

The ether was evaporated under reduced pressure and the sirupy residue taken up in alcohol. A small amount of amorphous solid separated and was removed by filtration. The alcoholic solution was poured into ether and the resulting solution washed thoroughly with water and then extracted with 5% sodium carbonate solution. The intensely red aqueous layer was separated and acidified and extracted with ether. The ether layer was washed with several portions of dilute ammonium carbonate solution, dried over sodium sulfate and evaporated to dryness. The yellow-brown, solid residue was extracted with 25 cc. of boiling xylene in several portions. The filtered xylene solution was allowed to stand for several days and slowly deposited a mixture of an amorphous yellow powder (40 mg.) and hard brown-yellow nodules (190 mg.). The nodules were partially purified by solution in cold, dilute aqueous-alcoholic sodium hydroxide followed immediately by precipitation with dilute hydrochloric acid. The pigment was thus obtained as brownish-yellow needles. After several recrystallizations from dilute alcohol it formed golden-yellow needles, m. p. 214–215° (dec.); reported for butein, 211–213°, 212–213°, 214–215°. *Anal.* Calcd. for C₁₅H₁₂O₅: C, 66.20; H, 4.41. Found: C, 65.88; H, 4.84. The substance gives a yellow color in concentrated sulfuric acid, a brown color with ferric chloride and a deep red solution in aqueous sodium hydroxide.

The melting point was not depressed upon admixture with a synthetic sample of butein, m. p. 213–214° (preparation described below).

Butein Tetraacetate.—A solution of 10 mg. of the natural pigment and 20 mg. of anhydrous sodium acetate in 0.6 cc. of acetic anhydride was heated to boiling and allowed

to stand at room temperature overnight. The excess acetic anhydride was decomposed with ice; the acetate (15 mg.) separated in crystalline form, m. p. 125–127°. After two recrystallizations from dilute alcohol it formed nearly colorless needles, m. p. 129–130°; reported for butein tetraacetate, 129–131°, 128–129°.

A sample of butein tetraacetate prepared from synthetic butein by the above method melted at 129.5–130°. A mixture of this material with the acetate of the natural pigment melted at 129–130°.

Synthesis of Butein.—The following procedure is essentially that used by Nadkarni and Wheeler¹⁰ for the condensation of *p*-hydroxybenzaldehyde with resacetophenone.

Nitrogen was bubbled through an ice-cooled suspension of 5 g. of protocatechualdehyde and 5.5 g. of resacetophenone in 10 cc. of alcohol, a solution of 50 g. of potassium hydroxide in 35 cc. of water was added, with shaking, and the resulting mixture allowed to stand under nitrogen for five days at room temperature. The deep red mixture was poured onto enough ice to dilute it to twice the original volume and acidified with 6 *N* hydrochloric acid. The precipitate was collected, washed with water and recrystallized from 50% alcohol. There was obtained 2.4 g. of golden-yellow needles, m. p. 213–214°.

Summary

Butein (2',4',3,4-tetrahydroxychalcone) has been shown to be the anthochlor pigment of *Coreopsis Douglasii*.

(10) Nadkarni and Wheeler, *J. Chem. Soc.*, 1320 (1938).

LOS ANGELES, CALIFORNIA

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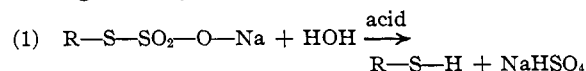
(9) Saiyad, Nadkarni and Wheeler, *J. Chem. Soc.*, 1737 (1937).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Use of Bunte Salts in Synthesis. I. The Preparation of Mercaptals

By HARRY E. WESTLAKE, JR., AND GREGG DOUGHERTY

Bunte salts, esters of sodium thiosulfuric acid, undergo acid hydrolysis as follows



It was of interest therefore to determine whether acid solutions of Bunte salts could be used to carry out mercaptan reactions without the necessity of isolating the latter.

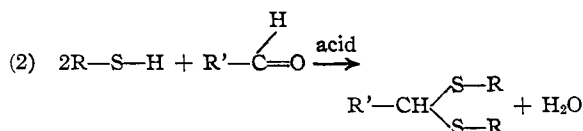
The literature revealed only two cases in which Bunte salts were used in reactions with compounds containing the carbonyl group. A patent was issued to Baeyer and Company for the preparation of acetone ethyl and methyl mercaptols by heating the Bunte salts with acetone and hydrochloric acid.¹ Also Gibson prepared the cyclic com-

pound, ethylene mercaptal or dithiolane, from formaldehyde and the reaction product of sodium thiosulfate and ethylene chloride.² No references were found in the literature to the use of Bunte salts in the synthesis of normal, open chain mercaptals.

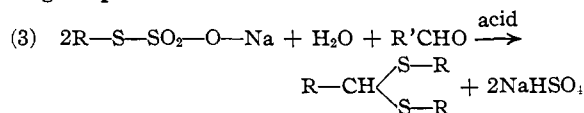
It has now been found that this method is generally applicable to mercaptal formation and the following have been prepared: formaldehyde dibenzyl mercaptal, benzaldehyde dibenzyl mercaptal, formaldehyde bis- β -oxyethyl mercaptal, formaldehyde dibutyl mercaptal, acetaldehyde dibutyl mercaptal, formaldehyde diethyl mercaptal. The obvious course of the reaction is a hydrolysis as in equation (1) followed by

(1) German Patent, *Ber.*, **22**, 115 (1889).

(2) Gibson, *J. Chem. Soc.*, 12 (1930).



However, there is some indication that the yields obtained by the present method are somewhat higher than those resulting from the direct action of mercaptans with aldehydes in the presence of dilute acids. Therefore it may be that some sort of a nascent state is involved or that the reaction is direct and is not in fact preceded by hydrolysis. On this account it is perhaps best, in our present state of knowledge concerning the mechanism of the process, not to assume intermediate mercaptan formation but to describe the reaction by the single equation



Experimental

The Bunte salts were prepared in the usual way. One mol of sodium thiosulfate was dissolved in 500–600 cc. water. To this was added 1 mol of the alkyl or aralkyl halide in 500–600 cc. of alcohol. The mixture was refluxed until the solution became homogeneous or until little or no sulfur was precipitated on the addition of a mineral acid. At this point the alcohol was removed by distillation. To the resulting Bunte salt solution 0.5 mol or a little less of the aldehyde was added and, after the addition of 2 cc. of concentrated hydrochloric acid, the mixture was refluxed gently for eight to ten hours. The reaction mixture was cooled and extracted with ether, the extract dried with anhydrous magnesium sulfate and the

ether removed by evaporation. The product remaining was either recrystallized from alcohol or distilled under vacuum depending on its nature. For confirmation of identity of the mercaptals some were analyzed and some were converted to the corresponding sulfones.

Formaldehyde Dibenzyl Mercaptal.—77% yield; m. p. 54–55°. *Anal.* Calcd. for $(\text{C}_7\text{H}_7\text{S})_2\text{CH}_2$: S, 24.63. Found: S, 24.76. **Benzaldehyde Dibenzyl Mercaptal.**—72% yield; m. p. 60–61°. *Anal.* Calcd. for $(\text{C}_7\text{H}_7\text{S})_2\text{CH}-\text{C}_6\text{H}_5$: S, 19.06. Found: S, 19.12. **Formaldehyde bis- β -Oxyethyl Mercaptal.**—The Bunte salt was prepared from ethylene chlorhydrin. The crude yield of mercaptal was 50%. *Anal.* Calcd. for $(\text{HO}-\text{C}_2\text{H}_4-\text{S})_2\text{CH}_2$: S, 38.10. Found: S, 38.29. This compound has not been reported before. It is a pale yellow oil of b. p. 52–54° at 5 mm. **Formaldehyde Dibutyl Mercaptal.**—60% yield. The methylene bis-butyl sulfone was prepared by oxidation of the mercaptal with chromic anhydride in glacial acetic acid; m. p. in the literature is 95–96°, obsd. m. p. 95–96°. **Acetaldehyde Dibutyl Mercaptal.**—Yield 50%. Ethylidene bis-butyl sulfone was prepared by oxidation of the mercaptal; m. p. in the literature 64°, obsd. m. p. 62–64°. **Formaldehyde Diethyl Mercaptal.**—46% yield. Methylene bis-ethyl sulfone was prepared by oxidation of the mercaptal with potassium permanganate and sulfuric acid; m. p. in the literature 104°, obsd. m. p. 102–104°.

Summary

Sodium alkyl thiosulfates react with aldehydes in the presence of acid to give mercaptals, possibly by means of an acid hydrolysis to the mercaptan. This provides a new method for the preparation of these compounds as was demonstrated by the preparation of a group of representative mercaptals, including one not hitherto known.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Bond Moment Additivity and the Electric Moments of Some Halogenated Hydrocarbons

BY ARTHUR A. MARYOTT, MARCUS E. HOBBS AND PAUL M. GROSS

A problem that has received considerable attention is that of bond moment additivity and induction effects¹ between polar groups in the same molecule. A related problem is that of the magnitude and direction of the effects produced by solvents on the observed dipole moments.² In

(1) (a) Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929); (b) Smallwood and Herzfeld, *THIS JOURNAL*, **52**, 1919 (1930); (c) J. W. Williams, *Chem. Rev.*, **60**, 549 (1929); (d) Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

(2) (a) Higasi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **28**, 284 (1936); (b) Franck, *Proc. Roy. Soc. (London)*, **A152**, 171 (1935); (c) H. Mueller, *Physik. Z.*, **35**, 346 (1934).

order to treat either of these considerations satisfactorily it is necessary to have accurate values of the net electric moment of the molecule. The determination of these values may be made with the least ambiguity through measurements in the gas phase, as there the environmental influences are completely eliminated or considerably minimized. With a view to extending the list of accurately determined values we have measured several halogen substituted compounds, namely: methylene chloride, chloroform, methyl