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 $(\alpha)^{20}_{D}$ $-22.5°$ 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