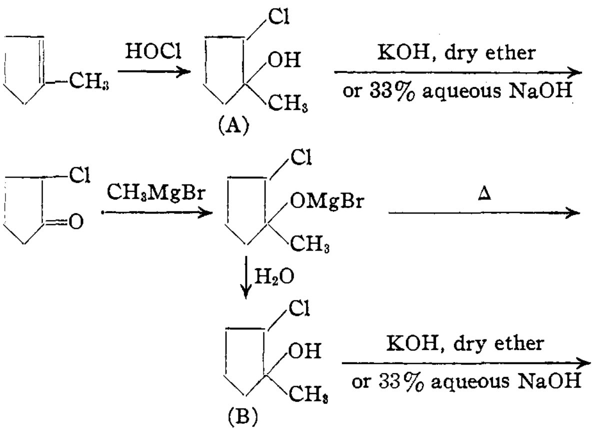
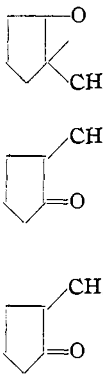
Cis- and *Trans-*Chlorohydrins of Δ^1-Methylcyclopentene

BY PAUL D. BARTLETT AND RALPH V. WHITE

The isomeric chlorohydrins (A) and (B) have been obtained by methods parallel to those used in the cyclohexane series,[1] and are found to react as shown.



The (B) isomer alone is new, (A), m. p. 35–37°, having been studied by Chavanne and de Vogel.[2] In two respects these isomers contrast with the homologous compounds, previously described, containing the six-membered ring. (1) There is only one ketone formed from the B isomer, whatever method of dehydrohalogenation is employed, no ring contraction occurring. (2) These isomers show marked differences in their physical properties, which is not the case with the corresponding 6-ring compounds. If such differences (*e. g.*, in boiling point) are assumed due to some interaction of groups[3] in the *cis* compound which is impossible in the *trans*, then the absence of such effects in the cyclohexanes may be connected with the strainless 6-ring, which enables *trans* groups to approach each other as closely as *cis* groups.



Chavanne and de Vogel[2] obtained, along with our "Isomer A," an oil of b. p. 64–67.5° (10 mm.) which they believed to be an isomeric chlorohydrin. We also obtained a lower-boiling fraction (b. p. 38–43°, 8 mm.); it contained, however, 35.74% of chlorine, and did not react with boiling alcoholic alkali in thirty-five minutes. It was therefore not a chlorohydrin, and we believe that "Isomer A" represents the sole product of addition of hypochlorous acid to Δ^1-methylcyclopentene.

PROPERTIES OF THE ISOMERIC 2-CHLORO-1-METHYLCYCLOPENTANOLS

Isomer	B. p., °C.	d_{24}	n^{24}_D	Cl, % (calcd. 26.37)
A	61–64 (7 mm.)	1.131[a]	1.477[a]	26.28
B	50–57 (8 mm.)	1.059	1.4709	26.55

[a] Supercooled.

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RECEIVED NOVEMBER 2, 1934

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[1] Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[2] Chavanne and de Vogel, *Bull. soc. chim. Belg.*, **37**, 141–152 (1928).

[3] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1927, p. 147.

COMMUNICATIONS TO THE EDITOR

THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF WEAK BASES BY THE SILVER IODIDE ELECTRODE

Sir:

Among electrodes of the second kind, sufficiently insoluble in ammonia and organic bases to be used in the determination of their dissociation constants without liquid junctions, the silver–silver iodide electrode offers interesting possibilities. To avoid technical difficulties associated with the use of dilute hydriodic acid, the normal potential (E^0) may be obtained in alkaline solutions. The method is essentially a comparison of the silver iodide and silver chloride electrodes. Preliminary values of E^0 have been determined in borax buffers by reversing the calculation for the ionization constant of boric acid [Owen, THIS JOURNAL, **56**, 1695 (1934)], and should likewise be obtainable in solutions of a strong base from the ionization constant of water [Harned and Hamer, *ibid.*, **55**, 2194, 4496 (1933)]. Using the cell

$$H_2/NH_4OH(m_1),\ NH_4I(m_2)/AgI,\ Ag$$

in connection with the extrapolation function $\log K - B\mu = (E - E^0)/0.05915 + \log K_{H_2O}$

$+ \log (NH_4^+) (I^-)/(NH_4OH) - 0.5/\sqrt{\mu}$, $K = 1.75 \times 10^{-5}$ was obtained for ammonium hydroxide at 25°. Since this result depends upon a single series of measurements, and a preliminary determination of E^0, it can only be regarded as tentative, but it is sufficiently close to the accepted value, 1.81×10^{-5} ["Int. Crit. Tables," Vol. VI], to demonstrate the potential usefulness of the indirect procedure herein outlined. Further work on this problem is in progress.

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RECEIVED OCTOBER 3, 1934

THE EMISSION OF γ-RAYS IN NUCLEAR REACTIONS

Sir:

It has been shown recently[1] that all known nuclear reactions which result in actual disintegration, and which are induced by a nuclear projectile of ordinary energy (up to 8 to 15 mev) are of the type of a chemical double decomposition or metathesis. Thus: $A + B \longrightarrow AB^* \longrightarrow C^* + D$. Here C is starred to indicate the probability that at least one of the products is activated and shows either γ-ray activity or the emission of an electron or positron, which, since it is commonly delayed, is considered as an artificial radioactivity.

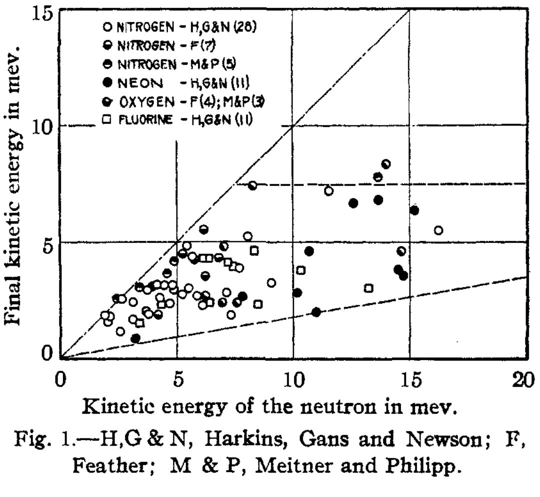

Fig. 1.—H,G & N, Harkins, Gans and Newson; F, Feather; M & P, Meitner and Philipp.

It is now possible to collect complete data where the projectile is a neutron for 71 such reactions, many of which were obtained in this Laboratory, and the others by Feather [*Proc. Roy. Soc.* (London), **A136** (1932); **142,** 689 (1933); *Nature,* **130,** 237 (1932)] and Meitner and Philipp [*Z. Physik,* **87,** 484 (1934); *Naturwissenschaften,* **20,** 929 (1932)]. One such event, obtained by Kurie [*Phys. Rev.,* **43,** 672 and 771 (1933)], was not included since the nature of the reaction involved is supposed by him to be uncertain.

These reveal relations of considerable interest (Fig. 1).

1. Kinetic energy disappears in every reaction, or is rarely conserved.

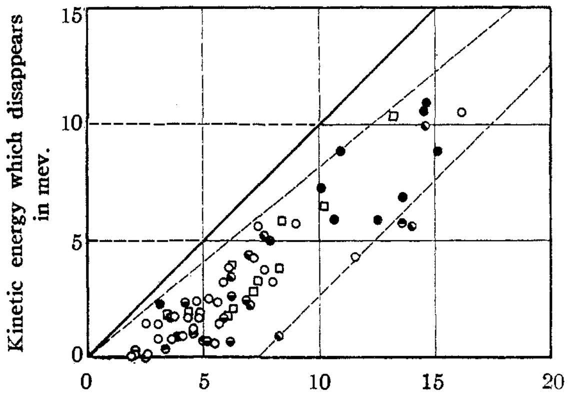

Fig. 2.

2. Though the kinetic energy of the neutron rises as high as 15 mev or slightly more, the maximum kinetic energy retained by the products of the reaction (C and D) is 8.5 mev.

3. The kinetic energy which disappears ($-\Delta KE$) in the reaction rises rapidly with the kinetic energy of the neutron, which is the initial kinetic energy of the system, since the velocity of the atom of A is relatively very small

4. The minimum kinetic energy which remains in the system (ordinates Fig. 1) increases with the kinetic energy of the neutron.

It may be assumed that some or all (depending on the mass change in the reaction) of the kinetic energy decrement is emitted as γ-rays, which are given off either by the atom AB^*, which has an excessively short life, or by the atom C^*. In experiments with fluorine, Harkins, Gans and Newson [*Phys. Rev.,* **44,** 945 (1933)] considered that if C^* is nitrogen 16, a new isotope found by them, it would be likely to be unstable and emit an electron to form oxygen 16. This has been verified by Fermi [Fermi, Amaldi, D'Agostino, Rasetti and Segrè, *Proc. Roy. Soc.* (London), **146,** 483 (1934)], who finds nitrogen 16 to be radioactive.

The ordinate of Fig. 2 ($-\Delta KE$) plus a con-

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(1) Harkins and Gans, *Phys. Rev.*, **46,** 397 (1934).

stant $(-\Delta E_m)$ for the reaction gives the total energy which disappears in the reaction.

If it is assumed that the energy escapes largely as γ-ray energy, then it follows that:

5. The total γ-ray energy emitted increases rapidly as the energy of the projectile, the neutron, increases.

6. A remarkable feature of Fig. 2 is the absence of points in the lower right-hand section. Thus the γ-ray energy is always high if the energy of the neutron is high.

Let it be supposed that the γ-ray levels are discrete. Then since all possible neutron energies are involved, the points for each level in Fig. 2 should lie on or close to a horizontal line. This would give a scattering along the x-axis, while the different levels would give a scattering along the y-axis. While the points in Figs. 1 and 2 have the general type of distribution suggested by this hypothesis, the accuracy of the values is not sufficient to resolve the levels which may exist. It is possible that the type of plot found may, on account of the existence of some unknown relation, be associated with a continuous rather than a line spectrum. On the whole it does not seem improbable that both types of spectra may be represented.

UNIVERSITY OF CHICAGO WILLIAM D. HARKINS
CHICAGO, ILL. DAVID M. GANS

RECEIVED OCTOBER 15, 1934

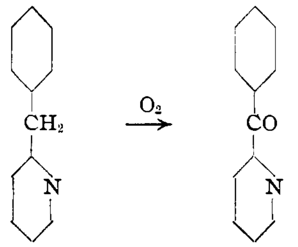
THE PHOTO-OXIDATION OF 2-BENZYLPYRIDINE AND PAPAVERINE

Sir:

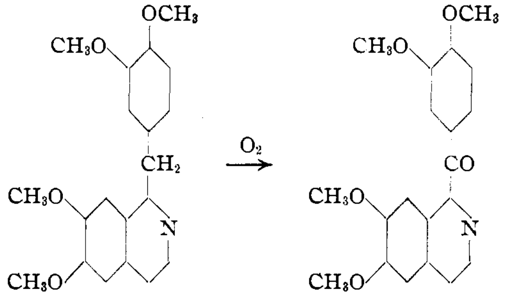
It has been established that the following reactions take place photochemically in air.

The second reaction is of plant physiological interest since these alkaloids occur together in nature.

2-Benzylpyridine in a glass bulb was exposed to a quartz mercury lamp (the liquid becomes brown[1]) and fractionally distilled *in vacuo* whereby a small quantity of the ketone, which is the chief product, was obtained and identified by isolating the semicarbazone and phenylhydrazone. A benzene solution of papaverine[2] in a quartz flask after three days in sunlight (the color becomes brown with the formation of a slight precipitate) yielded approximately 10% papaveraldine which was identified by analysis and mixed melting points with synthetic papaveraldine and by those of the hydrochlorides. In the solid state, papaverine and papaveraldine became brown after several hours in mercury light.



2-Benzylpyridine 2-Benzoylpyridine



Papaverine
(in benzene)

Papaveraldine
(or xanthaline)

Using glass bulbs sealed to mercury manometers, papaveraldine in benzene, 2-benzylpyridine and 2-benzoylpyridine in dry oxygen showed no absorption in the dark at 115°, but at lower temperatures in mercury light a strong absorption occurred and the practically colorless liquids became deep brown as in air. In the dark at 115°, papaverine in benzene absorbed oxygen but in air at 60° (20° higher than reached by the solution exposed in sunlight) no color appeared and evaporation (without crystallization) yielded unchanged papaverine. Similarly it was found that papaverine solutions in glass bulbs sealed off in high vacuum or with water remained unchanged after forty hours in mercury light. However, such bulbs containing papaveraldine solution or 2-benzoylpyridine so exposed soon became brown and later in the case of papaveraldine precipitates resulted. 2-Benzylpyridine in vacuum remained colorless but with water became pale yellow after exposure.

The effect of various spectral lines of the mercury lamp in so far as they produced color was studied. Filter paper strips impregnated with alcoholic solutions were exposed in place of a

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(1) This color change in light was first observed by H. Freytag and A. Müller, *Naturwiss.*, **21**, 720 (1933).

(2) E. Paternò, *Gazz. chim. ital.*, **44**, II, 104 (1914), simply reports that from a solution of papaverine in acetone contained in glass, after seven months in daylight, only the starting materials and traces of reaction products could be obtained. Although not mentioned, undoubtedly little or no air had access.

photographic plate in a quartz spectrograph until the effect became constant. For papaveraldine the lines were yellow-brown and distinct within an hour; 405, 365, 313, 302 and 297 appeared considerably stronger than those shorter (to 238 mμ). For papaverine essentially the same was found but with somewhat weaker intensity and 405 mμ was absent. For 2-benzoylpyridine lines 365 to shorter than 238 mμ appeared dull green, with those from 365 to 297 the strongest. This compound was the most sensitive, all lines appearing in ten minutes, much weaker, however, than on silver chloride print paper. For 2-benzylpyridine 280 to 238 (265 and 254, strongest) appeared within thirty minutes brown in color, and eight hours later, undoubtedly due to the formation of 2-benzoylpyridine, lines to 365 mμ which were dull green. None of these compounds were affected by lines longer than 405 mμ.

Other compounds related to 2-benzylpyridine were also studied which will be described in a forthcoming publication.

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UNIVERSITY OF VIENNA
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ADOLF MÜLLER
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RECEIVED NOVEMBER 5, 1934

ON THE APPLICATION OF THE PRINCIPLE OF OPTICAL SUPERPOSITION IN THE KETOSE SERIES. PREPARATION OF THE TRUE α-PENTAACETYLFRUCTOSE <2,6>

Sir:

In order to test the validity in the ketose series of the principle of optical superposition as applied by Hudson [THIS JOURNAL, **31**, 66 (1909)] in sugar chemistry, it is necessary to know the optical rotations of a true α,β-stereoisomeric pair of any ketose derivative. In the ketose series, contrary to the aldose, no such true α,β-pair has hitherto been known with certainty. It was *assumed* [Hudson, *J. Ind. Eng. Chem.*, **8**, 381 (1916); THIS JOURNAL, **46**, 477 (1924)] that the two known pentaacetates as well as the two chloroacetates of fructose constituted such α,β-pairs. The rotations of the latter were used to calculate the value of the constants A_{Cl} and $B_{\text{fruct. ac.}}$. Since the value of A_{Cl} resulting from this calculation *happened* to agree closely with the value of A_{Cl} for the aldoses, this was regarded as evidence that the substitution of —CH$_2$OAc for —H does not change the rotation of carbon atom 2. Subsequently, the constants for aldoses were used in calculations for the ketose series, but the calculated optical rotations never agreed with those actually observed. Assuming the principle of optical superposition be correct, the reason for this disagreement was obscure. However, it was recently proved [Pacsu and Rich, THIS JOURNAL, **54**, 1697 (1932); **55**, 3018 (1933)] that both "α-pentaacetylfructose" and "α-chloroacetylfructose" are derivatives of the open-chain fructose, and, therefore, all the calculations based on the assumption that the two pentaacetates and the two chloroacetates of fructose constitute α,β-stereoisomeric pairs, are invalid. This correction resulted in the present search for, and discovery of, the true α-pentaacetylfructose.

On replacement of the chlorine atom in β-chloroacetylfructose <2,6> by an acetoxyl radical, partial Walden inversion occurs on the carbon atom 2, if the reaction be carried out in boiling acetic anhydride solution with anhydrous sodium acetate. The mixture of the diastereomerides so formed consists of the well-known β-pentaacetylfructose <2,6> and its α-isomeride. After separation from the β-compound, the α-pentaacetylfructose <2,6> was obtained in pure, crystalline form; m. p. 122–123°; $[\alpha]^{20}_{\mathrm{D}}$ 47.4°, in chloroform. From the molecular rotations of the β-pentaacetate and the new acetate, the values of $A_{\mathrm{Ac}} = 32{,}850$ and $B_{\text{fruct. ac.}} = -14{,}350$ were obtained. Knowing the value of $B_{\text{fruct. ac.}}$, it is now possible to calculate the specific rotations of the α-derivatives. For instance, the calculated specific rotation of tetraacetyl-α-methylfructoside <2,6> is $[\alpha]^{20}_{\mathrm{D}}$ 45.5° in chloroform. Several years ago, Schlubach and Schröter [*Ber.*, **61**, 1216 (1928)] prepared a tetraacetylmethylfructoside with $[\alpha]^{20}_{\mathrm{D}}$ 45° in chloroform, to which they ascribed the α-configuration. The excellent agreement between these two values indicates that Schlubach's compound is really the α-isomeride of the tetraacetyl-β-methylfructoside <2,6>, and at the same time supports the validity of the principle of optical superposition in the ketose series. It is to be expected that several unknown α-derivatives can be prepared from this new fructose pentaacetate.

The details of this investigation will be published within a short time.

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EUGENE PACSU

RECEIVED NOVEMBER 17, 1934

THE TRITYLATION OF SUGAR MERCAPTALS

Sir:

In view of the publication of Micheel and Spruck [*Ber.*, **67,** 1665 (1934)] on the tritylation of galactose ethyl mercaptal, we wish to report the work completed in this Laboratory on the tritylation of a number of sugar mercaptals. The work herein reported was completed before the above article of Micheel and Spruck appeared and was also well under way before the publication of Micheel and Suckfüll [*Ann.*, **502,** 85 (1933)] on the action of mercuric chloride on 6-iodogalactose ethyl mercaptal tetraacetate. All compounds now reported were obtained in crystalline form and were recrystallized to constant melting point and rotation. All rotations are recorded in U. S. P. chloroform. *d*-Glucose ethyl mercaptal was successively treated in pyridine solution with triphenylchloromethane (trityl chloride) and benzoyl chloride to produce (I) 6-tritylglucose ethyl mercaptal tetrabenzoate (m. p. 161–162°; $[\alpha]_D$ +49°). This tritylation procedure was originally applied to carbohydrates by Helferich and co-workers [B. Helferich and J. Becker, *Ann.*, **440,** 1 (1924)]. Similar procedures produced the tetrabenzoate of 6-trityl-*d*-galactose ethyl mercaptal (m. p. 138–139°; $[\alpha]_D$ −22.5°). By substituting acetic anhydride for the benzoyl chloride there was obtained 6-tritylgalactose ethyl mercaptal tetraacetate (m. p. 123–124°; $[\alpha]_D$ −22.5°), trityl-*l*-arabinose ethyl mercaptal triacetate (m. p. 101–102°; $[\alpha]_D$ −24°), and trityl-*d*-xylose ethyl mercaptal triacetate (m. p. 149-150°; $[\alpha]_D$ −20.5°).

Attempts to hydrolyze the trityl group in 6-tritylglucose ethyl mercaptal tetrabenzoate with hydrogen bromide always produced (II) 6-bromoglucose ethyl mercaptal tetrabenzoate (m. p. 169–170°; $[\alpha]_D$ +39°). The position of the bromine atom was proved by the identity of this compound with the product obtained by benzoylation of the 6-bromoglucose ethyl mercaptal of E. Fischer [E. Fischer, B. Helferich and P. Ostmann, *Ber.*, **58,** 873 (1920)]. Iodine replacement of the bromine atom was effected by sodium iodide in acetone [J. C. Irvine and J. W. Oldham, *J. Chem. Soc.*, **127,** 2729 (1925)] to produce (III) 6-iodoglucose ethyl mercaptal tetrabenzoate (m. p. 165–166°; $[\alpha]_D$ +39°) with constants practically identical with those of the 6-bromo compound. The iodine was removed with silver nitrate in dilute acetone and the mercaptal groups with mercuric chloride and cadmium carbonate in moist acetone [M. L. Wolfrom, THIS JOURNAL, **51,** 2188 (1929)]. The product obtained was the glucopyranose tetrabenzoate of E. Fischer [E. Fischer and H. Noth, *Ber.*, **51,** 321 (1918)] and a benzoyl migration had accordingly occurred.

Cautious hydrolysis of 6-tritylgalactose ethyl mercaptal tetraacetate with hydrogen bromide produced 6-hydroxygalactose ethyl mercaptal tetraacetate (m. p. 96–97°; $[\alpha]_D$ −7°). More vigorous hydrolysis produced 6-bromogalactose ethyl mercaptal tetraacetate (m. p. 110–111°). Removal of the mercaptal groups from 6-hydroxygalactose ethyl mercaptal produced the galactose 2,3,4,5-tetraacetate hydrate of Micheel and Suckfüll. When recrystallized from water this substance melts sharply at 168°.

Removal of the mercaptal groups from 6-tritylgalactose ethyl mercaptal tetraacetate produced 6-tritylgalactose tetraacetate, isolated as a compound with one mole of ethanol (m. p. 153°; $[\alpha]_D$ −28°) and also as its semicarbazone ($[\alpha]_D$ +20°).

The above work on the glucose compounds was presented completely on March 30, 1934, at the 44th Meeting of the Ohio Academy of Science at Columbus, Ohio. Compounds I, II and III are recorded in the M.A. thesis of Mr. Clarence C. Christman, The Ohio State University, Dec. 15, 1933. Full details of all this work will be published at a later date.

DEPARTMENT OF CHEMISTRY
OHIO STATE COLLEGE
COLUMBUS, OHIO

M. L. WOLFROM
JOSEPH L. QUINN
CLARENCE C. CHRISTMAN

RECEIVED NOVEMBER 21, 1934

CRYSTALLINE β-GLUCOHEPTOSE AND ITS MUTAROTATION

Sir:

A sirup containing β-glucoheptose was synthesized by E. Fischer [*Ann.*, **270,** 87 (1892)] but he and subsequent workers were unable to obtain the crystalline sugar. The writer has now prepared β-glucoheptose in crystalline form. The mutarotation is very unusual and resembles that of ribose, reported in a previous publication [THIS JOURNAL, **56,** 747 (1934)].

The first crystals separated spontaneously from a product obtained by Fischer's method from β-glucoheptonic γ-lactone by reduction with sodium amalgam. The new sugar crystallizes in slender prisms, melting at 121°, very soluble in water but not deliquescent. After recrystallization from aqueous alcohol and drying over calcium chloride it was analyzed. *Anal.* Calcd. for $C_7H_{14}O_7$: C, 39.98; H, 6.72. Found: C, 40.06; H, 6.62.

MUTAROTATION OF β-GLUCOHEPTOSE AT 20° IN 5% AQUEOUS SOLUTION

$$[\alpha]^{20}_{D} = +11.31 \times 10^{-0.050t} - 11.28 \times 10^{-0.0108t} - 0.13$$

Time, minutes	$[\alpha]^{20}_{D}$ Obs.	k Initial period	$k_1 + k_2$ Final period	$[\alpha]^{20}_{D}$ Calcd. from eq.
0	(−0.1)	...	...	−0.1
1.3	−1.4	...	...	−1.31
3.2	−2.7	0.0496	...	−2.73
5.1	−3.7	.0489	...	−3.78
7.5	−4.7	.0497	...	−4.72
10	−5.2	.0483	...	−5.35
15	−5.8	.0487	...	−5.89
18	−5.93	.0503	...	−5.92
20	−5.9	.0507	...	−5.86
30	−5.2	...	...	−5.12
40	−4.3	...	...	−4.19
50	−3.4	...	0.0106	−3.38
60	−2.7	...	.0105	−2.67
70	−2.1	...	.0108	−2.11
80	−1.6	...	.0113	−1.67
90	−1.3	...	.0110	−1.33
100	−1.1	...	.0106	−1.06
120	−0.7	...	.0108	−0.70
24 hrs.	−0.13	...	...	− .13

The mutarotation cannot be expressed by the usual first order equation but, as may be seen from the calculated values given in the table, it is adequately expressed by an equation containing two exponential terms corresponding to two well-defined reactions. The velocity constants for the initial reaction were calculated by the method of Lowry and Smith [*J. Phys. Chem.*, **33**, 9 (1929)]. The uniform values show that the initial change follows approximately the course of a first order reaction. The constants calculated from forty minutes on are uniform also, which shows that the final change follows the course of a first order reaction. The initial change is approximately five timee as fast as the final and is sufficiently large to permit its study in more detail than is possible with ribose and other known sugars which exhibit this type of mutarotation.

The complex character of the mutarotation reaction is evidence that the original substance on dissolving in water changes into another form or forms which slowly pass, at least in part, into one or more additional substances. The various substances may contain different ring structures or possibly the changes in rotation may be due in part to the presence of endocyclic bridge isomers [Fuson, *Chem. Reviews*, **7**, 347 (1930)] of one ring type. In any case the new crystalline form of β-glucoheptose may contain an open chain, furanose or pyranose structure. Hence the writer refrains from classifying it until its reactions and properties have been studied further.

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.
HORACE S. ISBELL

RECEIVED NOVEMBER 22, 1934

THE REACTION OF ETHYLENE OXIDE WITH ACETYLENIC GRIGNARD REAGENTS

Sir:

In a recent article Faucounau [*Compt. rend.*, **199,** 605 (1934)] describes the preparation of some acetylenic alcohols by the action of ethylene oxide on acetylenic Grignard reagents and the subsequent hydrolysis of the products obtained. During the past year we have been working on the same reaction [Danehy, Master's dissertation University of Notre Dame, 1934] and have prepared 3-nonyn-1-ol and 1-phenyl-1-butyn-4-ol as reported by Faucounau, obtaining yields corresponding with his; we have also prepared 3-octyn-1-ol, b. p. 97° (15 mm.); n^{25}_{D} 1.4542; d^{25}_{4} 0.8765. We also have obtained other products from these reactions in yields at least as large as the yields of the alcohols by extracting the aqueous layer with ether after hydrolysis of the Grignard complex. Faucounau has failed to report these non-alcoholic products. Because of the water solubility, molecular weight and other physical properties of these compounds, it is very likely that the phenyl-substituted product (b. p. (15 mm.) 55°) isolated by us along with the 1-phenyl-1-butyn-4-ol is identical with the 2-phenyl-4,5-dihydrofuran obtained by Faucounau in a series of reactions subsequently carried out with the 1-phenyl-1-butyn-4-ol, and that the amyl and butyl compounds isolated by us are similar in nature. We are investigating the structures of these compounds.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
JAMES P. DANEHY
RICHARD R. VOGT
J. A. NIEUWLAND

RECEIVED NOVEMBER 30, 1934