Full details of this and further work will be published in *Helvetica Chimica Acta*.[14]

(14) Drs. E. J. Corey and W. R. Hertler also have been concerned with this problem and our results are published simultaneously with theirs by friendly agreement.

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ACYL AMIDES AS EPIMERIZATION REAGENTS[1,2]

Sir:

We wish to report the novel epimerizing action of acyl amides on certain tosylates.

β-Cholestanyl tosylate in a 2.5% solution in N,N-dimethylformamide[3] (DMF) heated at 78°, reacted completely in 23 hours to form a product which when chromatographed on Florisil[4] was cleanly separated into 75% of α-cholestanyl formate (m.p. 114.5–116.0°, $[\alpha]_D$ +30.3° chf, $\lambda_{max}^{CS_2}$ 5.82; 8.40, 8.45, 8.65μ.[5] *Anal.* Found: C, 81.00; H, 11.80), identical with the ester prepared from epicholestanol[1] and formic acid, and 22% of 2-cholestene.[6] However, chromatography on alumina[7] instead of Florisil resulted in hydrolysis of the formate, permitting a facile quantitative separation[8] into α-cholestanol and olefin.

In DMF purified[9] by treatment with barium oxide and distillation, the reaction, although slower (60 hr.), gave essentially the same yields of products. At reflux temperature, with untreated DMF, the product contained 35% formate and was predominantly olefin.

Methyl 3α-tosyloxycholanate with untreated DMF at 78° gave when chromatographed on Florisil 78% methyl 3β-formoxycholanate (m.p. 104–107.5°, $[\alpha]_D$ +13.4° chf., $\lambda_{max}^{CS_2}$ 5.77, 5.82; 8.45, 8.68μ. *Anal.* Found: C, 74.90; H, 10.27) identical with the product of esterification of methyl 3β-hydroxycholanate[10] with formic acid, and 20% methyl 3-cholenate. Chromatography on alumina similarly yielded methyl 3β-hydroxycholanate and olefin quantitatively.

Obtained at 78° from DMF and the corresponding epimeric tosylates were: β-cholestanyl formate,[11] 45 hr., 36%, m.p. 85–86.0°, $[\alpha]_D$ + 14.4° chf, $\lambda_{max}^{CS_2}$ 5.82; 8.47μ (*Anal.* Found: C, 80.91; H, 11.85); androsterone formate, 45 hr., 73%, m.p. 181–181.5°, $[\alpha]_D$ +94.2° chf, $\lambda_{max}^{CS_2}$ 5.76, 5.82; 8.44, 8.65μ. (*Anal.* found: C, 75.25; H, 9.60). Cholesteryl tosylate under these conditions in 40 hr. gave 54% of cholesteryl formate,[12] m.p. 97.5–98.0°, $[\alpha]_D$ −49.1° chf, $\lambda_{max}^{CS_2}$ 5.81; 8.45, 8.52μ.

With N,N-dimethylacetamide,[3] β-cholestanyl tosylate required 92 hr. for complete reaction (disappearance of strong tosylate infrared bands), yielding 21% of α-cholestanyl acetate,[13] and much ether-insoluble product.

Formamide did not react with β-cholestanyl tosylate because of the extremely low solubility, but when heated for 65 hr. at 78° with methyl 3α-tosyloxycholanate, formed 53% of methyl 3β-hydroxycholanate and 32% of methyl 3-cholenate.

Observed facts pertinent to a study of the mechanisms of the reactions reported are: the alcoholic products are stereochemically nearly homogeneous; the reaction in formamide yields inverted alcohol, not formate; purified DMF gives the same yields as untreated DMF, albeit more slowly; an equimolar amount of dimethylammonium *p*-toluenesulfonate was recovered (from DMF reaction); DMF with added *p*-toluenesulfonic acid does not formylate epicholestanol to any appreciable extent under the conditions of the inversion; formamide does not hydrolyze methyl 3β-formoxycholanate under like conditions; cholesterol is formylated without rearrangement.[14]

Full details and further work on this reaction will be reported subsequently.

(1) Paper VII in Seroflocculating Steroids series. Previous paper VI, *Chem. & Ind.*, in press (1958).

(2) This work is supported by grants CS-9053, C-2249 and C-3407 from the National Cancer Institute, of the National Institutes of Health, Public Health Service.

(3) Eastman Kodak Co. product, "Eastman" grade, used as purchased.

(4) Floridin Co. product, 60–100 mesh.

(5) The very strong carbonyl band at 5.82 μ permits estimation of the formate concentration. Such estimates were found to check actual isolations by chromatography to within 1%. Furthermore, the C—O stretching bands near 8.5 μ appear to be characteristic of the 3-formates (L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1956, p. 161).

(6) Elsevier's "Encyclopaedia of Organic Chemistry," Vol. III, 14 Supplement, 1422S.

(7) Fisher Scientific Co. product A-540.

(8) In another experiment in which β-cholestanyl tosylate was heated for 29 hr. at 78° as a 5% solution in DMF, some unreacted tosylate remained, and 3.5% of β-cholestanol was obtained as the final fraction from the chromatography on alumina.

(9) *Cf.* G. R. Leader and J. F. Gorley, THIS JOURNAL, **73**, 5731 (1951). S. R. Ross and M. M. Labes (*ibid.*, **79**, 4155 (1957)), report that DMF purified similarly contains 0.09–0.13% water, more than the equimolar proportions needed for reaction.

(10) R. T. Blickenstaff and F. C. Chang, *ibid.*, **80**, 2726 (1958).

(11) Elsevier's "Encyclopaedia of Organic Chemistry," Vol. III, 14, p. 58.

(12) Elsevier's "Encyclopaedia of Organic Chemistry," Vol. III, 14, p. 1630S.

(13) C. W. Shoppee, *J. Chem. Soc.*, 1138 (1946).

(14) *Cf.* S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948).

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RECEIVED MARCH 28, 1958

THE REACTION OF SODIUM BOROHYDRIDE WITH MUSCLE PHOSPHORYLASE[1]

Sir:

The presence of a firmly bound, non-protein constituent in skeletal muscle phosphorylase has been investigated independently in two different laboratories.[2,3,4] Identification of this material as pyridoxal 5′-phosphate (PLP) was first reported by Baranowski, *et al.*[2] Cori and Illingworth[3] found

(1) Supported by the Institutional Grant to the University of Washington by the American Cancer Society, the Initiative 171 Fund of the State of Washington, and the United States Public Health Service (Grant No. A-850).

(2) T. Baranowski, B. Illingworth, D. H. Brown and C. F. Cori, *Biochim. et Biophys. Acta*, **25**, 16 (1957).

(3) C. F. Cori and B. Illingworth, *Proc. Nat. Acad. Sci.*, **43**, 517 (1957).

(4) A. B. Kent, E. G. Krebs and E. H. Fischer, *J. Biol. Chem.*, in press.