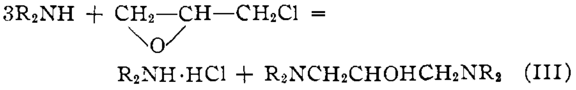
$$4R_2NH + BrCH_2CH_2CH_2Br = 2R_2NH \cdot HBr + R_2NCH_2CH_2CH_2NR_2 \quad (II)$$



$$3R_2NH + CH_2{-}CH{-}CH_2Cl\ (\text{epoxide, }{-}O{-}) = R_2NH \cdot HCl + R_2NCH_2CHOHCH_2NR_2 \quad (III)$$

As a representative example, the synthesis of 1,3-dimorpholinopropane (IID) is reported in detail: 8 g. of trimethylene bromide (Dow) and 14 g. (= 2% excess) of morpholine (Carbide & Carbon) were mixed with 20 ml. of dry benzene and placed in a flask fitted with reflux condenser. (Undiluted, morpholine and trimethylene bromide would react with explosive violence.) The mixture warmed up slightly and crystallization began soon. After standing overnight, the reaction mixture was refluxed for four hours on the water-bath, cooled, filtered from morpholinium bromide, the benzene removed and the residual oil distilled; yield 7.0 g. (77%).

TABLE III

NEW BASES

Compound	Formula	B.p., °C. at 760 ± 5 mm.	Nitrogen, % Calcd.	Found
IB	$C_{10}H_{20}N_2$	236	16.65	16.63
IIB	$C_{11}H_{22}N_2$	256	15.37	15.31
IIIB	$C_{11}H_{22}ON_2$	286	14.13	14.08
ID	$C_{10}H_{20}O_2N_2$	285	13.99	13.99
IID	$C_{11}H_{22}O_2N_2$	317	13.08	12.99
IIID	$C_{11}H_{22}O_3N_2$	352	12.17	12.14

The basicities were determined from the *p*H titration curves by means of the Henderson–Hasselbach equation. The *p*H titrations were carried out as described in detail for pyridine bases.[8]

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[8] A. Gero and J. J. Markham, *J. Org. Chem.*, **16**, 1835 (1951).

LABORATORY OF ORGANIC CHEMISTRY
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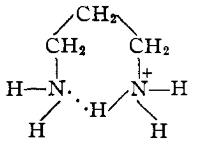
Inductive Effect and Hydrogen Bonding as Factors in the Base Strength of Polymethylenediamines

BY ALEXANDER GERO

RECEIVED MAY 8, 1954

The following factors may be expected to be important for the base strength of polymethylenediamines $NH_2(CH_2)_nNH_2$: (1) the inductive effect of the two nitrogen atoms on each other will mutually hinder their basic action, the more so the closer they are, *i.e.*, the smaller *n* is in the formula. (2) If one of the amino groups coördinates with a proton, its inductive effect on the other, non-ionic, amino group will be greatly enhanced. In this case the electrostatic repulsion between the positive N^+ and a H_3O^+ ion approaching the uncharged N also must be taken into consideration; this repulsion, being inversely proportional to the square of the distance between the two positive charges, should fall off even more rapidly with increasing distance between the two nitrogens. (3) Considerable intramolecular hydrogen bonding may be expected between the two amino groups if one of them is ionized and the other is not. This hydrogen bond should be especially strong in trimethylenediamine where it forms a six-membered chelate ring



This chelate ring should stabilize the mono-cation of trimethylenediamine.

From the foregoing premises it may be concluded that ethylenediamine should be the weakest base among polymethylenediamines and that both ionization constants should increase with increasing length of the carbon chain, the second more than the first so that in long enough chains both ionization constants should become about equal. Besides, the first ionization constant (but not the second in which chelation cannot occur) of trimethylenediamine should be anomalously high.

A search of literature did not reveal any determinations of ionization constants of polymethylenediamines since those of Bredig[1] and Osaka[2] in the last century. Therefore this writer determined the thermodynamic ionization constants of the first four members of the polymethylenediamine series from their *p*H titration curves, by means of the Henderson–Hasselbach equation. The results (Fig. 1) bear out all predictions of the preceding paragraph, except that even in *n* = 5 the two ionization constants are not yet quite equal; but they are already so close as to make separate determination by *p*H titration barely possible.

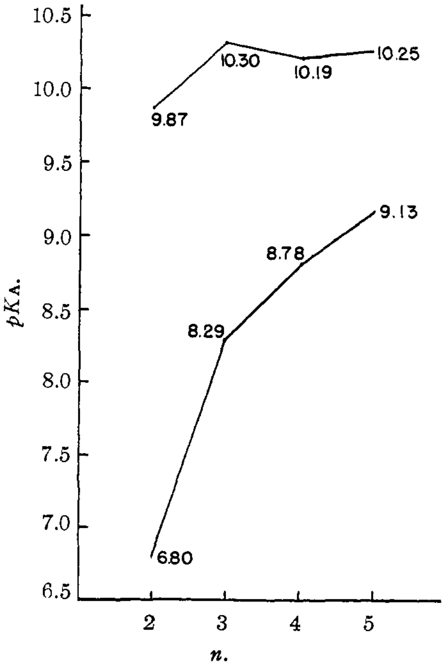


Fig. 1.

Experimental

Ethylenediamine was generously donated by Carbide & Carbon Chemicals Corp., trimethylenediamine by American Cyanamid Co. Putrescine and cadaverine were obtained from Bios Laboratories. All bases were purified by vacuum

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[1] G. Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

[2] Y. Osaka, *ibid.*, **35**, 661 (1900).

distillation. The *p*H titrations were carried out as described for pyridine bases.[3]

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(3) A. Gero and J. J. Markham, *J. Org. Chem.*, **16**, 1835 (1951).

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The Preparation of Vinylacetylene

BY G. F. HENNION, CHARLES C. PRICE AND THOMAS F. MCKEON, JR.[1]

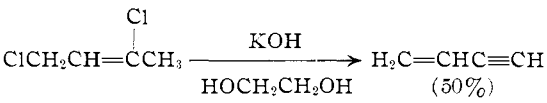
RECEIVED MAY 13, 1954

Several methods for the preparation of vinylacetylene have been reported. Perhaps the best known of these methods is the dimerization of acetylene discovered by Nieuwland.[2]

$$HC{\equiv}CH \xrightarrow{\text{Cat.}} H_2C{=}CHC{\equiv}CH + H_2C{=}CHC{\equiv}CCH{=}CH_2 \; (+ \; H_2C{=}CHCl)$$

Not only is this method inconvenient as a laboratory procedure, but it also suffers from the difficulty that appreciable amounts of divinylacetylene, formed as a by-product, must be eliminated before the vinylacetylene may be safely employed. It is also difficult to remove small amounts of vinyl chloride contaminating the product. Other methods reported[3a,b] are also not readily adapted to laboratory synthesis.

We have found that the preparation of vinylacetylene by the dehydrohalogenation of 1,3-dichloro-2-butene using potassium hydroxide in ethylene glycol offers a number of advantages for a laboratory scale preparation since it is a one-step process, all the starting materials are readily available, the yields of pure vinylacetylene are better than 50% and there are no hazardous or difficulty-removed by-products.



$$ClCH_2CH{=}\overset{\overset{\displaystyle Cl}{|}}{C}CH_3 \xrightarrow[HOCH_2CH_2OH]{KOH} \underset{(50\%)}{H_2C{=}CHC{\equiv}CH}$$

The apparatus for the dehydrohalogenation is arranged as follows. A 2-l., three-necked flask, heated by means of a Carbowax bath, is equipped with a motor-driven, oil-sealed stirrer, a bulb reflux condenser and a 250-ml. dropping funnel. The dropping funnel is connected to the flask by means of a side-arm test-tube with the end removed. This side-arm is connected through a calcium chloride drying tube and a bubbler to a nitrogen tank.

The top of the condenser is connected to a horizontal tube (*ca.* 2 × 25 cm.) partially filled with calcium chloride. This in turn is connected to a 100-ml. graduated cylinder immersed in an acetone-Dry Ice mixture. The cylinder is also equipped with an escape tube which is protected by a calcium chloride drying tube.

A typical preparation of vinylacetylene is carried out as follows. Four hundred grams of powdered technical potassium hydroxide flakes is placed in the flask and 500 ml. of ethylene glycol is added. This mixture is stirred vigorously while adding 100 ml. of *n*-butyl cellosolve. The system is swept with a rapid stream of nitrogen for 15-20 minutes while the temperature of the wax-bath is raised to 165-170°. The flow of nitrogen is then reduced to a rate just sufficient to maintain an atmosphere of nitrogen in the system.

One hundred twenty-five grams (1.0 mole) of 1,3-dichloro-2-butene is then added from the dropping funnel at a rate of about three drops per second. The addition should be complete in less than an hour. During the addition the temperature of the wax-bath is maintained at 165-170° and the reaction mixture is stirred vigorously. Heating is continued for one hour after the addition of dichlorobutene is complete.

The yields of crude product obtained in typical runs were 39-42 ml. (31.2-33.6 g.,[4] 60-64.7%). The product was purified by distillation through a Davis low temperature column to yield 37-40 ml. (56.9-61.6%) of vinylacetylene, b.p. 0-6°.

The vinylacetylene was identified by formation of the silver salt, using ammoniacal silver nitrate, and by conversion to ethylvinylacetylene, b.p. 83-84°, n^{20}_{D} 1.4515, d^{20}_{20} 0.7536, 35% yield, using the method of Jacobson and Carothers,[5] lit.[4] n^{20}_{D} 1.4522, d^{20}_{4} 0.7492.

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[1] General Tire and Rubber Co. Fellow, 1952-1954.

[2] J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, THIS JOURNAL, **53**, 4197 (1931).

[3] (a) R. Willstätter and T. Wirth, *Ber.*, **46**, 535 (1913); (b) W. J. Croxall and J. O. Van Hook, U. S. Patent 2,623,077 (Dec. 23, 1952, to Rohm & Haas Co.); THIS JOURNAL, **76**, 1700 (1954).

[4] Calculated on basis of d^{-80} 0.80, extrapolated from data at higher temperatures; K. Kuchinskaya and Anitima, *Khim. Referat. Zhur.*, **2**, 65 (1939) (*C. A.*, **34**, 2783⁷ (1940)).

[5] R. A. Jacobson and W. H. Carothers, THIS JOURNAL, **55**, 1622 (1933).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
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The Preparation of 1-C¹⁴-Labeled Glucose, Mannose and Fructose[1]

BY H. G. HERS,[2,3] J. EDELMAN[2] AND V. GINSBURG

RECEIVED JUNE 1, 1954

As no convenient method has been described for the direct synthesis of 1-C^{14}-labeled fructose, the authors have used a procedure, based upon the cyanohydrin method of Isbell, *et al.*,[4] to prepare this sugar on a millimole scale in addition to 1-labeled glucose and mannose. This was achieved by epimerization of a mixture of the labeled aldoses in phosphate buffer. As no carrier was added at any stage of the reaction or purification the specific activity of the hexoses was equal to that of the starting cyanide.

The procedure of Isbell, *et al.*, was simplified by omitting the separation of the epimeric gluconic acid and γ-mannolactone, thus obtaining, after reduction, a mixture of glucose and mannose instead of the individual sugars. Such a mixture is suitable for epimerization as it theoretically yields the same ratio of glucose, mannose and fructose as does any one of the pure sugars. After epimerization the products were separated and purified chromatographically.

Experimental

C^{14}-Labeled $BaCO_3$ was converted to $KC^{14}N$,[5] and then to $NaC^{14}N$ by distillation of the regenerated $HC^{14}N$ into NaOH. The reaction between D-arabinose and $NaC^{14}N$ was carried out in the presence of $CaCl_2$ by the procedure of Isbell, *et al.* The resultant mixture of epimeric hexonic acids was converted by slow concentration in methyl cellosolve to the corresponding lactone mixture, and this sirup was reduced directly by sodium amalgam in oxalate buffer to yield glucose and mannose. Isbell's procedure was then followed until the deionized sugar solution was collected from the

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[1] This work was supported in part by a research contract with the U. S. Atomic Energy Commission.

[2] Rockefeller Foundation Research Fellow.

[3] Chercheur qualifié F.N.R.S.

[4] H. S. Isbell, J. V. Karabinos, H. L. Frush, N. B. Holt, A. Schwebel and T. T. Galkowski, *J. Research Natl. Bur. Standards*, **48**, 163 (1952).

[5] J. A. McCarter, THIS JOURNAL, **73**, 483 (1951).