nitrobenzoate. Absolutely consistent determinations of the composition of the mixture were obtained by the use of all of these methods.

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RECEIVED MAY 31, 1934

PREPARATION OF CRYSTALLINE β-*d*-[α-GALAHEPTOSE][1]

Sir:

Fischer [*Ann.*, **288**, 139 (1895)] prepared the two galaheptoses from galactose and crystallized β-galaheptose, but was unable to obtain α-galaheptose in crystalline condition. We have now succeeded in crystallizing this sugar.

The first crystalline material was obtained from an aqueous sirup resulting from the reduction of crystalline α-galaheptonic lactone in acid solution by sodium amalgam. Following removal of the sodium salt of α-galaheptonic acid by repeated treatments with methyl alcohol, the sirup crystallized after standing in a loosely covered beaker at laboratory temperature for several weeks. With these crystals it was possible to nucleate other sirups and obtain crystallization readily.

β-*d*-(α-Galaheptose) monohydrate crystallizes in clusters of colorless glistening prisms, stable at room temperature upon drying *in vacuo* over calcium chloride or sulfuric acid. When slowly heated in a capillary tube it melts at 77–78° (corr.) to a colorless sirup. Its solution in water shows $(\alpha)^{20}_{\mathrm{D}}$ $-22.5°$ for the monohydrate after three minutes and an equilibrium value of $-14.1°$ in 180 minutes, at 20°. These data establish the fact that the sugar is the less dextrorotatory form of a sugar in the *d*-series, and according to the usual nomenclature [Hudson, THIS JOURNAL, **31**, 66 (1909)] it is to be designated as the β-form. Studies of the *d*-galaheptoses, which closely resemble *l*-mannose and *l*-glucose in configuration, are in progress.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

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RECEIVED JUNE 4, 1934

PHOTOCHEMICAL DECOMPOSITION OF KETENE

Sir:

In a recent paper Ross and Kistiakowsky [THIS JOURNAL, **56**, 1112 (1934)] have confirmed our experimental results on the photochemical decomposition of ketene [*J. Chem. Soc.*, 1533 (1933)]. They have in addition measured the quantum efficiency and find average values of about 1.0 at 3130 Å. and 0.3 at 3650 Å. While agreeing with our primary change

$$CH_2{=}CO \longrightarrow CH_2 + CO$$

they suggest that the secondary change

$$CH_2 + CH_2 \longrightarrow C_2H_4$$

is in better agreement with the unit quantum yield at 3130 Å. than is that postulated by us

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO + 9 \text{ k. cal.}$$

This reaction cannot, however, be eliminated on such evidence alone. It is not necessarily true that the higher of the two values of the quantum efficiency is its maximum value. Further, it is now apparent that for polyatomic molecules the quantum yield of the primary reaction may be less than unity throughout a considerable portion of a region of continuous absorption. This is true of acetone ($\gamma = 0.2$ for λ 3130 and 0.4 for λ 2650) as has been shown by Damon and Daniels [THIS JOURNAL, **55**, 2363 (1933)] and recently confirmed by us. If the radiationless transition which follows absorption of light be viewed as an Auger effect confined to the carbon atom of the chromophoric (carbonyl) group, we may suppose that it does not in all cases lead to dissolution of the C=C link but that instead it may lead to the degradation of the electronic energy of excitation to molecular vibration, and its dissipation as heat. The relative probabilities of these alternatives would not be expected to remain constant throughout the absorption band but as the wave length of the absorbed radiation decreased the fraction of molecules decomposing would increase.

The spectroscopic observations of ketene made by Lardy [*J. chim. phys.*, **21**, 353 (1924)] and ourselves (Ref. 2) are completely in agreement with these ideas. The absorption spectrum consists of completely diffuse bands throughout its *entire* range. The substance shows no fluorescence. The low quantum yield of 0.3 at λ 3650 increases to 1.1 at λ 3130 (Ref. 1) in full agreement with this theory. As with acetone the value of the quantum yield may be expected to increase toward the theoretical maximum value as the magnitude of the absorbed quantum exceeds by greater amounts the energy necessary to decompose the molecule. This would lead to a maximum over-all quantum yield of 2 if our mechanism is correct, or of 1 if that of Ross and Kistiakowsky is right. The fact that the values of Ross and Kistiakowsky are less than unity at 3650 and somewhat exceed it at 3130 lends probability to the correctness of our theory.

If this view is not taken it is difficult to reconcile the low value of the quantum efficiency at λ 3650 Å. with the diffuse character of the absorption in that region. It is improbable that the fraction of excited molecules which do not decompose could lose their energy by collision for this would involve a life of the excited state of the order of 10^{-8} second, which is about 10^5 times greater than that necessary to produce so diffuse a spectrum.

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RECEIVED JUNE 7, 1934

THE ADDITION OF HYDROGEN BROMIDE TO PENTENE-1 AND HEPTENE-1

Sir:

In reply to the communication by Kharasch, Hinckley and Gladstone in which they question the validity of our conclusions concerning the importance of the solvent as an influencing factor in hydrogen bromide addition to pentene-1 and heptene-1, we would emphasize the particular conditions under which our addition reactions were carried out. The highly purified hydrocarbons gave no test for peroxide before the addition of hydrogen bromide nor did they give the colored reaction mixtures which we have always obtained in hydrogen bromide addition to hydrocarbons known to contain peroxide. The addition reactions in organic solvents, where we obtained the so-called "abnormal" products, 1-bromopentane and 1-bromoheptane, took place in the absence of air, whereas in water solution the reaction mixtures were shaken for many days in contact with air. The probability of a peroxide effect in the latter solvent is therefore much greater than in the organic solvents but our results gave conclusive evidence of the formation of only the "normal" product 2-bromopentane and 2-bromoheptane in water solution. Careful analysis of the experimental data would seem to justify our conclusion that any peroxide effect was eliminated in these reactions.

Furthermore, our reactions were carried out at atmospheric pressure while those of Kharasch and co-workers must have taken place under increased pressure. This factor complicates any comparison of results since the effect of pressure may be of importance in determining the products of the reaction. In drawing conclusions from our experiments there was no intentional disregard of the importance of the peroxide effect in hydrogen halide addition to unsaturated compounds which has been demonstrated by Kharasch and co-workers. Our results, however, seem to give conclusive evidence that in the absence of peroxide the solvent is an influencing factor.

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RECEIVED JUNE 11, 1934

PREPARATION OF PURE METALLIC HYDROXIDES

Sir:

A recent article by J. H. Long, J. C. W. Frazer and Emil Ott [THIS JOURNAL, **56**, 1101 (1934)] refers to a dissertation by O. G. Bennett [Johns Hopkins University, 1930] which describes the purification of metallic hydroxides by washing the oxides (or hydroxides) by decantation until peptization occurs and then electrodialyzing to remove the alkali salts adsorbed by the oxide hydrate at the moment of precipitation and which cannot be removed from the (usually gelatinous) oxide by mere washing. This ultrapurification is necessary if one is to obtain cobalt or nickel trioxides or manganese dioxides in a state sufficiently pure so as to be capable of catalyzing the reaction of carbon monoxide with oxygen at room temperature.

According to Bennett's dissertation, which was kindly made available by Dr. J. C. W. Frazer, the process of electrodialysis is long and tedious, sometimes requiring weeks. If the oxide could be precipitated in the absence of alkali or metal compound other than manganese or nickel salts, respectively, it would not be necessary to remove adsorbed salts by electrodialysis. It has been found in this Laboratory that passing ozone through neutral solutions of manganous acetate or chloride precipitated a manganese oxide which, after a short washing with concentrated nitric acid and drying by evacuation at 100°, was a very active catalyst for the oxidation of carbon monoxide. The electrolysis of manganous nitrate