of formaldehyde bis-(β-ethoxyethyl)-acetal, b. p. 108° (13 mm.)[1]; d^{24}_{24} 0.9688; $n^{24}\mathrm{D}$ 1.4200; mol. refraction, 50.21 (calcd., 50.33). The colorless substance, which is only sparingly soluble in water, liberates formaldehyde upon treatment with dilute sulfuric acid.

Anal. Calcd. for $C_9H_{20}O_4$: C, 56.3; H, 10.4. Found: C, 56.5; H, 10.4.

(b) The same reaction, carried out with 134 g. (1 mole) of diethyleneglycol monoethyl ether, gave 65 g. of potassium chloride and 30 g. (21%) of formaldehyde bis-[β-(β-ethoxyethoxy)-ethyl]-acetal, b. p. 170–174° (19 mm.); d^{24}_{24} 1.033; $n^{24}\mathrm{D}$ 1.4445; mol. refraction, 72.00 (calcd., 72.09). The substance is easily soluble in water.

Anal. Calcd. for $C_{13}H_{28}O_6$: C, 55.7; H, 10.0. Found: C, 55.4; H, 9.8.

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(1) Palomaa and Aalto (*Ber.*, **66**, 468 (1933)) mention this substance, without describing its preparation or physical constants.

THE GROSVENOR LABORATORY
LONDON, ENGLAND
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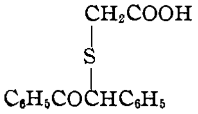
Reaction of Benzoins with Thioglycolic Acid

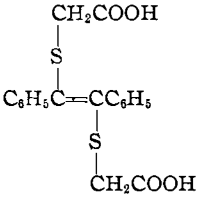
BY SYLVIA TEICH[1] AND DAVID Y. CURTIN

The reaction of benzoin with thioglycolic acid at 100° in the presence of hydrogen chloride has been shown to lead to S-desylthioglycolic acid (I) and a lesser amount of the substituted stilbene (II).[2]



$$\begin{matrix} & \mathrm{CH_2COOH} & \\ & | & \\ & \mathrm{S} & \\ & | & \\ \mathrm{C_6H_5CO} & \mathrm{C} & \mathrm{HC_6H_5} \end{matrix}$$

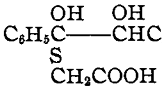
I



$$\begin{matrix} & \mathrm{CH_2COOH} & & \\ & | & & \\ & \mathrm{S} & & \\ & | & & \\ \mathrm{C_6H_5} & \mathrm{C} & = & \mathrm{CC_6H_5} \\ & & & | \\ & & & \mathrm{S} \\ & & & | \\ & & & \mathrm{CH_2COOH} \end{matrix}$$

II

While the over-all result of the reaction is an acid-catalyzed replacement of hydroxyl by the mercaptan,[3] it seemed possible that its course might be a more complicated one involving the hemimercaptol (III) as an intermediate. A pinacol-type rearrangement of III with migration of hydrogen would lead to I.



$$\begin{matrix} & \mathrm{OH} & & \mathrm{OH} \\ \mathrm{C_6H_5} & \mathrm{C} & \text{——} & \mathrm{CHC_6H_5} \\ & \mathrm{S} & & \\ & \mathrm{CH_2COOH} & & \end{matrix}$$

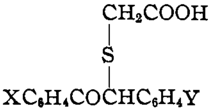
III

We had hoped to decide between these two alternatives by subjecting unsymmetrically substituted benzoins to the reaction. When a molecule with structure IV undergoes the reaction, a direct replacement should lead to V but a mechanism involving attack at the carbonyl group followed by rearrangement should give VI.

Five unsymmetrical benzoins (Table I) were prepared and treated with thioglycolic acid and hydrogen chloride. The desyl thioglycolic acids were not isolated but were cleaved with dilute sodium hydroxide to the corresponding desoxybenzoins. This cleavage reaction has been found to give desoxybenzoins in good yields without rearrangement.[1,4] The results are summarized in Table I. The mixtures of desoxybenzoins were analyzed either by isolation of the constituents or, in the case of the *p*-chlorodesoxybenzoins, by the use of a melting point diagram.

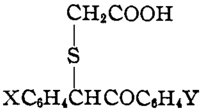
$XC_6H_4COCHOHC_6H_4Y$

IV



$$\begin{matrix} & \mathrm{CH_2COOH} & \\ & | & \\ & \mathrm{S} & \\ & | & \\ \mathrm{XC_6H_4CO} & \mathrm{C} & \mathrm{HC_6H_4Y} \end{matrix}$$

V



$$\begin{matrix} & \mathrm{CH_2COOH} & \\ & | & \\ & \mathrm{S} & \\ & | & \\ \mathrm{XC_6H_4} & \mathrm{C} & \mathrm{HCOC_6H_4Y} \end{matrix}$$

VI

It will be seen that a nearly identical mixture of products was obtained from either the 4- or 4′-substituted benzoin. This suggests either that equilibrium is established between the two benzoins prior to reaction (or between two intermediates during the reaction) or that the two isomers react by way of a common intermediate. A small amount of 4′-chlorobenzoin could be recovered from the reaction of 4-chlorobenzoin with thioglycolic acid.

The acid-catalyzed isomerization of 4′-methoxybenzoin has been reported by Blum-Bergmann[5]

TABLE I

REACTION OF BENZOINS $X\text{–}C_6H_4COCHOHC_6H_4\text{–}Y$ WITH THIOGLYCOLIC ACID

Benzoin $X\text{—}C_6H_4COHOHC_6H_4\text{—}Y$	Ref. to synthesis	Conditions °C.	Conditions Minutes	Yield of ketones, % $X\text{—}C_6H_4COCH_2C_6H_4\text{—}Y$	Yield of ketones, % $X\text{—}C_6H_4CH_2COC_6H_4\text{—}Y$	% yield of stilbene deriv. $X\text{—}C_6H_4C(SCH_2COOH)\text{=}C(SCH_2COOH)C_6H_4\text{—}Y$
X = *p*CH_3O–	[a]	100	30	70	0	10[b]
Y = H		45	30	60	0	10
X = H	[c]	45	35	60	0	10
Y = *p*-CH_3O–		0	30	35	0	10
X = H	[d]	100	30	35	20	20[e]
Y = *p*-Cl						
X = *p*-Cl	[f]	100	30	35	20	20
Y = H						
X = *p*-$(CH_3)_2N$–	[g]	80	45	50	40	
Y = H						

[a] Jenkins, THIS JOURNAL, **54**, 1155 (1932). [b] Recrystallized from ethyl acetate–petroleum ether (b. p. 65–110°), m. p. 189–190° (dec.). *Anal.* Calcd. for $C_{19}H_{18}O_5S_2$: C, 58.5; H, 4.8; neut. equiv., 390. Found: C, 5.86; H, 4.8; neut. equiv., 391. [c] Ref. 4. [d] Arnold and Fuson, THIS JOURNAL, **58**, 1295 (1936). [e] Recrystallized from aqueous formic acid or ethyl acetate–petroleum ether (b. p. 30–60°), m. p. 183–184 (dec.). *Anal.* Calcd. for $C_{18}H_{15}O_4S_2Cl$: C, 54.8; H, 3.8; neut. equiv., 395. Found: C, 54.7; H, 4.0; neut. equiv., 395. [f] Ref. 11. [g] Staudinger, *Ber.*, **46**, 3535 (1913).

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[1] American Cyanamid Fellow, 1947–1948. Present address: Department of Chemistry, Amherst College, Amherst, Massachusetts.

(2) Behagel and Schneider, *Ber.*, **68**, 1588 (1935).

(3) Compare Holmberg, *J. prakt. Chem.*, [2] **141**, 93 (1934).

(4) Teich and Curtin, in press.

(5) Blum-Bergmann, *J. Chem. Soc.*, 723 (1938).

who found that it could be converted amost completely to 4-methoxybenzoin when heated under reflux for four hours with a mixture of acetic and concentrated hydrochloric acids. In spite of this, the isomerization of the unsymmetrical benzoins during the thioglycolic acid reaction was unexpected for two reasons. First, a number of unsymmetrical benzoins (both stable and unstable isomers) have been prepared with no apparent isomerization in a medium containing strong Lewis acids (aluminum chloride, stannic chloride)[6] and, second, the reaction with thioglycolic acid is extremely rapid. For example, as shown in Table I, 4′-methoxybenzoin when treated with thioglycolic acid and hydrogen chloride at 0° for twenty minutes gave after basic cleavage a 35% yield of 4-methoxydesoxybenzoin and a 10% yield of the corresponding stilbene derivative.

On the basis of these experiments it is not possible to choose between the alternatives of direct replacement of hydroxyl or replacement with rearrangement. The lack of reactivity of mandelic acid (which may be regarded as derived from benzoin by replacement of a phenyl by hydroxyl) is consistent with the idea that the facile reaction of benzoin and its derivatives is due to the ability of the carbonyl group of benzoin to undergo a preliminary addition reaction to form a thiohemiacetal. Thus when mandelic acid was treated with thioglycolic acid and hydrogen chloride for thirty minutes in a boiling water-bath less than 8% of the thioglycolic acid had reacted as shown by iodine titration. Under the same conditions a 90% yield of desylthioglycolic acid and a 10% yield of the substituted stilbene are obtained from either benzoin or benzoin methyl ether. It may be noted that benzoin is probably not an intermediate in this reaction since benzoin methyl ether can be quantitatively recovered from a reaction mixture in which the thioglycolic acid has been replaced by acetic acid.

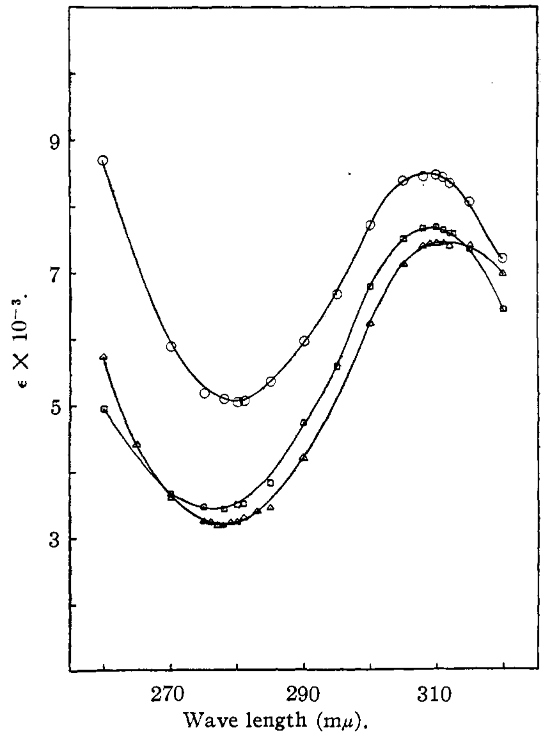

Fig. 1.—Ultraviolet absorption spectra in ethanol of: □, stilbene-α,β-bis-thioglycolic acid (II); △, *p*-chlorostilbene-α,β-bis-thioglycolic acid (VII); ○, *p*-methoxystilbene-α,β-bis-thioglycolic acid (VIII).

During the course of this work the structure previously proposed for the stilbene (II) and its analogs has been confirmed by the quantitative reduction with Raney nickel to dibenzyl and by the ultraviolet absorption spectra of II and its *p*-chloro (VII) and *p*-methoxy (VIII) derivatives which are given in Fig. 1. The maxima at 310 mμ (ϵ = 7.4–8.5 × 10^3) are roughly comparable with those of *cis*- and *trans*-stilbene (*cis*, max. 280 mμ; ϵ 10 × 10^3; *trans*, max. 295 mμ; ϵ 25 × 10^3.)[7] The shift of the maximum toward longer wave lengths found here has been observed in the case of other vinyl sulfides.[8]

Experimental[9]

Reaction of Benzoins with Thioglycolic Acid.—The procedure used was modified from that of Behagel and Schneider.[2] The thioglycolic acid was redistilled and titration against a standard solution of iodine[10] gave values of 100 ± 1% thioglycolic acid. The benzoins were synthesized by known methods which are referred to in Table I. A rapid stream of dry hydrogen chloride was passed through a mixture of 5–10 g. of the benzoin and a three- to fivefold excess of thioglycolic acid. The reaction mixture was heated in a water-bath at the desired temperature. It was then made neutral to litmus and 25–50 cc. of 20% aqueous sodium hydroxide was added. The solution was heated for fifteen minutes longer and the neutral and acidic fractions were separated in the conventional manner. The neutral fraction in each case was reasonably pure desoxybenzoin or a mixture of two desoxyben-

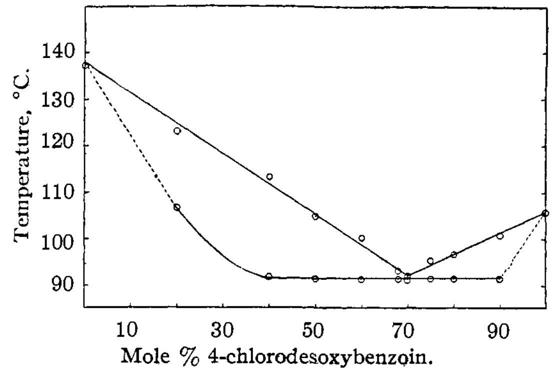

Fig. 2.—Melting point diagram for the system 4-chlorodesoxybenzoin and 4′-chlorodesoxybenzoin.

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[6] See Ide and Buck in Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 286.

[7] Solmssen, This Journal, 65, 2370 (1943).

[8] Bowden, Braude and Jones, *J. Chem. Soc.*, 948 (1946).

[9] All melting points are corrected. Analyses were carried out by Miss Lois May and the Clark Microanalytical Laboratories.

[10] Klason and Carlson, *Ber.*, 39, 738 (1906).

zoins. The acidic fraction contained the stilbene-α,α'-bis-thioglycolic acid.

The mixtures of chlorodesoxybenzoins were analyzed as follows. The original chlorodesoxybenzoin mixture (isolated in 55% yield in each case) was recrystallized from ligroin (b. p. 70–90°). The mixture was shown to give the correct carbon and hydrogen analysis. The melting point was determined and also the melting point of the unknown mixture to which had been added a small amount of pure 4- or 4′-chlorodesoxybenzoin. The composition of the mixture was then read from the melting point diagram, the preparation of which is described below. It was shown that crystallization from ligroin did not effect a change in the composition of a known mixture of the two chlorodesoxybenzoins.

The mixture of dimethylaminodesoxybenzoins was separated by a procedure of Jenkins, Bigelow and Buck[11] involving fractional crystallization from ethanolic hydrochloric acid.

Melting Point Diagram for the System 4-Chlorodesoxybenzoin and 4′-Chlorodesoxybenzoin (Fig. 2).—A procedure similar to that described by Rheinboldt[12] was used. 4-Chloro- and 4′-chlorobenzoin were prepared by the method of Jenkins[13] and purified by recrystallization from ligroin (b. p. 70–90°). Mixtures totalling 0.500 ± 0.0002 g. were weighed out, brought to complete fusion and cooled slowly while stirring. This fusion was repeated three to five times to ensure adequate mixing. A small portion of each was powdered with an agate mortar and pestle. Samples were introduced into capillary tubes 0.5–1 mm. in diameter and were 4–5 mm. in height. The melting points were determined in an aluminum block which had a lens of high magnifying power so that the samples could be seen clearly. The rate of heating of the block was controlled by a variable voltage transformer. A 360° thermometer, calibrated in degrees, was used. All readings were corrected. The temperature of the block was brought rapidly to within 5° of the melting range, and then allowed to rise at the rate of one degree per ten minutes. The melting point range was recorded as the point where the first liquid appeared (lower curve) and the point where the last crystal disappeared (upper curve). Several samples from the same mixture were taken to determine whether adequate mixing had occurred, and samples were subjected to remelting to prove that no decomposition had occurred during fusion. The m. p. ranges were reproducible to within 1° which corresponded to an error of ±4% in composition of the mixture.

Treatment of Mandelic Acid with Thioglycolic Acid.—The procedure described for the benzoins was followed except that the reaction mixture was neutralized to congo red paper (acid to litmus) and a sample, withdrawn by pipet and diluted, was titrated with a solution of iodine in ethanol. Titration showed that 92% of the initial thioglycolic acid remained.

Reaction of Benzoin Methyl Ether with Thioglycolic Acid.—Benzoin methyl ether was prepared by the method of Fischer.[14] When it was treated in the manner described above for benzoin an 88% yield of desoxybenzoin was obtained, as well as 12% of the stilbene-α,β-bis-thioglycolic acid. When a stream of hydrogen chloride was passed into a solution of benzoin methyl ether in acetic acid for thirty minutes at 100° the ether could be recovered quantitatively.

Ultraviolet Absorption Curves (Fig. 1).—The instrument used was a Beckman quartz spectrophotometer model DU. The solvent was 95% ethanol and the concentration ranged from 2.5–3.5 × 10^{-5} mole per liter. The average deviation in ϵ was 0.1, and this corresponded to an error of 1.5% in the region of the maximum.

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RECEIVED NOVEMBER 7, 1949

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[11] Jenkins, Bigelow and Buck, THIS JOURNAL, **52**, 4495 (1930).

[12] Rheinboldt, *J. prakt. Chem.*, [2] **111**, 242 (1925).

[13] Jenkins, THIS JOURNAL, **56**, 682 (1934).

[14] Fischer, *Ber.*, **26**, 2412 (1893).

High-Silica Fluosilicic Acids

BY S. MILTON THOMSEN

Current chemical literature teaches that the end-product of the reaction of aqueous hydrofluoric acid on silica, with silica in excess, is fluosilicic acid, having the composition represented by the formula H_2SiF_6.

Tannanaev,[1] reported in 1936 that more silica may be present in fluosilicic acids (giving them a higher Si/F ratio) than the formula indicates. In agreement with that report, it has been found here that the reaction end-product (silica-saturated fluosilicic acid) has a composition very nearly approaching that represented by the formula $H_2SiF_6 \cdot SiF_4$ (fluodisilicic acid). Little more than 5 moles of HF suffices to "dissolve" one mole of silica, the product being almost 20% higher in silica than the formula H_2SiF_6 indicates.

Two consequences of the presence of "extra" silica are readily demonstrated: (1) Much heat is evolved when silica-saturated fluosilicic acid is mixed with hydrofluoric acid. The temperature rise is roughly proportional to the amount of extra silica in a less-than-saturated acid. (2) Mixing sodium chloride solution (in excess) with fluosilicic acid produces a granular precipitate of sodium fluosilicate which settles rapidly, followed by a slow precipitation of the extra silica.

Most commercially available fluosilicic acids have compositions approximating that of H_2SiF_6 (30% by weight) and will dissolve approximately 30 g. of silica per liter.

[1] Ivan Tannanaev, *J. Gen. Chem. U. S. S. R.*, **6**, 1430 (1936).

RCA LABORATORIES
PRINCETON, N. J.
RECEIVED MARCH 9, 1950

Chemical Properties of Berkelium

BY S. G. THOMPSON, B. B. CUNNINGHAM AND G. T. SEABORG

The recent production by Thompson, Ghiorso and Seaborg[1] of a radioactive isotope of berkelium (atomic number 97) makes it possible to investigate the chemical properties of this transuranium element by means of the tracer technique. This isotope has been prepared through the bombardment of Am^{241} with about 35 Mev. helium ions in the 60-inch cyclotron of the Crocker Laboratory and is believed to have the mass number 243, or possibly 244. This Bk^{243} has a half-life of 4.6 hours and decays by electron capture with about 0.1% branching decay by alpha-particle emission.

In the present tracer chemical experiments, the radiations accompanying the electron capture process were used as a means of detection and were counted in two ways. Where the sample deposits on the platinum plates were essentially weightless, as was the case following the evapora-

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[1] S. G. Thompson, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 838 (1950).