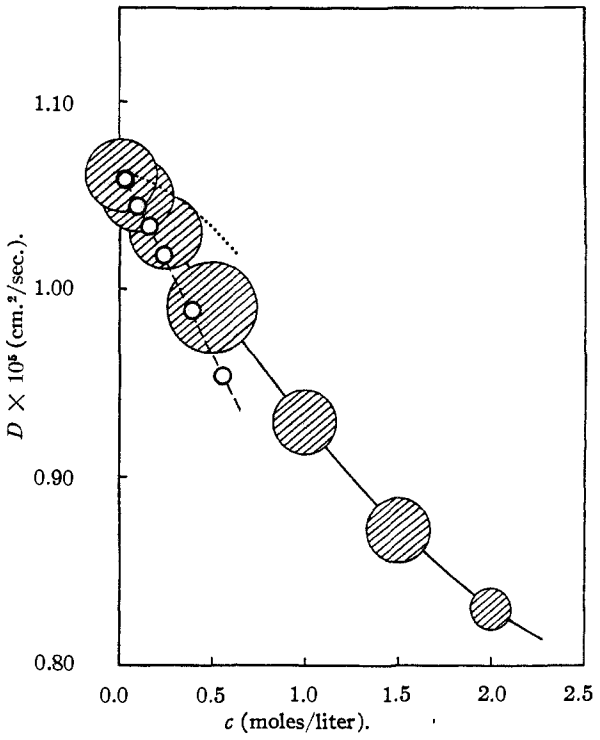


Fig. 1.—Diffusion coefficients of isoelectric glycine in its aqueous solution at 25°: ●, self-diffusion coefficients determined in the present work; O, chemical concentration gradient diffusion coefficients determined by Lyons and Thomas.

by Lyons and Thomas from their data. It may be seen from Fig. 1 that these values, which when corrected for "hydrodynamical effect" would represent the mobilities for chemical concentration gradient diffusion, are higher than the self-diffusion coefficients of isoelectric glycine at the corresponding concentrations. From this we may infer that the actual mobilities for the chemical concentration gradient diffusion of isoelectric glycine are still higher than the corresponding self-diffusion coefficients.

A possible cause of this decrease in self-diffusion coefficient of isoelectric glycine with increasing concentration in dilute solutions is that the actual driving force for self-diffusion (equal to the absolute temperature times the entropy gradient) is opposed by a smaller but finite force due to the time of relaxation effect. This time of relaxation effect is due to the interaction between dipolar ions and therefore should presumably increase with concentration of the solution. The effect of interaction between dipolar ions on the equilibrium properties of these solutions in the dilute concentration range have been discussed by Fuoss.[7] But the quantitative formulation of a theory for the relaxation effect in the self-diffusion of dipolar ions analogous to that for the diffusion of simple spherical ions[8] appears to be difficult because of the absence of spherical symmetry of charge distribution of both the diffusing dipolar ion and its surrounding atmosphere of dipolar ions. Thus, the equilibrium charge distribution surrounding a diffusing dipolar ion can be disturbed both by the translational motion of the center of mass of the dipolar ion (as in the case of self-diffusion of simple spherical ions), or by a pure rotation of the latter. Since these two mechanisms are probably linked together in the actual process of diffusion, it is difficult at this time to make quantitative calculations of the relaxation effect without introducing further simplifying assumptions of doubtful validity. It appears advisable, therefore, to postpone detailed discussion of the present subject until more data on the self-diffusion of dipolar ions have become available.

**Acknowledgment.**—The present work is supported by a du Pont de Nemours Grant-in-Aid and by Contract AT-(30-1)-1375 between the U. S. Atomic Energy Commission and Yale University.

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(7) R. M. Fuoss, THIS JOURNAL, **56**, 1024 (1934); *ibid.*, **58**, 982 (1936).

(8) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

## The Uronic Acid Component of Chondroitinsulfuric Acid[1]

BY M. L. WOLFROM AND W. BROCK NEELY

RECEIVED FEBRUARY 13, 1953

Hexosamine glycosides hydrolyze with difficulty and when hexosamines are glycosidically linked to a hexuronic acid, as in the cartilage heteropolysaccharide chondroitinsulfuric acid,[2,3] the acid conditions requisite to break this bond lead largely to the destruction of the uronic acid moiety. In the case of the related polysaccharides heparin and "mucoitinsulfuric acid,"[4] this difficulty was overcome by the employment of an oxidative hydrolysis with bromine and concentrated sulfuric acid at 0°, whereby the D-glucuronic acid entity present was recovered as D-glucaric (D-glucosaccharic) acid. We report herein the extension of this procedure to cartilage chondroitinsulfuric acid whereby its hexuronic acid component is adequately identified as D-glucuronic acid, in confirmation of the work of Bray, Gregory and Stacey,[5] who isolated a crystalline methyl ether of this substance on acid hydrolysis of the methylated, degraded polysaccharide. In early experiments, Levene and Jacobs[6] obtained a silver salt on treatment of chondroitinsulfuric acid, designated glycothionic acid by them, with hydrobromic acid and bromine under unspecified conditions. The silver content of this salt was in agreement with that required by a hexuronic acid but the substance was not further characterized.

### Experimental

An amount of 500 mg. of purified barium chondroitinsulfate (from cartilage)[3] was dissolved at 0° in a mixture of 10 ml. of concentrated sulfuric acid (sp. gr. at 15.56°, 1.84), 4 ml. of water and 10 drops of bromine and maintained at 3° for 6 days. Additional quantities of bromine were added

(1) Supported by fellowship funds granted by The Ohio State University Research Foundation to the university for aid in fundamental research (Project R-11670-P369).

(2) P. A. Levene, *J. Biol. Chem.*, **140**, 267 (1941).

(3) M. L. Wolfrom, R. K. Madison and M. J. Cron, THIS JOURNAL, **74**, 1491 (1952).

(4) M. L. Wolfrom and F. A. H. Rice, *ibid.*, **68**, 532 (1946); **69**, 1833 (1947).

(5) H. G. Bray, J. E. Gregory and M. Stacey, *Biochem. J.*, **38**, 142 (1944).

(6) P. A. Levene and W. A. Jacobs, *J. Exptl. Med.*, **10**, 557 (1908).

at intervals to hold it in excess. After bromine removal by aeration, the reaction mixture was poured slowly into 125 ml. of ice and water and the acid was neutralized in the cold with barium carbonate. The precipitate was removed by filtration and triturated with 30 ml. of 1% aqueous potassium hydroxide and again filtered. The combined filtrates were neutralized with acetic acid and concentrated under reduced pressure at 30–40° to a sirup which was treated with 80 ml. of a 1% solution of hydrogen chloride in anhydrous methanol and again concentrated under reduced pressure to a sirup. The sirup was extracted with 30 ml. of absolute ethanol, filtered and again concentrated to a sirup under reduced pressure. This sirup was dissolved in 4 ml. of water and the solution brought to *ca.* *p*H 7 with solid potassium bicarbonate. Glacial acetic acid (4 ml.) was added and the solution was maintained at 15° overnight. Crystals formed which were removed by filtration and were recrystallized by dissolving in aqueous potassium bicarbonate and adding an equal volume of glacial acetic acid; yield 50 mg., $[\alpha]^{24}D$ +10° (*c* 1.8 as the dipotassium salt). The rotation was assayed by solution in water containing an equivalent (to phenolphthalein) quantity of potassium bicarbonate and was in agreement with the previously recorded[4] value (+10°). X-Ray powder diffraction data were in exact agreement with those produced by an authentic specimen of potassium acid D-glucarate (D-glucosaccharate): 4.439 (1), 3.934 (3), 3.302 (5), 2.771 (2), 2.392 (4).[7]

On repeating the above procedure with omission of the bromine oxidant, no potassium acid D-glucarate was isolable.

(7) Interplanar spacing in Å. of the five most intense lines; estimated visually; 1 = strongest; λ = 1.5418 Å.

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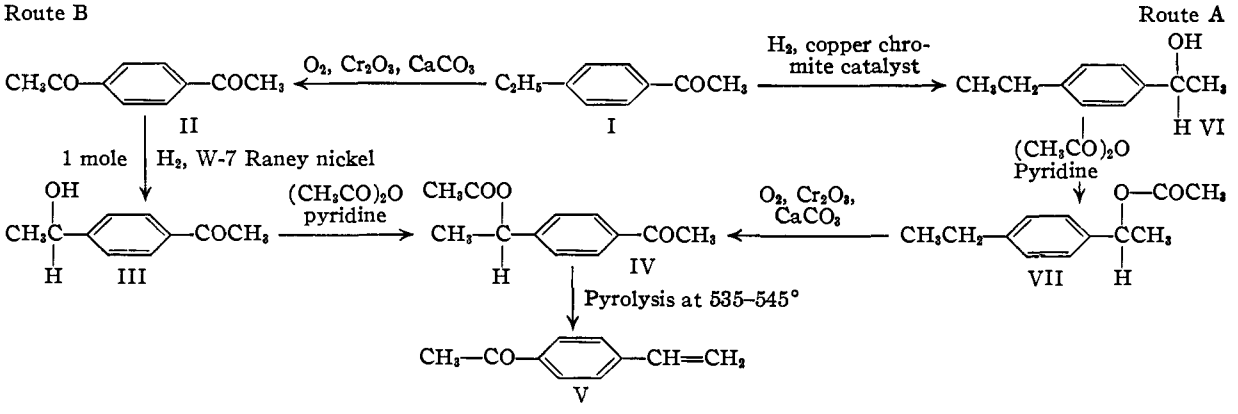
## *p*-Vinylacetophenone: The Disproportionation of *p*-Acetophenylmethylcarbinol[1]

BY J. L. R. WILLIAMS

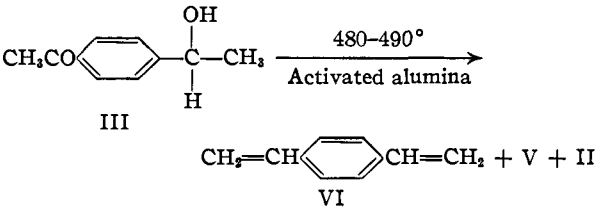
RECEIVED JANUARY 29, 1953

Two routes for the preparation of *p*-vinylacetophenone from *p*-ethylacetophenone which have been found are shown below.

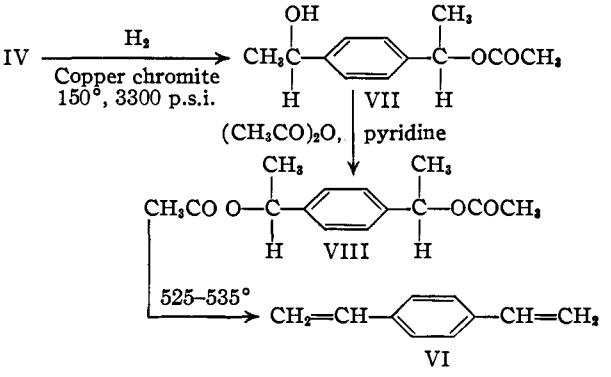



In route A, *p*-ethylacetophenone (I) was hydrogenated to *p*-ethylphenylmethylcarbinol (VI) which was acetylated and oxidized to *p*-acetophenylmethylcarbinol acetate (IV). By route B, *p*-ethylacetophenone was oxidized to *p*-diacetylbenzene (II) which was hydrogenated over W-7 Raney nickel to *p*-acetophenylmethylcarbinol (III) and then converted by acetylation to *p*-acetophenylmethylcarbinol acetate (IV). *p*-Acetophenylmethylcarbinol acetate from both routes was pyrolyzed at 530–545° over glass beads to yield *p*-vinylacetophenone (V).

*p*-Acetophenylmethylcarbinol (III) was alternately prepared by de-esterification of *p*-acetophenylmethylcarbinol acetate (IV) using sodium methoxide and methanol. Vapor-phase dehydration of *p*-acetophenylmethylcarbinol over activated alumina yielded not only *p*-vinylacetophenone but also *p*-diacetylbenzene (II) and *p*-divinylbenzene (VI) by disproportionation.




*p*-Divinylbenzene was also prepared from *p*-acetophenylmethylcarbinol acetate by the following scheme




### Experimental

***p*-Ethylphenylmethylcarbinol Acetate (VII), Route A.**—A mixture of 250 g. (1.69 moles) of *p*-ethylacetophenone and 25 g. of copper chromite catalyst (Harshaw Cu-X-649-57-P) was hydrogenated in the usual way at 125° and 4500 p.s.i. until 1.69 moles of hydrogen had been absorbed. The resulting material was heated on the steam-cone for 16 hours with 250 cc. of acetic anhydride and 5 cc. of pyridine. Distillation through a 12-in. Vigreux column yielded 220 g. (66% of theory) of *p*-ethylphenylmethylcarbinol acetate, b.p. 79° (0.9 mm.), $n^{25}D$ 1.4956.

***p*-Acetophenylmethylcarbinol Acetate (IV), Route A.**—In a liquid phase oxidizing apparatus consisting of a large test-tube equipped with a gas disperser, and a water take-off and reflux condenser, there was placed 220 g. (1.15 moles) of *p*-ethylphenylmethylcarbinol acetate, 1 g. of chromium sesquioxide and 15 g. of calcium carbonate. Air was forced through the disperser, and the temperature of the reaction mixture was maintained at 130–140° for 28 hours by means

(1) Communication No. 1535 from the Kodak Research Laboratories.