sion with anhydrous ether and low-boiling petroleum ether. The crystals (0.64 g., 49.3%) decomposed at 143–145°. The filtrate deposited an additional amount of product which weighed 0.33 g. (25%) and decomposed at 137–145°. The product with the higher decomposition point was submitted directly for microanalysis.

Anal. Calcd. for $C_{26}H_{26}NO_3B_3$: C, 72.13; H, 6.06; N, 3.24. Found: C, 71.95; H, 5.98; N, 2.98.

Morpholine–Benzeneboronic Anhydride Complex.—A 10-ml. aliquot, which contained 0.26 g. of morpholine, of an ether solution of technical grade morpholine was added to 0.94 g. of benzeneboronic anhydride. The anhydride dissolved, but no precipitation occurred. After the solution was filtered by gravity filtration and the filtrate was reduced in volume to *ca.* 5 ml. on a water-bath, the complex separated in clumps of white needles. The white needles were collected by suction filtration and were rinsed with ether and petroleum ether. The crystals (0.68 g., 58%) melted at 183–187°. The filtrate deposited an additional amount of product which weighed 0.17 g. (14.5%) and melted at 165–171°. An analytical sample was prepared by one recrystallization of the higher melting crystals from ether. The analytical sample melted at 188–189°.

Anal. Calcd. for $C_{22}H_{24}NO_4B_3$: C, 66.25; H, 6.07; N, 3.51. Found: C, 66.44; H, 6.32; N, 3.49.

Attempted Preparation of an Acridine–Benzeneboronic Anhydride Complex.—A 15-ml. aliquot, which contained 0.54 g. of acridine, of an ether solution of acridine was added to 0.94 g. of benzeneboronic anhydride in a conical flask. A precipitate was always present in the flask. Thus it was not possible to distinguish between insolubility of the anhydride in the acridine solution and dissolution of the anhydride in the solution accompanied by simultaneous precipitation of the complex. After several hours, the precipitate was collected by suction filtration, and washed with ether and petroleum ether. The infrared spectrum of this precipitate was essentially identical with that of benzeneboronic anhydride.

3,6-Diaminoacridine–Benzeneboronic Anhydride Complex.—The 3,6-diaminoacridine used in this reaction was prepared by treatment of the sulfate salt (Eastman Kodak Co., practical grade) with excess base and crystallization of the free amine from dimethylformamide. A mixture of 0.32 g. of 3,6-diaminoacridine and 40 ml. of tetrahydrofuran was heated to reflux on a steam-bath to effect solution. The solution was filtered rapidly while hot to remove a minute amount of insoluble material. The filtrate was added to 0.90 g. of benzeneboronic anhydride. Within a few minutes the anhydride dissolved completely to give an orange-red solution which exhibited an intense green fluorescence. The solution was reduced in volume to *ca.* 12 ml. on a steam-bath. A small amount of amorphous, colored material which deposited upon cooling was removed from the solution by filtration. When the filtrate was further reduced in volume to *ca.* 2–3 ml., a red precipitate separated on cooling. The red precipitate was collected by suction filtration and washed in succession with tetrahydrofuran and anhydrous ether. These ether washes removed the red color and left a brilliant yellow, crystalline product on the filter. The yellow crystals were rinsed with petroleum ether. These crystals (0.32 g., 25%) melted at 252–255°. Additional highly colored material deposited in the filtrate, but no attempt was made to isolate more of the product. The yellow crystals were submitted for microanalysis without further purification.

Anal. Calcd. for $C_{49}H_{41}N_3O_6B_6$: C, 70.66; H, 4.96; N, 5.05. Found: C, 70.66; H, 5.00; N, 5.10.

Preparation of Analytical Samples *via* Complexes. A. Benzeneboronic Anhydride.—Ten milliliters of water was added to 0.27 g. of the pyridine–benzeneboronic anhydride complex in a conical flask and the mixture was boiled on a hot-plate. The complex gradually dissolved in the boiling water, and then the volume of solution was reduced to *ca.* 3 ml. The flask was stoppered and allowed to stand overnight; white crystals of benzeneboronic acid deposited. The crystals were collected by suction filtration, dried in a vacuum desiccator over calcium chloride, and then converted to benzeneboronic anhydride in an oven at 105° for 17 hours. The product was submitted for microanalysis without further purification.

Anal. Calcd. for C_6H_5OB: C, 69.43; H, 4.85. Found: C, 69.52; H, 4.96.

B. **3,6-Diaminoacridine.**—Ten ml. of 2 *N* sodium hydroxide solution was added to *ca.* 150 mg. of the 3,6-diaminoacridine–benzeneboronic anhydride complex, and the mixture was allowed to stand for one or two hours. The complex appeared to decompose, and a yellow solid deposited in the dark brown solution. The yellow solid was collected by suction filtration and rinsed well with water. The solid was dried in an oven at 105° overnight and submitted for microanalysis without further purification.

Anal. Calcd. for $C_{13}H_{11}N_3$: C, 74.63; H, 5.31; N, 20.09. Found: C, 74.36; H, 5.07; N, 20.07.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. I. The Structure of Poly-(diallylammonium Halides)[1,2]

BY GEORGE B. BUTLER, ALLAN CRAWSHAW AND W. LAMAR MILLER

RECEIVED JANUARY 13, 1958

Two of the soluble, linear polymers obtained from monomers of the general formula $[(CH_2{=}CHCH_2)_2NR_2]^+Br^-$ have been degraded by well-known methods. Both poly-(diallylammonium bromide) and poly-(diallyldimethylammonium bromide) have given products resulting from the cleavage of piperidinium bromide rings present in the structures. The results confirm the structure previously proposed for these polymers.

Polymerization of diallylammonium halides of the general formula $[(CH_2{=}CHCH_2)_2NR_2]^+X^-$ leads to soluble linear polymers.[3] To explain the formation of such polymers, a chain propagation mechanism was proposed which involved alternate intramolecular and intermolecular growth steps. The resultant polymer structure consisted of a linear chain of recurring N-substituted piperidinium halide units alternating along the chain with methylene groups. The polymers appeared to contain a small amount of residual unsaturation, suggesting the occurrence of occasional pendant allyl groups along the polymer chains. In more recent work, extensive purification has afforded polymers in which no unsaturation could be detected. It appears, therefore, that the proposed

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract number AF 18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, New York, N. Y., September, 1957.

(3) G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).

mechanism is followed almost exclusively under the polymerization conditions employed.

Other workers[4,5] have described similar results with monomers that have the requisite seven-membered chain containing a 1,6-diene system.

An investigation of the structure of the poly-(diallylammonium halides) and of the polymerization mechanism has been undertaken. In attacking the problem of the structure, two degradation procedures that would lead to the opening of piperidine type rings were most successful.

Results and Discussion

In the earlier work,[3] diallylammonium chloride was the only monomer in this series that gave an insoluble polymer. This is probably because of the decreased steric assistance given to the intramolecular step in this case when compared to the polymerization, under identical conditions, of diallyldimethyl- and diallyldiethylammonium halides. Using more dilute solutions of diallylammonium chloride for the polymerization, a soluble polymer could be obtained readily and purification gave fully saturated products. This monomer, and the corresponding bromide, provide further examples of this type of polymerization.

Degradation of Poly-(diallylammonium Bromide.).—This monomer was degraded by the method shown in Fig. 1. The bromide I was purified by prolonged extraction until residual unsaturation no longer be could detected by quantitative hydrogenation experiments. An aqueous solution of I on treatment with excess sodium hydroxide gave the polyamine II as a light-brown colored gum which became solid on vacuum drying.

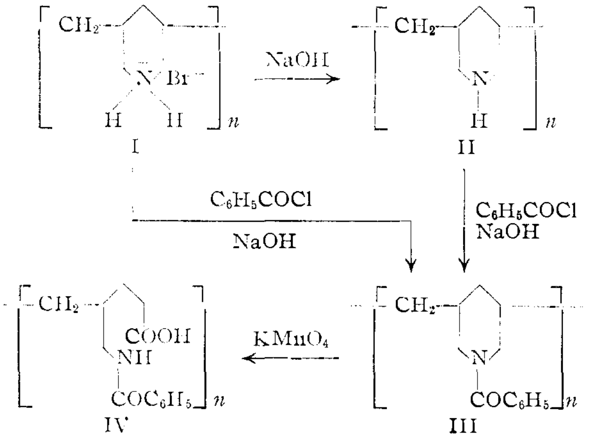

Fig. 1.

Benzoylation of the polyamine II under the Schotten-Baumann conditions was then undertaken. The isolated polyamine II under these conditions always led to products containing some unreacted amine units, which were recognized by their absorption in the NH stretching region of the infrared. However, the dropwise addition of a solution of the polybromide I to a mixture of excess potassium hydroxide solution and benzoyl chloride led to the separation of the polyamine II in small amounts in the benzoylating medium and gave a completely benzoylated product. This polymeric benzoate III, purified to an almost white powder by using a chloroform–ethyl acetate combination, showed a negligible absorption at the NH stretching vibration frequency in the infrared. This fact, along with a correct nitrogen analysis for this structure, showed that all the units had undergone this benzoylation. The spectrum also contained several bands in the region 5.76–6.5 μ, assignable to the benzoylamino group. A determination of intrinsic viscosity gave a value of 0.17 for the polymeric benzoate III, but no data are available for correlating intrinsic viscosity to molecular weight in this case. The value suggests a relatively low degree of polymerization.

The analogous benzoylpiperidine ring can be opened by various reagents.[6] Oxidation using potassium permanganate solution proved to be the most effective for opening the rings of the polymeric benzoate III. The conditions used were similar to those described for the oxidation of benzoylpiperidine to 5-benzoylaminovaleric acid by this reagent.[7] The time required for the oxidation was much longer than for the simpler analog, the optimum time required being about 45 hours. The product was obtained, after purification, as a white solid which was shown to have the ring-opened carboxylic acid structure IV by the following: (a) The analysis is that required for this structure. (b) Potentiometric titrations in dimethylformamide solution afforded typical titration curves for carboxylic acids under these conditions. (c) The infrared spectrum showed absorption bands that correlate with such a structure. (d) On heating a little above its softening point, the product yields a sublimate of benzoic acid and the residual polymer was clearly cross-linked, being insoluble and forming gels with several solvents. The analogous 5-benzoylaminovaleric acid also loses benzoic acid on heating, and cyclization occurs to give 2-ketopiperidine.[8] With the polymeric product IV some degree of intermolecular elimination of benzoic acid giving rise to cross-linkages might be expected.

More prolonged potassium permanganate oxidation of III results in the slow removal of the benzoyl groups by hydrolysis, under the mildly alkaline conditions of the reaction. For example, an oxidation of eight days duration gave a yield of benzoic acid corresponding to the hydrolysis of approximately 50% of the benzoyl groups present.

The final product IV of the degradation has thus resulted from the cleavage of rings present in the original poly-(diallylammonium bromide) I. The analytical results confirm the exclusiveness of the ring formation process under the polymerization conditions used.

Degradation of Poly-(Diallyldimethylammonium Bromide).—The dimethyl polymer was suitable for degradation by the exhaustive methylation method, the reaction scheme being shown in Fig. 2. The polymer V was obtained free of residual unsatura-

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[4] C. S. Marvel and R. D. Vest, THIS JOURNAL, **79**, 5771 (1957).

[5] J. F. Jones, paper read before the Division of Polymer Chemistry, American Chemical Society, New York, N. Y., September, 1957.

[6] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1937, p. 539.

[7] C. Schotten, *Ber.*, **17**, 2544 (1884).

[8] C. Schotten, *ibid.*, **21**, 2235 (1888).

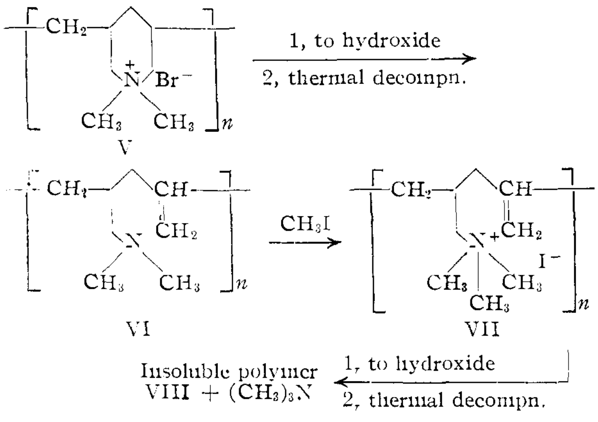

Fig. 2.

tion by prolonged extraction of the finely-ground material. The conversion of the polymer V to its hydroxide was achieved readily by passing an aqueous solution through a column of Amberlite 410 or Nalcite in their hydroxide forms. Usually a sufficient amount of the resin was used to allow complete conversion of V to its hydroxide in one passage through the column. Decomposition of the hydroxide occurred slowly on heating at 55° *in vacuo*. The progress of the decomposition was followed by measuring the *p*H of 0.1% solutions of the product. After 72 hours, the *p*H showed that just over 80% of the units had undergone decomposition. A potentiometric titration at this stage gave a curve showing two end-points, corresponding to neutralization of the remaining units in the hydroxide form and of those in the amine form VI. The concentration of each, estimated from these end-points, confirmed the above ratio of amine to hydroxide units. The hydrochloride of this product was prepared in solution by titrating with dilute hydrochloric acid and then was hydrogenated. Absorption of hydrogen occurred to about 40% of the theoretical amount for the structure. For steric reasons, a quantitative uptake of hydrogen seems unlikely, but qualitatively the results showed that unsaturation had been introduced, and it is apparent that this must be a result of ring cleavage in the starting material V.

Decomposition of the hydroxide at higher temperatures or for a longer period than 72 hours gave an increasingly less soluble product; probably because of the formation of cross-linkages by the newly-formed double bonds. For further work, a soluble polymer was preferable, so the degradation was continued using the polymer having over 80% of its units in the amine form VI.

This polymer was methylated with methyl iodide in methanol solution, from which the poly-(quaternary ammonium iodide) VII precipitated as a pale-yellow, water-soluble solid. Iodine analysis showed that virtually complete addition of methyl iodide had occurred. To complete the degradation, a repetition of the earlier steps was necessary. The polymeric iodide VII was converted to its hydroxide on passage through a prepared ion-exchange column. As before, the hydroxide showed considerable stability and decomposed only slowly at moderate temperatures. A volatile amine, characterized as trimethylamine through its picrate, was produced. The polymeric fragment was not obtained free of nitrogen, since the loss of trimethylamine in the final stage could only occur with those units in the ring-opened quaternary ammonium hydroxide form. The residual polymer, after the vacuum removal of the evolved trimethylamine, was a brown, insoluble solid VIII. It appears that the temperature required to decompose the poly-(quaternary ammonium hydroxide) is sufficient to produce cross-linking in the product. A heterogeneous, alkaline potassium permanganate oxidation of this product gave a filtrate containing formate ions, confirming the presence of pendant methylene groups in the structure.

Thus, this degradation also has given products that can only reasonably be explained by assuming a structure for poly-(diallyldimethylammonium bromide) V as shown.

Experimental

Linear Poly-(diallylammonium Chloride).—Diallylammonium chloride (1.7 g.) dissolved in water (1.7 ml.), was treated with *t*-butyl hydroperoxide (60%, 0.05 ml.) and the solution kept at 65° for four days. The resultant polymer, after powdering and vacuum drying, was obtained as a pale-brown hygroscopic solid (1.6 g.), readily soluble in water. This is in contrast to the cross-linked product described previously.[3]

Poly-(diallylammonium Bromide) I.—A solution of the monomer (3.79 g.) in water (1.9 ml.) and *t*-butyl hydroperoxide (60% 0.12 ml.) was kept at 65° for four days. The crude polymer was ground, vacuum dried, reground to less than 100 mesh particle size, and extracted with absolute ethanol for nine days. The product was an almost white solid (2.5 g.), which decomposed at 350°. *Anal.* Calcd. for $(C_6H_{12}NBr)_n$: N, 7.87; Br, 44.87. Found: N, 7.73; Br, 42.76. Quantitative hydrogenation of this polymer (0.653 g.) in ethanol–water (1:1) solution (35 ml.), using Adams catalyst (0.11 g.) at atmospheric pressure and pre-reducing the catalyst in the usual manner, resulted in a negligible absorption of hydrogen by the polymer.

Degradation of Poly-(diallylammonium Bromide). I to II.—Poly-(diallylammonium bromide) I (0.5 g.) dissolved in water (3 ml.) was treated with excess concentrated sodium hydroxide solution. The viscous product which separated was washed several times with water and vacuum dried to afford a pale-brown solid, readily soluble only in glacial acetic acid of the commoner solvents tested. A solvent combination for purification could not be found.

II to III.—The above product (0.5 g.) was shaken with potassium hydroxide solution (10%, 10 ml.) and benzoyl chloride (1.5 ml.) for 30 minutes, the mixture being cooled in ice occasionally. The product separated during this time as a cream-colored plastic mass from which the excess benzoyl chloride and potassium hydroxide were removed in the usual way. After vacuum drying, dissolution in chloroform and reprecipitation with ethyl acetate gave the polymer as a white powder. The infrared spectrum showed a small band at 2.95 μ (NH stretching), proving incomplete benzoylation.

I to III.—A mixture of benzoyl chloride (4.8 ml.) and potassium hydroxide (4.8 g.) in 35 ml. of water was cooled in ice and stirred vigorously. A solution of the bromide I (2.4 g.) in 10 ml. of water was added dropwise over a period of 30 minutes. Isolation and purification of the product, as described above, gave a white powdery polymer III (2.3 g., 85% yield), softening point 170°, soluble in chloroform, dimethylformamide and several other organic solvents. *Anal.* Calcd. for $(C_{13}H_{15}NO)_n$: N, 6.96. Found: N, 7.15. The infrared spectrum showed bands at 5.83 (weak), 6.15 (strong), 6.32 (medium) and 6.45 μ (weak shoulder) assignable to the benzoyl group, and negligible absorption in the NH stretching region. The intrinsic viscosity of this polymer (0.834 and 1.060% solutions in chloroform at 30.0°) was 0.17.

III to IV.—The finely powdered polymer III (3 g.) was stirred with water (300 ml.) at 60–65°, and 180 ml. of aqueous potassium permanganate solution (2%) was added, in portions, over a period of 45 hours. The precipitated manganese dioxide was removed and the colorless filtrate acidified with dilute hydrochloric acid. The product separated as a gelatinous white precipitate, which was filtered off, washed and vacuum dried. The resultant white powder (2.65 g., 77% yield) was purified by dissolving in pyridine and reprecipitating with dilute hydrochloric acid; softening point (with some decomposition) 175–180°. *Anal.* Calcd. for $(C_{13}H_{13}NO_3)_n$: C, 66.89; H, 6.58; N, 6.00. Found: C, 66.88; H, 6.93; N, 6.10. The following results provided further support for the structure IV: (a) Infrared absorption bands at 3.7 (medium, broad shoulder), 5.81 (medium) and 7.70 μ (medium) for the COOH group, and a broad shoulder at 3.1 μ (medium) for the NH group, both the OH and NH bonds apparently being hydrogen bonded fairly strongly. The absorption bands due to the benzoyl group between 6.15 and 6.45 μ, quoted previously, were present also in this spectrum. (b) Potentiometric titration of this product in dimethylformamide with sodium methoxide in methanol–benzene solution, and using a glass–calomel electrode system afforded curves typical of carboxylic acids under these conditions.[9] (c) The product IV was heated in a dry tube at 230° (Woods metal-bath) for 15 minutes. A white sublimate of benzoic acid was formed, m.p. and mixed m.p. 117–118°. The residual polymer was insoluble and formed gels on standing with dimethylformamide and pyridine.

Degradation of Poly-(diallyldimethylammonium Bromide), V to VI.—The polymer V[3] was first ground, in a dry-box, to less than 100-mesh particle size and extracted with absolute ethanol for 48 hours. Quantitative hydrogenation work showed that the polymer was fully saturated after such treatment. A solution of V (20 g.) in water (50 ml.) was passed through a column of Amberlite resin (Rohm and Haas, Grade IRA 410; about 150 g. of moist resin) that had previously been converted to its hydroxide form by repeated elution with sodium hydroxide solution. The column was washed with water and the collected, bromide-free effluent (250 ml., *p*H greater than 13.0) evaporated down under reduced pressure at room temperature. The resultant semisolid mass was vacuum dried and decomposed by heating at 55° *in vacuo* for 72 hours. The solid product (*p*H of 0.1% solution 11.07) was somewhat hygroscopic, readily soluble in methanol and slowly soluble in water. The following experiments were performed on this product: (1) Potentiometric titration with 0.1 *N* hydrochloric acid followed by back-titration with 0.1 *N* sodium hydroxide solution using a glass-calomel electrode system gave the following values: pK_B 8.60, units in the amine form 81%, units remaining in the hydroxide form 19%. (2) The product (0.225 g.) was titrated with 0.1 *N* hydrochloric acid to a *p*H of 3.05 and the solution hydrogenated quantitatively, using Adams catalyst and at atmospheric pressure in the usual way. The observed uptake of hydrogen was 8.2 ml. (S.T.P.).

VI to VII.—The polyamine VI (1.018 g.), dissolved in absolute methanol (200 ml.), was refluxed gently at 55° with methyl iodide (15 ml.) for four hours. The precipitated product was filtered, washed, and vacuum dried to afford a pale-yellow, water-soluble solid, m.p. 312° (closed capillary), yield 1.68 g. (78%). *Anal.* Calcd. for $(C_9H_{18}NI)_n$: I, 47.5. Found: I, 44.7.

VII to VIII.—The poly-(quaternary ammonium iodide) VII (0.91 g.) was converted to its hydroxide by passing an aqueous solution through a prepared column of Amberlite 410, as previously described. The iodide-free solution of hydroxide was evaporated under reduced pressure at room temperature to a small volume of pale-brown viscous solution. This was heated in a micro distillation apparatus leading into a saturated solution of picric acid in benzene. At a bath temperature of 170°, crystals formed momentarily in the picric acid solution. Water was removed from the benzene by azeotropic distillation and, on cooling, yellow crystals separated. Subsequent recrystallization from benzene afforded trimethylamine picrate, m.p. and mixed m.p. 214.5–215.5°, literature m.p. 215°.

A further portion of the viscous solution of the hydroxide was vacuum dried and heated at 50° for 72 hours *in vacuo*. The polymeric residue was insoluble in all solvents.

Oxidation of VIII.—A sample of the insoluble polymer was stirred vigorously at room temperature for 16 hours with excess alkaline potassium permanganate solution. In a test for formate ion,[10] a portion of the filtered solution readily reduced mercuric chloride.

Acknowledgment.—The analyses reported in this paper were carried out by Galbraith Laboratories, Knoxville, Tenn., or by Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

GAINESVILLE, FLORIDA

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[9] For examples see J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951).

[10] F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., New York, N. Y., 1954, p. 246.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

The Acid-catalyzed Dehydration of 2,2,4-Trimethyl-1,3-pentanediol[1]

BY M. A. PERRY, F. C. CANTER, R. E. DEBUSK AND A. G. ROBINSON

RECEIVED DECEMBER 13, 1957

The acid-catalyzed, vapor-phase dehydration of 2,2,4-trimethyl-1,3-pentanediol led to products resulting from rearrangement rather than simple dehydration. The major product was 2,3,4-trimethylvaleraldehyde, which was formed in 45% conversion and 60% yield. Minor products identified were tetrahydro-2,2,4,4-tetramethylfuran, tetrahydro-2,3,4,4-tetramethylfuran and the cyclic acetal of 2,3,4-trimethylvaleraldehyde and 2,2,4-trimethyl-1,3-pentanediol. Triethyl phosphate was found to be an excellent catalyst for accomplishing this reaction. Mechanisms rationalizing the formation of these products are given.

Of the three reported[2-4] dehydrations of 2,2-dialkyl-1,3-diols, two[2,3] involved rearrangements, apparently through carbonium ion formation. Isovaleraldehyde and 3-methyl-2-butanone were reported to be formed when 2,2-dimethyl-1,3-propanediol was heated in a sealed tube at 200° with dilute sulfuric acid.[2,5] When 2,2,4-trimethyl-1,3-pentanediol was refluxed with dilute sulfuric acid, tetrahydro - 2,2,4,4 - tetramethylfuran was formed.[3] No rearrangement was reported in the dehydration of 3-ethyl-2,2-dimethyl-1,3-pentanediol, which gave 3-ethyl-2,2-dimethyl-3-penten-1-ol as the product.[4]

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[1] Presented at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., November 14–16, 1957.

[2] A. Fischer and B. Winter, *Monatsh.*, **21**, 301 (1900).

[3] A. Franke, *ibid.*, **17**, 89 (1896).

[4] M. Letellier, *Compt. rend.*, **146**, 344 (1908).

[5] Little evidence was presented by Fischer and Winter[2] to distinguish the reported product, isovaleraldehyde, from 2-methylbutyraldehyde. The latter aldehyde closely resembles isovaleraldehyde in all properties reported and its formation can be explained more readily than the formation of isovaleraldehyde.