[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Configurations of the 2-Butenes

BY M. H. THOMAS AND F. E. W. WETMORE

For certain geoisomeric derivatives of ethylene it has been shown[1] that the rate of mercuration of the *trans* isomer is less than that of the corresponding *cis* isomer. In connection with other work on the 2-butenes, the authors have used this method to confirm the structures established by previous investigations.

Experimental

Materials.—The samples of butene were drawn from portions prepared by Kistiakowsky and co-workers[2]; before use these were dried and the purity confirmed by measurements of the vapor pressures. All other materials were the usual C. P. grade.

Rate of Reaction.—For a trial experiment butene was fed at atmospheric pressure from a gas buret into an oscillating chamber containing mercuric acetate dissolved in methanol. At 25°, 25 ml. of methanol dissolved at least 850 ml. of low boiling 2-butene (I), 760 ml. of high boiling 2-butene (II), quantities far in excess of that required for complete reaction; the reaction was much too rapid to be followed with accuracy. By using water as solvent the rate was made measurable, but appeared to be simply that of the absorption of the butene.

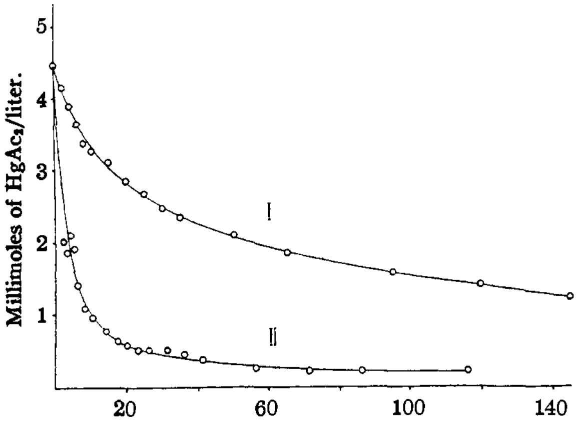

Fig. 1.—Rate of mercuration of 2-butene at 0.8°.

In the second method 0.05 to 0.12 g. of liquid butene was sealed off in a small ampoule; this was placed in a flask containing such a quantity of 0.00447 *M* solution of mercuric acetate in methanol that the butene concentration was also 0.00447 *M*. The whole was brought to 0.8° with continuous shaking and the ampoule was then broken. At regular intervals 4-ml. samples were withdrawn and immediately subjected to vacuum (water pump); this removed all of the unchanged butene and most of the methanol. The mercurial product was removed by dissolving the remainder of the sample in 10 ml. of water, then extracting five times with 5-ml. portions of chloroform; this extraction was shown to be sufficiently complete for the accuracy desired. The mercuric acetate remaining in the aqueous layer was titrated with 0.0102 *N* potassium thiocyanate in the presence of 1 ml. of concd. nitric acid and 1 ml. of ferric alum indicator.

The results of these rate studies are shown in Fig. 1. It is clear that this evidence is in support of the assignment of the *trans* structure to I.

Mercurials.—The solution resulting from the reaction between mercuric acetate and butene in methanol was treated with 10% aqueous sodium hydroxide solution to precipitate any mercurous salt present and the black precipitate filtered off. The remaining liquid was evaporated under vacuum, the mercurial taken up in chloroform and the inorganic salts filtered off. The mercurial (2-acetoxymercuri-3-methoxybutane) could not be crystallized from ethanol, chloroform, carbon tetrachloride or petroleum ether, but persisted in separating as an oil, even in the cold. Therefore to the solution before evaporation saturated aqueous sodium chloride solution was added and the solution allowed to stand one hour. The resultant mercurial (2-chloromercuri-3-methoxybutane) was extracted as before and found to crystallize readily from cold ethanol. The addition of a few drops of water to the cold ethanol solution was sufficient to cause opalescence and initiate a more complete precipitation. The crystals were washed with small portions of cold water, then with cold ethanol, and were dried by vacuum. In like fashion 2-chloromercuri-3-hydroxybutanes were obtained from the reaction of aqueous solutions of mercuric acetate with the 2-butenes. All four mercurials are white solids.

III. 2-Chloromercuri-3-methoxybutane from I.—M. p. 65.5. *Anal.* Calcd. for $C_5H_{11}OHgCl$: C, 18.58; H, 3.43; OCH_3, 9.60. Found: C, 18.58; H, 3.51; OCH_3, 9.79.

IV. 2-Chloromercuri-3-methoxybutane from II.—M. p. 23.6. *Anal.* Calcd. as for III. Found: C, 18.46; H, 3.50; OCH_3, 10.09.

V. 2-Chloromercuri-3-hydroxybutane from I.—M. p. 80. *Anal.* Calcd. for C_4H_9OHgCl: C, 15.53; H, 2.93. Found: C, 15.56; H, 2.98.

VI. 2-Chloromercuri-3-hydroxybutane from II.—M. p. 59. *Anal.* Calcd. as for V and Hg, 64.86; Cl, 11.48. Found: C, 15.42; H, 2.98; Hg, 64.89; Cl, 11.62.

Mixed melting points were determined for V and VI; the eutectic temperature lies in the vicinity of 43°, but this method is not considered satisfactory for determining relative quantities of I and II in a mixture.

Methoxyl Determinations

Although the observed and calculated analytical values for carbon, hydrogen, mercury and chlorine are within allowable error (2%), even the best values for methoxyl are inordinately high (over 4%). Both methoxymer-

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[1] Wright, THIS JOURNAL, 57, 1993 (1935).

[2] Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, 57, 878 (1935).

curials gave variable results as much as 77% too high when analyzed here by the Vieböck–Schwappach method[3] and also in a commercial laboratory. It was obvious that the fault lay with the compounds when analysis of the hydroxymercurials showed an apparent methoxyl content of a few per cent. A suspicion that this error was caused by co-distillation of methyl and butyl iodides was confirmed by analysis of *n*-butyl *o*-methoxybenzoate (VII); this compound gave consistent results indicating two alkoxyl groups per mole. The *n*-butyl iodide which must have carried over in this last methoxyl determination to give such high results was actually isolated (49% yield) in a comparable macro-experiment and identified by conversion to *n*-butyl S-isothiourea picrate, m. p. 174.[4] Although it was not possible to isolate butyl halide from the analyses of III, IV, V and VI, there is little doubt that the methoxyl analyses of these are in error from the same cause.

The difficulty could be partly though not wholly avoided by elimination of the phenol ordinarily used in this determination.[5] Under these conditions the methoxymercurials gave values only 4% too high, while VII gave apparent methoxyl values between one and two groups per mole. Similar discrepancies have been noted before.[6] It seems necessary to question the reliability of the usual analytical procedure, not only with compounds where other alkoxyl groups are present, but also, as in the case of the methoxymercurials, where there exists any possibility that other alkyl halides may be formed.

Acknowledgment.—The authors are grateful for the generosity of the authors of reference 2 in making samples of 2-butene available. They wish to express their thanks also to Miss J. Romeyn and Miss G. Stonestreet for assistance in the microanalyses and to Dr. G. F. Wright for his helpful advice throughout this work.

Summary

1. The methoxy- and hydroxy-mercurials of *cis*- and *trans*-2-butene have been prepared.

2. The rates of mercuration indicate that the low-boiling 2-butene has the *trans* configuration.

3. Errors in methoxyl determinations have been shown and corrected.

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(3) (a) Vieböck and Brecher, *Ber.*, **63**, 3207 (1930); (b) Vieböck and Schwappach, *ibid.*, **63**, 2818 (1930).

(4) Brown and Campbell, *J. Chem. Soc.*, 1699 (1937).

(5) (a) Friedrich, "Die Praxis der quantitativen Mikroanalyse," F. Deuticke, Leipzig; (b) Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937).

(6) King, *ibid.*, **61**, 2383 (1939).

[CONTRIBUTION FROM THE BIOPHYSICAL LABORATORY OF THE DEPARTMENT OF PHYSICS, UNIVERSITY OF MISSOURI]

Ultraviolet Absorption in a Series of Chloropyrimidines in the Vapor State and in Solution

BY FRED M. UBER AND ROGER WINTERS

In view of the importance of compounds which contain the pyrimidine ring in their structure, it is desirable to have more knowledge concerning the absorption spectra of pyrimidine itself and of its simpler substitution products. Moreover, recent progress in the interpretation of the spectra of benzene and pyridine make it appear hopeful that the spectrum of a six-membered heterocyclic ring with two nitrogen atoms might also be amenable to analysis. With the great interest in the correlation of absorption spectra and chemical constitution, as evidenced in several recent papers,[1] additional data on the behavior of absorption within a series of compounds should prove valuable.

Ultraviolet absorption measurements on solutions of various pyrimidine derivatives have been reported in two papers by Heyroth and Loofbourow,[2] who were able to correlate their spectra with the degree of saturation of the pyrimidine ring. It seemed evident from their published absorption curves that considerable fine structure must exist in spectra of the vapor state, particularly in pyrimidine, and this has now been confirmed.

The absorption behavior of a number of amino- and oxypyrimidines has been determined by Williams, Ruehle and Finkelstein.[3]

Experimental

Method.—As a source of continuous ultraviolet for the vapor spectra a hydrogen discharge tube has been used. The quartz spectrograph was a medium Hilger instrument. Quartz absorption cells for the vapor had lengths of 1.0, 3.0, and 11.0 cm. Side tubes permitted filling and sealing-off, the latter being done while maintaining a vacuum. Arrangements were made whereby the temperature of any cell could be varied in order to secure the most favorable conditions for photographing fine structure in the absorption spectra. Eastman "33" photographic plates were employed. The wave lengths were measured on tracings made with a Leeds and Northrup recording microphotometer.

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(1) Smakula, *Angew. Chem.*, **47**, 657 (1934); Dimroth, *ibid.*, **52**, 545 (1939); Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(2) Heyroth and Loofbourow, THIS JOURNAL, **53**, 3441 (1931); *ibid.*, **56**, 1728 (1934).

(3) Williams, Ruehle and Finkelstein, *ibid.*, **59**, 526 (1937).