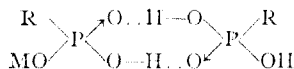


bility in hydrocarbon solvents, also appears to support such a formulation.

When a phosphonic acid is gradually neutralized by addition of a base, the above formulation would indicate the possibility of initial neutralization of the "free" chain ends and a preservation, in whole or in part, of the essential structure of the chain.

In experiments with *n*-butanephosphonic acid, which is a readily available experimental material, the acid was neutralized in aqueous solution with sodium hydroxide added in small steps. Specimens of solutions so obtained ranging up to the point of exact half-neutralization in 5% steps were carefully evaporated to dryness. The products obtained by neutralization up to one-quarter of all available hydrogen ions, *i.e.*, up to empirical formulation of $\text{RPO}_3\text{H}_2:\text{RPO}_3\text{HNa}$, were waxy substances which melted well below the melting point of the free acid (m.p. 106°); generally the softening began at $60\text{--}70^\circ$ and extended to approximately 110° , with formation of a very viscous transparent liquid. At the point of "25%" neutralization the nature of the products underwent a decided change. The substance obtained at this juncture was a freely mobile powder which showed the first sign of partial liquefaction only at 143° and the translucent jelly-like consistency was maintained even at well above 200° . Extraction of these lower products with hot benzene resulted in slow removal of the free acid from specimens containing less than 25% neutralized material; the residual matter was identical with the "quarter" salt described above. Since the free acid is rapidly soluble in hot benzene on heating, the relative slowness of the extraction of the partial salts (0.5–1.0 hour) may serve as an indication of the time requirement for the separation of the chain fragments of the residual phosphonic acid chain from the neutralized portion, possibly through cleavage of monomer units which then associate.

The "quarter-neutralized" product was not soluble in hot benzene and its solubility in water at 25° was appreciably lower than that of the free acid: approximately 17 weight per cent. against 31 weight per cent. This suggests that the essentially chain-linked free acid has been transformed at this juncture into a ring-linked structure, similar to that found in phosphonous acids,⁴ *i.e.*



The analogy is obviously incomplete, since the phosphonous acids appear to form a trimeric ring, lacking free hydroxyl groups.

Products obtained by further neutralization of the acid are freely flowing powders of microcrystalline appearance; they shrink and sinter at temperatures that rise from 143° shown by the "quarter" salt to 245° shown by the "half" salt, *i.e.*, product corresponding to RPO_3HNa . The latter is less soluble than the "quarter" salt, dissolving only to the extent of 13 weight per cent. in water at 25° . The behavior of this salt suggests the structure similar to that of the "quarter" salt with the hydroxyl being replaced by ONa group, thus affording a very symmetrical aggregate. Heated to red heat the

substance decomposes with evolution of an organic phosphine, a behavior that is not observed with the free acid and thus suggesting a different aggregation of the constituents. Such a reaction is rather typical of phosphonous acids on pyrolysis and underlines the apparent similarity of the overall structures of these two classes of substances. The amounts of the generated phosphine were too small for positive identification but absorption in strong nitric acid resulted in formation of an acid that appears to be butanephosphonic acid.

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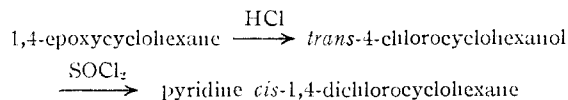
cis-1,4-Dichlorocyclohexane^{1,2}

BY T. W. LUNNEY, A. M. WHALEY AND H. W. DAVIS

RECEIVED JANUARY 12, 1952

Of the seven possible dichlorocyclohexanes, the *trans*-1,2- is well known and the 1,1- and *cis*-1,2- have recently been reported.³ In regard to other isomers, Rothstein⁴ obtained a mixture of 1,4-dichlorocyclohexanes from which a solid melting at 102° , considered to be the *trans* isomer, was separated. The *cis*-1,4- was apparently not completely separated from the *trans* isomer as it remained liquid on cooling to -15° .

It was thought that the *cis*-1,4-dichlorocyclohexane might be obtained in satisfactory purity by means of the reactions



These reactions did furnish a dichloro derivative which, on the basis of its history and the mechanisms generally accepted for the reactions by which it was made, is assumed to be the *cis*-1,4-dichlorocyclohexane. Since the preparation of *trans*-4-chlorocyclohexanol from 1,4-epoxycyclohexane has recently been described,⁵ only the conversion of the chlorohydrin to the dichloride is reported here.

Reaction of thionyl chloride on 4-chlorocyclohexanol in the absence of pyridine produced no dichloride.

Experimental

A mixture of 48.6 g. (0.36 mole) of *trans*-4-chlorocyclohexanol, 100 ml. of chloroform and 34.4 g. (0.43 mole) of pyridine (freshly distilled) was stirred until the chlorohydrin dissolved, then 51.5 g. (0.43 mole, 20% excess) of thionyl chloride was added dropwise. The temperature was allowed to rise until reflux started and refluxing was continued for one hour after all the thionyl chloride was added. After cooling, the mixture was washed twice with water, the water extracted with ether and the ether combined with the chloroform solution. After drying, the solvents were

(1) This paper represents part of a thesis submitted by T. W. Lunney to the University of South Carolina in partial fulfillment of the requirements for the degree of Master of Science.

(2) Part of a paper presented before the Southwide Chemical Conference, Wilson Dam, Ala., October, 1951.

(3) (a) B. Carroll, D. C. Knibler, H. W. Davis and A. M. Whaley, *This Journal*, **73**, 5382 (1951); (b) H. C. Stevens and O. Grummitt, *International Congress of Pure and Applied Chemistry*, Sept. 10–13, 1951, New York, N. Y.

(4) B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

(5) E. A. Felnel, S. Goodyear and J. Berkowitz, *This Journal*, **71**, 4978 (1951).

evaporated and the residue distilled at reduced pressure through a 1" × 14" Vigreux column. Obtained were 16 g. of material, probably 4-chlorocyclohexene, b.p. 40–45° (13 mm.) and 21 g. (38% of theoretical) of *cis*-1,4-dichlorocyclohexane, b.p. 80–81° (13 mm.). Redistillation gave a sample having the following properties: m.p. 18°; b.p. 80.3° (12.5 mm.), 96° (25 mm.), 113.2° (50 mm.), 133° (100 mm., dec.), 193° (756.5 mm., dec.); n_D^{20} 1.4942, n_D^{25} 1.4920; d_4^{20} 1.1900, d_4^{25} 1.1847.

Anal. Calcd. for $C_6H_{10}Cl_2$: Cl, 46.33; mol. ref., 37.44. Found: Cl, 46.49; mol. ref., 37.45.

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Trifunctional Aminocyclanols. Synthesis of 3-Aminocyclohexanediol-1,2

By G. E. McCASLAND, T. J. MATCHETT AND MARSHA HOLLANDER

RECEIVED JANUARY 30, 1952

Through previous studies¹ on 2-aminocyclanols and 2-aminocyclohexanepentols (inosamines) we became interested in the synthesis of alicyclic compounds having three neighboring amino and/or hydroxy functional groups. Of the cyclohexane derivatives with such substituents, the 1,2,3-triols have been thoroughly characterized by Posternak²; however, the corresponding triamines and the aldimines apparently are wholly unknown, and only one investigation³ of the aminediols has been reported.

A suitable starting material for preparation of the aminediols appeared to be 1-ethoxy-2,3-epoxycyclohexane, whose preparation *via* the iodohydrin,⁴ and also directly from 1-ethoxycyclohexene-2 by peracid treatment,³ had been described. We found that a procedure using the chlorohydrin is somewhat more convenient, but the peracid method does give much better yields.

The reaction of the ethoxy-epoxide with ethanolic ammonia gave us an aminediol monoethyl ether⁵ of m.p. 132–134°. Its *N-p*-nitrobenzoyl derivative melted at 201–203°. Cleavage of the aminediol ether with hydrobromic acid gave the aminediol as its hydrobromide, m.p. 167–168°. The aminediol was further characterized by conversion of the hydrobromide to the *N-p*-nitrobenzoyl derivative, which melted at 182–183°.

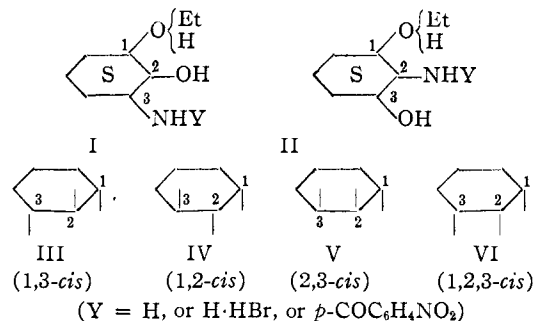
(1) For related publications see G. E. McCasland and Donald A. Smith, *THIS JOURNAL*, **73**, 5184 (1951), and references there cited.

(2) T. Posternak, *Helv. Chim. Acta*, **30**, 441 (1947).

(3) M. Mousseron, F. Winternitz and G. Combes, *Bull. soc. chim.*, [5] **14**, 79 (1947); M. Mousseron and R. Granger, *ibid.*, [5] **14**, 850 (1947); M. Mousseron, G. Manon and G. Combes, *ibid.*, [5] **16**, 396 (1949).

(4) L. Brunel, *Compt. rend.*, **150**, 986 (1910); *Ann. chim. phys.*, [8] **6**, 269 (1905).

(5) Mousseron, *et al.*,³ reportedly obtained by the amination of this same ethoxy-epoxide an aminediol monoethyl ether of m.p. 110°, b.p. 148–150° (15 mm.), whose hydrochloride melted at 160° and contained 9.7% N (calcd. 7.2%). The free base reportedly reacted with nitrous acid to give 1-ethoxy-2-formylcyclopentane (semicarbazone m.p. 204–205°). Yields were not reported, and the compounds were not further characterized. The product of m.p. 110° could be an isomer, but is perhaps merely a less pure sample, of the compound of m.p. 134° now reported. In early 1947 Mousseron, *et al.*, assigned their product structure I, but later wavered between I and II. It should be noted that, according to current interpretations of the pinacolic rearrangement (*e.g.*, see G. E. McCasland, *THIS JOURNAL*, **73**, 2293 (1951)), both structures I and II might be expected to yield the above aldehyde.



For each of these four derivatives two structures (I or II) are possible, depending on whether the parent aminediol is 3-aminocyclohexanediol-1,2 or 2-aminocyclohexanediol-1,3. Structure I will result if the nucleophilic attack by $:NH_3$ on 1-ethoxy-2,3-epoxycyclohexane occurs at position 3, structure II if the attack is at position 2.

In order to determine the structure, periodic acid studies were carried out. The aminediol *N-p*-nitrobenzoyl derivative consumed nearly the theoretical amount of periodic acid for one $-CHOHCH_2OH-$ grouping, thus supporting structure I.⁶

For each structure (I or II) four diastereomeric configurations (III, IV, V, VI) are possible.⁷ Since oxirane ring opening generally occurs in the *trans* manner, the aminediol of structure I might have configuration III or IV but not V or VI. To decide between III and IV one must know not only the position of nucleophilic attack, but also the configuration of the ethoxy-epoxide used. The configuration of the epoxide must be either *d,l*-V or *d,l*-VI, since the cyclohexane-oxirane ring-fusion is necessarily *cis*.^{8,8a}

Possible evidence on the configuration of the ethoxy-epoxide may be found in the work of Posternak,² who showed that it is hydrolyzed by water to give (after ether-cleavage by hydrobromic acid, which presumably causes no inversion) predominantly the *meso*-triol of configuration III.⁹ Unfortunately, it is not known whether the presumed nucleophilic attack by $:OH_2$ on the oxide ring is at position 2, or at position 3. Hence the configurations of the ethoxy-epoxide and of our aminediol derivatives remain uncertain.

An earlier attempt to prepare an aminediol of structure II from the corresponding nitrodiol was

(6) It is conceivable that a periodic acid solution of low pH might cause $N \rightarrow O$ acyl migration in a compound of structure $-CHOHCH_2(NHCOR)CHOH-$. This would produce a structure $-CH(OCOR)-CHNH_2CHOH-$ scissionable by periodate. So far as we know, no one has found, or looked for, such an effect. However, since in any case the periodate oxidation of a 2-aminocyclanol is very slow at low pH, we regard it as improbable that the observed periodate uptake was due to acyl migration.

(7) For structure II, configurations IV and V become identical when both hydroxyl groups are free; therefore only three diastereomers would be predicted for such derivatives.

(8) The possible presence of both diastereomers in the ethoxy-epoxide as ordinarily prepared has not been entirely excluded.

(8a) FOOTNOTE ADDED IN PROOF.—Dr. J. A. McRae and Dr. R. Y. Moir of Queens University (Kingston), advise in a private communication that they have actually found two diastereomers in the ethoxy-epoxide prepared from the chlorohydrin, and will describe the separation and identification of these diastereomers in a forthcoming publication.

(9) A small proportion of the *d,l*-triol of configuration IV (= V) is simultaneously formed. The *meso*-triol of the all-*cis* configuration VI is obtained by hydrogenating pyrogallol.