Table I. Thioglycidaldehyde Diethylacetal-Amine Addition Compounds

[3-Substituted Amino-2-thiol-propanal diethylacetals, II]

Amine	Yield, %	B.P., °C. (Mm.)	n_D^{25}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Diethyl-amine	83	75–76 (0.5)	1.4542	56.12	10.70	56.12	10.50
Ethylen-imine	47	62–63 (0.2)	1.4662	52.65	9.33	52.82	9.49
Pyrrol-idine	87	83–84 (0.3)	1.4728	56.61	9.93	56.15	9.92
Piper-idine	78	85–86 (0.2)	1.4758	58.26	10.19	58.04	10.06
tert-Butyl-amine[a]	55.5	71–72 (0.3)	1.4518	56.12	10.70	56.14	10.80

[a] Secondary addition compound boiled at 149–50° (0.3 mm.); n_D^{25} 1.4716. Anal. Calcd. for $C_{18}H_{39}NO_4S_2$: C, 54.37; H, 9.89. Found: C, 54.43; H, 9.90.

Structure II, based on opening of the thiirane ring at the primary carbon to give a secondary thiol, is assigned by analogy to previously reported work with 1,2-epithiopropane (*1*) and with 1-chloro-2,3-epithiopropane (*2*).

The only primary amine, *tert*-butylamine, used in this investigation gave, in addition to the primary addition product, the expected secondary product resulting from addition of two molecules of I to one of the amine,

$$(CH_3)_3C{-}N[CH_2\underset{\underset{SH}{|}}{C}HCH(OC_2H_5)_2]_2$$

Although a ratio of 2 moles of amine to 1 of the sulfide was employed in an effort to avoid this secondary reaction, 18% of I was converted to the secondary product and 55.5% was converted to the primary product.

As in the previously reported reactions of cyclic sulfides with bromine (*3*, *4*), I could be titrated quantitatively with a solution of bromine in chloroform. The addition product, however, was not stable to distillation and even on standing at room temperature in solution it became steadily darker and appeared to be decomposing. Acetyl chloride also reacted with I to form an unstable product which decomposed on attempted distillation.

EXPERIMENTAL

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Boiling points are uncorrected.

Thioglycidaldehyde Diethylacetal (I). The general method used previously (*5*) was followed, except that a 50% molar excess of potassium thiocyanate was employed, and no ether extraction was found necessary. Improved yields of 65 to 68% were obtained {b.p. 69–71° (7 mm.); n_D^{30} 1.4570 [lit. (*1*) b.p. 84° (14 mm.); n_D^{20} 1.4613]}.

Reactions of Amines and I. A mixture of I with a 30% molar excess of the amine was allowed to stand at room temperature for 1 to 2 days and then heated on a steam bath for ½ hour. The product was then isolated by vacuum distillation with argon ebullition aid.

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Acylation of Tetrahydroxy-*p*-benzoquinone

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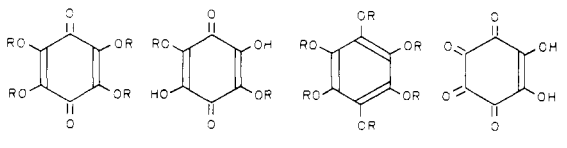
Unreported di- and tetraacetates of tetrahydroxy-*p*-benzoquinone have been prepared and characterized. Acetylation of tetrahydroxy-*p*-benzoquinone in the presence of pyridine gave benzenehexol (hexahydroxybenzene) hexaacetate and rhodizonic acid in nearly equal proportions believed to be formed by disproportionation.

DI- AND TETRA-ACETATES of tetrahydroxy-*p*-benzoquinone (1a) were not described by Verter and coworkers (*14*, *15*) in their recent report on the preparation of propionates (*14*), butyrates (*14*), and other fatty acid esters (*15*) of 1a. The only report in the literature on the preparation of an acetyl derivative of 1a is that of Nietzki and Kehrmann (*9*), who described a yellow diacetate (m.p. 205°) which they supposed was 2b. The author has studied their product by thin-layer chromatography (silica gel G; acetic acid) and found that it is a mixture of the di- and tetraacetates (2b and 1b). The author unsuccessfully attempted to prepare diacetate 2b by the method (*14*) used in the preparation of the dipropionate of 1a; however, a procedure employing simultaneous acetylation and hydrolysis (hydrolytic acetylation) that gave 2b in 85% yield was successful. The acetyl groups in 2b show remarkable stability in the presence of strong acids—e.g., 2b can be recrystallized from warm 4*N* hydrochloric acid with only little decomposition. However, 2b is easily hydrolyzed with bases; even dissolution of 2b in distilled water at room temperature yields a red solution, owing to hydrolysis to



1 2 3 4

a. R = H
b. R = CH_3CO—
c. R = CH_3CH_2CO—
d. R = $CH_3CH_2CH_2CO$—
e. R = $(CH_3)_2CHCO$—

the parent compound 1a. Dipropionate 2c was prepared in a yield of over 60% by this procedure; however, only traces of the corresponding dibutyrate 2d or diisobutyrate 2c were obtained, indicating the difficulty in effecting hydrolysis of acyl groups as the length of the carbon chain increases. Ultraviolet and visible spectra of diacetate 2b (and tetraacetate 1b) were analogous to the spectra of the dipropionate and dibutyrate (and corresponding tetraacetates) of 1a [prepared according to Verter and Frank (*14*)], indicating their structural similarities.

Refluxing of tetrahydroxy-*p*-benzoquinone (1a) with acetic anhydride for 3 minutes gave tetraacetate 1b in 75–80% yield; only traces of diacetate 2b were formed and were isolated from the wine-red filtrate. When 1a was similarly treated with propionic anhydride, tetrapropionate (1c) was obtained in 70–75% yield. Similarly, the following esters were obtained: tetrabutyrate 1d (66–70% yield) and tetraisobutyrate 1e (78–81% yield). This self-catalyzed acylation [1a is known (*12*) to have a pK_1 of 4.8] for the preparation of esters 1c, 1d, and 1e is simpler, less time-consuming, and gives better yields than those hitherto reported (*14, 15*).

In contrast, treatment of 1a with acetic anhydride and pyridine (or other basic catalysts) at 60–65° yields benzenehexol (hexahydroxybenzene) hexaacetate (3b) and rhodizonic acid (4) in nearly equal proportions (about 50% yields of each). This finding provides additional support to earlier reports (*8, 13*) that, in moderately basic media (above pH 6), 1a disproportionates into 3a and 4. Similar reactions have now been observed when 1a is treated with pyridine and the appropriate anhydride (at 60–70°) to give benzenehexol hexapropionate 3c (48% yield), hexabutyrate 3d (46% yield), and hexaisobutyrate 3e (47% yield). The yields of esters 3d and 3e are comparable to, or better than, those obtained by direct acylation (*1*). Treatment of diacetate 2b with pyridine and acetic anhydride gave 1b and 3b, each in 50% yield.

The diacetate of 4 could not be prepared; treatment of 4 with acetic anhydride and 100% phosphoric acid, under conditions described for preparation of the diacetate of the enediol of croconic acid (*3*), produced tetraacetate 1b as the only acetate isolated, a result that indicates disproportionation of 4 in acid media; rhodizonic acid (4), as reported (*2*), disproportionates into tetrahydroxy-*p*-benzoquinone (1a) and croconic acid.

EXPERIMENTAL

The melting points were observed in capillary tubes (silicone-oil bath) and are uncorrected. The samples were dried at 0.05 mm. at 78° or 140° for 2 hours before analysis (analyses by R. Paulson and W. Schmidt of the Microchemical Analysis Section). Infrared spectra were obtained (Nujol mulls) with a Perkin-Elmer Model 257 grating spectrophotometer; UV spectra were determined, 15 minutes after dissolution, with a Beckman DK-2 spectrophotometer.

Tetrahydroxy-*p*-benzoquinone Diacetate (2b). A mixture of tetrahydroxy-*p*-benzoquinone (1a) (*4, 5*) (3 grams, 17.4 mmoles) in acetone (50 ml.) and acetic anhydride (20 ml.) containing 20 drops of concentrated sulfuric acid was placed in a water bath at 50° and stirred until the solid had dissolved (5 minutes). The rather dark solution was filtered through carbon, which was then washed with 10 ml. of acetone. The filtrate and washing were combined and concentrated to about 25 ml., and the solution was poured into a mixture of 50 ml. of concentrated hydrochloric acid and 75 grams of crushed ice. The mixture was stirred for 15 minutes at room temperature, and the resulting product was filtered off, washed with ice-cold hydrochloric acid (6*M*), and dried in a vacuum desiccator over potassium hydroxide; the yield of lustrous, gold-orange plates of diacetate (2b) was 2.5 grams. Cooling of the filtrate (ice-bath) for 3 to 4 hours gave an additional crop (1.3 grams); total yield 3.8 grams (85%), m.p. 246–248° C. The product was recrystallized quickly from warm glacial acetic acid (prolonged heating causes decomposition) or from hot nitromethane, m.p. 250–251° C. (with effervescence); lit. (*9*) m.p. 205° C.

On contact with silica gel or other adsorbent used for thin-layer chromatography, 2b produced a pink spot owing to hydrolysis to the parent compound 1a; (silica gel, 9 to 1 (v./v.) glacial acetic acid–water, 60 minutes, solvent A); R_f 0.70 ± 0.01. γ_{max}^{MeOH} 292 (ε ~17,500), 425 nm. (ε ~200); γ_{max}^{MeCN} 279 (sh) (ε ~18,300), 288 (ε ~20,900), 412 nm. (ε ~250); ν_{max}^{Nujol} 3320 (OH), 1757, 1730 (ester C=O), 1680 (conj. C+C), a doublet at 1660 and 1650 (conj. C=O), 1205 cm.$^{-1}$ (acetate). Anal. Calcd. for $C_{10}H_8O_8$: C, 46.88; H, 3.15. Found: C, 46.90; H, 3.25.

When exposed to air and light at room temperature, a colorless solution of diacetate 2b in methanol (10^{-2} to $10^{-3}M$) rapidly turns pink (λ_{max} 512 nm.) owing to hydrolysis to the parent compound 1a; other diacyl derivatives of 1a (compounds 2c, 2d, and 2e) show similar instability.

Tetrahydroxy-*p*-benzoquinone Dipropionate (2c). This compound was prepared by a method similar to that for 2b; yield 60%, deep-orange plates (from glacial acetic acid); m.p. 232–234° C., lit. (*14*) m.p. 231–233° C.

Tetrahydroxy-*p*-benzoquinone Tetraacetate (1b). A suspension of 1a (1.0 gram, 5.8 mmoles) and acetic anhydride (10 ml.) was heated with stirring at 135–140° (oil bath) until dissolution occurred (3 minutes). The brown-red solution was then cooled, successively diluted with ice water (10 to 20 ml.) and methanol (10 to 20 ml.), and stirred (ice bath) until a solid formed (10 minutes). The solid was separated by decantation (or filtration), triturated with cold 50% aqueous methanol (10 ml.), and filtered. The product (1.5 grams, 76%) was dried and recrystallized from acetone-pentane or glacial acetic acid, giving light-yellow prisms or needles, m.p. 174–176° C.

The product shows a pale-yellow spot on a thin-layer chromatogram (silica gel, 4:1:1 (v./v.) benzene–acetic acid–2-butanone, 60 minutes) R_f 0.81 ± 0.01; in about 10 minutes after drying of a plate, the yellow spot (1b) turns wine red owing to hydrolysis to 1a; solvent A, R_f 0.95 ± 0.01. A sulfuric acid–methanol (1.5*M*) spray and heating of the plate facilitate detection of the spot; γ_{max}^{MeOH} 262 (ε ~16,000) and 350 nm. (ε ~800); ν_{max}^{Nujol} 1790 (ester C=O); a quintet at 1205, 1190, 1180, 1158, and 1148 cm.$^{-1}$ (acetate). Anal. Calcd. for $C_{14}H_{12}O_{10}$: C, 49.41; H, 3.55. Found: C, 49.55; H, 3.66.

No hydrolysis of tetraacetate 1b or other tetraacyl derivatives of 1a in dilute methanol solution was observed. However, on storage at room temperature, tetraacetate 1b was slowly converted (about 95% in one year) into the thermodynamically more stable diacetate 2b; this change is associated with a change in color from pale yellow to deep yellow and can readily be followed spectrophotometrically; the other tetraacyl esters of 1a showed similar instability.

Other esters were similarly obtained: tetrapropionate 1c, m.p. 103–105° (from 95% ethanol), lit. (*14*) m.p. 104–105° C.; tetrabutyrate 1d, m.p. 77–78° C. (from 95% ethanol), lit. (*14*) m.p. 76–77° C.; tetraisobutyrate 1e, m.p. 126–127° C. (from absolute ethanol), lit. (*15*) m.p. 127° C.

Acetylation of Tetrahydroxy-*p*-benzoquinone (1a) to Benzenehexol Hexaacetate (3b and 4). A suspension of tetrahydroxy-*p*-benzoquinone (1a) (1 gram, 5.8 mmoles), acetic anhydride (20 ml.), and anhydrous pyridine (3 ml.) was heated, with stirring, at 60–65° for 15 minutes, to give first a brown-red solution and then crystallization of the product, first visible in 6 to 8 minutes. The suspension was cooled to room temperature (10 minutes) and then poured into ice-water (75 ml.) to yield colorless cubes of

3b, yield 1.24 grams (50%). Recrystallization from warm glacial acetic acid yielded a product having m.p. 203–204° and containing one molecular proportion of acetic acid, lit. (*10*) m.p. 203°, 203–205° (*7*), and 202–203° (*6*); recrystallization of 3b from warm ethyl acetoacetate afforded the unsolvated product, m.p. 218–220°, lit. (*1*) m.p. 222°.

The dark-red filtrate (ca. 100 ml.) was treated with 1.5*M* barium chloride (5 ml.) and then carefully neutralized at 50° with sodium carbonate; the resulting greenish red precipitate was filtered off, washed with water, and dried (yield 0.2 gram). A sample (0.1 gram) of this material was digested for 10 minutes at 50° with 2*M* hydrochloric acid (10 ml.) to give insoluble, lustrous yellow plates (0.01 gram) of barium croconate (*5*). The small amount of croconic salt (*5*) isolated from the reaction mixture presumably resulted from a benzilic acid-type of rearrangement of rhodizonic acid in the presence of air and base; this type of rearrangement was discovered by Nietzki (*10, 11*). The neutralized filtrate gave red crystals of barium rhodizonate (*5*) (0.08 gram).

Similarly, the following esters of benzenehexol (3a) were prepared: hexapropionate 3c, m.p. 140–141° (from ethanol), lit. (*1*) m.p. 137°; hexabutyrate 3d, m.p. 137–139° (from ethanol), lit. (*1*) m.p. 135°.

For the hexaisobutyrate 3e, m.p. 169–170° shrinking at 157° (from ethanol), lit. (*1*) m.p. 157°, Anal. Calcd. for $C_{30}H_{42}O_{12}$: C, 60.59; H, 7.12. Found: C, 60.50; H, 7.05.

To facilitate the isolation of the acyl derivatives 3c, 3d, and 3e, decomposition of the reaction mixture was performed with aqueous ethyl alcohol.

Acetylation of 2b into 3b and 1b. A mixture of diacetate 2b (1 gram), acetic anhydride (20 ml.), and pyridine (3 ml.) was treated according to the procedure already described. The crude reaction mixture was dried and extracted with warm ethanol (15 ml.); the undissolved solid was 3b (47%). Addition of water (5 ml.) and cooling of the filtrate gave 1b (42%). By use of different anhydrides with compound 2b, this procedure may be employed for the preparation of mixed acyl derivatives.

Formation of Tetraacetate (1b) from Rhodizonic Acid (4). Rhodizonic acid dihydrate [4, 1 gram (*5*)] was thoroughly mixed with ice-cold acetylating mixture (*3*) (25 ml.; 5 ml. of 100% phosphoric acid and 20 ml. of acetic anhydride) and kept in a refrigerator (3°) for 48 hours; decomposition of the light-yellow solution with ice water yielded light-yellow crystals of 1b (0.32 gram, 20%).

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Preparation of Substituted Aziridinium Salts

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Cyclizations of several β-substituted β-chloramines, $R_2NCH_2CR(Cl)X$, to the corresponding, novel aziridinium salts have been carried out in 30 to 90% yields with silver perchlorate in benzene or acetone when X was H, alkyl, CH_2Cl, CH_2OR, CH_2SO_2R, or $Si(CH_3)_3$. However, no cyclization products could be isolated, although the chloramines did decompose, when X was Cl, Br, F, or CF_3.

RECENT REPORTS of the synthetic usefulness of simple alkyl aziridinium salts (*5, 6, 10*) prompted this study of some novel, ring-substituted analogs from the β-chloramines, I, which were readily available via the free radical addition of *N*-chloramines to substituted olefins (*8, 9*). Using substantially the method of Leonard and Paukstelis (*7*), several of the desired salts were isolated in high yield (Table I and Equations 1 through 3).

The structures of compounds IIa-h, IV, VI, VIII, and IX were assigned on the basis of their NMR spectra and combustion analyses (Tables II and III). The NMR absorptions due to the $\geq NCH_2-$ protons at τ 6.5–6.9 appear at unusually high field and are characteristic of the aziridinium ring protons (*5*). An illustration of this is provided by the aziridinium salt IIa, which had a broad singlet at τ 6.6, and the 6-membered ring dimer (piperazinium salt, IX), which showed the singlet at τ 6.2. Although the absorption patterns in the τ 6–7 region were highly complex in the spectra of the other aziridinium salts, the absorption near τ 7 was definitive (*5*) in all cases (see Table II). The non-equivalence of the *N*-alkyl groups (except in IIa) confirmed the presence of an unsymmetrical quaternary structure, and conclusive evidence of the presence of aziridinium rings was obtained from the following chemical behavior of the salts.

Aziridinium salts react rapidly with water, methanol, and lithium chloride (*5*), in contrast to piperazinium salts such as IX, which was quantitatively recovered after 24 hours of boiling in water or methanol, or from lithium chloride in acetonitrile at room temperature. Therefore the last reaction was applied as a facile diagnostic test for the presence of the aziridinium ring in the five representative compounds IIe, IIf, IIh, IV, and VI; all except IIh afforded only the corresponding original β-chloramine (Ie, If, III, and V), as judged by NMR and thin-layer chromatography.

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