methanol was allowed to stand at room temperature for 48 hours with frequent shaking. The clear solution was then decanted, and the solid residue was extracted with chloroform in a Soxhlet extractor for 4 hours. Evaporation of the methanol solution gave solid material which was similarly extracted with chloroform. The chloroform extracts were finally combined and concentrated yielding 32.5 g. of **N,N-dimethylcycloheptylmethylamine methiodide**, which was purified by recrystallization from ethyl acetate containing 3% of ethanol. The product separated as large colorless prisms, m.p. 235.7° dec. (literature[39] value 223°).

A solution of 30.2 g. of the quaternary iodide in 150 ml. of water was treated with a slight excess of freshly prepared silver oxide, and the mixture was stirred rapidly for 30 min. and filtered. The residue was washed with water, and the filtrate and washings were then concentrated to small volume under reduced pressure and finally heated to 160–180°. The distillate was collected and washed with 5 portions of water to remove trimethylamine, and, after drying, was refluxed for 3 hours with sodium. Distillation afforded 5.6 g. of methylenecycloheptane, b.p. 130–135°, which was purified by redistillation through a 120-plate concentric tube column, b.p. 135°, n^{25}_{D} 1.4600.

Preparation of 1-Methylcycloheptene.—1-Methylcycloheptanol, prepared from cycloheptanone and methylmagnesium iodide, was dehydrated by distillation in the presence of a small amount of iodine. The olefin in the distillate was separated and, after washing with water and drying over anhydrous sodium sulfate, was distilled through a 75-plate center-rod column. 1-Methylcycloheptene, b.p. 136°, n^{25}_{D} 1.4563 (literature[44] values b.p. 137.5–138.5°, $n^{19.5}_{\mathrm{D}}$ 1.4581) was obtained by this procedure.

Preparation of Ethylidenecyclopentane.—Ethylidenecyclopentane, b.p. 110–111°, was prepared by the procedure of Wallach and von Martius.[17a] Vapor phase chromatography of the product indicated contamination by 1-ethylcyclopentene, and the specimen that was employed for the hydrogenation work was purified chromatographically.

Preparation of 1-Ethylcyclopentene.—1-Ethylcyclopentanol (31 g.), prepared by the action of ethylmagnesium bromide on cyclopentanone, and 0.6 g. of iodine were heated in a distillation flask at atmospheric pressure. The olefin fraction that distilled was washed with water, dried over anhydrous magnesium sulfate and fractionated. The crude product (12 g.) was redistilled through a 75-plate center-rod column and furnished 9 g. of 1-ethylcyclopentene, b.p. 106.2–106.9° (literature value[17d] 107.3°). The product gave a single peak on vapor phase chromatography.

Preparation of Ethylidenecyclohexane.—Ethylidenecyclohexane was prepared as described by Wallach and his associates.[5b] Distillation of the product through a Podbielniak column furnished material boiling at 134.5°, n^{27}_{D} 1.4656 (literature[17d] values b.p. 136.8°, n^{20}_{D} 1.4623). The infrared spectrum of the product revealed no detectable amounts of 1-ethylcyclohexene.

Preparation of 1-Ethylcyclohexene.—1-Ethylcyclohexene was obtained by the iodine-catalyzed dehydration of 1-ethylcyclohexanol according to the method of Mosher.[40] Fractionation of the crude product in a 75-plate center-rod column gave material boiling at 136.2° (literature value[45] 135.7–136.6°).

Isomerization Experiments.—Samples (0.5 ml.) of methylenecyclopentane, methylenecyclohexane, ethylidenecyclopentane and ethylidenecyclohexane were dissolved in 1.0-ml. portions of glacial acetic acid containing catalytic amounts of *p*-toluenesulfonic acid. The mixtures were sealed under vacuum in bent tubes arranged in such a manner that total reflux could be obtained during the reaction period. The solutions were then heated to 100° for 6 hours, at the end of which time the tubes were tilted, and the contents were distilled into the second limb which was cooled in liquid nitrogen. In the cases of methylenecyclohexane and ethylidenecyclopentane the distillate was analyzed directly by vapor phase chromatography. Since methylenecyclopentane and and 1-methylcyclopentene, as well as ethylidenecyclohexane and 1-ethylcyclohexene, were not separable under the chromatographic conditions employed, the products obtained in these experiments were separated from the acetic acid by water dilution, and, after thorough washing with water and drying, were analyzed in the infrared.

---

(44) O. Wallach and H. Kohler, *Ann.*, **345**, 139 (1906).

(45) F. K. Signaigo and P. L. Cramer, THIS JOURNAL, **55**, 3326 (1933).

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Heats of Hydrogenation. VI. Heats of Hydrogenation of Some Substituted Ethylenes[1]

BY RICHARD B. TURNER, DONALD E. NETTLETON, JR., AND M. PERELMAN

RECEIVED MAY 14, 1957

The heats of hydrogenation of several substituted ethylenes have been measured in acetic acid solution at 25°. The compounds included in this investigation and the ΔH values (kcal./mole) obtained are as follows: 2,4-dimethyl-1-pentene (−26.7), 2,4-dimethyl-2-pentene (−25.2); 2,4,4-trimethyl-1-pentene (−25.5), 2,4,4-trimethyl-2-pentene (−26.8); 4-methyl-*cis*-2-pentene (−27.3), 4-methyl-*trans*-2-pentene (−26.4); 4,4-dimethyl-*cis*-2-pentene (−30.8), 4,4-dimethyl-*trans*-2-pentene (−26.5); 2,2,5,5-tetramethyl-*cis*-3-hexene (−36.2), 2,2,5,5-tetramethyl-*trans*-3-hexene (−26.9).

The nature of the directive forces responsible for elimination in the senses of the Hofmann and Saytzeff rules has long been a matter of concern to organic chemists. In recent years considerable attention has been devoted to Hofmann-type eliminations that occur under certain circumstances in alkyl halides and in related compounds that customarily undergo elimination with Saytzeff orientation.[2] In particular, the observation that solvolysis of 2-halo-2,4,4-trimethylpentanes (I) furnishes olefin mixtures in which 2,4,4-trimethyl-1-pentene (II) largely predominates over the isomeric 2,4,4-trimethyl-2-pentene (III) has been extensively discussed.[3,4] This result is contradictory to normal expectations based upon the Saytzeff rule, and to the fact that under similar conditions 2-bromo-2,4-dimethylpentane yields larger amounts of 2,4-dimethyl-2-pentene (IV) than of 2,4-dimethyl-1-pentene (V).[5]

First order eliminations (E1) in I have been carried out under a wide variety of conditions, and a decision as to whether the ratio of olefinic products

---

(1) This work was supported by a grant from the National Science Foundation.

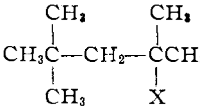
(2) For leading references see H. C. Brown and I. Moritani, THIS JOURNAL, **78**, 2203 (1956).

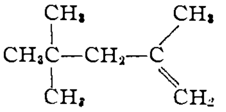
(3) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953); H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955).

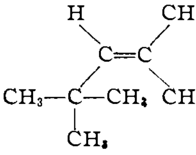
(4) E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.*, 3827 (1953).

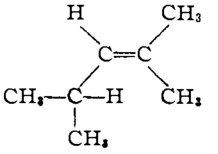
(5) H. C. Brown and M. Nakagawa, THIS JOURNAL, **77**, 3610 (1955).

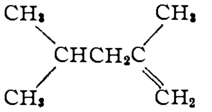
is subject to equilibrium or to kinetic control cannot always be made. However, the greater stability of II as compared with III has been clearly established by equilibrium studies, and an equilibrium constant of about 5.7 in favor of the Δ^1-isomer has been obtained in 80% ethanol at 25°.[4] To the extent that the transition states for the elimination steps possess olefinic character, the factors governing stability in the unsaturated compounds should be operative in the transition states as well.[6]


I


II


III


IV


V

In seeking an explanation for the failure of the 2-halo-2,4,4-trimethylpentane eliminations to show adherence to the Saytzeff rule, Hughes, Ingold and Shiner[4] noted that, although only five hydrogen atoms are available for hyperconjugation in II as compared with six in III, forms of type VI may make an important contribution toward stabilizing the Δ^1-product (II). Brown and his associates,[3,5,7] on the other hand, have emphasized the fact that the stability of III is adversely affected by the conflicting steric requirements of the adjacent *cis*-methyl and *t*-butyl groups, and that predominance of steric over hyperconjugative effects in this olefin provides a reasonable basis for interpretation of the 2,4,4-trimethyl-1-pentene – 2,4,4-trimethyl-2-pentene stability relationship. The present investigation was undertaken in the hope that evaluation of the magnitudes of steric interactions in systems of this type by the hydrogenation method might shed some light on this problem. The results of the hydrogenation work are listed in Table I.

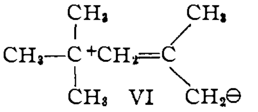

VI

TABLE I

HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION

Compound	Mmoles	PtO_2, mg.	$-\Delta H$, kcal./mole, 25°
2,4-Dimethyl-1-pentene	3.596	100.50	26.67
	3.444	100.00	26.66
Average, $-\Delta H$ = 26.67 ± 0.04[a]			
2,4-Dimethyl-2-pentene	3.455	100.30	25.02
	3.780	100.44	25.27
Average, $-\Delta H$ = 25.15 ± 0.13			
2,4,4-Trimethyl-1-pentene	3.380	100.16	25.61
	3.568	100.50	25.42
Average, $-\Delta H$ = 25.52 ± 0.10			
2,4,4-Trimethyl-2-pentene	3.320	99.77	26.96
	3.671	100.56	26.62
Average, $-\Delta H$ = 26.79 ± 0.17			
4-Methyl-*cis*-2-pentene	4.122	100.12	27.38
	3.354	99.75	27.26
Average, $-\Delta H$ = 27.32 ± 0.07			
4-Methyl-*trans*-2-pentene	4.089	99.96	26.35
	4.304	100.34	26.41
Average, $-\Delta H$ = 26.38 ± 0.04			
4,4-Dimethyl-*cis*-2-pentene	3.085	100.36	30.86
	3.066	99.70	30.74
Average, $-\Delta H$ = 30.80 ± 0.07			
4,4-Dimethyl-*trans*-2-pentene	3.570	100.02	26.34
	3.827	99.64	26.67
Average, $-\Delta H$ = 26.51 ± 0.16			
2,2,5,5-Tetramethyl-*cis*-3-hexene	1.770	98.58	36.41
	1.801	99.10	36.06
Average, $-\Delta H$ = 36.24 ± 0.18			
2,2,5,5-Tetramethyl-*trans*-3-hexene	2.404	99.58	26.86
	2.617	99.37	26.87
Average, $-\Delta H$ = 26.87 ± 0.05			

[a] Deviations include uncertainty in the heat of hydrogenation of the catalyst.

The heats of hydrogenation of 2,4,4-trimethyl-1-pentene and of 2,4,4-trimethyl-2-pentene were measured in the gas phase (82°) by Kistiakowsky and his collaborators[8] in 1937. The values obtained for these substances (−27.2 and −28.4 kcal./mole, respectively), while consistent with the more recently obtained equilibrium data, were at the time unexpected. Thus, although the heat of hydrogenation of 2,4,4-trimethyl-1-pentene seemed reasonable in comparison with results for other unsymmetrically disubstituted ethylenes, the value for 2,4,4-trimethyl-2-pentene appeared to be inordinately high. In considering possible causes for this discrepancy, the question of purity was carefully examined, and the presence of 2% contamination in the latter olefin was demonstrated by freezing point determinations.[9] Although it is unlikely that this amount of impurity could seriously affect the hydrogenation results, a redetermination of the heats of hydrogenation of the diisobutylenes II and III seemed desirable. The values obtained for purified specimens of 2,4,4-trimethyl-1-pentene (−25.5 kcal./mole) and of 2,4,4-trimethyl-2-pentene (−26.8 kcal./mole)[10] are completely consistent with the Kistiakowsky results if allowance

---

(6) Of interest in this connection is the observation of H. C. Brown, I. Moritani and Y. Okamoto, THIS JOURNAL, **78**, 2193 (1956), that E2 elimination in 2-bromo-2,4,4-trimethylpentane yields II in considerable excess of its equilibrium concentration.

(7) H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

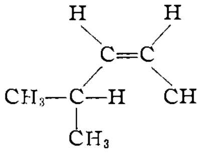
(8) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *ibid.*, **59**, 831 (1937).

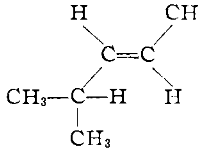
(9) G. S. Parks, S. S. Todd and C. H. Shomate, *ibid.*, **58**, 2505 (1936).

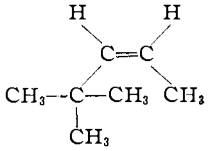
(10) The samples were obtained from the American Petroleum Institute and contained, respectively, 0.09 ± 0.03 and 0.08 ± 0.05 mole % impurity (see Experimental section).

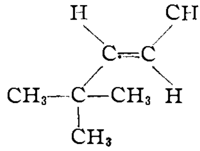
is made for the differences between solution and gas phase data,[11] the heat of isomerization of the Δ^2- into the Δ^1-olefin in acetic acid solution being −1.3 kcal./mole as compared with the gas phase value of −1.2 kcal./mole. Since the free energy difference calculated from the equilibrium constant of 5.7 is approximately −1.0 kcal./mole, the entropy change in passing from the Δ^2- to the Δ^1-compound would appear to be negligible. The heats of hydrogenation of 2,4-dimethyl-1-pentene (V) and of 2,4-dimethyl-2-pentene (IV) have also been measured and are found to be −26.7 and −25.2 kcal./mole, respectively. Substitution of hydrogen for methyl in the *t*-butyl branch of diisobutylene therefore leads to an inversion of the $\Delta^1 - \Delta^2$ enthalpy difference which is in accord with predictions based upon the elimination evidence.[5] In this connection it has been noted that rotation of the isopropyl group in IV permits a conformation in which repulsive interactions between the isopropyl and methyl groups are minimized. With respect to *cis* interference, the effective bulk of the isopropyl group in such an arrangement cannot be much greater than that of methyl, since the enthalpy difference between IV and V (1.5 kcal./mole) is essentially the same as that reported for trimethylethylene and *asym*-methylethylethylene (1.6 kcal./mole).[12] In these cases the greater degree of substitution of the Δ^2- as compared with the Δ^1-isomer appears to be the governing factor.

For the purpose of evaluating the magnitudes of steric effects involved in compounds of this series, the heats of hydrogenation of 4-methyl-*cis*-2-pentene (VII) (−27.3 kcal./mole), 4-methyl-*trans*-2-pentene (VIII) (−26.4 kcal./mole), 4,4-dimethyl-*cis*-2-pentene (IX) (−30.8 kcal./mole) and of 4,4-dimethyl-*trans*-2-pentene (X) (−26.5 kcal./mole) have been determined. In each pair of *cis–trans* isomers, hyperconjugative and inductive effects[13] should be nearly constant. The enthalpy difference between the *cis* and *trans* forms therefore provides a measure of the difference in the steric strains associated with these molecules, which to a first approximation reflects the *cis* R → CH_3 interaction.


VII

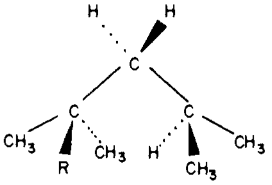

VIII

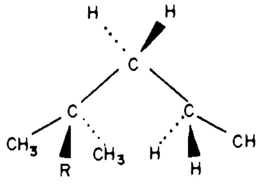

IX


X

The difference between the heats of hydrogenation of 4-methyl-*cis*-2-pentene (VII) and 4-methyl-*trans*-2-pentene (VIII) is 0.9 kcal./mole. The fact that this value is essentially identical with that recorded for the *cis*- and *trans*-butenes by Kistiakowsky and his associates (1.0 kcal./mole)[14] lends further support to the idea that in compounds of this type the preferred conformations are those in which the isopropyl group is sterically equivalent to methyl. For reasons of symmetry such equivalence is not possible in the case of the *t*-butyl group, and the enthalpy difference between 4,4-dimethyl-*cis*-2-pentene (IX) and 4,4-dimethyl-*trans*-2-pentene (X) is accordingly raised to 4.3 kcal./mole.[15] The strain involved in the opposition of methyl and *t*-butyl groups would therefore appear to be of a magnitude sufficient to account for the relative stability of 2,4,4-trimethyl-1-pentene (II) and 2,4,4-trimethyl-2-pentene (III) without recourse to the arguments of Hughes, Ingold and Shiner.[4]

Although the possibility that hyperconjugation of the type indicated in VI may play some part in stabilizing 2,4,4-trimethyl-1-pentene (II) cannot be summarily dismissed, a clear demonstration of such participation is lacking. The fact that the heat of hydrogenation of 2,4,4-trimethyl-1-pentene (II) is 1.2 kcal./mole lower than that of 2,4-dimethyl-1-pentene (V), although consistent with the premise that hyperconjugation involving the *t*-butyl group should be more important than that involving the isopropyl group,[4] is not acceptable as evidence on this point, since other interpretations also may be invoked. Thus, an equally plausible explanation can be formulated on the basis of the assumptions that steric strain in 2,4,4-trimethylpentane (XIa) is greater than that in 2,4-dimethylpentane (XIb), and that the strain difference is in all probability larger for the saturated hydrocarbons than for the olefins, in which the number of non-bonded interactions is reduced by the presence of unsaturation.[16]


XIa, R = CH_3
b, R = H


XIIa, R = CH_3
b, R = H

An approximation of the difference between the steric strains associated with the two paraffins XIa and XIb can be obtained in the following manner. The difference in the heats of formation (vapor phase, 25°) of 2,4,4-trimethylpentane (XIa) (−53.57 kcal./mole) and of 2,4-dimethylpentane (XIb) (−48.30 kcal./mole) is 5.3 kcal./mole.[17] The corresponding difference for the reference substances 2,2-dimethylpentane (XIIa) (−49.29 kcal./

---

[11] (a) R. B. Williams, THIS JOURNAL, **64**, 1395 (1942); (b) R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

[12] J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

[13] *Cf.*, R. W. Taft and M. M. Kreevoy, THIS JOURNAL, **79**, 4011 (1957).

[14] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 137 (1936).

[15] This value is comparable with the figure of 5.6 ± 0.8 kcal./mole obtained for the enthalpy difference between *o*-*t*-butyltoluene and the corresponding *m*- and *p*-isomers from combustion data [results of E. J. Prosen quoted by H. C. Brown, *J. Chem. Soc.*, 1248 (1956)].

[16] See the discussion of a related problem in ref. 5.

[17] "Selected Values of Properties of Hydrocarbons," Circular C 461 of the National Bureau of Standards, U. S. Printing Office, Washington, D. C., 1952.

mole) and 2-methylpentane (XIIb) (−41.66 kcal./mole) is 7.6 kcal./mole.[17] The discrepancy of 2.3 kcal. between these two values may be taken as the difference in strain between the compounds XIa and XIb. Unfortunately estimation of a corresponding factor for the olefins II and V is not possible by this method. It will be observed, however, that if the olefin strain difference does not exceed about 1 kcal./mole, the difference of 1.2 kcal./mole in the heats of hydrogenation of these compounds can be accounted for on the basis of steric effects alone.

In connection with this investigation we have also had an opportunity to examine the heats of hydrogenation of the *cis*- and *trans*-di-*t*-butylethylenes (2,2,5,5-tetramethyl-3-hexenes), samples of which were kindly provided by Prof. M. S. Newman. The values obtained for these substances are, respectively, −36.2 and −26.9 kcal./mole. The enthalpy difference of 9.3 kcal./mole in favor of the *trans* isomer is in this case comparable to that found in the *cis*-cyclooctene–*trans*-cyclooctene system (9.2 kcal./mole in favor of the *cis*-modification),[18] but is considerably lower than the value of 25.5 kcal./mole estimated by Brown, Gintis and Domash[19] for the strain energy in *o*-di-*t*-butylbenzene.

The heat of hydrogenation obtained for *cis*-di-*t*-butylethylene (−36.2 kcal./mole) represents the highest value that we have yet encountered. The spread of 15.5 kcal./mole between this figure and the *cis*-cyclodecene result (−20.7 kcal./mole),[18] which amounts to about 75% of the total heat change accompanying reduction of the latter olefin, serves to emphasize in a striking manner the important influence that steric phenomena may exert on thermochemical properties.

Experimental

The heats of hydrogenation reported in this paper were obtained in acetic acid solution (25°) by the previously described procedure.[11b]

Materials.—Samples of 2,2,5,5-tetramethyl-*cis*-3-hexene (*cis*-di-*t*-butylethylene) and of 2,2,5,5-tetramethyl-*trans*-3-hexene (*trans*-di-*t*-butylethylene) were prepared by Dr. W. H. Puterbaugh at Ohio State University. The *cis* isomer was obtained by partial hydrogenation of the corresponding acetylene and was purified by successive fractional distillation; b.p. 143°, n^{20}_{D} 1.4269 (literature values[20] b.p. 144.2–144.4°, n^{20}_{D} 1.4271). Hydrogenation of this sample proceeded with the absorption of only 95% of the theoretical amount of hydrogen and gave a ΔH value of −35.53 ± 0.06 kcal./mole (based on hydrogen uptake). It was subsequently determined by vapor phase chromatography that the material contained about 5% of a compound with the same retention time as 2,2,5,5-tetramethylhexane as well as a second minor impurity. Through the courtesy of Drs. Newman and Puterbaugh of Ohio State and Drs. Doering and Saunders at Yale a second sample was purified by vapor chromatography. The latter material showed a single chromatographic peak and was flask distilled immediately before use; n^{20}_{D} 1.4264. The hydrogenation values reported in Table I were obtained with this specimen. The *trans* compound was prepared by pyrolysis of 2,2,5,5-tetramethyl-3-hexyl acetate, and after repeated fractionation furnished a sample boiling at 125.1°, n^{20}_{D} 1.4117, f.p. −4.8° (literature values[21] b.p. 125.01°, n^{20}_{D} 1.4115, f.p. −4.75°).

The remainder of the substances employed in this investigation were American Petroleum Institute Standard Samples. The compounds together with the A.P.I. sample numbers and impurity indexes are listed in Table II.

TABLE II

AMERICAN PETROLEUM INSTITUTE SAMPLES

Pentene	Sample	Impurity, mole %
2,4-Dimethyl-1-	1044-5S	0.13 ± 0.09
2,4-Dimethyl-2-	1027-5S	.14 ± .04
2,4,4-Trimethyl-1-	545-5S	.09 ± .03
2,4,4-Trimethyl-2-	546-5S	.08 ± .05
4-Methyl-*cis*-2-	537-5S	.08 ± .07
4-Methyl-*trans*-2-	536-5S	.25 ± .07
4,4-Dimethyl-*cis*-2-	582-5S	.21 ± .11
4,4-Dimethyl-*trans*-2-	574-5S	.09 ± .03

The homogeneity of these samples was further checked by vapor phase chromatography.

HOUSTON, TEXAS

---

[18] R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

[19] H. C. Brown, D. Gintis and L. Domash, *ibid.*, **78**, 5387 (1956).

[20] G. F. Hennion and T. F. Banigan, *ibid.*, **68**, 1202 (1946).

[21] F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz *ibid.*, **68**, 2121 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND NUTRITION, COLLEGE OF AGRICULTURE, UNIVERSITY OF NEBRASKA]

Reversible Transgalactosylation[1]

BY JOHN H. PAZUR, JEAN M. MARSH AND CARL L. TIPTON

RECEIVED SEPTEMBER 5, 1957

Allolactose (6-*O*-β-D-galactopyranosyl-D-glucose) is disproportionated to glucose, galactose and a new trisaccharide by an enzyme preparation from *S. fragilis*. In the disproportionation, galactosyl units of allolactose are transferred by the enzyme to accepting carbohydrate or water molecules. Evidence from isotope experiments indicates that the reactions are reversible.

The enzymatic conversion of disaccharides into new oligosaccharides *via* transglycosylation type reactions has been observed with enzymes from animal and microbial sources.[2,3] In a few instances, reversibility of enzyme action has been demonstrated.[4,5] Reversibility has now been observed for the transgalactosylation reactions catalyzed by a transferring enzyme from *Saccharomyces fragilis*. Because the transgalactosylation

---

[1] Published with the approval of the Director as Paper No. 801, Journal Series, Nebraska Agricultural Experiment Station. Supported in part by a grant from the National Science Foundation.

[2] B. L. Horecker and A. H. Mehler, *Ann. Rev. Biochem.*, **24**, 207 (1955).

[3] J. Edelman, *Adv. Enz.*, **17**, 189 (1956).

[4] S. C. Pan, L. W. Nicholson and P. Kolachov, *Arch. Biochem. Biophys.*, **42**, 406 (1953).

[5] J. H. Pazur, *J. Biol. Chem.*, **216**, 531 (1955).