the refractive index, a decrease in the iodine value, and a shortening of the drying time; all of which indicated a shift of the polyethenoid bonds toward a conjugated system.

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THE SYNTHESIS OF ALDOBIONIDES

Sir:

Aldobionic acids are disaccharides containing a uronic acid as one of the sugar constituents. These sugar acids were found among the products of hydrolysis of the immunologically specific carbohydrates of certain encapsulated pathogenic microörganisms [M. Heidelberger and W. F. Goebel, *J. Biol. Chem.*, **70**, 613 (1926); W. F. Goebel, *ibid.*, **74**, 619 (1927)]; they have since been obtained from various plant gums as well. The synthesis of two aldobionic acids, gentiobiuronic acid and the aldobionic acid of gum acacia, has been described recently [R. D. Hotchkiss and W. F. Goebel, *J. Biol. Chem.*, **115**, 285 (1936)]. The chemical constitution of a third aldobionic acid, cellobiuronic acid obtained from the specific polysaccharide of pneumococcus, Types III and VIII, have also been established [R. D. Hotchkiss and W. F. Goebel, *ibid.*, **121**, 195 (1937)].

Since it is our desire to prepare for chemo-immunological study, artificial carbohydrate-protein antigens containing these three aldobionic acids, a method for the synthesis of aldobionides has now been developed. The preparation of the acetobromo derivatives of the methyl esters of the acacia aldobionic acid (6-β-glucuronosido-galactose) and of cellobiuronic acid (4-β-glucuronoside-glucose) was achieved in the following manner.

When the heptaacetyl methyl ester of cellobiuronic acid or of the acacia aldobionic acid, is allowed to stand in the presence of acetic acid saturated with hydrogen bromide, the α-bromohexaacetyl methyl ester of the corresponding aldobionic acid is in each instance formed. The derivatives may be isolated from the reaction mixtures in excellent yields. The α-bromohexaacetyl methyl ester of 4-β-glucuronosido-glucose is obtained as glistening needles melting at 200° (uncorrected) $[\alpha]^{24}D$ +99.4° in $CHCl_3$ (*C*, 1%) (found, Br, 11.66). The α-bromohexaacetyl methyl ester of 6-β-glucuronosido-galactose crystallizes as rosets of needles. The melting point of the pure substance is 201–202° (uncorrected) $[\alpha]^{23}D$ +194.7° (*C*, 1%) (found, Br, 11.52). When the latter derivative is condensed with methyl alcohol in the presence of silver oxide the methyl ester of hexaacetyl-6-β-glucuronosido-methylgalactoside is formed in yields of 60%. The derivative crystallizes as prismatic needles melting at 134° (uncorrected) $[\alpha]^{25}D$ +86.4° (*C*, 1%) (found, OCH_3 9.96). We have certain evidence which indicates that the synthetic methyl glycoside of the aldobionic acid derivative is the α instead of the anticipated β-glycoside.

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FREE ROTATION ABOUT CARBON–CARBON BONDS

Sir:

Montgomery, McAteer and Franke [THIS JOURNAL, **59**, 1768 (1937)] find for the reaction

$$n\text{-}C_4H_{10} \rightleftharpoons i\text{-}C_4H_{10}$$

an equilibrium constant of about 4.0 in the liquid phase at 27°; the corresponding value for the vapor phase is calculated to be 5.5. This result when combined with Rossini's accurate value $\Delta H_{298} = -1630$ cal. gives $\Delta S_{298} = -2.08 \pm 0.55$ e. u. The third law measurements of Parks, Shomate, Kennedy and Crawford [*J. Chem. Phys.*, **5**, 359 (1937)] gave -5.8 ± 1.2 e. u. Statistical calculations of Pitzer [*ibid.*, **5**, 473 (1937)] assuming potential barriers of 3400–3800 cal. opposing free rotation gave -4.3 e. u., as compared with -4.1 e. u. calculated by Kassel [*ibid.*, **4**, 276 (1936)] on the basis of free rotation. Direct experiment thus shows isobutane to be significantly more stable than is indicated by any calculation; unpublished work done in this Laboratory supports this conclusion.

A major argument against the assumption of free rotation has been the consistency with which statistical entropies based on it exceeded third law determinations. It now appears, however, that the difference of the third law values for the two butanes is in error by 3.7 e. u. Modern determinations of this sort can only be wrong by failure to attain equilibrium in the crystal, and hence can only be low. The third law value for isobutane must therefore be at least 3.7 e. u. low, and the correct value of S_{298} is at least 73.7 e. u.