Sodium 3-phenylpropane-1-sulfinate was oxidized to **2** with an acidic solution of cobaltic sulfate, using the general procedure for conversion of *n*-alkanesulfinates to α-disulfones developed by Denzer et al.[12] The crude product was recrystallized from benzene–ethanol, giving pure 3-phenylpropyl α-disulfone (19%): mp 114–116 °C; IR (KBr) 1113 and 1345 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.31 (quintet, 2 H), 2.82 (t, 2 H), 3.42 (t, 2 H), 7.10–7.46 (m, 5 H). Anal. Calcd for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05; S, 17.50. Found: C, 59.10; H, 6.04; S, 17.56.

Procedure for Kinetic Runs. The apparatus used for the kinetic runs was of a design previously described[3a] and shown to be effective for following the progress of reactions that evolve substantial amounts of sulfur dioxide. The desired amounts of α-disulfone and purified bromobenzene were placed in the reaction flask and deaerated by passing a slow stream of dry nitrogen through the solution for 1 h at room temperature, after which the reaction vessel was placed in a constant-temperature bath to initiate decomposition. A stream of nitrogen was passed through the solution during the decomposition to sweep out sulfur dioxide as it was formed. The nitrogen stream was subsequently passed through a trap containing standard iodine solution where the sulfur dioxide was absorbed, and the rate of evolution of sulfur dioxide was followed in the manner outlined by Kice, Parham, and Simons.[3a]

Products of Decomposition of 2. Benzyl α-disulfone (0.62 g, 2 mmol) was decomposed in 50 mL of bromobenzene at 138 °C, using the same apparatus and means of estimating the amount of sulfur dioxide produced (1.6 mmol/mmol of **2**) as in the kinetic runs. After decomposition was complete the bromobenzene was removed under reduced pressure at 90 °C. The residue was chromatographed on silica gel, using successively hexane, various hexane–benzene mixtures, benzene, benzene–ether, ether, ether–methanol, and finally methanol as eluents. Elution with hexane afforded a white solid which was recrystallized from ethanol, giving 0.150 g (0.82 mmol) of bibenzyl, mp 50–53 °C (lit.[13] mp 52–53 °C), identical in all respects with a known sample. Elution with 1:1 benzene–ether gave a fraction, also recrystallized from ethanol, that was dibenzyl sulfone (0.06 g, 0.24 mmol), mp 146–148 °C (lit.[14] mp 151–152 °C), identical with an authentic sample. There was also a small fraction eluted with methanol that was not identified, although the presence of strong absorption in the infrared at 1180–1220 and 1050 cm^{-1} suggested that it was either the hydrate of a sulfonic acid or a sulfonate salt.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. 2, 76625-87-1; **3**, 77357-66-5; 1-bromo-3-phenylpropane, 637-59-2; 3-phenylpropylsulfinyloxymagnesium bromide, 77357-67-6; 3-phenylpropane-1-sulfinic acid, 70385-57-8; sodium 3-phenylpropanol-1-sulfinate, 77357-68-7; sulfur dioxide, 7446-09-5; $(CH_3SO_2)_2$, 10383-49-0.

(12) Denzer, G. C., Jr.; Allen, P., Jr.; Conway, P.; van der Veen, J. M. *J. Org. Chem.* **1966**, *31*, 3418.

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Communications

Reductive Cyclization of Keto Acids to Polycyclic Aromatic Hydrocarbons by Hydroiodic Acid–Red Phosphorus

Summary: Hydroiodic acid–red phosphorus in acetic acid causes ring closure of *o*-naphthoylbenzoic acids and of *o*-naphthoylnaphthoic acids to yield benz[*a*]anthracene and dibenzanthracenes.

Sir: Although hydroiodic acid–red phosphorus (HI/P) was introduced as a reagent into organic chemistry over a century ago[1] it has been only sporadically used in the past. Examples of its use are hydrogenations,[1] deoxygenations of alcohols,[2] ketones,[3] keto acids,[3] and quinones,[4] cleavage of phenol ethers,[5] and reductive cleavage of lactones.[6]

A recent report[4] on the reductive cyclization of 2-(9-phenanthroyl)benzoic acid in the presence of HI/P to dibenz[*a*,*c*]anthracene ascribes the ease of cyclization in this special case to the relatively high olefinic character of the phenanthrene 9,10 bond.

We have found that reductive cyclization with HI/P can quite generally be applied to *o*-naphthoylbenzoic acids and to *o*-naphthoylnaphthoic acids. The use of HI/P therefore provides a simple high-yield route to benz[*a*]anthracene, dibenz[*a*,*h*]anthracene, and dibenz[*a*,*j*]anthracene as well as to their hydroxylated derivatives (Table I).

The keto acids **1–6** were prepared in 70–80% yield by the addition of the Grignard reagent from a suitable aromatic bromo compound to an aromatic 1,2-dicarboxylic acid anhydride as described by LaBudde and Heidelberger,[14] modified according to Braun.[15]

The classic way to transform these keto acids to the corresponding polycyclic aromatic hydrocarbons consists of Friedel–Crafts cyclization with sulfuric acid or polyphosphoric acid to the quinones and reduction with aluminum tricyclohexoxide[16] or zinc/pyridine/acetic acid[17] to polycyclic aromatic hydrocarbons. Both steps, especially the cyclization of **4–6**, afford low yields.[14]

Reductive cyclization with HI/P is therefore a very convenient method to overcome the disadvantages of the classic synthesis of dibenzanthracenes.

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(2) Meakins, G. D.; Swindells, R. *J. Chem. Soc.* **1959**, 1044. Ho, T. L.; Wong, C. M. *Synthesis* **1975**, 161.
(3) Ansell, L. L.; Rangarajan, T.; Burgess, W. M.; Eisenbraun, E. J. *Org. Prep. Proced. Int.* **1976**, *8*, 133.
(4) Harvey, R. G.; Leyba, C.; Konieczny, M.; Fu, P. P.; Sukumaran, K. B. *J. Org. Chem.* **1978**, *43*, 3423.
(5) Guerrero, T. H.; Deulofeu, V. *Chem. Ber.* **1937**, *70*, 947.
(6) Giebe, G. *Chem. Ber.* **1896**, *29*, 2533.
(7) Hemilian, W. *Chem. Ber.* **1878**, *11*, 837.
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(11) Fieser, L. F.; Dietz, E. M. *Chem. Ber.* **1929**, *62*, 1827.
(12) Clar, E. *Chem. Ber.* **1929**, *62*, 350.
(13) Cook, J. W. *J. Chem. Soc.* **1932**, 1472.
(14) LaBudde, J. A.; Heidelberger, C. *J. Am. Chem. Soc.* **1958**, *80*, 1225.
(15) Braun, M. *Angew. Chem.* **1978**, *90*, 1000.
(16) Coffey, S.; Boyd, V. *J. Chem. Soc.* **1954**, 2468.
(17) Manning, W. B.; Muschik, G. M.; Tomaszweski, J. E. *J. Org. Chem.* **1979**, *44*, 699.

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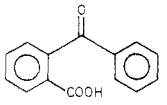
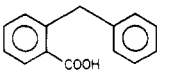
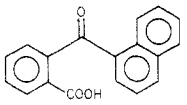
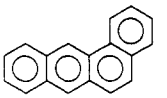
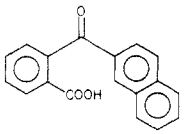
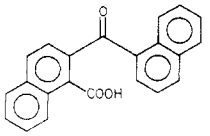
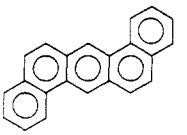
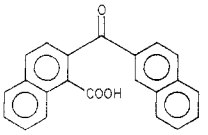
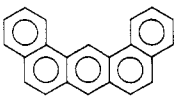
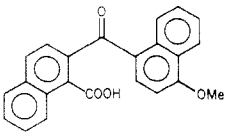
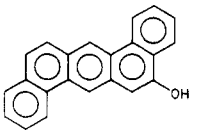
Table I. Reductive Cyclization of Keto Acids with HI/P

keto acid[a]	mp, °C (lit. mp, °C)	reaction time, h	product[a]	mp, °C (lit. mp, °C)	% yield[b]
 1	129 ($EtOH/H_2O$) (127)[7]	120	 7	118 ($AcOH/H_2O$) (118)[10]	85
 2	176 ($CHCl_3$/benzene) (176)[8]	24	 8	159 (benzene) (157)[11]	80
 3	166 (benzene) (165)[8]	36	8		73
 4	180 ($CHCl_3$) (184)[9]	24	 9	260 (acetone) (262)[12]	82
 5	204 ($CHCl_3$)	120	 10	195 ($CHCl_3$/EtOH) (196)[13]	84
 6	239 ($CHCl_3$)	48	 11	264 (acetone)	68

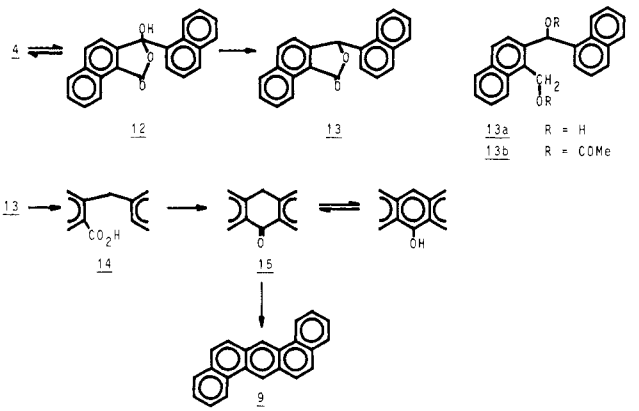
[a] The identity of the products was confirmed by NMR, UV, and mass spectrometry. All compounds gave satisfactory elemental analyses. [b] The yield refers to isolated product after recrystallization.

In the case of methoxy keto acid **6**, the reaction product was the cyclized phenol **11** which is as expected in view of the ability of HI to cleave ethers.[5] This indicates the simplicity by which polycyclic aromatic phenols may be synthesized from methoxy-substituted keto acids by using HI/P. Since most if not all bromomethoxynaphthalenes are described in the literature, the synthesis of these methoxy keto acids in the same way as **6** should pose no major problem.

The proposed reaction sequence[4] of the reductive cyclization with HI/P has to be modified according to our results and is outlined in Scheme I.

The pseudoacid **12** is reduced to the lactone **13**,[9,18] which could be isolated after short reaction times as the sole product. The intermediate formation of a quinone could be positively excluded by TLC in all cases. The (naphthylmethyl)naphthoic acid **14** could not be detected although the transformation of **1** to **7** by HI/P suggests the formation of **14** as an intermediate. The reduction of the ketone **15**—formed by HI-catalyzed intramolecular Friedel–Crafts acylation of **14**—to **9** is consistent with a recent report by Konieczny and Harvey[19] on the reduction of similar phenols to polycyclic aromatic hydrocarbons with HI.

Scheme I. Proposed Reaction Sequence of Reductive Cyclization with HI/P



The experimental simplicity of the reductive cyclization with HI/P is demonstrated by the synthesis of **9** from **4**. A mixture of **4** (326 mg, 1 mmol), red phosphorus (370 mg, 12 mmol), and 57% HI (3 mL) in glacial acetic acid (30 mL) is heated under reflux for an appropriate time. The reaction can easily be monitored by TLC and is stopped when the initially formed lactone **13** has disappeared. The reaction mixture is filtered while hot and diluted with

(18) The structure of the lactone **13** [mp 172 °C (lit.[9] mp 171 °C)] was further supported by reduction to the corresponding dialcohol **13a** by lithium aluminum hydride and subsequent transformation to the diacetate **13b**.

(19) Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4813.

water, and the precipitate isolated and recrystallized (acetone) to yield 9 (228 mg, 82%) as white platelets.

According to Scheme I, HI/P could be used to transform suitable phthalide derivatives (e.g., 13) prepared by tandem-directed metalation[20] to polycyclic aromatic hydrocarbons in an efficient manner.

Work on this and other applications of HI/P is in progress and will be reported in due course.

(20) Newman, M. S.; Kannan, R. *J. Org. Chem.* **1979**, *44*, 3388. Watanabe, M.; Snieckus, V. *J. Am. Chem. Soc.* **1980**, *102*, 1457.

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Additions and Corrections

Vol. 44, 1979

Thomas J. Curphey. Trifluoroacetylation of Amino Acids and Peptides by Ethyl Trifluoroacetate.

Page 2807. Column 1. Line 31 should read L-serine (1.05 g, 10 mmol) not L-serine (1.5 g, 10 mmol).

R. B. King,* J. Bakos, C. D. Hoff, and L. Markó. Poly(tertiary Phosphines and Arsines). 17. Poly(tertiary Phosphines) Containing Terminal Neomethyl Groups as Ligands in Asymmetric Homogeneous Hydrogenation Catalysts.

Page 3096. The carbon-13 NMR data for NmenP(H)Ph listed in Table I (sixth entry in the table) are in error. The correct values are as follows: C-1, 31.6 (8), 31.3 (4.9); C-2, 40.9; C-3, 39.0 (12.2), 38.3 (18.3); C-4, 49.8 (8.6), 49.4 (12.2); C-5, 27.7 (12.2), 27.3 (12.2); C-6, 38.8; C-7, 23.6; C-8, 37.0 (9.8), 36.6 (9.8); C-9, 22.3; C-10, 21.9.

Frederic C. Chang. Potential Bile Acid Metabolites. 2. 3,7,12-Trisubstituted 5β-Cholanic Acids.

Page 4570. In the third column of Table I under δ,[d] the third entry (7α-OH) should read 3.92, the fourth entry (12α-OH) 3.97, and the sixth entry (3α-OTs) 4.35.

Herbert V. Ansell and Roger Taylor.* Electrophilic Aromatic Substitution. 25. Acid-Catalyzed Hydrogen Exchange of 9-Tritiated Polymethylphenanthrenes: Effect of Ring Distortion on Aromatic Reactivity and Substituted Effects.

Page 4907. Compound 4 in Table I has been misprinted. The 2-methyl substituent is missing. The compound should be 2,4,5,7-tetramethylphenanthrene-9-T.

Vol. 45, 1980

Arthur F. Kluge,* Michael L. Maddox,* and Graham S. Lewis. Formation of Quinoxaline Monoxides from Reaction of Benzofurazan Oxide with Enones and ^{13}C NMR Correlations of Quinoxaline *N*-Oxides.

Page 1911. In the monoxide portion of Table II compounds **15** and **16** should be **17** and **18** and compounds **19–23** should be deleted. In the dioxide portion, compounds **17–21** and **23** should be **19–24**, respectively.

Howard Alper* and Khaled Hachem. Rhodium(I)-Catalyzed Biphasic Isomerization of Allylic Alcohols.

Pages 2269–2270. The concentration of sodium hydroxide used is 6 M, not 8 M.

Roy Odle, Burke Blevins, Matt Ratcliff, and Louis S. Hegedus.* Conversion of 2-Halo-*N*-allylanilines in Indoles via Palladium(0) Oxidative Addition–Insertion Reactions.

Page 2710. In the aniline column of Table I, 2-bromo-3,4-dimethoxy-*N*-allyl should be 2-bromo-4,5-dimethoxy-*N*-allyl.

Thomas N. Sorrell* and Paul S. Pearlman. Preparation of Aldehydes from Acid Chlorides Using Copper Tetrahydroborate Complexes.

Pages 3449–3451. The work described by our paper is a compilation of results both from our laboratory and from the laboratory of Dr. G. W. J. Fleet at Oxford. Although we included the references to his work, it may not be readily apparent what input each group has made except to those closely associated with the field. The use of triphenylphosphine in the reaction of $(Ph_3P)_2CuBH_4$ with acid chlorides and the use of cuprous chloride for removing triphenylphosphine from organic reaction mixtures were both introduced by Fleet (*Tetrahedron Lett.* **1978**, 1437–1440). Furthermore, the large-scale preparation of $(Ph_3P)_2CuBH_4$ described in our manuscript is identical with Fleet's original synthesis (*Tetrahedron Lett.* **1979**, 975–978) except that because we could not obtain product with as high a melting point as he reported, we added what amounts to a purification step wherein the crude product is treated with additional triphenylphosphine and sodium borohydride. We did not intend that our report constitute a new procedure, and Dr. Fleet deserves full credit for developing a practical method for preparing this synthetically useful reagent.