refractivity values of other authors[13] are used. The refractivity increment per methylene group appears to be less than the estimated value of 4.65 generally given.[13]

The Eykman constant was computed over the range 20–26° and appears constant within the estimated limits of experimental error.

CHEMISTRY RESEARCH BRANCH
AERONAUTICAL RESEARCH LABORATORY
DIRECTORATE OF RESEARCH
WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

---

(13) (a) W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, 4th Ed., Vol. II, p. 142, Akademische Verlag., Leipzig, Germany, 1943. (b) A. I. Vogel, *A Textbook of Practical Chemistry*, 3rd Ed., p. 1035, Longmans, Green and Co., Inc., New York, N. Y., 1956. (c) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd Ed., p. 107, John Wiley and Sons, Inc., New York, N. Y., 1940.

High Temperature Chlorination of Dioxane to Give Trichloroacetyl Chloride

N. B. LORETTE

Received February 7, 1957

Several workers[1–4] have reported the chlorination of *p*-dioxane at temperatures of 130–160° to give a number of chlorinated dioxanes. Boeseken, *et al.*[2] noted that the ring was broken and that "acid chlorides were probably present" when dioxane was subjected to prolonged chlorination at 130–150°.

When trichloroacetyl chloride was isolated from the products of a dioxane chlorination experiment, the work described below was carried out to determine the extent to which trichloroacetyl chloride was formed. Although the experiment was stopped before the ultimate yield of trichloroacetyl chloride was obtained, sufficient information was obtained to show that trichloroacetyl chloride is a major product of the prolonged high temperature chlorination of dioxane. The factors which account for the different results of the previous and present work are the temperature, which was kept near or above 160° when trichloroacetyl chloride was formed, and the large excess of chlorine which was used in this work.

EXPERIMENTAL

Two hundred and sixty g. (2.95 moles) of *p*-dioxane was heated to 90° in a flask equipped with a condenser, an inlet tube, and a thermometer. Chlorine was added at a rate of 20 to 30 g. per hr. At the end of 60 hr. the pot temperature had risen to 115° and the net weight increase was 530 g. Infrared analysis indicated less than 2% carbonyl chloride present. Chlorination was continued at 155–160° for 11 hr. Distillation of the crude products at 75 mm. gave 144 g. of trichloroacetyl chloride, b.p. 47–48, n_D^{24} 1.4662, confirmed by the infrared spectrum. The residue was then chlorinated for 15 hr. at 165–180° after which reduced pressure distillation yielded 88 g. of trichloroacetyl chloride. Again the distillation residue was chlorinated at 175–190° for 10 hr.; no condenser was used and the vent gases were passed directly into a cold trap. During this period 160 g. was collected. Distillation of the condensate gave 84 g. of trichloroacetyl chloride. The pot residue solidified on cooling. Infrared and chlorine analysis showed the solid to be hexachloroethane. The total yield of trichloroacetyl chloride was 316 g. (1.74 moles).

An attempt was made to distill the reaction residue (462 g.) at 2 mm. The column and condenser immediately plugged with hexachloroethane. According to the infrared spectrum, the residue contained above 20% hexachloroethane.

THE DOW CHEMICAL COMPANY
FREEPORT, TEX.

---

(1) C. L. Butler and L. H. Cretcher, *J. Am. Soc.*, **54**, 2987 (1932).

(2) J. Boeseken, F. Tellegen, and P. C. Henriquez, *J. Am. Chem. Soc.*, **55**, 1284 (1933).

(3) J. J. Kucera and D. C. Carpenter, *J. Am. Chem. Soc.*, **57**, 2346 (1935).

(4) R. K. Summerbell, R. R. Umboeffer, and G. R. Lappin, *J. Am. Chem. Soc.*, **69**, 1352 (1947).

Preparation of Malonaldehyde bis-Bisulfite, Sodium Salt

L. D. SASLAW AND V. S. WARAVDEKAR

Received February 12, 1957

Malonaldehyde (I) reacts with 2-thiobarbituric acid to give a characteristic pink coloration. This reaction is useful for the estimation of 2-deoxysugars and nucleosides containing 2-deoxysugars. For this purpose, it is considered important to have a stable derivative of I, since I has been reported[1] as an unstable crystalline monomer. This report is concerned with the preparation of a stable crystalline bisulfite addition compound suitable for investigations of reactions of I.[2]

EXPERIMENTAL[3]

A suspension of 10 ml. of malonaldehyde bis(dimethyl acetal)[4] in 5.5 ml. of 3.7% aqueous hydrochloric acid was shaken for 1 min. in a water bath at 60° to effect dissolution. The resulting yellow solution was kept at room temperature for 40 hr. and then cooled to 4°. A freshly prepared saturated solution of sodium *meta*-bisulfite was chilled in an ice bath

---

(1) R. Hüttel, *Ber.*, **74**, 1825 (1941).

(2) U. S. Patent No. 2,671,800 has been granted for a related process for preparing bisulfite addition products of malonaldehyde [*Chem. Abstr.*, **49**, 4014 (1955)]. However, no proof of identity of the proposed compounds is recorded, and apparently no physical or chemical studies were undertaken to characterize the compounds.

(3) Microanalyses for C, H, S, and Na were performed by Dr. W. C. Alford and his associates.

(4) Obtained from Kay-Fries Chemicals, Inc., 180 Madison Ave., New York 16, N. Y.

and 40 ml. was mixed with the malonaldehyde solution. After 5 hr. at 4°, the slowly separating crystals were collected and washed successively with cold 15 ml. aliquots of saturated bisulfite solution and 50% ethanol. Substantial quantities of crystals were obtained by mixing the mother liquor with an additional 40 ml. of saturated bisulfite solution and storing for several days in a refrigerator.

The sodium salt of malonaldehyde *bis*-bisulfite (II) was recrystallized, after storage at 4°, from saturated aqueous solution by the dropwise addition of $^1/_4$ volume of absolute ethanol. A second crop was obtained by bringing the total ethanol concentration to about 50%. The combined crops were washed with cold 70% ethanol and anhydrous ether and stored overnight in a vacuum desiccator over calcium chloride. The colorless oblong hexagonal plates (40% yield) darkened above 185° without melting.

Anal. Calcd. for $C_3H_6O_8S_2Na_2.2H_2O$: C, 11.39; H, 3.19; S, 20.28; Na, 14.54; H_2O, 11.39. Found: C, 11.57; H, 3.30; S, 20.16; Na, 14.58; wt. loss (vac. oven, 70°), 11.39.

Concentrated aqueous solutions of II exhibit a maximum in the ultraviolet at 265 mμ. Distillates of concentrated aqueous solutions of II exhibit a maximum at 245 mμ and also give the red color, characteristic of I, with aqueous ferric chloride.[5]

Reaction with 2-thiobarbituric acid aids in identification of I. Three ml. of an aqueous solution of 5.5 micrograms of II and 12 mg. of 2-thiobarbituric acid, in a test tube fitted with a tear-drop condenser, was immersed in boiling water for 20 min. Examination of the visible absorption spectrum of the pink solution, with the use of a Warren Spectracord, revealed a maximum at about 530 mμ which was in agreement with spectra reported by other workers.[6,7]

A highly sensitive method of estimating 2-deoxysugars based upon oxidation with periodate and subsequent estimation of the resulting I with 2-thiobarbituric acid has been developed. The usefulness of the bisulfite compound in enzymic studies based upon the observations of others[8,9,10] has been explored. These studies will form the subject of separate communications.

Laboratory of Chemical Pharmacology
National Cancer Institute
National Institutes of Health
Bethesda, Md.

---

[5] L. Claisen, *Ber.*, **36**, 3664 (1903).

[6] S. Patton and G. W. Kurtz, *J. Dairy Sci.*, **34**, 669 (1951).

[7] W. G. Jennings, W. L. Dunkley, and H. G. Reiber, *Food Research*, **20**, 13 (1955).

[8] F. Bernheim, K. M. Wilbur, and C. B. Kenaston, *Arch. Biochem.* and *Biophys.*, **38**, 177 (1952).

[9] A. Ottolenghi, K. M. Wilbur, and F. Bernheim, *Arch. Biochem.* and *Biophys.*, **56**, 157 (1955).

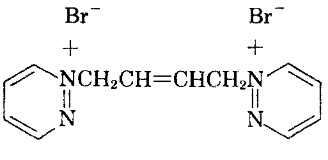
[10] C. W. Shuster, *Proc. Soc. Exp. Biol. Med.*, **90**, 423 (1955).

Some Quaternary Salts of Pyridazine

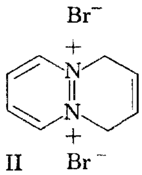
A. E. Blood and C. R. Noller

Received February 13, 1957

The reaction of either *cis*- or *trans*-1,4-dibromo-2-butene with pyridazine in mole ratios varying from 1:4 up to 4:1, in methanol, carbon tetrachloride, or acetone, and at different concentrations, gave only *trans*-1,4-dipyridazinium-2-butene bromide (I).



I



II

There was no evidence for the formation of the *cis* isomer, of *N*-(4-bromo-2-butenyl)pyridizanium bromide, of *N*,*N'*-di-(4-bromo-2-butenyl)pyridazinium bromide, of 9,10-diaza-1,4-dihydronaphthalene bromide (II), or of products that might result from allylic rearrangement of 1,4-dibromo-2-butene before or during reaction with pyridazine.

Attempts to prepare simpler diquaternary salts of pyridazine were equally unsuccessful. When pyridazine was heated with an excess of either methyl iodide or ethyl bromide at temperatures up to 100°, only the monoquaternary salts were obtained.

It has been pointed out[1] that compounds containing more than one tertiary nitrogen, phosphorus, or arsenic atom frequently do not give the maximum number of quaternary groups on reaction with alkyl halides. This behavior has been ascribed to the proximity of the positive charge produced when the first tertiary group forms a quaternary salt. However, hydrazine forms numerous diacid salts,[2] and both *p*-phenylenediamine[3] and 2,2'-dipyridyl[4] readily form diquaternary salts. Hence it cannot be predicted that the presence of a charge necessarily will prevent the introduction of an adjacent like charge or one separated by a conjugated system.

EXPERIMENTAL

trans-1,4-Dipyridazinium-2-butene bromide (I). To 25.6 g. (0.12 mole) of *cis*-1,4-dibromo-2-butene[5] dissolved in 35 cc. of carbon tetrachloride was added dropwise with cooling and stirring a solution of 5.5 g. (0.069 mole) of pyridazine[6] in 20 cc. of carbon tetrachloride. During the course of the addition a small amount of brown solid separated. The mixture was allowed to stand in an ice bath for 4 hr. during which time more solid was deposited. The carbon tetrachloride was decanted and the solid crystallized from 1-propanol to give 9.7 g. (71%) of gray hygroscopic crystals that melted with decomposition at 177–178°. Recrystallization for analysis raised the decomposition point to 179–180°.

Anal. Calcd. for $C_{12}H_{14}Br_2N_4$: C, 38.52; H, 3.77; Br, 42.73; N, 14.98. Found: C, 38.8; H, 3.5; Br, 42.6; N, 14.9.

Infrared spectrum, Nujol mull: maxima at 6.32, 7.05, 8.41, 9.16, 9.91, 10.0, and 12.56 μ. The lack of a band near 6μ indicates that the double bond is *trans* and symmetrically substi-

---

[1] F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948).

[2] L. F. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine*, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 177.

[3] A. W. Hofmann, *Proc. Roy. Soc.* (*London*) 12, 642 (1863).

[4] F. Blau, *Monatsh.*, **10**, 382 (1889).

[5] A. Vallette, *Ann. chim.*, (12) **3**, 644 (1948).

[6] N. Clausen-Kaas, S. Li, and N. Elming, *Acta Chem. Scand.*, **4**, 1233 (1950).