

Decompositions were carried out in a flask fitted with a nitrogen ebullator; a thermometer; and an absorption train consisting of a water-cooled condenser with receiver, a trap cooled by an ice salt freezing mixture, another trap containing concentrated sulfuric acid and finally, a U-tube containing Ascarite.⁵ Typically the pot containing the ester was heated to about 265°, at which temperature the ester would start to boil. A slow stream of nitrogen was used to sweep out the decomposition products. A liquid, n_D^{25} 1.3950, was collected in the receiver of the water-cooled condenser. This was identified as 1-butanol by preparation of an α -naphthylurethan which melted at 69–70.5° and did not depress the melting point of an authentic sample. Butene was absorbed in the sulfuric acid and carbon dioxide in the Ascarite. In preliminary experiments butene was identified by condensation in a cold trap, the liquid was evaporated, and the gas passed into a solution of bromine in carbon tetrachloride to give a liquid boiling at 164°; n_D^{25} 1.507; d_4^{25} 1.76. These values are in reasonable agreement with literature values⁶ for 1,2-dibromobutane: B.P. 166°, n_D^{25} 1.5125, d_4^{25} 1.787. These data indicate that the butene is primarily 1-butene, although there may have been some rearrangement. Decomposition was continued until evolution of volatile material had stopped.

Acknowledgment. The authors acknowledge their appreciation to J. L. O'Donnell for preparation of the esters.

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(5) Mention of firm names or trade products are furnished for convenience, and this information does not constitute an endorsement of them or their products by the Department of Agriculture.

(6) R. T. Dillon, W. G. Young, and H. J. Lucas, *J. Am. Chem. Soc.*, **52**, 1954 (1930); N. A. Lange, *Handbook of Chemistry*, Seventh Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 446.

Iodination of Benzoic Acid in Acetic Acid-Sulfuric Acid Mixture Containing Iodate

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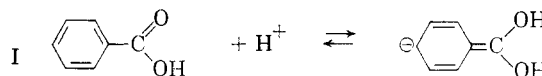
Received June 24, 1959

The direct halogenation of benzoic acid is inhibited by the deactivating influence of the carboxyl group. It is possible however, to obtain yields of *m*-chlorobenzoic acid as high as 50% by the use of potassium permanganate, hydrochloric acid, and benzoic acid in aqueous medium.¹ The iodination of benzoic acid was attempted in acidified aqueous medium in the presence of iodide and iodate. Perchloric, nitric, sulfuric, and acetic acids, respectively, failed to produce even the slightest yield of *m*-iodobenzoic acid.

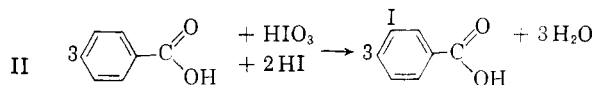
The use of 1:1 glacial acetic and sulfuric acids containing benzoic acid and sodium iodate produces a 70% yield of *m*-iodobenzoic acid when sodium iodide, dissolved in glacial acetic acid, is added

dropwise over a period of one hour to the heated (85°) mixture. Subsequently, it was determined that a mixture of 45% glacial acetic and 55% sulfuric acids by volume proved to be the most effective environment. Sodium iodide in acetic acid, or iodine plus sodium iodide, presented a convenient way in which to introduce iodine. The latter combination makes possible the solution of 20 g. of iodine in 50 ml. of acetic acid.

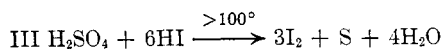
It would appear that in the presence of glacial acetic and sulfuric acids the benzoic acid is rather basic and may be considered a proton acceptor.² Acquiring a proton, the carboxyl group now permits more negativity at the *meta*- position (I), a situa-



tion which seems to facilitate iodination. The presence of water in this system provides a much stronger base than benzoic acid and thus hydronium ion is formed which effectively prevents a proton combination with the carboxyl group. The reaction (II) is most rapid in the presence of a slight excess of iodate and free iodine which is liberated on the addition of iodide as described above. The acetic acid solubilizes both iodine and benzoic acid which enhances the rate of reaction.



A temperature above 100° promptly stops the reaction. Lowering the temperature at this point does no good. Above 100° elemental sulfur (III) appears



on the colder parts of the reaction flask. At the optimum temperature for the reaction to proceed, an excess of iodide over the equivalent of iodate will stop the iodination. Iodate must always be in slight excess over the iodide added. The addition of more iodate when iodide is in excess will restore the iodination process.

EXPERIMENTAL

Benzoic acid (12.0 g.) was placed in a 3-necked flask, with condenser, along with glacial acetic acid (90 ml.) and stirred to dissolve the benzoic acid. Concentrated sulfuric acid (110 ml.) was added slowly with stirring. To this mixture was added sodium iodate (6.0 g.). The mixture was maintained at 85° throughout the reaction. Acetic acid (50 ml.), containing sodium iodide (10 g.), was added dropwise while the mixture was vigorously stirred mechanically. The free iodine concentration was permitted to be in considerable excess. As the reaction progresses the iodine color disappears and more iodide must be added to keep the rate optimum. In these circumstances the time required is approximately 50 min.

The mixture was decolorized by the use of sodium sulfite. The addition of water equivalent to 3 times the volume of the

(1) H. Y. Yee and A. J. Boyle, *J. Chem. Soc.*, 4139 (1955).

(2) L. P. Hemmet, *Chem. Revs.*, **16**, 67 (1935).

final mixture effectively brings down the *m*-iodobenzoic acid. The product recovered was recrystallized from glacial acetic acid by diluting the solution with water yielding 18.0 grams (75%) of pure product. M.p. and mixed m.p. 181–183°.

Anal. Calcd. for $C_7H_5O_2I$: 248. Found: Equiv. 246.

DETROIT 1, MICH.

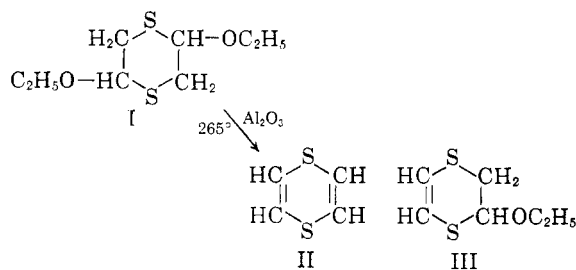
Heterocyclic Vinyl Ethers. XV. The Thermal Stability of 1,4-Dithiadene and Its Reaction with Chlorine.¹

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Received June 24, 1959

We now wish to report some terminal experiments with the heterocycle 1,4-dithiadene, including an improved method of synthesis, its thermal stability, and its reaction with chlorine.

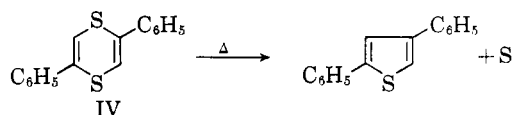
The preparation of 1,4-dithiadene (II), by the vapor phase dealkoxylation of 2,5-diethoxy-1,4-dithiane (I) on alumina, has been re-examined. The reaction temperature was accurately measured



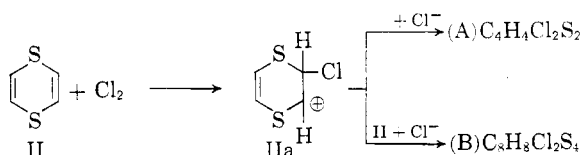
and carefully controlled. Optimum yields of II (47–60%) were obtained when molten I, in the absence of solvent, was reacted on alumina at 260–265°. The use of higher temperatures (310°), as previously reported,² gave only viscous oils and neither II nor III could be isolated.

1,4-Dithiadene was previously reported² to decompose at its boiling point (181°/735 mm.). We have subsequently found that the thermal stability of II is quite dependent upon its purity. Pure 1,4-dithiadene can be distilled at atmospheric pressure under nitrogen with no apparent decomposition. A sample of pure II was maintained at the reflux temperature in a nitrogen atmosphere for 50 minutes with no evidence of decomposition; however, after that time a rapid decomposition initiated. The infrared spectra of the crude decomposition residue, and of the more volatile material obtained from the pyrolysis reaction in the preparation of II, did not reveal bands char-

acteristic of thiophene. Indophenine color tests for thiophene were also negative. Thus, the thermal stability of 1,4-dithiadene is in contrast with that of 2,5-diphenyl-1,4-dithiadene (IV). The latter decomposes at 180° to give 68% yields of 2,4-diphenylthiophene and sulfur.³

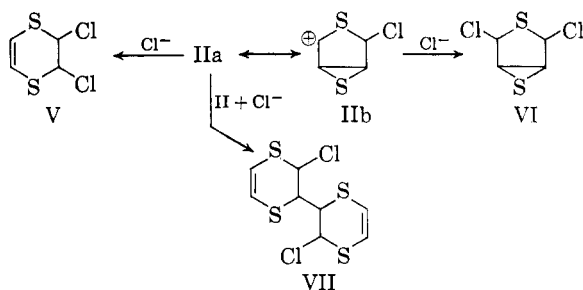


The reaction of 1,4-dithiadene, in carbon tetrachloride at zero degrees, with one molar equivalent of chlorine, resulted in the formation of two solid products: (A) m.p. 104.5–105.5° (22%), and (B) m.p. 157–158° dec. (29%).



(A) is relatively unstable in air, becoming first brown and then dark purple. Elemental analysis and molecular weight determinations established the molecular formula $C_4H_4Cl_2S_2$. Elemental analysis of (B) gave the empirical formula $C_4H_4ClS_2$, although attempts to determine the exact molecular weight were not successful, because of its very low solubility in suitable solvents at low temperatures, and of its thermal instability at higher temperatures. An approximate value obtained suggested the molecular formula $C_8H_8Cl_2S_4$.

Possible structures for (A) were considered to be V or VI, and for (B) the structure VII, or a product related to VI. Product VI could form, as shown in the above equations ($\text{IIa} \rightarrow \text{IIb} \rightarrow \text{VI}$),



a process related to that postulated for the thermal degradation of diaryl dithiadenes.^{3,4} The product (A) reacted readily with potassium iodide in acetone to liberate iodine; however, 1,4-dithiadene disulfone could not be recovered from the acetone solution subsequent to oxidation with hydrogen peroxide. Failure to isolate the disulfone from such mixtures was subsequently shown to be of little

(1) This work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022 ORD 2616.

(2) W. E. Parham, H. Wynberg and F. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).

(3) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954).

(4) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955).