Very convincing evidence of the identity of calcium altronate from celtrobiose with the calcium altronate from neolactose, as well as for their identity with samples of calcium altronate from *d*-ribose and from the 1,4-lactone of *d*-talomucic acid[19] is given in Table II. Here are recorded the changes in rotation which occur when calcium altronate is dissolved in 1 *N* hydrochloric acid and the liberated altronic acid undergoes lactone formation.

This work has been materially aided by a grant to one of us (N. K. R.) from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Acetochloroceltrobiose has been obtained in 40–45% yield by the action of a mixture of aluminum chloride and phosphorus pentachloride on cellobiose octaacetate in chloroform.

2. Both the α- and the β-octaacetates of celtrobiose have been prepared. A double compound of the two acetates crystallizes with the composition 2α-octaacetate·1β-octaacetate·3-ether.

3. Both the α- and the β-heptaacetates of celtrobiose have been prepared. A third heptaacetate is believed to possess an ortho ester structure.

4. Celtrobiose monohydrate has been obtained in crystalline form. It has $[\alpha]^{20}D + 13.6°$, without mutarotation. Acetylation shows it to be the β-form.

5. Acid hydrolysis of celtrobiose indicates that the component hexoses are *d*-altrose and *d*-glucose. Oxidation to celtrobionic acid, followed by acid hydrolysis, yielded *d*-glucose, and *d*-altronic acid which was identified as calcium *d*-altronate·3.5H_2O. These data lead to the conclusion that celtrobiose is 4-β-*d*-glucosido-*d*-altrose.

(19) Steiger and Reichstein, *Helv. Chim. Acta*, **19**, 195 (1936).

WASHINGTON, D. C. RECEIVED OCTOBER 19, 1936

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Asymmetric Oxidation of Sugars by Optically Active Alkaline Copper Solutions[1]

BY NELSON K. RICHTMYER AND C. S. HUDSON

In a recent paper dealing with neolactose and *d*-altrose[2] we had occasion to compare the reducing powers of the *d*- and *l*-forms of altrose toward the alkaline copper reagent of Shaffer and Hartmann.[3] The *d*-altrose was found to have only about 56% the reducing power of *l*-altrose; similarly, *d*-arabinose was found to have only 76% the reducing power of *l*-arabinose. The suggestion was made that, since the copper carbonate reagent contains an optically active substance, namely, *d*-tartaric acid. the *d*- and *l*-forms of the reducing sugars may behave differently in its presence.

A number of investigators[4] have compared the reducing powers of various sugars as determined by the methods of Hagedorn–Jensen, Folin–Wu, Shaffer–Hartmann, and others, but the behavior of a pair of antipodal sugars toward these reagents, and toward copper reagents containing other than the ordinary *d*-tartaric acid, has not been studied previously. The results of our experiments, in which *d*-glucose, *d*- and *l*-altrose, and *d*- and *l*-arabinose were compared by oxidation with the Hagedorn–Jensen–Hanes ferricyanide reagent, and with four modifications of the Shaffer–Hartmann–Somogyi Reagent 50 with 1 g. of potassium iodide, containing the *d*-, *l*-, racemic, and *meso* tartaric acids, respectively, are shown in Tables I and II.

The first three columns of figures in Table I show clearly that with the ferricyanide reagent, and with the alkaline copper reagents containing *meso* and racemic tartaric acids, the *d*- and *l*-forms of altrose have identical reducing powers, and the same is true of the *d*- and *l*-forms of arabinose, within the limits of experimental error. In the fourth and fifth columns, however, striking differences appear between *d*- and *l*-altrose in their behavior with the alkaline copper solutions containing *d*- and *l*-tartaric acids, respectively. Thus, *d*-altrose (1.2 mg.) requires 5.82 cc. of

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Richtmyer and Hudson, THIS JOURNAL, **57**, 1716 (1935).

(3) Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 377 (1921).

(4) *E. g.*, Bertrand, *Bull. soc. chim.*, **35**, 1285 (1906); Thomas and Dutcher, THIS JOURNAL, **46**, 1662 (1924); Willaman and Davison, *J. Agric. Research*, **28**, 479 (1924); Greenwald, Samet and Gross, *J. Biol. Chem.*, **62**, 397 (1924); Rowe and Wiener, THIS JOURNAL, **47**, 1698 (1925); Pucher and Finch, *Proc. Soc. Exptl. Biol. Med.*, **23**, 468 (1926); Hawkins, *J. Biol. Chem.*, **84**, 79 (1929).

TABLE I

CC. OF 0.005 *N* THIOSULFATE EQUIVALENT TO AMOUNT OF REAGENT CONSUMED IN 15 MINUTES

Sugar 1.20 mg.	Reagent: Ferricyanide	Meso tartaric	Racemic tartaric	*d*-tartaric	*l*-tartaric
d-Glucose	7.12	10.50	10.97	10.94	10.82
d-Altrose	5.67	8.44	7.34	5.82	9.47
l-Altrose	5.63	8.34	7.26	9.41	5.78
d-Arabinose	6.58	8.07	8.42	8.00	9.18
l-Arabinose	6.56	8.03	8.29	9.09	7.89

TABLE II

RELATIVE REDUCING POWERS TOWARD VARIOUS REAGENTS, WITH GLUCOSE AS STANDARD IN EACH CASE

Sugar	Reagent: Ferricyanide	Meso tartaric	Racemic tartaric	*d*-tartaric	*l*-tartaric
d-Glucose	100	100	100	100	100
d-Altrose	79.6	80.4	66.9	53.2	87.5
l-Altrose	79.1	79.4	66.2	86.0	53.4
d-Arabinose	92.4	76.9	76.7	73.1	84.8
l-Arabinose	92.1[a]	76.5	75.6	83.1	72.9

[a] This is in accord with the value of 92 found by Pucher and Finch, ref. 4, and the value of 94 found by the ferricyanide gasometric method of Hawkins, ref. 4.

0.005 *N* thiosulfate, which is a measure of the amount of oxidation brought about by the reagent containing *d*-tartaric acid, whereas the same amount of *l*-altrose requires 9.41 cc. of thiosulfate; the ratio 5.82:9.41 indicates that toward the *d*-tartaric reagent the *d*-altrose has only 61.8% the reducing power of its *l*-isomer. On the other hand, using the copper reagent containing *l*-tartaric acid, the relations are reversed, the *l*-altrose requiring 5.78 cc., and the *d*-altrose 9.47 cc. of thiosulfate; the ratio of these values shows that toward the *l*-tartaric acid reagent the *l*-altrose has only 61.0% the reducing power of its *d*-isomer. It is noted that the figure for the *d*-sugar with the *d*-reagent, 5.82 cc., is identical, within the experimental limits, with the value 5.78 cc. for the *l*-sugar plus the *l*-reagent; likewise, the *d*-sugar with the *l*-reagent, and the *l*-sugar with the *d*-reagent, give practically identical values of 9.47 and 9.41 cc., respectively.

In the case of the arabinoses, the differences in behavior are strictly parallel, although not so marked. Using the *d*-reagent, the ratio 8.00:9.09 gives the *d*-arabinose 88.0% the reducing power of the *l*-arabinose,[5] with the *l*-reagent the situation is reversed, and the ratio 7.89:9.18 shows *l*-arabinose to have 86.0% the reducing power of its *d*-isomer. For both the altroses and the arabinoses, with the reagent containing racemic tartaric acid, the values lie between those found for the *d*-reagent and those for the *l*-reagent.

In the case of *d*-glucose, the values in Table I show no difference, within the experimental limits of accuracy, between its behavior with the copper reagents containing the *d*-, *l*- and racemic tartaric acids. The value obtained with the *meso* tartaric acid is somewhat smaller; this is not unexpected, since *meso* tartaric acid differ from the other tartaric acids in chemical and physical properties, and a reagent containing it might be expected to differ as much as would a reagent containing citric, trihydroxyglutaric, or other hydroxy acid which might be used to prevent precipitation of the copper hydroxide.

Table II shows the relative reducing powers found for the pairs of altroses and arabinoses, compared with glucose as a standard with each of the five oxidizing agents. The relationships are similar to those already discussed, and show, for example, that each of the two altroses has about 80% the reducing power of *d*-glucose toward the ferricyanide reagent and toward the copper reagent containing meso tartaric acid, and about 66.5% of the reducing power of *d*-glucose toward the racemic tartaric acid reagent. However, toward the *d*-tartaric reagent the *d*-altrose has 53% the reducing power and *l*-altrose 86% the reducing power of *d*-glucose, while toward the *l*-tartaric reagent the reverse situation exists, the *d*-altrose having 87% and the *l*-altrose 53% the reducing power of *d*-glucose.

Having accomplished the primary objects of the research, and having a certain amount of copper reagents on hand, we decided to examine the behavior of other available sugars as far as the supply of reagents would permit. These additional results are presented in Table III. In the last three columns are compared the reducing powers of a single sugar against each of the three alkaline copper reagents employed, which is a somewhat different method of interpreting a portion of the data previously discussed.

The most striking examples were found in the cases of *d*- and *l*-altrose and *l*-allose. For example, *d*-altrose reduces the copper reagent containing *l*-tartaric acid 163% as much as it does the reagent containing *d*-tartaric acid; on the other hand, *l*-altrose reduces the *l*-tartaric reagent

(5) The discrepancy between the value 88% and the value 76% previously reported may be due in part to the fact that the samples of arabinose used earlier were not purified by us, and in part to the difference in composition of the alkaline copper reagents as used in the two sets of experiments. The present values are believed to be correct at least to within ±2%.

TABLE III

COMPARISON OF SUGARS

Sugar	Time of heating, min.	Cc. of 0.005 *N* thiosulfate equivalent to amount of reagent consumed by 1.20 mg. of sugar: Reagent *d*-tartaric	Reagent *l*-tartaric	Reagent Racemic	Relative reducing powers of the sugar toward the three copper reagents, with the *d*-tartaric acid reagent as standard: Reagent *d*-tartaric	Reagent *l*-tartaric	Reagent Racemic
d-Glucose	15	10.94	10.82	10.97	100	99	100
d-Mannose	15	8.21	8.69	9.01	100	106	110
d-Mannose	35	10.45	10.62	10.88	100	102	104
d-Galactose	35	9.21	7.64	8.67	100	83	94
d-Altrose	15	5.82	9.47	7.34	100	163	126
d-Altrose	25	5.78	9.50	..	100	164	...
l-Altrose	15	9.41	5.78	7.26	100	61	77
l-Altrose	25	9.41	..	..	100	...	...
l-Allose	35	7.84	4.77	6.37	100	61	81
d-Fructose	15	10.57	10.91	11.23	100	103	106
d-Fructose	35	10.61	10.86	11.29	100	102	106
d-Manno-heptulose	15	7.94	6.99	8.10	100	88	102
d-Manno-heptulose	35	7.94	6.88	8.17	100	87	103
d-Arabinose	15	8.00	9.18	8.42	100	115	105
d-Arabinose	35	8.49	9.83	9.37	100	116	110
l-Arabinose	15	9.09	7.89	8.29	100	87	91
l-Arabinose	35	9.69	8.34	9.50	100	87	99
d-Xylose	35	10.65	10.51	10.76	100	99	101
l-Rhamnose	35	9.07	9.41	9.88	100	104	109
l-Fucose	35	6.86	7.73	7.48	100	113	109
Neolactose	15	5.47	4.95	5.51	100	90	101
Celtrobiose	15	5.86	5.65	6.03	100	96	103
Lactose	15	5.27	4.87	5.25	100	92	100

only 61% as much as it does the *d*-tartaric reagent; yet the fourth column shows that the *d*- and *l*-altrose solutions reduce to the same extent the reagent containing racemic tartaric acid. The *l*-allose also reduces the *l*-tartaric reagent only 61% as much as it does the *d*-reagent.

The arabinose pair of sugars behaves like the altrose pair, although to a lesser extent, the values being 115 and 87%, respectively, for the *d*- and *l*-sugars. *d*-Galactose and *l*-fucose also showed very marked differences in their behavior toward the copper reagents, with values of 83 and 113%, respectively. *l*-Rhamnose, the ketone sugar *d*-mannoheptulose, and the disaccharides lactose, neolactose, and celtrobiose all show differences well outside the limits of error.

The time of heating was varied in several cases, since Shaffer and Somogyi[6] have found that with their Reagent 50, glucose and fructose are oxidized completely in fifteen minutes, while mannose and xylose require thirty-five and thirty minutes, respectively. With the altroses, fructose and mannoheptulose the reaction appeared to be complete within fifteen minutes; with the two arabinoses, and *d*-mannose, a longer period was required, the time of thirty-five minutes being chosen arbitrarily. For the three disaccharides the fifteen-minute period only was tried, while for *d*-xylose, *l*-rhamnose and *l*-fucose a thirty-five minute heating was allowed.

Certain correlations between the configurations of the sugars and the relative reduction of the *d*-, *l*- and racemic reagents may be cited. *d*-Xylose and *d*-glucose, each with the *d*-xylose configuration on the second, third, and fourth carbon atoms, show practically no difference in their behaviors, the ratios being 100:99:101 and 100:99:100, respectively. *d*-Arabinose, *d*-altrose, and *l*-fucose, each with the *d*-arabinose configuration on the second, third and fourth carbon atoms, form a series with the ratios 100:115:105, 100:163:126, and 100:113:109, while *l*-arabinose, *l*-altrose and *d*-galactose, each with the *l*-arabinose configuration, form another series with the ratios 100:87:91, 100:61:77, and 100:83:94, respectively. The other aldoses including lactose, and the two ketoses, are not closely related to themselves or any of the foregoing series, so a further and complete correlation will require more data. All the facts given, however, are in full accord with the recognized theories of stereochemistry.

The above examples of asymmetric oxidation may be considered as belonging to the larger group of phenomena called asymmetric degradations. Pasteur's classical experiment on the preference of *Penicillium glaucum* for the *d*- over the *l*-form of tartaric acid, the selective fermentation of the *d*- but not the *l*-forms of glucose, mannose and fructose, and the peculiarities of other enzymes and micro-organisms in their behavior toward optical antipodes, are well known. A purely chemical asymmetric degradation was first studed by Bredig and his associates.[7] They were able to show that the rates of decomposition of the *d*- and *l*-forms of camphor- and bromocamphor-carboxylic acids were unequally accelerated by the addition of a small amount of optically active base as catalyst; for example, the *l*-camphor carboxylic acid in acetophenone at 75° decomposed about 46% faster than did the *d*-acid

(6) Shaffer and Somogyi, *J. Biol. Chem.*, **100**, 695 (1933).

(7) Bredig and Fajans, *Ber.*, **41**, 752 (1908); Fajans, *Z. physik. Chem.*, **73**, 25 (1910); Creighton, *ibid.*, **81**, 543 (1913); Bredig and Joyner, *Z. Elektrochem.*, **24**, 285 (1918); Pastanogoff, *Z. physik. Chem.*, **112**, 448 (1924). See also Rona and Reuter, *Biochem. Z.*, **249**, 455 (1932).

when quinine was added, while the reverse effect was produced when quinidine was added.

Recently Y. Shibata and his co-workers[8] have described the asymmetric oxidations brought about by the oxidase-like action of ammonochlorodiethylenediamine cobaltic bromide [Co$en_2NH_3Cl]Br_2$. Their experiments have led to the conclusion that the *l*-form of 3,4-dihydroxyphenylalanine is oxidized more rapidly than the *d*-form by the *l*-cobalt complex; and that *d*-catechin is oxidized more rapidly by the *d*-cobalt than by the *l*-cobalt complex.

To return to the data in Table III, we find that in the members of the *d*- and *l*-arabinose series, and also in the case of *l*-allose, the reducing power of each sugar toward the racemic tartaric acid reagent was intermediate between the value found for the *d*-reagent and that found for the *l*-reagent. In other cases, notably those of *d*-fructose, *l*-rhamnose, *d*-mannoheptulose and the three disaccharides, the reducing power was not intermediate in value, but was equal to or even greater than the reducing power toward either the *d*- or the *l*-reagent. The reason for this might be learned if we knew more about the mechanism underlying these sugar oxidations. Nef[9] states that the oxidation of *l*-arabinose by alkaline copper hydroxide solution leads to the formation of carbon dioxide, formic and glycolic acids and the optically active arabonic, ribonic, erythronic, threonic and glyceric acids. Thus are produced a number of other optically active acids which would intensify or mitigate the effects already initiated by the tartaric acids, and the reaction becomes so complex that almost any final result would be conceivable.

Similarly, Shibata reports that the oxidation of *d*-catechin by the *d,l*-cobalt complex takes a course closely resembling that of the system *d*-catechin plus *l*-complex as if there were no *d*-complex salt in the solution. Willstätter, Kuhn and Bamann[10] found that if racemic mandelic ester is subjected to the action of an esterase extracted from liver, the (+)-ester is hydrolyzed more rapidly than the (−)-ester, but the relation is reversed if the two forms are examined separately: here the (−)-ester is hydrolyzed faster. This is explained by assuming that the ratio of reaction velocites with which the *d*- and *l*-forms in the racemate are cleaved is conditioned by (1) the ratio of affinities of the esterase for the *d*- and *l*-forms, and (2) the ratio of the velocities at which the esterase—*d*-ester complex and the esterase—*l*-ester complex are hydrolyzed.

It is possible that the asymmetric oxidation of sugars by alkaline copper solutions containing optically active tartrates, or even by alkaline ferricyanide reagents to which tartrates have been added, may become a practical method for identifying sugars, especially in working with very small amounts and before isolation of the crystalline material. The behavior of a *d*-galactose solution toward the *d*- and *l*-reagents would clearly distinguish it from solutions containing *d*-glucose, *d*-mannose, *d*-fructose, *d*-xylose, *l*-rhamnose and *d*-arabinose, although *l*-arabinose would remain a possibility. Because of the difficulties involved in preparing *l*-tartaric acid from the common *d*-acid, it might be advantageous to use other antipodal acids, such as the *d*- and *l*-araboglutaric acids which may be prepared by oxidation of the now readily procurable *d*- and *l*-arabinoses. The use of *d*- and *l*-alanine might also be suggested, since Benedict[11] has substituted alanine for tartaric acid, in part at least, in his sugar reagent.

Experimental

Tartaric Acids.—The **racemic** and **meso tartaric acids** were Eastman Kodak Co. products; the former had no detectable optical activity, while the latter appeared to have the very slight specific rotation of +0.07°. The ***d*-tartaric acid** was a commercial brand, thrice recrystallized from water, having $[\alpha]^{20}D$ +13.5° in water (*c*, 10.1). The ***l*-tartaric acid** was obtained by resolving racemic tartaric acid with cinchonine according to Marckwald.[12] The recrystallized cinchonine *l*-acid tartrate monohydrate was decomposed with excess ammonia and the cinchonine removed by filtration. The filtrate was made barely acid with acetic acid, and lead acetate solution added until no further precipitation occurred. Upon standing overnight the amorphous lead tartrate changed to fine needles which were filtered, washed, suspended in water and the lead removed by hydrogen sulfide precipitation. The clear solution was evaporated *in vacuo* to a small volume and the *l*-tartaric acid allowed to crystallize slowly in a desiccator. After several recrystallizations from water it showed $[\alpha]^{20}D$ −13.5° in water (*c*, 10.3).

Sugars.—The *l*-altrose and *l*-allose were samples kindly supplied by the late Dr. W. C. Austin.[13] The *d*-altrose and the disaccharides neolactose and celtrobiose have been

(8) Shibata and Tsuchida, *Bull. Chem. Soc. Japan*, **4**, 142 (1929); Shibata, Tanaka and Goda, *ibid.*, **6**, 210 (1931); Shibata and Sakai, *J. Chem. Soc. Japan*, **55**, 841 (1934), in C. A. **30**, 6354 (1936).

(9) Nef, *Ann.*, **357**, 251 (1907).

(10) Willstätter, Kuhn and Bamann, *Ber.*, **61**, 886 (1928). *Cf.* Rona and Ammon, *Biochem. Z.*, **181**, 49 (1927).

(11) Benedict, *J. Biol. Chem.*, **92**, 141 (1931).

(12) Marckwald, *Ber.*, **29**, 42 (1896); *cf.* Bremer, *ibid.*, **13**, 351 (1880); Pasteur, *Ann. chim.*, [3] **38**, 437 (1853).

(13) Austin and Humoller, THIS JOURNAL, **56**, 1153 (1934).

described by the present authors.[14] The *d*-arabinose, prepared in this Laboratory by the method of Hockett and Hudson,[15] showed $[\alpha]^{20}D$ −103.4°; the *l*-arabinose, from the Difco Laboratories in Detroit, after one recrystallization, rotated +104.2° in water (*c*, 6). The other sugars were either high grade commercial products or prepared by other workers in this Laboratory. All sugar solutions were made up to contain 1.20 mg. of anhydrous substance in each 5 cc. of solution.

The Alkaline Ferricyanide Reagent.—The procedure of Hagedorn and Jensen[16] as modified by Hanes[17] was used, except that the oxidizing solution contained 6.60 g. instead of 8.25 g. of potassium ferricyanide per liter; thus 5 cc. of this solution was equivalent to 5 cc. of the alkaline copper solutions, each requiring about 20 cc. of the same 0.005 *N* thiosulfate solution in the blank determinations.

The Alkaline Copper Reagents.—According to the latest procedure of Shaffer and Somogyi,[6] four solutions were prepared, the only variation being in the use of an equivalent amount of the sodium tartrates instead of the sodium potassium tartrate (Rochelle salt) recommended. Thus, 3.32 g. of *d*-tartaric acid (or 3.32 g. of the *l*-acid, or 3.72 g. of the *meso* or racemic acid monohydrates) was dissolved in 50 cc. of water, and neutralized with *N* sodium hydroxide, with phenol red as indicator. Then were added in succession 6.25 g. of anhydrous sodium carbonate, 1.875 g. of copper sulfate pentahydrate in 20 cc. of water, 5.00 g. of sodium bicarbonate, 0.25 g. of potassium iodide and 50 cc. of standard potassium iodate solution, 0.1 *N* as to iodine. The mixture was diluted exactly to 250 cc., and allowed to stand for several days before filtering through washed and dried filter paper into a Pyrex flask. This reagent should be the exact equivalent of the "Shaffer–Somogyi Copper Iodometric Reagent 50 with 1 g. KI;" 5 cc. of it required about 20 cc. of 0.005 *N* thiosulfate in a blank determination. The preparation and standardization of the solutions, and the oxidations of the sugars, were carried out as directed, observing all the precautions noted by the original writers. The solutions were kept, and the titrations performed, in a room equipped with a white light and kept constant at 20°.

(14) Richtmyer and Hudson, ref. 2, and THIS JOURNAL, **58**, 2534 (1936).

(15) Hockett and Hudson, *ibid.*, **56**, 1632 (1934).

(16) Hagedorn and Jensen, *Biochem. Z.*, **135**, 46 (1923).

(17) Hanes, *Biochem. J.*, **23**, 99 (1929).

Summary

1. A study of the oxidation of the *d*- and *l*-forms of altrose and of arabinose by an alkaline ferricyanide reagent and by four modifications of an alkaline copper reagent containing the *d*-, *l*-, racemic and *meso* forms of tartaric acid, respectively, has been made.

2. The reagents which are optically inactive show no difference in their relative oxidizing power on the *d*- and *l*-forms of the sugars.

3. The reagents which are optically active oxidize the *d*- and *l*-forms of the sugars asymmetrically. Striking relationships have been noted in the four systems composed of the *d*- and *l*-sugars with the *d*- and *l*-reagents. The results are in full accord with the classical theories of stereochemistry.

4. The behavior of twelve other sugars toward the *d*-, *l*- and racemic copper reagents has been studied.

5. The practical adaptation of this asymmetric oxidation for the identification of sugars has been suggested.

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

On the Formation and Reactions of the Substituted Thiazolidones. IV

BY FLOYD A. EBERLY AND F. B. DAINS

Previous papers from this Laboratory[1] have shown that the alkylation of the 2-arylthiazolidones gave both the 2-aryl-2-alkyl and the 2-aryl-3-alkyl derivatives. This paper is a study of the influence of allyl groups, of acyl groups and of phenyl and diphenylchloroacetyl chlorides in the formation and properties of such thiazolidones. Thus from mono-allylthiourea was obtained the 3-allyliminothiazolidone (the unstable form of Wheeler and Johnson) which did not rearrange; while allylphenylthiourea formed a thiazolidone in which the allyl group assumed position 2 with the phenyl at 3. Allyl iodide and the sodium salt of monophenyl thiazolidone gave the two remaining isomers of phenylallylthiazolidone.

The symmetrical benzoyl and carbethoxyphenylthiourea yielded thiazolidones with the acyl radical at 2. Dixon had erroneously assigned the reverse formula to his carbethoxyphenylthiazolidone.

Our work also indicated that the stable form of phenyl-5-phenylthiazolidone is the 2-phenyl isomer and not the 3-phenyl as was suggested by Wheeler and Johnson since it gave alkylation

(1) Eberly and Dains, THIS JOURNAL, **55**, 3859 (1933); Davis and Dains, *ibid.*, **57**, 2627 (1935); Long and Dains, *C. A.*, **28**, 2356 (1934); *Kan. Acad. Sci.*, **16**, 119 (1933).