yield was obtained; mp 125–129 °C, after recrystallization from ether–hexane.

1-[(5-Bromo-2-methyl-3-indolyl)acetyl]-4-phenylpiperidine (4b). From **9b** and 4-phenylpiperidine (**11**) a 64% yield was obtained, mp 175–180 °C, after recrystallization from chloroform–hexane.

1-[(5-Fluoro-2-methyl-3-indolyl)acetyl]-4-phenylpiperidine (4c). From **9c** and 4-phenylpiperidine (**11**) a 75% yield of **4c** was obtained, mp 165–166 °C, after recrystallization from acetonitrile.

1-[(5,6-Dichloro-2-methyl-3-indolyl)acetyl]-4-phenylpiperazine (4d). From **9d** and *N*-phenylpiperazine (**10**) a 28% yield was obtained, mp 209–219 °C, after recrystallization from acetonitrile.

1-[(5,6-Dimethoxy-2-methyl-3-indolyl)acetyl]-4-(2-pyridyl)piperazine (4f). From **9a** and *N*-(2-pyridyl)piperazine (**12**) a 35% yield was obtained, mp 172–174 °C, after recrystallization from ethanol.

8-[(5,6-Dimethoxy-2-methyl-3-indolyl)acetyl]-1-phenyl-1,3,8-triazaspiro[4.5]decan-4-one (4g). From **9a** and 1-phenyl-1,3,8-triazaspiro[4.5]decan-4-one (**13**) a 42% yield was obtained, mp 250–254 °C, after recrystallization from ethanol.

Reduction of the Amides 4. General Procedure. To a stirred mixture of 0.49 g (13 mmol) of lithium aluminum hydride and 200 mL of tetrahydrofuran was added a tetrahydrofuran solution of 5 mmol of an indolylamide **4** dropwise during 10 min under nitrogen at room temperature. The reaction was stirred at room temperature for 16 h, and then the excess hydride was decomposed by the cautious addition of saturated aqueous sodium sulfate. Filtration and ether workup gave the crude indole **2**.

5-Bromo-2-methyl-3-[2-(4-phenylpiperidino)ethyl]indole (2b). From **4b** a 61% yield was obtained after recrystallization from acetonitrile; mp 138–141 °C.

5-Fluoro-2-methyl-3-[2-(4-phenylpiperidino)ethyl]indole (2c). From **4c** a 21% yield was obtained after recrystallization from acetonitrile; mp 132–134 °C.

5,6-Dichloro-2-methyl-3-[2-(4-phenyl-1-piperazinyl)-ethyl]indole (2d). From **4d** a 87% yield was obtained after recrystallization from acetonitrile; mp 196–199 °C.

5,6-Dimethoxy-2-methyl-3-[2-[4-(2-pyridyl)-1-piperazinyl]ethyl]indole Hydrochloride (2f). The crude indole from **4f** was dissolved in ethanol and made acidic with ethanolic HCl. Addition of ether produced a white crystalline precipitate which was collected by filtration. The salt deliquesced upon exposure to air and resolidified after a few days in the air to give a gray solid, mp 220 °C dec, in 35% yield.

8-[2-(5,6-Dimethoxy-2-methyl-3-indolyl)ethyl]-1-phenyl-1,3,4-triazaspiro[4.5]decan-4-one (2g) was prepared in 16% yield from **4g** after recrystallization from acetonitrile; mp 238–241 °C.

5-(4-Phenyl-1-piperazinyl)-2-pentanone(4-fluorophenyl)hydrazone (15). A solution of 7.5 g (60 mmol) of (4-fluorophenyl)hydrazine, 19.7 g (80 mmol) of 5-(phenyl-1-piperazinyl)-2-pentanone,[23] and 10 drops of glacial acetic acid in 100 mL of ethanol was heated under reflux for 90 min. The clear solution was concentrated in vacuo, and the residue was recrystallized from ethanol to give 6.4 g (30%) of cream-colored crystals, mp 80–85 °C. A 1.0-g sample was recrystalized from ethanol to give 0.45 g of white crystals, mp 98–103 °C.

5-Fluoro-2-methyl-3-[2-(4-phenyl-1-piperazinyl)ethyl]-indole (2h). A mechanically stirred portion of 175 g of polyphosphoric acid was heated to 100 °C (oil bath temperature), and 16.9 g (50 mmol) of **15** was added in portions during 2 min. The stirred mixture was heated at 100 °C for 5 min and then poured onto a mixture of chopped ice and 250 mL of concentrated NH_4OH. A brown precipitate formed and was collected. This solid was partially dissolved in 600 mL of hot chloroform and filtered. The chloroform solution was concentrated to give 7.6 g (45%) of a brown glass.

Acknowledgment. The spectral data were obtained by W. E. Fulmor, G. Morton, Dr. R. T. Hargreaves, and staff. The microanalyses were carried out by L. Brancone and staff. We wish to thank Dr. Lantz Crawley for carrying out some of the reduction experiments and for helpful discussion.

Registry No. **1a**, 71987-48-9; **1b**, 72016-61-6; **1c**·2HCl, 72016-62-7; **1d**·HCl, 71987-49-0; **1f**·HCl, 72016-63-8; **1g**·HCl, 71987-50-3; **1h**·HCl, 71987-51-4; **2a**, 153-87-7; **2b**, 71987-52-5; **2c**, 71987-53-6; **2d**, 71987-54-7; **2f**·HCl, 71987-55-8; **2g**, 72016-64-9; **2h**, 71987-56-9; **4a**, 71987-57-0; **4b**, 71987-58-1; **4c**, 71987-59-2; **4d**, 71987-60-5; **4f**, 71987-61-6; **4g**, 72016-66-1; **5**, 72016-67-2; **6a**·HCl, 20329-82-2; **6b**·HCl, 41931-18-4; **6c**·HCl, 40594-35-2; **6d**·HCl, 71987-62-7; **7**, 123-76-2; **8a**, 13697-78-4; **8b**, 72016-68-3; **8c**, 17536-39-9; **8d**, 71987-63-8; **8e**, 71987-64-9; **9a**, 71987-65-0; **9b**, 71987-66-1; **9c**, 71987-67-2; **9d**, 71987-68-3; **10**, 92-54-6; **11**, 77-10-1; **12**, 34803-66-2; **13**, 1021-25-6; **14**, 25699-21-2; **15**, 71987-69-4; triethylsilane, 617-86-7; trifluoroacetic acid, 76-05-1; **3**, 72016-65-0.

Supplementary Material Available: Table III, nonhydrogen coordinates and anisotropic temperature parameters for **1a**; Table IV, hydrogen coordinates and isotropic temperature parameters for **1a**; Table V, bond distances and angles of osculant atoms; Table VI, spectral data for the new compounds (11 pages). Ordering information is given on any current masthead page.

Efficient Reduction of Polycyclic Quinones, Hydroquinones, and Phenols to Polycyclic Aromatic Hydrocarbons with Hydriodic Acid

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A series of polyarene quinones, hydroquinones, and phenols (or their esters or methyl ethers) undergo reduction directly to the corresponding fully aromatic hydrocarbons in high yield on treatment with hydriodic acid alone or in refluxing acetic acid. Phosphorus is generally not required (except for 1-hydroxynaphthalene) and has a deleterious effect through promotion of undesired hydrogenation of the aromatic products.

Although reduction of several polycyclic quinones with phosphorus and hydriodic acid was described over a century ago,[1] this reagent has never gained wide acceptance and is rarely employed today. Reasons for neglect include the high temperatures (>200 °C) traditionally employed and the complex mixtures of phenols and polyhydrogenated products frequently obtained.[2] We recently

(1) The earliest example of this reaction described in the literature appears to be the reduction of anthraquinone with HI/P to afford anthrone, anthracene, dihydroanthracene, and further hydrogenation products. Cf.: Graebe, C.; Liebermann, C. *Justus Liebigs Ann. Chem., Suppl.* **1870**, *7*, 287. Liebermann, C.; Topf, A. *Chem. Ber.* **1876**, *9*, 1201. Liebermann, C. *Justus Liebigs Ann. Chem.* **1882**, *212*, 1.

(2) Clar states: "The reduction of quinones with hydriodic acid and red phosphorus at 200 °C yields mostly hydrogenated hydrocarbons. These can be dehydrogenated by sublimation over copper at 400 °C." Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964; Vol. I, p 171.

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Table I. Reduction of Polycyclic Quinones with HI in Acetic Acid[a]

quinone[b]	product	yield, %	mp, °C	lit.[c] mp, °C
3	anthracene[d]	89	217-218	216.1
4	benz[a]anthracene[e]	99	158-159	158-159
5	chrysene	96	252-254	250, 254
6	dibenz[a,c]anthracene	98	206-207	200-201.5
1	9-hydroxyphenanthrene	98	154	152[f]
1	9-hydroxyphenanthrene[g]	98	154	152[f]
1	phenanthrene[h]	99	99	101

[a] Reactions were conducted under the standard conditions described in the Experimental Section except as otherwise specified. [b] 3, anthracene-9,10-dione; 4, benz[a]anthracene-7,12-dione; 5, chrysene-5,6-dione; 6, dibenz[a,c]anthracene-9,14-dione. [c] Heilbron, I. "Dictionary of Organic Compounds"; Oxford University Press: New York, 1965. [d] Reduction of anthraquinone with P/HI/I_2 is reported to afford 9,10-dihydroanthracene (77%).[12] [e] When the reaction time was decreased from 15 to 3.5 h, 6% unreacted quinone was detected in the product. [f] Reference 14. [g] Reaction was conducted in the presence of 2.5 mmol of red phosphorus. [h] Reaction of 1 (500 mg, 2.4 mmol) in HI (20 mL) was conducted at reflux for 15 h.

Table II. Reduction of Polycyclic Phenol and Hydroquinone Derivatives with HI[a]

compd	product	yield, %	mp, °C	lit.[b] mp, °C
9-hydroxyphenanthrene (2)[c]	phenanthrene	96	100	101
9-acetoxyphenanthrene	9-hydroxyphenanthrene	99	153	152
7-acetoxybenz[a]anthracene[d]	benz[a]anthracene	99	159-160	158-159
7-methoxybenz[a]anthracene	benz[a]anthracene	95	158-159	158-159
7,12-diacetoxybenz[a]anthracene	benz[a]anthracene	100	159-160	158-159
1-hydroxynaphthalene[e]	naphthalene	52	80-81	80-83

[a] Reactions were conducted following the general procedure described in the Experimental Section except as specified. [b] Heilbron, I. "Dictionary of Organic Compounds"; Oxford University Press: New York, 1965. [c] A solution of 2 (500 mg, 2.8 mmol) in 57% HI (20 mL) was heated at reflux for 15 h, poured into 1% aqueous bisulfite solution, and worked up conventionally. [d] Similar reaction conducted in the presence of red phosphorus (10 mg for 500 mg of the acetate) gave 7,12-dihydrobenz[a]anthracene (19%) along with benz[a]anthracene. [e] A solution of 1-hydroxynaphthalene (1.0 g, 7.0 mmol) in acetic acid (10 mL) and 57% HI (25 mmol) was heated in the presence of red phosphorus (300 mg, 10 mmol) at reflux for 48 h.

observed, however, that reduction of dibenz[a,c]-anthracene-9,14-dione with HI without phosphorus in refluxing acetic acid could be controlled to afford either dibenz[a,c]anthracene or its 9,14-dihydro derivative in excellent yield.[3] Since no entirely satisfactory general method is currently available for the reduction of polyarene quinones directly to the parent hydrocarbons,[4] we undertook an investigation of the utility of HI for this purpose.

We now report that hydriodic acid in refluxing acetic acid *without phosphorus* is a convenient general reagent for the reduction of polycyclic quinones directly to the parent polyarene in a single step. Moreover, since hydroquinones and phenols are found to be intermediates in these reactions, their reduction to hydrocarbons may also be conveniently achieved with this same reagent.

Treatment of a series of quinones with HI in refluxing acetic acid afforded smoothly the corresponding fully aromatic hydrocarbons in high yield (Table I). Under the conditions employed, the dihydro and further hydrogenated derivatives of the hydrocarbons, the usual major products of reduction of quinones with HI in the presence of phosphorus under more vigorous conditions, were not encountered. Incomplete reduction was observed only in the case of phenanthrene-9,10-dione (1) which furnished the phenolic intermediate 9-hydroxyphenanthrene (2) as the principal product of reaction conducted under the standard conditions.[13] Attempted reductions of 1 under similar conditions employing red phosphorus or reaction periods up to 3 days also failed to proceed beyond the phenolic stage. However, reduction of 1 to phenanthrene took place smoothly and essentially quantitatively in refluxing HI in the absence of red phosphorus or acetic acid.

Since hydroquinone and/or phenolic intermediates are likely to be involved in all these reductions, the susceptibility of these types of compounds to reduction with HI was also examined. 9-Hydroxyphenanthrene underwent smooth reduction to phenanthrene essentially quantitatively in refluxing HI with or without phosphorus present (Table II). In contrast, treatment of 9-acetoxyphenanthrene with HI in glacial acetic acid following the general procedure employed for reduction of quinones gave only the free phenol 2 (99%). 7-Acetoxy-, 7-methoxy-, and 7,12-diacetoxybenz[a]anthracene[15] (**4b–d**) on treatment

(3) Harvey, R. G.; Leyba, C.; Konieczny, M.; Fu, P. P.; Sukumaran, K. B. *J. Org. Chem.* **1978**, *43*, 3423.

(4) Reagents other than HI/P employed for the reduction of polycyclic quinones include $LiAlH_4$,[5] $NaBH_4$,[6] $NaBH_4$–BF_3,[6a,7] $Al(OR)_3$,[8] diborane,[9] Zn/NaOH or Zn/NH_4OH,[10] and diphenylsilane.[11] Products include dihydro diols, hydroquinones, phenols, dihydro arenes, and arenes. While Zn in alkaline solution is generally most effective for reduction to the arene, reactions are often erratic and complicated by experimental difficulties including frothing and emulsions.

(5) (a) Harvey, R. G.; Goh, S. H.; Cortez, C. *J. Am. Chem. Soc.* **1975**, *97*, 3468. (b) Harvey, R. G.; Fu, P. P. In "Polycyclic Hydrocarbons and Cancer: Environment, Chemistry, and Metabolism"; Gelboin, H. V., Ts'o, P. O. P., Eds.; Academic Press: New York, 1978; Vol. 1, Chapter 6, p 133.

(6) (a) Rerick, M. In "Reduction"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1968; p 39. (b) Criswell, T. R.; Klanderman, B. H. *J. Org. Chem.* **1974**, *39*, 770. (c) Cho, H.; Harvey, R. G. *J. Chem. Soc.* **1976**, 836.

(7) Sanchorawala, C. J.; Subba Rao, B. C.; Unni, M. K.; Venkataraman, K. *Indian J. Chem.* **1963**, *1*, 19.

(8) Coffey, S.; Boyd, V. *J. Chem. Soc.* **1954**, 2468.

(9) Bapat, D. S.; Subba Rao, B. C.; Unni, M. K.; Venkataraman, K. *Tetrahedron Lett.* **1960**, 15.

(10) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964; Vols. I and II.

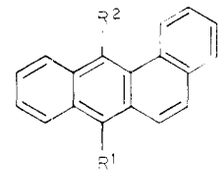
(11) Gilman, H.; Diehl, J. *J. Org. Chem.* **1961**, *26*, 4817.

(12) Renaud, R. N.; Stephens, J. C. *Can. J. Chem.* **1974**, *52*, 1229.

(13) Reduction of 1 with fuming HI was reported in an early study[14] to provide 2, while a similar reaction conducted in acetic acid in the presence of a large excess of phosphorus gave 9-acetoxy-10-hydroxyphenanthrene (yields unspecified).

(14) Japp, F. R.; Klingemann, F. *J. Chem. Soc.* **1893**, *63*, 770.

(15) The acetate derivatives were employed to minimize decomposition of the air-sensitive free hydroquinone and phenolic compounds.



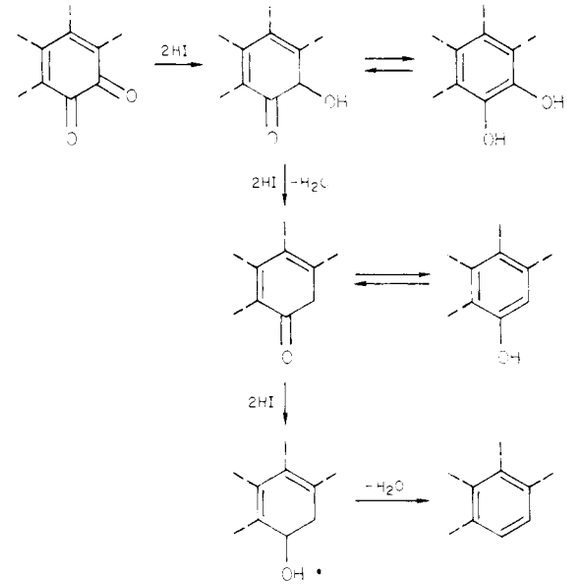
4a, $R^1 = R^2 = H$
b, $R^1 = OAc$; $R^2 = H$
c, $R^1 = OCH_3$; $R^2 = H$
d, $R^1 = R^2 = OAc$

with HI in acetic acid by the same general procedure all underwent facile conversion to benz[*a*]anthracene (**4a**). Similar reaction of 7-acetoxybenz[*a*]anthracene conducted in the presence of red phosphorus gave 7,12-dihydrobenz[*a*]anthracene (19%) in addition to benz[*a*]anthracene as principal products. 1-Hydroxynaphthalene proved resistant to reduction by HI in acetic acid (with or without phosphorus), or even in HI alone, but underwent conversion to naphthalene in refluxing HI in the presence of red phosphorus.

Deoxygenation of phenols is conventionally achieved by catalytic hydrogenation or metal–ammonia reduction of the phosphate ester or other appropriate derivatives.[16] Recently, reduction of phenolic diethyl phosphate esters with titanium metal generated in situ has been introduced as an alternative procedure.[17] The HI method offers the advantages over these methods that deoxygenation may be effected directly on the phenol without the necessity for preparation of a special derivative, and secondary hydrogenation of polycyclic ring systems with HI is poorly competitive in comparison with the alternative methods where this is often a serious problem.[18] Moreover, phenolic methyl ether or ester derivatives do not require prior conversion to the free phenols, since HI effects concurrent demethylation and deesterification readily under the conditions employed. This is particularly advantageous with air-sensitive phenols or hydroquinones which are commonly isolated and purified as their ether or ester derivatives.

These findings are consistent with a mechanism involving successive protonation and hydride transfer from HI with formation of 1 molar equiv of I_2 and dehydration at each stage (Scheme I).[21] Relative rates of reduction of different compounds are anticipated to be a function of the energies necessary to surmount the unfavorable keto–phenol equilibria at each stage. Thus, the relative resistance to reduction of **2** in comparison with 7-hydroxybenz[*a*]anthracene (presumed to be formed from the acetate derivative **4b** in situ) is readily understood as a consequence of the thermodynamically less favorable keto–phenol equilibrium in the former case. Phosphorus,

Scheme I



although it does apparently serve to scavenge the I_2 produced, is not essential in most cases and can have a deleterious effect through promoting hydrogenation of the aromatic ring system of the desired products.

In summary, it appears that HI in acetic acid without phosphorus is a convenient general reagent for the reduction of polycyclic quinones, hydroquinones, and phenols (or their esters or ethers which are readily cleaved under the conditions employed) *to fully aromatic hydrocarbons*. In resistant cases, HI may be employed without a cosolvent or with phosphorus, but these conditions are not recommended for general use for reasons of economy and the probability of undesired overreduction. It is likely that with appropriate modification of reactant ratios and experimental conditions these reductions may be controlled in many cases to afford the thermodynamically stable hydroquinone or phenolic intermediates or driven further under more severe conditions to dihydro and polyhydro aromatic products.

Experimental Section

Phenanthrene-9,10-dione, anthracene-9,10-dione, and benz[*a*]anthracene-7,12-dione were commercial samples (Aldrich) employed without further purification. Chrysene-5,6-dione was recrystallized from benzene prior to use, and dibenz[*a*,*c*]anthracene-9,14-dione,[3] 7-acetoxybenz[*a*]anthracene,[22] and 7,12-diacetoxybenz[*a*]anthracene[23] were synthesized as described previously. 9-Acetoxyphenanthrene was prepared through acid-catalyzed elimination of acetic acid from 9,10-diacetoxy-9,10-dihydrophenanthrene by the method reported.[5a] The HI employed was the colorless 57% aqueous solution (Fisher) preserved with ~1% hypophosphorous acid and stored under N_2 to prevent air oxidation.

The ^1H NMR spectra were obtained on a Varian T-60 spectrometer using tetramethylsilane as internal standard in $CDCl_3$. All products exhibited NMR spectra essentially identical with those of the authentic compounds. All melting points are uncorrected.

General Procedure for Reduction with HI. A mixture of the quinone (1.0 mmol) and 57% HI (1 mL, 7.5 mmol) is heated in refluxing acetic acid (10 mL) for 15 h. The hot solution is then poured into a 1% aqueous sodium bisulfite solution (100 mL), and the resulting precipitate is collected by filtration, washed with water, and air-dried. The crude product is dissolved in a small volume of benzene and purified by passage through a short column

(16) Procedures for the catalytic hydrogenation of tosylate esters, mesylate esters, potassium arylsulfonates, phenyl ethers, methyl ethers, 1-phenyl-5-tetrazolyl ethers, *O*-arylisoureas, and phenylurethanes are described in the literature.[17] Alkali metals in liquid ammonia have been employed for the reduction of mesylate esters, 2,4-diaminophenyl ethers, and diethyl phosphate esters.[17]

(17) Welch, S. C.; Walters, M. E. *J. Org. Chem.* **1978**, *43*, 4797.

(18) For example, benz[*a*]anthracene, obtained in high yield from reduction of **4** with HI, is known to undergo facile catalytic hydrogenation[19] and Li/NH_3 reduction.[20]

(19) Fu, P. P.; Harvey, R. G. *Tetrahedron Lett.* **1977**, 415. Fu, P. P.; Lee, H. M.; Harvey, R. G. *Ibid.* **1978**, 551.

(20) Harvey, R. G.; Urberg, K. *J. Org. Chem.* **1968**, *33*, 2206.

(21) Formation of the phenolic intermediates may conceivably also occur via a vicinal dihydro diol intermediate followed by dehydration rather than via the keto intermediate depicted; these pathways cannot be distinguished on the basis of the available evidence. Precedent for formation of a keto intermediate is provided by the reduction of benzil to benzoin by HI in acetic acid reported by: Reusch, W.; LeMahieu, R. *J. Am. Chem. Soc.* **1964**, *86*, 3068.

(22) Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1938**, *60*, 1893.

(23) Cho, H.; Harvey, R. G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 836.

of silica gel (5 g) eluted with benzene (50–100 mL). Concentration of the eluant affords the products in Tables I and II.

7-Methoxybenz[*a*]anthracene (4c). To a solution of sodium methoxide prepared from sodium (500 mg, 22 mmol) in absolute methanol (25 mL) under nitrogen was added **4b** (700 mg, 2.45 mmol). The resulting suspension was heated at reflux for 1 h, cooled, treated cautiously with dimethyl sulfate (10 mL), and stirred at room temperature for 20 h. The reaction mixture was poured into 5% aqueous NaOH (300 mL), and stirred for an additional hour. The product was removed by filtration, dried, and filtered through a short column of silica gel eluted with benzene–hexane (1:1). Evaporation of the solvent afforded **4c** (500 mg, 89%), mp 109–110 °C (lit.[24] 110.5–111.0 °C).

Acknowledgment. This research was supported by a grant (CA 11968) and a training grant (CA 09183) from the National Cancer Institute, DHEW.

Registry No. 1, 84-11-7; 2, 484-17-3; 3, 84-65-1; 4, 2498-66-0; **4a**, 56-55-3; **4b**, 25040-01-1; **4c**, 6366-20-7; **4d**, 60699-25-4; 5, 2051-10-7; 6, 3228-74-8; anthracene, 120-12-7; chrysene, 218-01-9; dibenz[*a*,*c*]-anthracene, 215-58-7; phenanthrene, 85-01-8; 9-acetoxyphenanthrene, 957-82-4; 1-hydroxynaphthalene, 90-15-3; naphthalene, 91-20-3; 7,12-dihydrobenz[*a*]anthracene, 2498-66-0; HI, 10034-85-2.

(24) Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1937**, *59*, 1028.

Stereochemistry and Mechanism of the Base-Induced Loss of Thiophenol from 1,1,3-Tris(phenylthio)alkanes to Form Cyclopropanone Dithioketals

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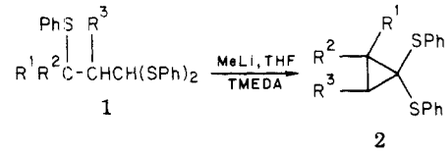
Received August 10, 1979

The indicated aspects of the title reaction were investigated by subjecting *trans*-2-(bis(phenylthio)-methyl)-1-(phenylthio)cyclohexane (**9**) and the corresponding cis isomer (**5**) to the action of methyllithium for 50 h and quenching the mixtures with deuterium oxide. The trans isomer gave the ring-closed product (**10**) in 51% yield, and 29% of the undeuterated starting material was recovered. The cis isomer gave a variety of decomposition products, 13% of starting material which was completely deuterated at the thioacetal carbon atom, and no ring-closed product (**10**). It is concluded that the ring closure is an intramolecular nucleophilic displacement of phenylthiolate ion by the thioacetal anion.

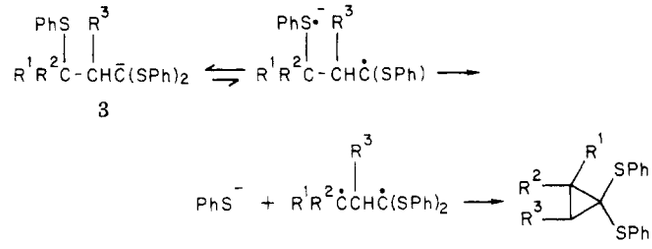
It has recently been found that cyclopropanone bis(phenylthio)ketals (**2**) are produced in excellent yields by the loss of thiophenol from 1,1,3-tris(phenylthio)alkanes (**1**) induced by methyllithium in a tetrahydrofuran (THF) solution containing tetramethylethylenediamine (TMEDA).[1] The recently developed synthesis of complex cyclopropanone thioketals by a connective version of this ring closure[2] and the reductive lithiation of the ring-closed products to sulfur-stabilized anions[3] suggest that this type of ring closure will have considerable synthetic utility, and we have thus carried out an investigation of its stereochemistry and mechanism, a study which was also designed to allow an assessment of its potential for preparing cyclopropanone dithioketals fused to larger rings.



1 2

It has been demonstrated[4] that the thioacetal proton of 1 (R^1 = Me; R^2 = R^3 = H) can be removed by methyllithium, and it is assumed that the anion **3** (Scheme I) is an intermediate in the ring closure. A direct intramolecular "S_N2" reaction with explusion of the thiophenoxide ion appeared questionable (1) because this ion has apparently never been observed as a leaving group in an S_N2 reaction and (2) because of very high yields, 100 and 90%, respectively, observed in the ring closures of 1 (R^1 = R^2 = Me; R^3 = H)[3] and 1 (R^1 = Me; R^2 = SPh; R^3 = H), where

Scheme I



the nucleophile and the carbon bearing the leaving group are both tertiary.[1] A mechanism involving expulsion of thiophenoxide ion from the negatively charged carbon atom of **3** to form a carbene,[5] intramolecular capture of the carbene by the 3-thiophenoxy group to form a four-member ring ylide,[6] and Stevens rearrangement of the ylide to produce the cyclopropane product[6] was excluded by a labeling experiment in which it was demonstrated that the thiophenoxide group on the 3-carbon atom is the one that is lost.[1]

There is still at least one more alternative to the intramolecular nucleophilic displacement. Sulfur-stabilized anions appear to be capable of one-electron donation to suitable acceptors,[7,8] and phenylthioethers can apparently

(1) Cohen, T.; Daniewski, W. M. *Tetrahedron Lett.* **1978**, 2991.
(2) Cohen, T; Weisenfeld, R. B.; Gapinski, R. E., submitted.
(3) Cohen, T.; Daniewski, W. M.; Weisenfeld, R. B. *Tetrahedron Lett.* **1978**, 4665.
(4) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218.
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