(Continued from page 102A)

the systems studied are: lecithin-cholesterol-water; lecithin-lysolecithin-water; cephalin-cholesterol-water; bile salt-cholesterol-water; bile salt-lecithin-water; bile acid-lecithin-water; bile salt-lecithin-cholesterol-water; bile salt-soap-water and soap-fatty-acid water. A variety of crystal, liquid crystal (lamellar, hexagonal, cubic, etc.) and isotropic aqueous phases have been found. Certain insoluble amphipaths are solubilized in liquid crystal phases of swelling amphipaths and in turn these liquid crystals can be dispersed as mixed micelles by soluble amphipaths. The phase equilibria of mixtures of biologically important lipids as well as the structure and some physical characteristics of the individual phases will be discussed and correlated with certain biological phenomena.

— 17 —

ROLE OF LIQUID CRYSTALLINE STRUCTURES IN LIPIDS

J. L. Ferguson and G. H. Brown

Most lipids do not pass on heating directly from a crystalline structure to an isotropic structure. They are often characterized by a number of intermediate phases ranging from the plastic crystal where the center of gravity of the molecule may rotate about one or more axes while the three-dimensional order of the crystal remains to nematic liquid crystals which have birefringent properties of crystals and yet are characterized by completely random ordering of the molecular centers. The smectic and cholesteric liquid crystalline structures are most commonly encountered in lipids. The structural characteristics of these systems will be discussed.

Of particular interest in living systems are liquid crystals which are formed by cholesteric esters and many protein materials and the two-dimensional crystals (smectic structure) formed by fatty acid derivatives. The mechanisms of energy transfer and the mechanical alignment in these liquid crystalline systems are unique and require different considerations than one finds adaptable to liquids or solids. The properties of liquid crystals which might best be associated with living systems will be discussed. These will include surface properties for catalytic processes and diffusivity.

— 18 —

VOLATILE PRODUCTS FROM OXIDATION OF CIS,CIS-6,9-OCTADECADIENE

G. Fuller, R. J. Horvat, W. H. McFadden and T. H. Applewhite

The hydrocarbon analog of linoleic acid, *cis,cis*-6,9-octadecadiene, was prepared from methyl linoleate by a series of reactions. The hydrocarbon was then used as a model oxidation system and subjected to oxidation both at ambient temperature and at 185C. The volatile oxidation products were separated and analyzed by a tandem gas chromatographic-mass spectral technique. Major products from the hydrocarbon were similar at high and low temperatures, but some of the minor products were quite different, reflecting differences in mechanism and in techniques of product isolation. Volatiles included hydrocarbons, aldehydes, ketones, esters and cyclic compounds. Some mechanistic interpretation of product formation and the relationship to oxidation processes with linoleate derivatives will be discussed.

Calendar of Ladies' Program Spring Meeting—New Orleans

Monday, May 8, 1967

Assembly and Continental Breakfast—9:00–9:30 AM. Rendezvous Room—Roosevelt Hotel

Boat trip through canals and bayous to the Barataria area aboard cruise boat "Voyageur"—Departure 10:00 AM. Bus transportation to dock at foot of Canal Street will be provided. Picnic lunch aboard "Voyageur"—return to hotel about 2:30 PM.

Tuesday, May 9, 1967

Assembly and Continental Breakfast—9:00–9:30 AM. Rendezvous Room—Roosevelt Hotel

Bus tour of city through the French Quarter and near uptown area, followed by brunch in the Grand Court—Pontchartrain Hotel, St. Charles Avenue near Lee Circle. Menu will feature typical Creole breakfast cuisine. Return to Roosevelt Hotel by street car. Schedule will leave afternoon free.

Wednesday, May 10, 1967

Assembly 9:00–9:30 AM. Rendezvous Room—Roosevelt Hotel, followed by short walk to Kolbs Restaurant on St. Charles Avenue near Canal. Coffee party in Kolbs' Tyrolean Room. Exhibit of research products of the Southern Regional Research Laboratory, featuring newest in cotton fabrics and wearing apparel. Return to Roosevelt Hotel will be timed to permit those who wish to attend the Awards Luncheon, 12:30 PM.

— 19 —

THE KINETICS OF EPOXIDATION OF METHYL-12,13-EPOXYOLEATE WITH PERACETIC ACID

M. E. Snook, Jr., W. E. Scott and H. L. Rothbart

The kinetics of epoxidation of methyl-12,13-epoxyoleate (methyl vernolate) with peracetic acid was studied in benzene and chloroform at a variety of temperatures from 25C to 40C. The rate of disappearance of the ester and formation of the *syn* and *anti* diepoxyesters was followed with the aid of gas-liquid chromatography. Rate constants, and energies and entropies of activation were determined for the second-order disappearance of monoepoxy ester and the formation of the diepoxides. Error analysis indicates that knowledge of the initial concentrations and temperature control are extremely important for the accurate determination of the rate constants for this relatively slow reaction. Although the entropies of activation for the formation of the two isomeric diepoxides, on the order of 30 eu., are known to only one significant figure the differences in these two entropies of activation, about 1 eu., may be determined. These small differences lead to large differences in the yields of the diepoxides.

— 20 —

SPECIFICITY OF A LIPASE FROM GEOTRICHUM CANDIDUM FOR CIS-9-UNSATURATION

T. A. Marks, J. G. Quinn, J. Sampugna and R. G. Jensen

A lipase from *Geotrichum candidum* did not differentiate between oleate and palmitoleate when glyceryl 1-palmitoleate 2,3-dioleate was the substrate. The enzyme released equimolar quantities of oleate and linoleate from glyceryl 1-oleate 2,3-dilinoleate and from equimolar mixtures of triolein and trilinolein. When glyceryl 1-*cis*-vaccenate 2,3-dioleate was the substrate oleate comprised 92.8 M% of the FFA. When glyceryl 1-palmitoleate 2,3-dipetroselinate was the substrate the FFA contained 94.6 M% palmitoleate. Since earlier, it was found that the lipase would not hydrolyze elaidate, the enzyme apparently has a specificity at least for *cis*-9 unsaturation and probably also for *cis*-9, *cis*-12 unsaturation.

— 21 —

RATE OF REACTION OF HEXAHALOCYCLOPENTADIENES WITH LONG CHAIN MONOENES

C. K. Lyon, G. Fuller and T. H. Applewhite

Second-order rate constants were calculated for the Diels-Alder type reaction of hexachlorocyclopentadiene and hexabromocyclopentadiene with various monounsaturated fatty esters and a model alkene. Diene concentrations during reaction were determined by measurement of ultraviolet absorption at 322 mμ (hexachloro diene) or 346 mμ (hexabromo diene). The following structural effects were noted on the rate of reaction of hexachlorocyclopentadiene at 150C: 1) Terminal double bonds reacted about 12 times as fast as mid-chain double bonds; 2) The presence of a homoallylic hydroxyl group (ricinoleate esters) reduced the reaction rate about 35%; 3) *cis*-double bonds reacted 5 to 6 times as fast as *trans*-double bonds. At 130C, hexabromocyclopentadiene reacted about one half as fast with ricinoleate esters as did hexachlorocyclopentadiene. The bromo-compounds were considerably less stable to heat than the chloro-compounds. We conclude that steric factors have a pronounced effect on the rate of reaction and stability of these heavily substituted dienes.

— 22 —

SOME REACTIONS OF THE STEAROYLATED ENOLIC FORM OF ACETONE

E. S. Rothman

After observing the ease of addition of acetyl hypobromite to the olefin, oleic acid, we considered that similar addition of stearoyl hypobromite to isopropenyl acetate would give rise to the highly unusual geminal diester structure. During a short-cut procedural try using commercially available isopropenyl acetate and stearic acid with a trace of acid catalysis we found that acid-ester interchange occurred instead to give the new enol ester, isopropenyl stearate. Isopropenyl stearate is a powerful stearoylating agent at elevated temperatures under conditions of acid-catalysis and performs such unusual stearoylations as that of N-butylstearamide and maleiimide. Extension of these principles to dioic acids gave diisopropenyl esters which are potential polymer-formers. Thus diisopropenyl sebacate reacts with N,N′-dimethylazelaiamide to form a linear polyimide, and with sucrose to form a three-dimensional network polymer. There is evidence to believe that the effective causative, intermediary agent is hexadecylketene. We have prepared and characterized the cyclobutanedione and four-membered-ring-lactone dimers supporting this conclusion. In situ preparation of hexadecylketene in the presence of hydroxylamine has enabled the preparation of the previously unknown di- and trihydroxamic acids. We have also observed a rearrangement of isopropenyl stearate to heneicosane-2,4-dione.

— 23 —

THE ROLE OF DETERGENT IN AUTOMATIC DISHWASHING PERFORMANCE

F. W. Gray, V. J. Richter and R. C. Odioso

The ability of automatic dishwashing products to perform satisfactorily in mechanical machines is dependent upon a number of factors, including machine design and composition of product. Although most leading dishwashers are highly satisfactory for food soil removal, the detergent composition and its usage can affect performance characteristics.

In this paper, the objectionable tendency of automatic dishwashing detergent compositions to cause glassware spotting or filming, fading of fine china decoration, and silverware tarnishing is considered. The means to minimize these deficiencies are presented.

— 24 —

THE EFFECT OF WATER HARDNESS ON DETERGENCY

Sadao Kakegawa, Michio Aoki and Haruhiko Argai

The effect of ionic or nonionic detergents, and builders on oil removal efficiency in hard water has been studied. As ionic detergent (sodium dodecyl benzene sulfonate), maximum oil removal efficiency