzo[a]pyrene-4,5-dione (2). A solution of 0.576 g (2.00 mmol) of the acid **12A**, mp 205.5–207 °C, in 35 mL of methanesulfonic acid was stirred under N_2 for 30 min at 50 °C. Workup as described for **3** provided the phenol **13** as a yellow-green solid which was directly oxidized with Fremy's salt as above for 1 h. The red-brown precipitate formed during the reaction was collected and heated with 5% aqueous Na_2CO_3, releasing the bright orange-red quinone (**2**). Chromatography over silica gel followed by crystallization from $CHCl_3$/ethyl acetate gave 0.48 g (85% overall) of **2** as red-orange crystals; mp 256–257.5 °C (reported[11] mp 255–256 °C); IR (KBr) 1665 (COCO), 1440, 1380, 1286, 1275, 1168, 910, 850, 750 cm^{-1}.

Ethyl Acetate-*1*-^{13}C (17) and Ethyl Acetate-*2*-^{13}C (18). A two-neck 1-L round-bottom flask equipped with a sealed Teflon paddle stirrer and a 12 in. Vigreux column leading to a condenser for downward distillation, receiver, and dry ice trap was charged with 82.6 g (0.996 mol) of sodium acetate-*1*-^{13}C (dried at 110 °C (0.01 Torr) for 2 h) and 300 mL of triethyl phosphate (Aldrich, redistilled). The reaction mixture was heated to 176–180 °C in an oil bath with stirring, and in that range of temperature ethyl acetate-*1*-^{13}C distilled freely (bp 76–78 °C at the top of the Vigreux column). Care had to be taken to keep the reaction from getting out of control by lowering the oil bath when the reaction became too vigorous. As the reaction proceeded the slurry of sodium acetate in triethyl phosphate turned to a homogeneous solution. After 45 min the reaction was essentially complete. The distillate amounted to 78.3 g and was put aside while the reaction mixture was allowed to cool to 60 °C. The system was placed under reduced pressure (25 Torr) in order to obtain a further amount of product which was collected in the dry ice/2-propanol bath cooled trap. This was added to the initial distillate to give a total yield of 86.6 g of colorless product. This was shown to contain a small amount of phosphate ester by VPC, and was redistilled through a 12 in. Vigreux column to give 81.6 g (92% yield) of colorless ethyl acetate-*1*-^{13}C (**17**), bp 72 °C. This product is labeled at C_1 with 90% ^{13}C. In a similar experiment ethyl acetate-*2*-^{13}C (**18**) was prepared in comparable yield.

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with Dr. Thomas W. Whaley regarding this work is also appreciated.

Registry No.—**1**, 50-32-8; **1a**, 67194-47-2; **1b**, 67194-48-3; **1c**, 67194-49-4; **1d**, 67194-50-7; **2**, 42286-46-4; **3**, 60657-26-3; **6**, 66267-06-9; **7**, 57652-74-1; **8**, 67194-42-7; **9**, 57652-75-2; **10A**, 67194-43-8; **10B**, 67194-44-9; **11A**, 67194-45-0; **11B**, 67914-46-1; **12A**, 57652-73-0; **12B**, 57652-76-3; **13**, 24027-84-7; **17**, 3424-59-7; **18**, 58735-82-3; *N*-isopropylcyclohexylamine, 1195-42-2.

References and Notes

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Mechanism of Aryl Group Migration in the Formation of Stilbenes from 1,1-Bis(*p*-hydroxyaryl)ethane 2-*O*-Aryl Ethers

Josef Gierer and Charles R. Nelson*

Department of Chemistry, Swedish Forest Products Research Laboratory, S-114 86 Stockholm, Sweden

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The base-catalyzed displacement of the aryloxy substituent in 1,1-bis(*p*-hydroxyaryl)ethane 2-*O*-aryl ethers, via an aryl participation (A_1-3) reaction, and subsequent transformation to the corresponding stilbenes have been investigated. The relative migratory aptitudes of the phenolic nuclei were determined by rate studies and by the use of C-1 deuterium labeled substrates. The two methods gave similar results and showed that the A_1-3 reaction is enhanced when the migrating phenolic nucleus is substituted with electron-donating substituents. The rate-determining step in this reaction was found to be the intramolecular nucleophilic displacement of the aryloxy substituent by a cyclohexadienone carbanion.

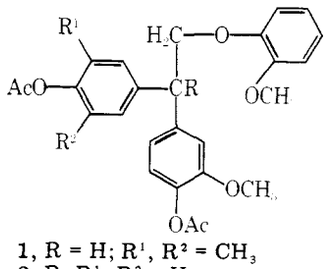
Recently, it was reported that the 1,1-bis(aryl)ethane 2-*O*-aryl ether **1** readily undergoes a base-catalyzed transformation to give, after reacetylation, stilbene **9**.[1] This transformation involves a [1,2] shift of an aryl group, and it was suggested that the mechanism may involve the displacement of the aryloxy substituent through an aryl participation (A_1-3) reaction (Scheme I). A priori, two possibilities for such a transformation can be formulated. As shown in Scheme I, the displacement can be brought about by an intramolecular nucleophilic attack by either carbanion **1b** or **1c** on the β-carbon atom, resulting in the formation of the spiro cyclohexadienone intermediate **8a** or **8b** which by rearrangement and elimination of a proton gives rise to stilbene **9a**.

This conversion of **1** → **9** by way of a spiro cyclohexadienone intermediate is based on well-established precedent, i.e., the alkaline solvolysis of 2-*p*-hydroxyphenylethyl bromide, which takes place by way of a spiro cyclohexadienone intermediate.[2,3] However, the transformation **1** → **9** involves a cyclohexadienone skeleton rearrangement, and the mechanism of this rearrangement with regard to the identity of the migrating group remains a point of considerable uncertainty and interest. Accordingly, in order to obtain more information about the reaction step in which the aryloxy substituent is split off, and to elucidate more fully the mechanism of this reaction, we have studied the effect of substituents on the migratory aptitude of phenolic nuclei in 1,1-bis(aryl)ethane 2-*O*-aryl ether compounds and have tried to correlate the resulting rate data with parameters characteristic for the electronic effect of the substituent. Some results of this study are now reported.

Results and Discussion

The 1,1-bis(aryl)ethane 2-*O*-aryl ether compounds **1–7** were synthesized in an average overall yield of 80–90% by reacting **19** or its deuterated analogue **20** with either phenol or one of three different ortho-substituted phenols in the presence of a small amount of hydrogen chloride,[4] followed by column chromatographic isolation and purification. The condensation products were subsequently used in the form of their crystalline acetate derivatives. Structural proof of new compounds was based on analytical and spectral data (NMR and MS).

Alkaline treatment (1 M NaOH, 170 °C, 2 h) of the 1,1-bis(aryl)ethane 2-*O*-aryl ethers **1–4**, followed by acetylation of the resulting reaction mixtures and gas chromatographic



1, R = H; R^1, R^2 = CH_3
2, R, R^1, R^2 = H
3, R, R^1 = H; R^2 = CH_3
4, R, R^1 = H; R^2 = OCH_3
5, R = ^2H; R^1, R^2 = CH_3
6, R = ^2H; R^1 = H; R^2 = CH_3
7, R = ^2H; R^1, R^2 = H

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