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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RECEIVED NOVEMBER 23, 1937

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 chemoimmunological 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) $[\alpha]^{24}_{\mathrm{D}}$ +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) $[\alpha]^{23}_{\mathrm{D}}$ +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) $[\alpha]^{25}_{\mathrm{D}}$ +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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RECEIVED NOVEMBER 20, 1937

FREE ROTATION ABOUT CARBON–CARBON BONDS

Sir:

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

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

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.

This result compares with 70.8 e. u. calculated by Pitzer and 74.04 by Kassel. The agreement in the latter case is to some extent fortuitous since there remains a discrepancy of 2.0 e. u. in the entropy of isomerization. Since 0.5 e. u. of this may be experimental error, however, the previously advanced belief [*ibid.*, **4,** 441 (1936)] that equilibrium constants could be calculated within a factor of 2 (1.4 e. u.) appears not to have been greatly over-optimistic.

Since the third law value for isobutane is wrong to a far greater extent than that for *n*-butane, it is perhaps reasonable that the still more highly branched molecule, tetramethylmethane, should give a particularly low third law value. The discrepancy actually found between third law measurements and free rotation calculations is 8.6 e. u. [Aston, Siller and Messerly, THIS JOURNAL, **59,** 1750 (1937)].

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RECEIVED NOVEMBER 13, 1937

CONTACT POTENTIALS OF MULTILAYER FILMS ON METAL PLATES

Sir:

Blodgett [THIS JOURNAL, **57,** 1007 (1935)] and Blodgett and Langmuir [*Phys. Rev.*, **51,** 664 (1937)] have recently described the building up of multilayer films of stearic acid on metal plates by successive dippings of the plates into aqueous solutions covered with a monomolecular layer of the acid under constant compression. If the solution contains $KHCO_3$ (10^{-3} *m*) and calcium ions (10^{-4} *m*) at a *p*H above 9 a layer of film is deposited only as the plate enters the liquid, and it is assumed that in each layer the molecules are oriented in the same direction. On the other hand, at a *p*H less than 7, after the first dip a layer is deposited both as the plate enters and as it is withdrawn from the solution, and in this case it is assumed that the molecules are oriented oppositely in successive layers. These two types of films have been termed by Langmuir *X* and *Y* films, respectively.

Clearly, if the hypothesis is correct, these two kinds of film should produce quite different effects on the contact potentials of the metal plates. In the case of the *Y* films, the potential changes due to successive layers should cancel one another; in the case of the *X* films, very large potential changes should result from the cumulative effect of the added layers. We have recently studied the potential changes associated with such films by means of the vibrating plate method [Zisman, *Rev. Sci. Instruments*, **3,** 7 (1932); E. F. Porter, THIS JOURNAL, **59,** 1883 (1937)]. Castor oil was used to provide constant surface pressure at a temperature of 25–26°. The very different results obtained with *X* and *Y* films are shown in the accompanying figure. A potential change of 8.6 volts was obtained with 170 similarly oriented layers of an *X* film, while the potential change remained constant at 0.12 volt from 10 to 220 layers of a *Y* film. In the former case the maximum slope is 62 millivolts per layer, and it should be noted that the sign of the potential change is such that the molecules in these layers are oriented with their negative ends toward the metal. These results are clearly in accord with Langmuir's hypothesis regarding the orientation of the molecules in the two types of film; nevertheless, they do not of themselves imply anything so specific. All that they demand is some continued electrical asymmetry in the arrangement of the

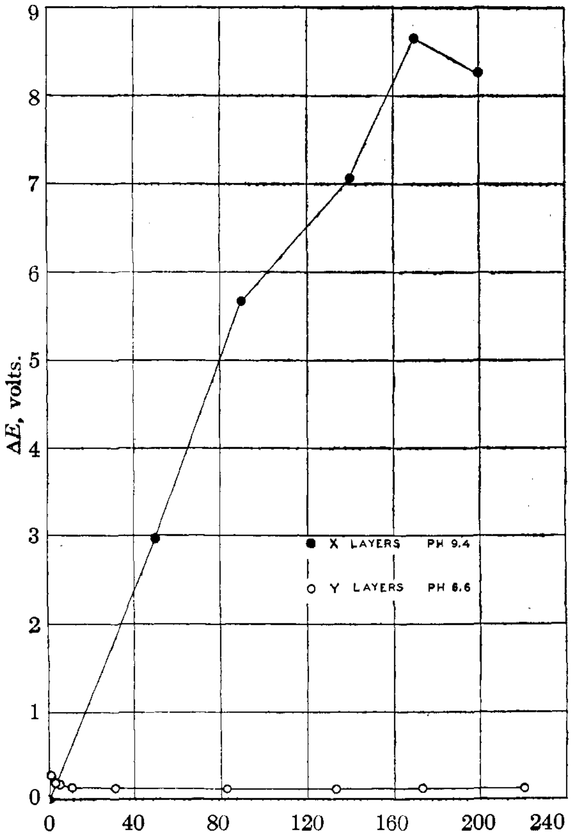

Fig. 1.