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Electron-bombardment and Pyrolysis of

meso- and *dl*-Hydrobenzoin Cyclic Sulfites

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Only a minor yield of sulfur dioxide positive ions is eliminated from the meso- and *dl*-hydrobenzoin cyclic sulfite molecules under electron bombardment. Among the principal fragmentation products for both sulfites are very similar yields of ions with m/e 154 and 126, which contain sulfur most probably attached to a phenyl ring. Positive ions apparently corresponding to those of diphenylacetaldehyde, desoxybenzoin, and stilbene are minor products of the positive-ion fragmentation process of the sulfites. These three compounds along with sulfur dioxide are the products of the pyrolysis of the sulfites at 240-250°. The principal product from the meso-sulfite is desoxybenzoin, and from the *dl*-sulfite it is diphenylacetaldehyde. Mechanistic details are discussed.

There has been much recent emphasis on the re-arrangement processes that occur in the course of the fragmentation of organic positive ions (2). We were interested to study the positive-ion fragmentation of the hydrobenzoin cyclic sulfite isomers in order to search for similarities to their contrasting pyrolysis reactions, one of which has been reported to involve a rearrangement (3). This paper reports the results of this study, in which the mass spectrometer was used to analyse the pyrolysis products formed in the vapor phase in the same apparatus as was used to lead the pure sulfites into electron bombardment.

RESULTS

The mass spectra of the hydrobenzoin cyclic sulfite isomers showed only very slight changes with time and temperature for temperatures of the mass-spectrometer inlet-system ranging from 60-150°. A set of data is presented in Table I for 110° and shows that the spectra are very similar for both isomers. No parent-ions were observed (m/e 260).

TABLE I

Mass Spectra of *dl*- and meso-Hydrobenzoin Cyclic Sulfite Isomers for an Inlet-temperature of 110° Using 70-eV Bombarding Electrons

m/e	Relative Yield (a) *dl*	meso	Assignment
196	0.04	0.06	$C_{16}H_{12}O^+$
195	0.03	0.02	
194	0.04	0.03	
180	0.24	0.18	$C_{16}H_{12}^+$
179	0.30	0.21	
178	0.29	0.22	
167	1.05	0.53	$C_{15}H_{11}^+$
165	0.85	0.56	
156	0.68	0.64	
155	1.14	1.09	
154	13.86	12.94	$C_7H_6O_2S^+$
152	0.54	0.35	
128	0.41	0.40	
127	0.53	0.55	
126	6.86	7.16	$C_6H_6OS^+$
106	2.62	2.79	
105	13.35	14.92	$C_7H_5O^+$
91	0.86	0.66	$C_7H_7^+$
90	2.23	1.72	$C_7H_6^+$
89	2.86	2.10	$C_7H_5^+$
78	14.14	15.23	$C_6H_6^+$
77	10.75	11.78	$C_6H_5^+$
76	1.01	0.88	
65	0.95	0.81	
64	0.98	0.83	SO_2^+
63	1.87	1.53	
52	2.29	2.42	
51	9.38	9.74	$C_4H_3^+$
50	2.80	2.86	
48	0.95	1.05	SO^+

(a) $\Sigma_{48}^{196} = 100.00$ for both. Many ions of low yield are not listed.

Two characteristic fragments obtained in high yield were identified from their isotopic ratios as the sulfur-containing ions $C_7H_6O_2S^+$ (m/e 154) and $C_6H_6OS^+$ (m/e 126). The yields of m/e 64 and 48, which correspond to SO_2^+ and SO^+, were small.

As the temperature of the vapor of each sulfite was raised to approach 250° in the inlet-system of the mass spectrometer, the production of sulfur dioxide became evident through the appearance of more substantial yields of m/e 64 and 48, and the characteristic features of the stable spectra of the sulfites that were observed at 110° were gradually replaced by spectra that corresponded principally to mixtures of desoxybenzoin and diphenylacetaldehyde, and which were characteristic of the original sulfite isomers. Table II shows a spectrum for the decomposition products of the meso-sulfite recorded after 1 hour at 240°, after which time the peaks for m/e 154 and 126 had almost disappeared and showed no change. In the case of the dl-sulfite the reaction was slower and the spectrum was recorded after 3 hours at 245° (Table II).

TABLE II

Mass Spectra (a) of Pyrolysis Products from meso- and dl-Hydrobenzoin Cyclic Sulfite Isomers for 70-eV Electrons, and Derived Spectrum of Diphenylacetaldehyde

m/e	Original data (a)		Residues for diphenyl-acetaldehyde	
	meso	dl		
197	0.60	2.0	0.6	0.6
196	3.12	11.5	3.2	3.5
181		7.1		1.5
180	0.70	24.0		1.8
179	0.68	16.5		
178	0.55	10.8		0.3
169	0.71	16.2	1.4	5.3
168	8.78	52.5	17.6	17.2
167	50.00	305.0	100.0	100.0
166	6.65	41.0	12.8	13.1
165	17.10	106.0	31.8	31.9
164	1.65	10.0	3.1	3.3
163	1.28	7.5	2.3	2.4
153	1.90	11.5	3.7	3.7
152	10.00	63.0	19.0	19.8
151	1.10	7.1	2.1	2.0
139	1.90	12.8	3.4	4.1
128	1.41	9.1	2.6	2.9
115	2.55	18.6	5.0	5.6
106	8.50	11.5	2.0	1.3
105	100.00	100.00		
102	0.74	7.2	1.2	1.2
91	8.50	20.0	2.7	4.0
90	1.50	8.8	1.0	1.6
89	3.70	22.8	3.3	3.0
83	2.30	14.2	4.4	4.6
82.5	2.75	17.2	5.1	4.9
82	2.00	12.0	3.8	3.9
78	3.52	13.0	1.4	2.7
77	42.80	70.8	4.2	7.5
76	3.15	20.0	2.4	2.7
75	1.90	10.5	1.9	2.5
74	1.92	10.3	1.9	2.7
66 (SO₂)	1.64	5.2		
66 (Ar) (c)	0.16	1.3		0.3
65 (SO₂)	0.35	0.9		
65 (Ar) (c)	8.77	25.3	3.6	5.6
64 (SO₂)	37.35	117.9		
64 (Ar) (c)	0.85	2.1		
63	6.68	35.4	7.0	9.2
62	2.10	11.5	2.2	3.1
52	2.40	13.0	1.9	2.9
51	20.50	67.6	8.3	13.5
50 (SO)	1.06	3.4		
50 (Ar) (c)	6.43	27.8	3.7	6.3
48 (SO)	24.00	77.2		
39	11.00	44.0	8.6	9.6
Σ^{197}_{39}	372.6 (b) (=Σmeso)	1430.4 (b) (=Σdl)	309 (b)	353 (b)

(a) Many small yields are omitted for brevity. (b) Includes contributions from all observed ions except SO^+ and SO_2^+. It was assumed that all m/e 48 was due to SO^+ and almost all of m/e 64 was due to SO_2^+, cf. Table III. (c) Derived from aromatic fragments.

For comparison with the spectra of the pyrolysis products, Table III shows the spectrum of desoxybenzoin recorded separately after 1 hour in the inlet-system at 240° (during which time the spectrum was constant) and, in a separate experiment, after 3 hours at 245° (during which time minor change occurred). Stilbene was suspected as a pyrolysis product and, accordingly, the spectrum of the stable trans-isomer was recorded after 3 hours at 240° and showed no change during that time (Table III).

TABLE III

Mass Spectra (a) of Desoxybenzoin and Stilbene (trans), for 70-eV Bombarding Electrons

m/e	Desoxybenzoin (240°) (b)	Desoxybenzoin (245°) (b)	Stilbene (240°) (c)	
197	0.28	0.10		
196	1.50	0.85		
181			.09	2.4
180			.76	18.5
179			.68	16.5
178			.41	10.0
167	0.12	0.10		
166	0.21	0.12	.04	1.0
165	0.85	0.60	.34	8.2
164	0.10			
163	0.09			

TABLE III
(Continued)

m/e	Desoxybenzoin (240°) (b)	Desoxybenzoin (245°) (b)	Stilbene (240°) (c)	
152	0.40	0.30	.09	2.1
151			.05	1.1
139	0.18	0.12		
128	0.10	0.08		
115	0.25	0.20	.05	1.2
106	7.48	7.50		
105	100.00	100.00		
102			.14	3.4
91	7.10	6.35	.06	1.5
90	0.88	0.72	.13	3.2
89	1.62	1.41	.51	12.3
83	0.10	0.10		
82.5	0.12	0.12	.09	2.1
78	2.75	2.91	.07	1.8
77	40.50	43.50	.19	4.5
76	1.55	1.51	.46	10.2
75	0.85		.09	2.1
74	0.88		.06	1.4
66	0.40	0.40		
65	6.90	6.81	.05	1.3
64	0.80	0.80	.05	1.3
63	2.98	2.75	.21	5.1
62	0.95	0.85	.05	1.3
52	1.31	1.35	.12	2.8
51	16.00	17.20	.37	9.1
50	4.44	4.40	.16	4.0
39	6.44	8.00	.27	6.5
	$\Sigma_{ket}^{240°}=212.07$	$\Sigma_{ket}^{245°}=213.37$	$\Sigma_{St}=5.89$	$\Sigma_{St}=141.8$

(a) Several ions of low yield, which are not treated in Table II, are not included here for brevity. (b) Normalized to base-peak (105) = 100.00. (c) Normalized to m/e 179 = 0.68 and 16.5, $cf.$ Table II.

These three spectra were used to obtain the analysis of pyrolysis products shown in Table V (the spectrum of diphenylacetaldehyde was not required, see Experimental (4)).

DISCUSSION

The principal ion-fragments produced by electron bombardment of the sulfites can be accounted for as shown in Figure 1. The production of a high yield of $C_7H_6O_2S^+$ is consistent with the loss from the parent-ion of stable, neutral fragments like benzaldehyde or benzene plus carbon monoxide. The elimination of neutral desoxybenzoin or equivalent fragments, with the production of SO_2^+, is not so well favored. It is plausible that there should be a higher energy requirement for the production of SO_2^+ compared to the aromatic ion $C_7H_6O_2S^+$ (the
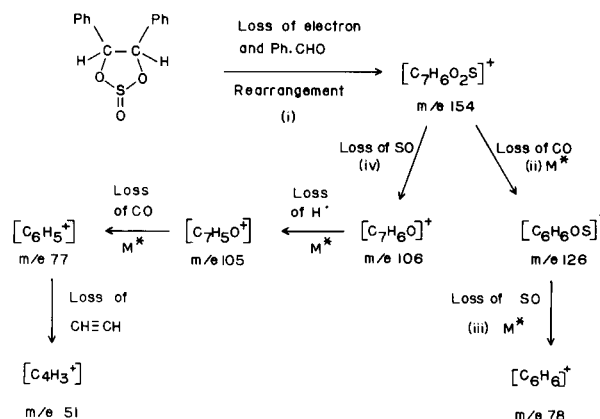

Figure 1. Illustration of probable main pathways of positive-ion fragmentation of hydrobenzoin cyclic sulfites under electron-bombardment. Odd-electron positive ion: $[....]^+$. Even-electron positive ion: $[....^+]$. Metastable transition: M*. (The processes are not necessarily consecutive but are presented that way for simplicity.)

ionization potential of SO_2 is $ca.$ 13.4 eV, $cf.$ 9-10 eV for aromatic aldehydes and ketones (5)). The observation of a broad "metastable" band centered at m/e 103.5 in the mass spectrum of the sulfites demonstrates that a fraction of the ions of m/e 154 decompose in flight by loss of carbon monoxide to give m/e 126 (Table IV). This strongly suggests

TABLE IV

Major Mestastable Transitions (M_f^2/M_i) observed in the Mass Spectra of meso- and dl-Hydrobenzoin Sulfites and Desoxybenzoin

Initial mass (M_i)	Final mass (M_f)	M_f^2/M_i	Mestastable observed (M*)
Hydrobenzoin sulfite isomers			
154 $\longrightarrow$ 126		103.1	103.5
126 $\longrightarrow$ 78		48.3	48.7
106 $\longrightarrow$ 105		104.0	104.2
105 $\longrightarrow$ 77		56.5	56.9
Desoxybenzoin			
106 $\longrightarrow$ 105		104.0	104.3
105 $\longrightarrow$ 77		56.5	56.7
91 $\longrightarrow$ 65		46.4	46.8

that the S=O group of the ion $C_7H_6O_2S^+$ becomes attached to the benzene ring through reaction of the sulfur with the neighboring phenyl group accompanied by a proton shift. This process is plausible when thought of as an intramolecular electrophilic substitution on the aromatic nucleus by the reagent $RO-S^+=O$ via a five-membered-ring transition state. Hence, a structure like I may be tentatively suggested for $C_7H_6O_2S^+$.

The "metastable" band centered at m/e 48.7 shows that, of those m/e 126 ions which were formed rapidly from short-lived m/e-154 ions, or possible directly from parent ions, a proportion lost sulfur monoxide in flight to give m/e-78 ions. This does not preclude the loss of sulfur monoxide directly from the shorter-lived m/e-154 ions to give m/e 106, and most of the yield observed for this ion no doubt comes by this path (Fig. 1, step iv, by analogy with steps ii and iii). The m/e-106 peak is 2-3 times higher than the expected C^{13} contribution from m/e 105. High yields of m/e 105, 78, 77, and 51 are usual in the spectra of aromatic aldehydes and ketones and their derivatives.

I
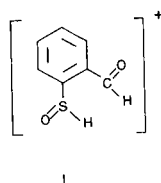
The most significant ions observed in the spectra of the decomposition products of the meso- and dl-hydrobenzoin sulfite are m/e 105 and 167, and the set ranging from 178-181. The yield of m/e 105 almost certainly comes entirely from desoxybenzoin, for which the principal fragmentation steps are shown in eq. 1 (cf. Tables III and IV). This ion is not given by stilbene (Table III) and it cannot be obtained from diphenylacetaldehyde by direct cleavage. It is very unlikely that the latter molecule should produce m/e 105 by a fragmentation process involving a double migration, of a phenyl group and a proton. Moreover, fragmentation of 1,1-diphenylacetanilide, a parallel case, produces no yield of m/e 105 (7). The ion-fragment m/e 167 is obtained in extremely small yield from desoxybenzoin and not at all from stilbene. However, this ion is one of the more abundant to be expected in the spectrum of diphenylacetaldehyde owing to loss of H· and CO. The most abundant ions in the spectrum of stilbene are m/e 178-180; these do not occur for desoxybenzoin and would not be expected from diphenylacetaldehyde (loss of H_2O, OH and O). This set of ions is evident in the spectra of the pyrolysis products of the sulfites, and stilbene is indeed a plausible pyrolysis product.
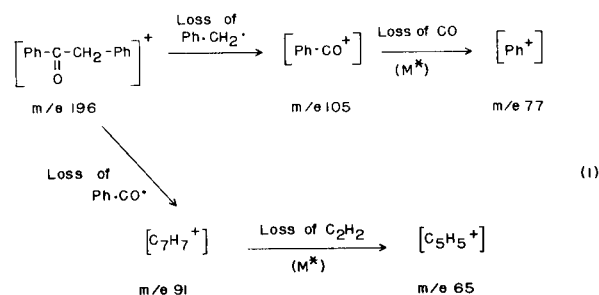

(1)

Table V shows the results of an analysis of the data in Table II using the above assumptions, and details of the calculation are given in the experimental section. The results are broadly consistent with a previously reported study of pyrolysis of the hydrobenzoin sulfites in the liquid phase (3). However, under our conditions a significant amount of elimination of sulfur trioxide occurs from the dl-isomer, and the free-energies of activation for the production of the aldehyde and ketone are evidently closer. No doubt the pyrolysis in the liquid phase involves medium effects that make the reaction more selective.

It can be shown that the mean temperature of molecules in the ion-source of the mass spectrometer is very close to the temperature of the source itself (250°) and is independent of the original temperature of the molecules in the inlet system, even though the mean residence-time within the source is less than 1 second. It is therefore possible that the spectra recorded for 110° (inlet temperature) contain a small contribution from a catalyzed pyrolysis at the stainless steel surfaces of the ion-source. However, the ratios of yields of m/e 180, 179, and 178, given by the meso-sulfite with and without intentional pyrolysis, do not agree; also, these yields are about the same for electron bombardment of the two sulfite isomers, whereas a 5:1 ratio of yields occurs when they are pyrolysed. Similarly, the ratios of yields of m/e 196, 167, 165, and 152 for the pyrolysis products differ substantially from these ratios for the sulfites run at 110°.

CONCLUSIONS

We conclude that the general features of all the observed spectra can be plausibly accounted for.

The similarity of the spectra of the two sulfite isomers strongly suggests that ring-opening is an immediate consequence of electron impact, so that there can be no characteristic effect of the differently oriented phenyl groups, as is observed in the pyrolysis. Ring-opening in saturated, heterocyclic, positive ions is probably a strongly favored process (8). Once ring-opening has occurred in the parent-ions of the sulfites, rearrangements and dissociations ensue to produce principally ion-fragments in which sulfur is attached to a phenyl ring. Contrastingly very low yields of ions that correspond

to the same products as are observed in the pyrolysis are obtained as very minor products of electron-impact on the sulfite molecules. The relative yields of these ions are different for decomposition of the sulfites by electron-impact alone and by intervening pyrolysis and electron-impact on the products; however, for the former case, although no molecular ions were observed at all in the spectra, it does not seem possible to decide whether these minor yields of ions result from dissociation of the parent-ions of the sulfites before or after ring-opening.

TABLE V

Yields of Products from Pyrolysis of meso- and dl-Hydrobenzoin Cyclic Sulfites

Product	Percent of total product meso	dl
Stilbene	2	10
Desoxybenzoin	57	15
Diphenylacetaldehyde	41	66
Unidentified	--	9

EXPERIMENTAL

Materials (9).

Meso-hydrobenzoin was prepared by reduction of 70 g. of benzil with sodium borohydride (10,11). The product was dried and crystallized from xylene, yielding 35 g. of white crystals, m.p. 136.5-137° (12).

The meso-hydrobenzoin was converted to the cyclic sulfite by treatment with thionyl chloride and pyridine, with benzene as diluent (13). The crude product was recrystallized twice from ethanol and then from hexane until the melting point reached 133°, yield 21 g.

Anal. (14) Calcd. for $C_{14}H_{12}O_3S$: C, 64.6; H, 4.6. Found: C, 64.5; H, 4.6.

A sample of pure dl-hydrobenzoin was prepared from stilbene (15) and was converted to the sulfite following the method of Price and Berti (3). The product was recrystallized from ethanol to a constant melting point of 86°. The overall yield was 30%.

Anal. Found: C, 64.5; H, 4.5.

Desoxybenzoin was a reagent-grade sample of m.p. 60° from the K. and K. Laboratories. trans-Stilbene was a reagent-grade sample from the Eastman Kodak Company.

Mass Spectra.

A Consolidated Electrodynamics Corporation Model 21-103C instrument equipped with a thermostated, all-glass inlet-system was employed (16). The samples were evaporated at a pressure in the order of 10^{-3} mm and held in a glass bulb, from which they were allowed to leak slowly into the ion-source of the spectrometer through a gold-foil leak that dropped the pressure about 100-fold. The ion-source was thermostated at 250° and a 10-μA beam of electrons accelerated to an energy of approximately 70 electron-volts was used to bombard the vapors of the samples. All spectra were recorded under "nonfocused" conditions (positive-ion repeller potentials varying at about 1.5% of the ion-accelerating voltage) and were scanned by varying the accelerating voltage downward from 3000 volts with a constant magnet current of 500 mA. All samples were scanned with the exit-pressure gauge reading within the range 1-3 x 10^{-6}mm.

Analysis of pyrolysis products.

Assuming that m/e 179 is due only to stilbene, the small contributions of this substance to Σ_{meso} and Σ_{dl} can be deducted out provided that the stilbene spectrum is normalized to m/e 179 = 0.68 and 16.5 for the respective cases (cf. Table II). The ratio of ionization cross-sections expected for stilbene and the aldehyde or ketone can be calculated from previously determined values of atomic constants, assuming additivity: (17) $C_{14}H_{12}/C_{14}H_{12}O = 0.955$. Hence, the fractions of stilbene present are $\Sigma_{St}/(0.955\ \Sigma_{meso})$ and $\Sigma'_{St}/(0.955\ \Sigma_{dl})$ for the two sets of decomposition products, respectively (Table V). The residual spectra of the pyrolysis products, after deduction of the

contribution due to stilbene, totaled 367 and 1289 for the meso and dl-sulfites (that is, Σ_{39}^{197} excluding SO_2^+ and SO^+ peaks, cf. Table II). From these residues were deducted the appropriate ketone spectra in Table III, which are suitably normalized to m/e 105 = 100, and the remaining peak-values are presented in the fourth and fifth column of Table II after renormalization to m/e 167 = 100 for mutual comparison. The fractions of desoxybenzoin present in the pyrolysis products were calculated from the expressions $\Sigma_{ket}^{240°}/\Sigma_{meso}$ and $\Sigma_{ket}^{245°}/\Sigma_{dl}$.

The spectrum shown in the fourth column of Table II is a reasonable one for diphenylacetaldehyde: the main fragmentation path involves loss of the aldehyde group to give m/e 167; the other fragments mostly range from $C_nH_n^+$ to $C_nH_{n-4}^+$ and are derived from the aromatic groups. The spectrum in the last column is similar but has a summation about 12% greater than that of the former (or 9% of the total product). Part of this results from experimental error; the remainder is due to "extra" contributions chiefly to m/e 181, 180, 169, 91, 63, 51 and 50, which represent either another aromatic product or possibly impurities leached from the walls of the spectrometer system after 3 hours. Nevertheless, the analytical procedure is proved to be sound by the reasonable consistency of columns 4 and 5 of Table II.

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(3) C. C. Price and G. Berti, J. Am. Chem. Soc., 76, 1211 (1954). These authors reported that, after 15 minutes at 245° in the liquid phase, dl-hydrobenzoin sulfite yielded not less than 95% of diphenylacetaldehyde and that, after 10 minutes at 240° similarly, the meso-sulfite gave at least 60% of desoxybenzoin plus "a trace" of aldehyde. To explain this apparently unlikely result, they proposed an ingenious mechanism involving alkenyl hydrogen sulfites as intermediates.

(4) To the best of our knowledge, free diphenylacetaldehyde has never been prepared in the liquid phase. Cf. C. D. Hurd and R. D. Kimbrough, J. Am. Chem. Soc., 82, 1373 (1960); A. Breuer and T. Zincke, Ann., 198, 156 (1879). Our attempts to prepare it in the liquid phase lead to a dimer, the spectrum of which there is no point in reproducing here. With hot saturated aqueous sodium bisulfite solution, the dimer gave an additional compound corresponding to $C_{14}H_{13}O_4SNa$, but all treatments of this to release the aldehyde gave only polymers.

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Gallegos has pointed out that the mass spectra of ethylene oxide and acetaldehyde are almost identical. Also, for a set of saturated, heterocyclic compounds containing either oxygen, sulfur, or nitrogen in three-membered and four-membered rings, Gallegos has shown that relative abundances of fragmentation products, which are consistent with experiment, can be calculated by application of modified quasi-equilibrium theory, assuming that the rate-controlling steps in the fragmentation involve dissociation of rapidly formed, open-chain, isomerized parent-ions.

(9) The authors wish to thank Miss Janet S. Hartman for assistance with the preparative work.

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