Pyrolysis of Silver Arenesulfinates

Ellis K. Fields*

Research and Development Department, Amoco Chemicals Corporation, P.O. Box 400, Naperville, Illinois 60540

Seymour Meyerson

Research Department, Standard Oil Company (Indiana), P.O. Box 400, Naperville, Illinois 60540

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Silver arenesulfinates decompose thermally to produce some bi- and polyaryls, just as do silver arenecarboxylates. Most of the products, however, contain sulfur and are probably formed by prior or concomitant disproportionation to silver salts of arenethiols and sulfonates. The relative amount of products from aryl radicals increases markedly from sulfinates in which expulsion of SO_2 is assisted by *o*-chloro substituents. A small amount of dichlorobiphenylene from pyrolysis of silver 2,5-dichlorobenzenesulfinate is postulated as arising via chloro-*o*-phenylene diradical, in fashion similar to formation of biphenylene in the pyrolysis of silver phthalate and silver diphenate.

Pyrolysis and photolysis of silver carboxylates produce metallic silver, carbon dioxide, and organic radicals:[1]

$$RCO_2Ag \xrightarrow{\Delta} Ag^0 + RCO_2\cdot \rightarrow CO_2 + R\cdot$$

Sulfur dioxide is a good leaving group from pyrolyzed organic molecules;[2] hence we expected silver sulfinates to behave like silver carboxylates upon being heated:

$$RSO_2Ag \rightarrow Ag^0 + RSO_2\cdot \rightarrow SO_2 + R\cdot$$

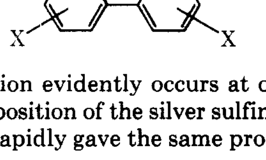
To test this hypothesis, we heated 12.4 g (50 mmol) of silver benzenesulfinate at 250 °C in a Pyrex tube under nitrogen flowing at 10 mL/min for 10 min. Sulfur dioxide evolved. The products other than sulfur dioxide are shown in Table I.

Indeed, biphenyl and terphenyl were formed, but they constituted only minor products. The major products contained sulfur and seem to have arisen apparently by disproportionation of the silver salt:

$$3C_6H_5SO_2Ag \rightarrow C_6H_5SAg + 2C_6H_5SO_3Ag$$

Such disproportionation was indicated by pyrolysis of silver thiophenolate and silver benzenesulfonate separately and determining the products. Silver benzenesulfonate at 380 °C gave benzene (20 mol %) and diphenyl sulfone (4 mol %) as the only ether-soluble products. Silver thiophenolate gave the products shown in Table II. Contributions to some of these products, as well as to some of the products in Table I such as thiophenol, dibenzothiophene, diphenyl sulfide, and thianthrene, also may have been made by prior formation of diphenyl disulfide and its decomposition in the heated inlet system of the mass spectrometer, on the gas chromatography column, and during the decomposition of the silver salts. Diphenyl disulfide, $D(C_6H_5S{-}SC_6H_5)$ = approximately 45.6 kcal/mol,[3] decomposes to an appreciable extent at 200–270 °C; among its degradation products are thiophenol, [4]thianthrene,[4] and diphenyl sulfide.[5]

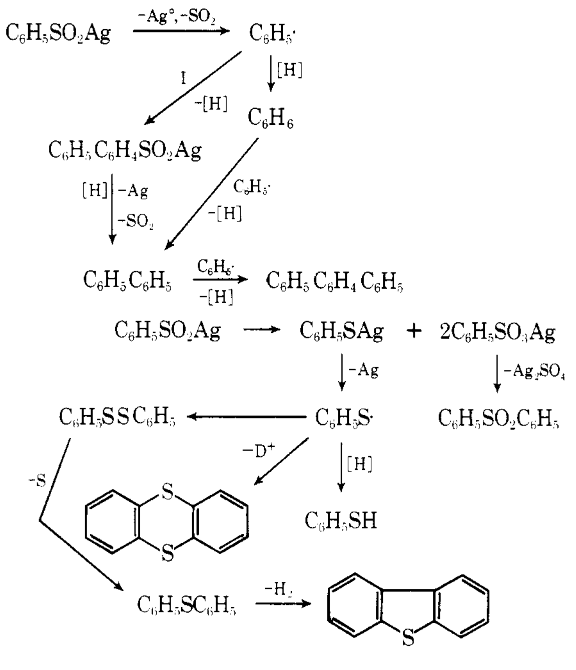
In our work, the compounds listed in Tables I and III as thianthrene and substituted thianthrenes may contain small contributions from the isomeric diphenylene 2,2′-disulfides, formed via loss of hydrogen from diphenyl disulfides.



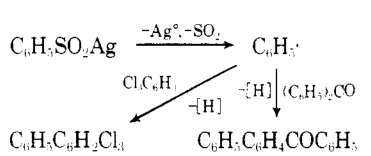
Disproportionation evidently occurs at or near the temperature of decomposition of the silver sulfinate. A sample of silver salt heated rapidly gave the same products and yields as another sample kept at 200 °C for 1 h before being decomposed.

The products listed in Table I can be rationalized by Scheme I.

Scheme I



To find if radicals from decomposition of silver benzenesulfinate would react with aromatic reagents, we refluxed mixtures of the silver salt with 1,2,4-trichlorobenzene and benzophenone separately. Of the products other than starting reagent, trichlorobenzene gave 16% of trichlorobiphenyl; benzophenone gave 41% of phenylbenzophenone. Both reactions thus give evidence of the formation of and arylation by phenyl radical from the silver benzenesulfinate.



Pyrolysis of silver salts of substituted arenesulfinic acids listed in Table III gave products generally similar to those from silver benzenesulfinate. A notable exception is the formation of dichlorobiphenylene from silver 2,5-dichlorobenzenesulfinate, presumably formed from dimerization of the corresponding benzyne:

Table I. Products from Pyrolyzed Silver Benzenesulfinate[a]

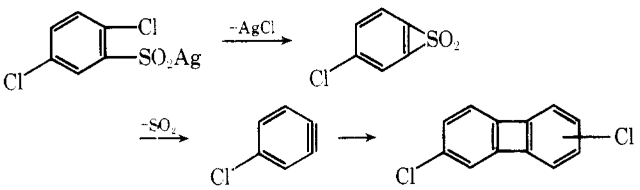
Products[b]	Concn[c]
Benzene	4.7
Thiophenol	3
Biphenyl	8.8
Dibenzothiophene	4.9
Diphenyl sulfide	45.9
Thianthrene	11.8
Diphenyl sulfone	2.0
Terphenyl	0.9
d	

[a] Conditions: 12.4 g (50 mmol) of silver benzenesulfinate, pyrolyzed at 300 °C, N_2 50 mL/min, ether-soluble products, 4.8 g. [b] Molecular composition determined by high-resolution, precise-mass measurements. [c] Percent of total ions in the 7.5-eV mass spectrum. [d] Remainder consisted of phenyl and phenylthio derivatives of those listed, as well as products of molecular weight lower by 2 units. Presumably the latter are ring compounds formed by loss of H_2.

Table II. Products from Pyrolyzed Silver Thiophenolate[a]

Products	Concn, wt %[b]
Benzene	2.8
Dibenzothiophene	0.6
Diphenyl sulfide	9.5
Thianthrene	3.0
Diphenyl disulfide	69.3
c	

[a] Conditions: 10.85 g (50 mmol) of silver thiophenolate pyrolyzed at 350 °C under N_2 at 50 mL/min. Ether-soluble products, 4.6 g. [b] By gas chromatography. [c] The remainder, analyzed by mass spectrometry, consisted of phenylthio derivatives of the compounds listed.



Pyrolysis of silver *o*-halobenzoates by Köbrich[6] and Simmons[7] gave no biphenylene, but other products that could be rationalized by intermediate formation of benzyne. We have obtained biphenylene in the pyrolysis of silver phthalate and silver diphenate in 1.4 and 4 mol % yields, respectively, in these reactions; diradical formation is implicated.

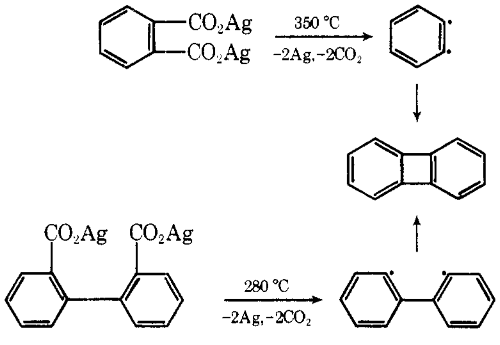


Table III. Products from Pyrolyzed Silver-Substituted Benzenesulfinates[a]

Registry no.	Substituted benzenesulfinate (wt of ether soluble products, g)	Products	Rel concn[b]
61558-20-1	4-F (1.8)	Fluorobenzene	11
		Fluorothiophenol	18.3
		Difluorobiphenyl[c]	4.5
		Difluorodibenzothiophene[c]	5.5
		Difluorodiphenyl sulfide	34.1
		Difluorothianthrene	4
		d	
61558-21-2	4-Cl (1.9)	Chlorobenzene	0.9
		Chlorothiophenol	5.5
		Dichlorodibenzothiophene[c]	3.5
		Dichlorodiphenyl sulfide	47.7
		Dichlorothianthrene[e]	2.8
		d	
61558-22-3	4-Br (2.0)	Phenol	7.3
		Bromobenzene	6.2
		Bromothiophenol	1.4
		Bromodiphenyl sulfide	10.2
		Dibromobiphenyl	4.9
		Dibromodiphenyl sulfide	48.1
		Tribromoterphenyl	0.8
		Dibromothianthrene	2.6
		d	
61558-23-4	2,5-Cl_2 (3.6)	Chlorophenol	3.6
		Dichlorobenzene	38.7
		Dichlorobiphenylene	2.0
		Tetrachlorobiphenyl	19.8
		Tetrachlorodibenzothiophene	1.9
		Tetrachlorodiphenyl sulfide	7.9
		Hexachloroterphenyl	5.7
		Octachloroquaterphenyl	1.4
		d	
61558-24-5	2,4,5-Cl_3 (4.1)	Trichlorobenzene	44.9
		Hexachlorobiphenyl	30.5
		Hexachlorodiphenyl sulfide	6.1
		Hexachlorothianthrene	3.2
		Nonachloroterphenyl-017.0	
		d	
39538-86-8	4-Me (2.1)[f]	Toluene	13
		Bitolyl	9
		Ditolyl sulfide	35
		Dimethylthianthrene	12
		Ditolyl sulfone	14
		d	

[a] Conditions: 20 mmol of Ag substituted benzenesulfinate pyrolyzed at 300 °C, N_2 50 mL/min. [b] Percent of total ions in the 7.5-eV mass spectrum. [c] And/or fragment ion. [d] Remainder consisted of substituted phenyl and substituted phenylthio derivatives of the listed products, as well as products of molecular weight 2 units lower. Presumably the latter are ring compounds formed by loss of H_2. [e] Confirmed by high-resolution precise-mass measurement. [f] In addition to 1.1 g of toluene distilled out of the pyrolyzed salt.

There were appreciable differences in the amount of substituted biphenyls formed from substituted silver benzenesulfinates, as shown in Table IV. The greater amounts of biphenyl derivatives from silver 2,5-dichloro- and 2,4,5-trichlorosulfinates evidently arise because of steric assistance by the *o*-chloro groups to the expulsion of SO_2 from $ArSO_2\cdot$ radicals, as well as weakening of the aryl–SO_2 bond in the more highly substituted sulfinates. Silver 4-chlorobenzenesulfinate, oddly enough, gave no detectable dichlorobiphenyl or tri-

Table IV

Substituent	Rel concn of biphenyl[a]
4-F	4.5
4-Cl	
4-Br	4.9
2,5-Cl_2	19.8
2,4,5-Cl_3	30.5

[a] On the scale of Table III.

Table V

Substituent	Yield, mol %	Mp, °C (acid)	Registry no.	Dec point, °C (Ag salt)
4-F	60	Syrup	369-51-7	220
4-Cl	35	92–93	100-03-8	304
4-Br	89	108	1195-33-1	251
2,5-Cl_2	90	99–101	61558-25-6	224
2,4,5-Cl_3	80	150–152	10439-21-1	218

chloroterphenyl. There was a considerable amount, 14.3 on the scale of Table II, of product of composition $C_{18}H_{11}Cl_3S$, confirmed by high-resolution precise-mass measurement, presumably having the structure $ClC_6H_4SC_{12}H_7Cl_2$, such as might arise from reaction of a chlorophenylthio radical and dichlorobiphenyl. The corresponding compound containing two fewer hydrogen atoms, tentatively pictured as chlorophenyl dichlorodibenzothiophene, also was confirmed by high-resolution precise-mass measurement.

Experimental Section

Benzene- and *p*-toluenesulfinic acids were purchased from Aldrich Chemical Co. The other benzenesulfinates were prepared by the method of Baldwin and Robinson,[8] by reduction of the corresponding benzenesulfonyl chlorides with aqueous sodium sulfite at 0–10 °C (Table V).

Silver salts were prepared by adding filtered solutions of sodium sulfinates to aqueous silver nitrate in 5% excess at 20 °C in dim light, collecting the precipitated silver salt on a filter, washing thoroughly with cold water, and drying in vacuo at 80 °C.

For pyrolysis, the silver salt, 20 mmol, was spread evenly in a Pyrex tube, swept with dry nitrogen, and heated in a furnace. The cooled products were extracted with ether, the ether solutions filtered and evaporated, and the residues analyzed by gas chromatography, 70-eV and low-voltage mass spectroscopy (low resolution), supplemented by high-resolution precise-mass measurements where shown in the tables, and directly coupled gas chromatography–mass spectrometry. Low-resolution mass spectra were measured on a Du Pont Model 21-104 instrument using electrical scanning, with normal and low-voltage electron energies set at 70 and 7.5 eV nominal, and with inlet and source temperatures of 350 and 250 °C, respectively. Directly coupled gas chromatography–mass spectrometry utilized a 5 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W, coupled via a jet-orifice separator to a Du Pont Model 21-491 mass spectrometer; electron energy was 70 eV and ion source temperature was 250 °C. High-resolution measurements were made on a CEC Model 21-110B mass spectrometer with 70-eV electrons and inlet and source temperatures approximating those used for the low-resolution spectra. Mass measurements were obtained via the A.E.I. DS50 system at a resolution of 10 000 (10% valley definition) except in cases where peaks of interest—especially some due to chlorinated species—were poorly resolved from perfluoroalkane reference peaks. In such cases, we resorted to peak matching at a resolution of 20 000. Silver phthalate and silver diphenate upon pyrolysis gave mostly black polymer as did other silver polycarboxylates.[1] The polymer was extracted with acetone; the small amount of distillate was dissolved in acetone, combined with the extract, and analyzed by gas chromatography. Biphenylene was prepared by the method of Logullo, Switz, and Friedman.[9]

Registry No.—Silver benzenesulfinate, 7449-23-2; silver thiophenolate, 22758-12-9.

References and Notes

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The Mechanism of the Photoreaction of 1,2-Benzocyclobutenedione in Ethanol. The Photochemistry of *o*-Carboethoxybenzaldehyde

Richard J. Spangler,* Leonard G. Henscheid, and Keith T. Buck

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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The ultraviolet irradiation of *o*-carboethoxybenzaldehyde (**8**) in ethanol gives the isomeric 3-ethoxyphthalide (**7**). The photoenol **9** of **8** can be trapped by a Diels–Alder reaction with maleic anhydride. Irradiation of **8** in ethanol-d_1 results in deuterium incorporation in **8** via the intermediate photoenol **9**. With the observation that **8** is photochemically isomerized to 3-ethoxyphthalide (**7**), *o*-carboethoxybenzaldehyde (**8**) is proposed as a likely intermediate in the known photoconversion of 1,2-benzocyclobutenedione (**1**) to 3-ethoxyphthalide (**7**).

In 1968 Staab and Ipaktschi reported that the ultraviolet irradiation of benzocyclobutenedione (**1**) at room temperature initially produced bisketene **2** which subsequently isomerized to oxacarbene **3**.[1,2] Chemical evidence was obtained supporting the intermediacy of both **2** and **3**. Specifically, irradiation of **1** with maleic anhydride gave an excellent yield of adduct **4** (presumably via bisketene **2**), irradiation of **1** with isobutylene gave the spirolactone **5** in 65% yield, and irradiation of **1** in inert solvents gave the dimers **6**. In 1971, Chapman, McIntosh, and Barber found that the photolysis of **1** at 77 K as a thin film gave dimers **6** but produced no detectable (by infrared spectroscopy) bisketene **2**.[3a] These workers thus concluded that bisketene **2** was not produced, at least under these experimental conditions, and that carbene **3** arose directly from **1**. Kolc also studied the low-temperature photochemistry of **1** matrix isolated in EPA at 77 K and sim-