Cl^- ions seems possible on the basis of D_{6h}^1, chiefly because of the 6-fold axis which forces cesium and chlorine, whose diameters are approximately equal to half the cell edge, to lie either directly on the axis or at a distance of half a lattice length away. The non-centrosymmetrical space groups, D_6^1 and C_{6v}^1, because of their 6-fold axes, are subject to the same difficulty. Only on the basis of D_{3h}^1 could chemically reasonable packings of the cesium and chloride ions be obtained. For at least two of these arrangements, positions could be found for the copper atoms which explained the intensities of the various orders of (0001) fairly satisfactorily. For other types of planes agreement with the observed intensities was unsatisfactory.

It seems probable that the difficulties encountered in this structure study may arise from some unknown and very perfect twinning. Hoard and Goldstein observed a case of this kind in their study of $Cs_3Tl_2Cl_9$,[5] and were fortunate in finding untwinned individuals. In this study no crystals were found whose diffraction effects showed different symmetry. In view of these results it has seemed unprofitable to pursue the study further at this time.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY OF THE
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Structure of Polyvinyl Alcohol

BY A. D. MCLAREN AND R. J. DAVIS

In connection with certain analytical procedures, it was necessary to look for possible existence of a small amount of 1,2-glycol structure in polyvinyl alcohol. Several investigators[1,2,3] have advanced evidence for a preponderance of 1,3-glycol structure in polyvinyl alcohol. The existence of some 1,2-glycol structure is indicated by the work of Staudinger[2] and of Nord,[4] but is doubted by Marvel and Denoon.[3] Reduction of periodic acid is considered specific for 1,2-glycol configuration. The latter authors found that polyvinyl alcohol was not appreciably oxidized by periodic acid at 0° in thirteen hours. We have reinvestigated the action of periodic acid upon polyvinyl alcohol.

Using polyvinyl alcohol[5] containing 0.31% residual vinyl acetate and yielding 0.39% of ash, oxidations with periodic acid were carried out as described previously[3] and at 25°. Results of a typical case using 25-cc. aliquots from a mixture of 150 cc. of 0.511% polyvinyl alcohol in water and 30 cc. of 1.2% periodic acid, at 25°, are given in Table I.

TABLE I

OXIDATION OF POLYVINYL ALCOHOL WITH PERIODIC ACID

Time, hours	Cc. 0.1 *N* $Na_2S_2O_3$ (for 0.511% alcohol)	Specific viscosity (for 0.4% alcohol)
0	0	0.065
1.0	0.1	.062
3.25	.15	.055
6.0	.17	...
18.0	.35	...
24.0	..	.051
48.0	.36	...

Viscosity data for a similar run, utilizing 10 cc. of 0.4% polyvinyl alcohol and 2 cc. of aqueous periodic acid, are also given in Table I.

These results indicate that oxidation takes place at an appreciable rate at 25° and is essentially complete in from six to eighteen hours for low concentrations of the polymer (up to 1%). The reaction proceeds at a very slow rate at 0° and is only about half complete in forty-eight hours. Execution of the periodic acid oxidation at 25° is not considered to modify the specificity of this test.[6]

For polyvinyl alcohol solutions ranging in concentration from 0.1–1.0%, the average titer corresponding to the periodic acid reaction with twenty-five cc. of 0.1% solution of the alcohol was 0.11 cc. of 0.1 *N* thiosulfate solution. This figure indicates that the fraction of vinyl alcohol residues united in 1,2-glycol configuration is 0.019 ± 0.007.

For some unknown reason, polymer solutions in the range of 2% or greater continue to react with periodic acid at room temperature, even after forty-eight hours have elapsed. This may, in part, be the result of cross-linkage with the periodic acid or oxidative side reactions.[6]

If actual cleavage of the polyvinyl alcohol molecule is expected to take place between 1,2-glycol carbon atoms,[6] a decrease in viscosity of aqueous solutions would be expected. Viscosity measurements were conducted with polyvinyl alcohol solutions containing periodic acid and it was observed that the specific viscosity of these mixtures fell off to a constant value after eight to twelve hours had elapsed. This approach to constancy of specific viscosity with time was anticipated since, for solutions of comparable concentration, the periodic acid uptake also ceases at about this time interval. In order to be certain that these viscosity decreases had probably no connection with acetal formation, similar observations were made with polymer solutions containing an equivalent normality of hydrochloric acid. The addition of hydrochloric acid caused an immediate rise in viscosity in accordance with previous findings.[7]

It is interesting to note that the small amount

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[1] Staudinger, *Ber.*, **59**, 3019 (1926).

[2] Staudinger, Frey and Stark, *ibid.*, **60**, 1782 (1927).

[3] Marvel and Denoon, THIS JOURNAL, **60**, 1045 (1938).

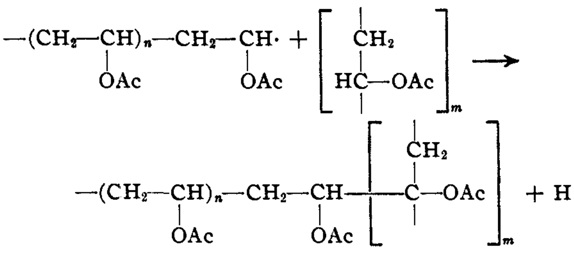
[4] Nord, *Naturwissenschaften*, **24**, 763 (1936).

[5] Osmotic molecular weight 30,000, courtesy of Dr. G. F. Lanzl.

[6] A general discussion of this test is presented by Jackson, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1944, p. 341.

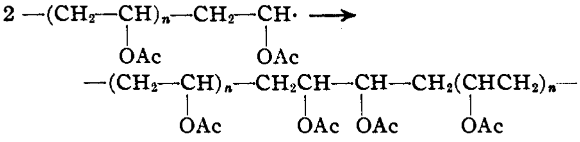
[7] Marvel and Inskeep, THIS JOURNAL, **65**, 1710 (1943).

of 1,2-glycol structure present need not arise from "head to head" polymerization; it might also be produced by a chain transfer mechanism whereby a growing free radical of polyvinyl acetate could become attached to a preformed chain



$$—(CH_2—\underset{OAc}{CH})_n—CH_2—\underset{OAc}{CH}\cdot + \left[\begin{array}{c} | \\ CH_2 \\ | \\ HC—OAc \\ | \end{array}\right]_m \longrightarrow —(CH_2—\underset{OAc}{CH})_n—CH_2—\underset{OAc}{CH}—\left[\begin{array}{c} | \\ CH_2 \\ | \\ C—OAc \\ | \end{array}\right]_m + H\cdot$$

or by a chain termination reaction.



$$2\ —(CH_2—\underset{OAc}{CH})_n—CH_2—\underset{OAc}{CH}\cdot \longrightarrow —(CH_2—\underset{OAc}{CH})_n—CH_2\underset{OAc}{CH}—\underset{OAc}{CH}—CH_2(\underset{OAc}{CH}CH_2)_n—$$

Subsequent hydrolysis in either case would liberate a 1,2-glycol group in the molecule.

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Synthesis of Arylpropylamines. II. From Chloroacetone[1]

BY T. M. PATRICK, JR.,[2] E. T. MCBEE AND H. B. HASS

During some work on the synthesis of pressor amines, the reaction of chloroacetone and benzene to give phenylacetone[3] came to our attention. It seemed worthwhile to study the reaction of chloroacetone with other aromatic compounds as a means of obtaining ketones which could be converted to desired amines.

From chlorobenzene there was obtained *p*-chlorophenylacetone in 11% conversion and 16% yield based on chloroacetone. Bromobenzene, fluorobenzene and anisole, however, failed to give the desired ketones by this method.

1-(*p*-Chlorophenyl)-2-propylamine, a compound of the benzedrine type, was prepared from *p*-chlorophenylacetone both by the modified Leuckart synthesis using formamide, and by sodium amalgam reduction of the ketoxime, in 20 and 35% yields, respectively.

Acknowledgment.—The authors wish to express their appreciation to the Abbott Laboratories for a grant which made this research possible.

Experimental

***p*-Chlorophenylacetone.**—A mixture of 175 g. (1.43 moles) of chlorobenzene and 82 g. (0.62 mole) of aluminum chloride held at 100° was agitated and 27.8 g. (0.30 mole) of chloroacetone was added dropwise over a period of forty-five minutes. Heating and stirring were continued for five hours longer. The cooled reaction mixture was shaken with crushed ice and hydrochloric acid. The organic layer was dried and rectified, giving 7 ml. (8.1 g.) of chloroacetone, 51 ml. (56 g.) of chlorobenzene, 4.7 ml. (5.8 g.) of a fraction boiling at 85–86° at 1 mm., and 2.8 ml. of intermediate fractions. The high boiling fraction had n^{20}_D 1.5452, d^{20}_{20} 1.1397, m. p. 6–8°. Permanganate oxidation of a small portion yielded *p*-chlorobenzoic acid.

Anal. Calcd. for C_9H_9OCl: C, 64.1; H, 5.4. Found: C, 64.1; H, 4.8.

The semicarbazone, m. p. 188°, was prepared in the conventional manner.

Anal. Calcd. for $C_{10}H_{12}ON_3Cl$: C, 53.2; H, 5.4. Found: C, 53.8; H, 5.4.

1-(*p*-Chlorophenyl)-2-propylamine.—Two methods of synthesizing the amine from the ketone were tried.

(a) Nine grams (0.053 mole) of *p*-chlorophenylacetone and 10 g. (0.22 mole) of 99% formamide were heated under reflux at 160–175° for three hours. The temperature was then raised to 185° for three hours. The liquid had become a clear dark brown. It was cooled and extracted with twice its volume of water to remove excess formamide. Five milliliters of concentrated hydrochloric acid was added, and the mixture was refluxed one hour to hydrolyze the formyl derivative of the amine. The solution was cooled, extracted with ether to remove non-basic components and finally made alkaline with 6 *M* sodium hydroxide. The basic solution was steam distilled. The distillate was extracted with ether and this extract was dried over anhydrous potassium carbonate. After the ether was evaporated, the residue was distilled, yielding 1.8 g. (20%) of 1-(*p*-chlorophenyl)-2-propylamine, b. p. 93–94° at 5 mm., n^{20}_D 1.5343, d^{20}_{20} 1.0762.[4]

(b) A 3.4-g. portion of *p*-chlorophenylacetone was dissolved in 14 ml. of ethanol and mixed with a solution of 1.4 g. of hydroxylamine hydrochloride and 1.6 g. of anhydrous sodium acetate in 5 ml. of water. The solution was allowed to stand overnight at room temperature. Cooling and diluting the mixture with water caused the oxime to separate as an oil. The crude oxime was dissolved in 35 ml. of glacial acetic acid, and reduced by the slow addition with cooling and shaking of 265 g. of 4% sodium amalgam. The aqueous phase was made basic with sodium hydroxide solution and extracted with ether. Distillation of the ether extract yielded 1.2 g. (35% based on the ketone) of 1-(*p*-chlorophenyl)-2-propylamine.

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[1] Based upon a thesis submitted by T. M. Patrick, Jr., to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, April, 1943.

[2] Abbott Laboratories Fellow, 1941–1942. Present address: Monsanto Chemical Co., Dayton 7, Ohio.

[3] Mason and Terry, THIS JOURNAL, **62**, 1622 (1940).

(4) Patrick, McBee and Hass, *ibid.*, **68**, 1009 (1946).

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The Exchange of Hydrogen and Tritium Ions During Alkylation, Catalyzed by Tritium Sulfuric Acid

BY T. D. STEWART AND DENHAM HARMAN

A recent paper by Ciapetta[1] stresses the role of hydrogen transfer during alkylation. An indication of very rapid exchange was found by us in a preliminary study of the alkylation of isobutane by 2-butene in the presence of tritium sulfuric acid. The alkylate was fractionated and the

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[1] F. G. Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945); see also C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936), and A. Farkas and L. Farkas, *Ind. Eng. Chem.*, **34**, 716 (1942), for exchange experiments with deuterium; T. M. Powell and E. B. Reid, THIS JOURNAL, **67**, 1020 (1945), for exchange involving tritium. S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1017 (1939), discuss the mechanism of alkylation reactions.