the initial dark brown solution not allowed to reflux. After the brown color of the aqueous extract diminished, the thimble was removed and dried overnight in a vacuum oven at 75° C. The dried thimble and its contents were transferred to a new thimble and extracted with boiling chloroform until the extract was essentially colorless. Fresh chloroform was supplied to the Soxhlet apparatus every few hours, as the bulk of the porphyrin was removed during the first 8 hours. Apparatus containing porphyrin solutions were wrapped with metal foil to minimize introduction of light. The combined porphyrin solutions were washed with water until the water layer was colorless; the chloroform was evaporated in vacuo to dryness and the residue was washed onto a funnel with methanol. The solid was washed repeatedly with cold methanol until the filtrate was essentially colorless, then dried in a vacuum dessicator (yield 100 mg., 66%, based upon **5**). The methanol washing removed mainly unreacted starting material. Some etioporphyrin I may be recovered from the washings by column chromatography on neutral alumina using benzene and ether for elution of the porphyrin. The porphyrin was best purified by successive recrystallizations from benzene (for quantitative measurements, Baker Spectrophotometer Analyzed reagent was stored over sodium ribbon and distilled before use) until a constant spectrum and extinction coefficients were obtained for the four visible bands. Recrystallization was preferred over chromatography for purification of the bulk of the porphyrin. After three recrystallization steps, maximum purity was obtained. When 100 grams of the fresh bromodipyrrylmethenes were reacted in 100 separate test tube melts, utilizing five Soxhlet extractors for the work-up, the yield of thrice crystallized etio I was 6.6 grams (44%) of beautiful violet needles. $\lambda^{C_6H_6}$ 399 mμ slit 0.070, log ε 5.223; 498, 0.025, 4.170; 530, 0.025, 4.026; 568, 0.025, 3.833; 623, 0.07, 3.780. These absorptivity data agreed closely with those of Dean and Girdler (*4*). Other absorptivity values for etio I have been determined in chloroform (*2*) and dioxane (*14*) solutions. δ^{CDCl_3} 10.1 (s, 4, *meso* —H), 4.13 (q, 8, J = 7.5 c.p.s., $-CH_2CH_3$), 3.68 (s, 12, $-CH_3$), 1.92 (t, 12, J = 7.5 c.p.s., $-CH_2CH_3$), −3.67 (s, 2, N—H). Anal. Calcd. for $C_{36}H_{38}N_4$: C, 80.29 H, 800 N, 11.71 Found C, 80.19 H, 7.94 N, 11.66.

ACKNOWLEDGMENT

The support of the American Petroleum Institute (Research Project 60) is gratefully acknowledged. We thank the Research Centre of BP (North America) Ltd. for providing some of the experimental details.

LITERATURE CITED

(1) Auwers, K. von, Jacobsen, H., *Ann. Chem.* **426**, 227 (1921).
(2) Bullock, E., Johnson, A.W., Markham, E., Shaw, K.B., *J. Chem. Soc. London* **1958**, p. 1430.
(3) Corwin, A.H., Viohl, P., *J. Am. Chem. Soc.* **66**, 1137 (1944).
(4) Dean, R.A., Girdler, R.B., *Chem. Ind. (London)* **1960**, p. 100.
(5) Erdman, J.G., Ramsey, V.G., Kalenda, N.W., Hanson, W.E., *J. Am. Chem. Soc.* **78**, 5844 (1956).
(6) Fischer, H., *Org. Syntheses Coll. Vol.* **3**, 513 (1955).
(7) Fischer, H., Baumann, E., Riedl, H.J., *Ann. Chem.* **475**, 205 (1929).
(8) Gray, C.H., Kulczycka, A., Nicholson, D.C., *J. Chem. Soc. London* **1961**, p. 2276.
(9) Johnson, A.W., Kay, I.T., Markham, E., Price, R., Shaw, K.B., *J. Chem. Soc. London* **1959**, p. 3416.
(10) Johnson, A.W., Markham, E., Price, R., Shaw, K.B., *J. Chem. Soc. London* **1958**, p. 4254.
(11) Kleinspehn, G.G., *J. Am. Chem. Soc.* **77**, 1546 (1955).
(12) Mironov, A.F., Naumova, B.S., Evstigneeva, R.P., Preobrazhenskii, N.A., *J. Gen. Chem. USSR* **34**, 3352 (1964).
(13) Siedel, W., *Z. Physiol. Chem.* **231**, 167 (1935).
(14) Stern, A., Wenderlein, H., *Z. Phys. Chem.* **170**, 337 (1934).
(15) Treibs, A., Schmidt, R., *Ann. Chem.* **577**, 105 (1952).

RECEIVED for review April 10, 1968. Accepted July 10, 1968.

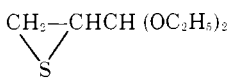
Reactions of Thioglycidaldehyde Diethylacetal

JOHN M. STEWART

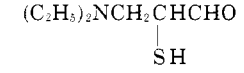
Department of Chemistry, University of Montana, Missoula, Mont. 59801

A procedure has been developed for the isolation of pure products (3-substituted amino-2-thiolpropanal diethylacetals) from the reaction of thioglycidaldehyde with primary and secondary amines. Yields, physical constants, and analytical data are given for the products from diethylamine, ethylenimine, pyrrolidine, piperidine, and *tert*-butylamine.

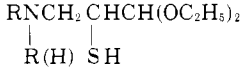
THE PREPARATION of thioglycidaldehyde diethylacetal (I)



was described in an article (*5*) on reactions of glycidaldehyde diethylacetal. It was reported that the reaction of I with diethylamine gave a product which decomposed on attempted distillation and that reaction of dilute hydrochloric acid with the crude product apparently gave a dimer of the hydrochloride of



Recent work in this laboratory has shown that the reaction products of amines and I can be prepared in good yield and are stable to distillation at reduced pressures sufficient to afford a reasonably low boiling point. The addition product of two molecules of I with one of piperazine, however, could not be distilled without decomposition—presumably because its boiling point was too high. These products have the general structure,



(II). Physical constants and analytical data are given in Table I. Several procedures were tried for hydrolysis of the addition compounds to the corresponding aldehydes, but even the use of 90% formic acid resulted in only polymeric material.

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.

LITERATURE CITED

(1) Snyder, H.R., Stewart, J.M., Ziegler, J.B., *J. Am. Chem. Soc.* **69**, 2672 (1947).
(2) Stewart, J.M., *J. Org. Chem.* **29**, 1655 (1964).
(3) Stewart, J.M., Burnside, C.H., *Ibid.*, **75**, 243 (1953).
(4) Stewart, J.M., Cordts, H.P., *J. Am. Chem. Soc.* **74**, 5880 (1952).
(5) Wright, J.B., *Ibid.*, **79**, 1694 (1957).

RECEIVED for review April 11, 1968. Accepted May 18, 1968.

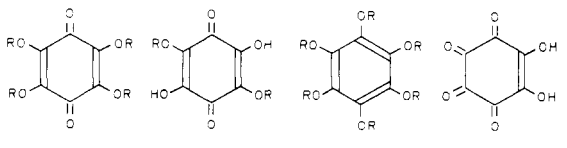
Acylation of Tetrahydroxy-*p*-benzoquinone

ALEXANDER J. FATIADI

Division of Anolytical Chemistry, Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234

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 = $(CH_3)_2CHCO$—