stant ($-\Delta E_m$) for the reaction gives the total energy which disappears in the reaction.

If it is assumed that the energy escapes largely as γ-ray energy, then it follows that:

5. The total γ-ray energy emitted increases rapidly as the energy of the projectile, the neutron, increases.

6. A remarkable feature of Fig. 2 is the absence of points in the lower right-hand section. Thus the γ-ray energy is always high if the energy of the neutron is high.

Let it be supposed that the γ-ray levels are discrete. Then since all possible neutron energies are involved, the points for each level in Fig. 2 should lie on or close to a horizontal line. This would give a scattering along the x-axis, while the different levels would give a scattering along the y-axis. While the points in Figs. 1 and 2 have the general type of distribution suggested by this hypothesis, the accuracy of the values is not sufficient to resolve the levels which may exist. It is possible that the type of plot found may, on account of the existence of some unknown relation, be associated with a continuous rather than a line spectrum. On the whole it does not seem improbable that both types of spectra may be represented.

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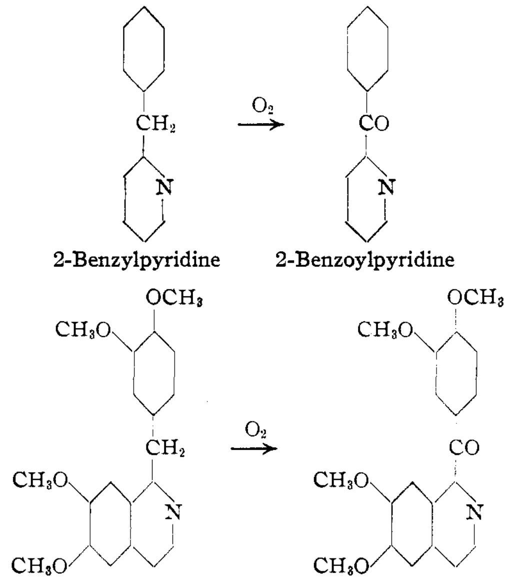
Received October 15, 1934

THE PHOTO-OXIDATION OF 2-BENZYLPYRIDINE AND PAPAVERINE

Sir:

It has been established that the following reactions take place photochemically in air.



Papaverine (in benzene) Papaveraldine (or xanthaline)

The second reaction is of plant physiological interest since these alkaloids occur together in nature.

2-Benzylpyridine in a glass bulb was exposed to a quartz mercury lamp (the liquid becomes brown[1]) and fractionally distilled *in vacuo* whereby a small quantity of the ketone, which is the chief product, was obtained and identified by isolating the semicarbazone and phenylhydrazone. A benzene solution of papaverine[2] in a quartz flask after three days in sunlight (the color becomes brown with the formation of a slight precipitate) yielded approximately 10% papaveraldine which was identified by analysis and mixed melting points with synthetic papaveraldine and by those of the hydrochlorides. In the solid state, papaverine and papaveraldine became brown after several hours in mercury light.

Using glass bulbs sealed to mercury manometers, papaveraldine in benzene, 2-benzylpyridine and 2-benzoylpyridine in dry oxygen showed no absorption in the dark at 115°, but at lower temperatures in mercury light a strong absorption occurred and the practically colorless liquids became deep brown as in air. In the dark at 115°, papaverine in benzene absorbed oxygen but in air at 60° (20° higher than reached by the solution exposed in sunlight) no color appeared and evaporation (without crystallization) yielded unchanged papaverine. Similarly it was found that papaverine solutions in glass bulbs sealed off in high vacuum or with water remained unchanged after forty hours in mercury light. However, such bulbs containing papaveraldine solution or 2-benzoylpyridine so exposed soon became brown and later in the case of papaveraldine precipitates resulted. 2-Benzylpyridine in vacuum remained colorless but with water became pale yellow after exposure.

The effect of various spectral lines of the mercury lamp in so far as they produced color was studied. Filter paper strips impregnated with alcoholic solutions were exposed in place of a

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[1] This color change in light was first observed by H. Freytag and A. Müller, *Naturwiss.*, **21**, 720 (1933).

[2] E. Paternò, *Gazz. chim. ital.*, **44**, II, 104 (1914), simply reports that from a solution of papaverine in acetone contained in glass, after seven months in daylight, only the starting materials and traces of reaction products could be obtained. Although not mentioned, undoubtedly little or no air had access.

photographic plate in a quartz spectrograph until the effect became constant. For papaveraldine the lines were yellow-brown and distinct within an hour; 405, 365, 313, 302 and 297 appeared considerably stronger than those shorter (to 238 mμ). For papaverine essentially the same was found but with somewhat weaker intensity and 405 mμ was absent. For 2-benzoylpyridine lines 365 to shorter than 238 mμ appeared dull green, with those from 365 to 297 the strongest. This compound was the most sensitive, all lines appearing in ten minutes, much weaker, however, than on silver chloride print paper. For 2-benzylpyridine 280 to 238 (265 and 254, strongest) appeared within thirty minutes brown in color, and eight hours later, undoubtedly due to the formation of 2-benzoylpyridine, lines to 365 mμ which were dull green. None of these compounds were affected by lines longer than 405 mμ.

Other compounds related to 2-benzylpyridine were also studied which will be described in a forthcoming publication.

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RECEIVED NOVEMBER 5, 1934

ON THE APPLICATION OF THE PRINCIPLE OF OPTICAL SUPERPOSITION IN THE KETOSE SERIES. PREPARATION OF THE TRUE α-PENTAACETYLFRUCTOSE <2,6>

Sir:

In order to test the validity in the ketose series of the principle of optical superposition as applied by Hudson [THIS JOURNAL, **31**, 66 (1909)] in sugar chemistry, it is necessary to know the optical rotations of a true α,β-stereoisomeric pair of any ketose derivative. In the ketose series, contrary to the aldose, no such true α,β-pair has hitherto been known with certainty. It was *assumed* [Hudson, *J. Ind. Eng. Chem.*, **8**, 381 (1916); THIS JOURNAL, **46**, 477 (1924)] that the two known pentaacetates as well as the two chloroacetates of fructose constituted such α,β-pairs. The rotations of the latter were used to calculate the value of the constants A_{Cl} and $B_{\text{fruct. ac.}}$. Since the value of A_{Cl} resulting from this calculation *happened* to agree closely with the value of A_{Cl} for the aldoses, this was regarded as evidence that the substitution of —CH$_2$OAc for —H does not change the rotation of carbon atom 2. Subsequently, the constants for aldoses were used in calculations for the ketose series, but the calculated optical rotations never agreed with those actually observed. Assuming the principle of optical superposition be correct, the reason for this disagreement was obscure. However, it was recently proved [Pacsu and Rich, THIS JOURNAL, **54**, 1697 (1932); **55**, 3018 (1933)] that both "α-pentaacetylfructose" and "α-chloroacetylfructose" are derivatives of the open-chain fructose, and, therefore, all the calculations based on the assumption that the two pentaacetates and the two chloroacetates of fructose constitute α,β-stereoisomeric pairs, are invalid. This correction resulted in the present search for, and discovery of, the true α-pentaacetylfructose.

On replacement of the chlorine atom in β-chloroacetylfructose <2,6> by an acetoxyl radical, partial Walden inversion occurs on the carbon atom 2, if the reaction be carried out in boiling acetic anhydride solution with anhydrous sodium acetate. The mixture of the diastereomerides so formed consists of the well-known β-pentaacetylfructose <2,6> and its α-isomeride. After separation from the β-compound, the α-pentaacetylfructose <2,6> was obtained in pure, crystalline form; m. p. 122–123°; $[\alpha]^{20}_{\text{D}}$ 47.4°, in chloroform. From the molecular rotations of the β-pentaacetate and the new acetate, the values of $A_{\text{Ac}} = 32{,}850$ and $B_{\text{fruct. ac.}} = -14{,}350$ were obtained. Knowing the value of $B_{\text{fruct. ac.}}$, it is now possible to calculate the specific rotations of the α-derivatives. For instance, the calculated specific rotation of tetraacetyl-α-methylfructoside <2,6> is $[\alpha]^{20}_{\text{D}}$ 45.5° in chloroform. Several years ago, Schlubach and Schröter [*Ber.*, **61**, 1216 (1928)] prepared a tetraacetylmethylfructoside with $[\alpha]^{20}_{\text{D}}$ 45° in chloroform, to which they ascribed the α-configuration. The excellent agreement between these two values indicates that Schlubach's compound is really the α-isomeride of the tetraacetyl-β-methylfructoside <2,6>, and at the same time supports the validity of the principle of optical superposition in the ketose series. It is to be expected that several unknown α-derivatives can be prepared from this new fructose pentaacetate.

The details of this investigation will be published within a short time.

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RECEIVED NOVEMBER 17, 1934