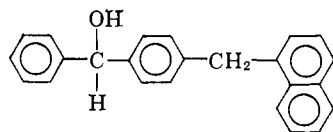


TABLE II  
PHOSPHORESCENCE MAXIMA, EPA AT 77°K. IN CM.<sup>-1</sup>

I	II	1-Methylnaphthalene
21,097	21,097	21,044
20,576	20,584	20,534
19,700	19,708	19,635
19,547	19,547	19,500

emission from benzophenone could have been detected (Fig. 2).

Apparently, efficient transfer of triplet excitation from the benzophenone moiety to the naphthalene moiety of I occurs. Singlet excitation transfer from a benzophenone to a naphthalene is unlikely since the first excited singlet level of benzophenone lies about 3000 cm.<sup>-1</sup> lower than the first excited singlet level of naphthalene. The lowest triplet state of benzophenone lies about 3000 cm.<sup>-1</sup> higher than the lowest triplet state of naphthalene and efficient triplet energy transfer can occur. Transfer of singlet excitation from the naphthalene unit to the benzophenone moiety is energetically possible and must occur with high efficiency<sup>11</sup> when I is excited with light adsorbed by the naphthalene nucleus. Fluorescence from 1-methylnaphthalene (O-O band 31,397 cm.<sup>-1</sup>) is nearly ten times more intense than fluorescence from I (O-O band 31,348 cm.<sup>-1</sup>). Direct involvement of the carbonyl group of I in fluorescence quenching is indicated by the fact that fluorescence of II (O-O band at 31,505 cm.<sup>-1</sup>) is as intense as that of 1-methylnaphthalene.



II

The large difference between the intensities of fluorescence from I and II is attributed to loss of singlet excitation from the naphthalene nucleus of I to the ketonic part of the molecule. While the excitation is in the carbonyl-containing unit, efficient intersystem crossing to a triplet state occurs and the excitation then returns to the naphthalene unit.

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(12) National Science Foundation Predoctoral Fellow.

HALL LABORATORY OF CHEMISTRY  
WESLEYAN UNIVERSITY  
MIDDLETOWN, CONNECTICUT  
CONTRIBUTION No. 2988

PETER A. LEERMAKERS  
GARY W. BYERS

GATES AND CRELLIN LABORATORIES  
OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA

ANGELO A. LAMOLA<sup>12</sup>  
GEORGE S. HAMMOND

RECEIVED JUNE 13, 1963

### The Role of $n \rightarrow \pi^*$ Triplet in the Photochemical Enolization of *o*-Benzylbenzophenone<sup>1</sup>

Sir:

The identification of reactive excited states in photochemistry is a subject of current interest. The  $n \rightarrow \pi^*$  triplet state of the aromatic ketones has been shown to be the intermediate in intermolecular photochemical

(1) The work was presented in part at the Photochemistry Symposium in Rochester, N. Y., on March 27, 1963.

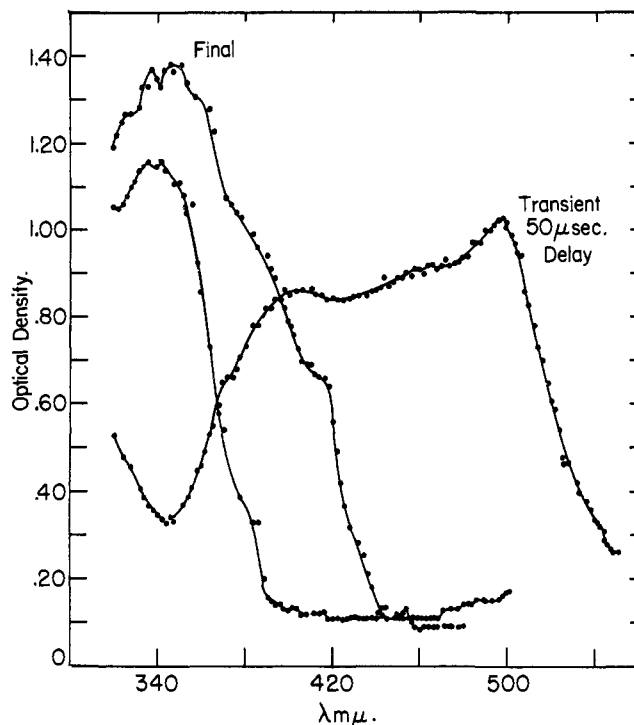
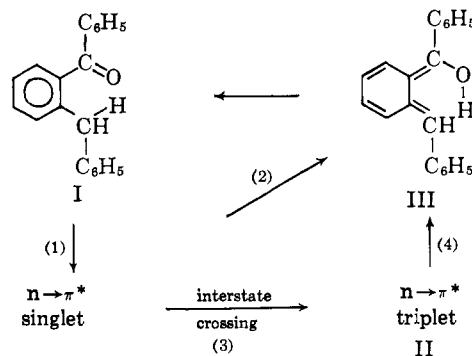


Figure 1.

reactions,<sup>2-6</sup> while in the intramolecular type II process the singlet excited state was suggested as the reactive intermediate.<sup>7</sup> *o*-Benzylbenzophenone undergoes an intramolecular photoenolization, a reaction analogous to the type II process,<sup>8</sup> and the photoenol thus formed reverts back to benzylbenzophenone in a dark reaction. On the basis of the two possible reactive excited states, the photoenolization may proceed directly through the  $n \rightarrow \pi^*$  singlet excited state (reactions 1 and 2) or it may proceed through the  $n \rightarrow \pi^*$  triplet as the intermediate (reactions 1, 3, and 4). By flash spectroscopy we have now demonstrated that the triplet is the reactive intermediate in this intramolecular reaction.



*o*-Benzylbenzophenone (I), the  $n \rightarrow \pi^*$  triplet state (II), and the enol (III) will all exhibit measurable electronic absorption spectra under the experimental conditions, while the  $n \rightarrow \pi^*$  singlet will have too short a lifetime to be detected. The flash photolysis and spectroscopy of I were carried out in cylindrical Pyrex cells ( $l = 26$  cm.) with full intensity of the flash light source

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in an apparatus previously described.<sup>9</sup> When the spectrum of 0.3 mM *o*-benzylbenzophenone in cyclohexane is measured several minutes after the flash excitation, it deviates only to a small extent from the initial absorption ( $\lambda_{\max}$  338 and 342 m $\mu$ ,  $\epsilon$  140).<sup>10</sup> However, 50  $\mu$ sec. after the flash excitation the absorption spectrum is markedly different with a new maximum at 500 m $\mu$  and a minimum at 344 m $\mu$  (Fig. 1). By studying the optical density at various wave lengths with kinetic spectrophotometry two transient intermediates were identified separately. A fast transient, the absorption maximum of which at 500 m $\mu$  is very similar to the triplet-triplet absorption of benzophenone,<sup>11</sup> was assigned as the  $n \rightarrow \pi^*$  triplet of *o*-benzylbenzophenone (II). Its rate of decay measured at 436 m $\mu$  and 480 m $\mu$  follows first-order kinetics with  $k = 1.9 \pm 0.2 \times 10^3 \text{ sec.}^{-1}$  which further substantiates the triplet assignment.<sup>11</sup> The slow transient, detected by the decay of optical density at 405 m $\mu$ , is tentatively identified as the enol (III). The decay is also of first order with  $k = 9.4 \pm 0.6 \times 10^{-2} \text{ sec.}^{-1}$ .

The interconversion relationship of the two intermediates was established by following the variation of the optical density at 345 m $\mu$ . The optical density at 345 m $\mu$  decreases to a minimum value immediately after the flash (Fig. 1), then it increases rapidly to a maximum a few msec. thereafter with a first-order rate constant,  $k = 3.2 \times 10^3 \text{ sec.}^{-1}$  ( $\pm 50\%$ ), which is of the same order of magnitude as that of the triplet decay. The maximum optical density attained at this wave length is approximately 0.1 unit higher than the final absorption. The decay of this maximum absorption to the final value also follows first-order kinetics with  $k = 8.7 \times 10^{-2} \text{ sec.}^{-1}$ , which is the same as the decay of the slow transient within experimental error. The above observations establish that (1) the fast transient is converted into the slow transient, *i.e.*, the  $n \rightarrow \pi^*$  triplet is the precursor of the enol, and (2) the enol is not formed directly from the  $n \rightarrow \pi^*$  singlet. If the  $n \rightarrow \pi^*$  singlet were the immediate precursor of the enol, there would be a strong absorption at 345 m $\mu$  immediately after the flash.

Our observations demonstrate that photoenolization of *o*-benzylbenzophenone, an intramolecular photochemical reaction analogous to the type II process, involves a reaction triplet intermediate. Although the enolization may occur theoretically within the lifetime of the singlet excited state, it is actually slower than the interstate crossing of the singlet to the triplet (reaction 3). This work supports the theory that the triplet state may be a reactive state in other similar intramolecular photochemical reactions.<sup>12,13</sup>

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(10) After several flash irradiations or a prolonged irradiation with a high intensity light source, the solution acquired a yellow tint with a blue fluorescence. From the reaction medium there was isolated a small yield of a dimer whose structure is being elucidated.

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(14) The work at the Illinois Institute of Technology is supported by the United States Public Health Service, Department of Health, Education and Welfare.

(15) The work at the University of Chicago is supported by the United States Atomic Energy Commission.

(16) Fellow of the Alfred P. Sloan Foundation.

DEPARTMENT OF PHYSICS<sup>14</sup>  
ILLINOIS INSTITUTE OF TECHNOLOGY  
CHICAGO 16, ILLINOIS

E. F. ZWICKER  
L. I. GROSSWEINER

DEPARTMENT OF CHEMISTRY<sup>15</sup>  
UNIVERSITY OF CHICAGO  
CHICAGO 37, ILLINOIS

N. C. YANG<sup>16</sup>

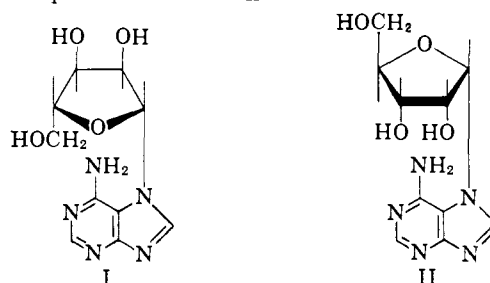
RECEIVED MAY 14, 1963

## The Synthesis of the Anomeric 7-D-Ribofuranosyladenines and the Identification of the Nucleoside from Pseudovitamin B<sub>12</sub><sup>1</sup>

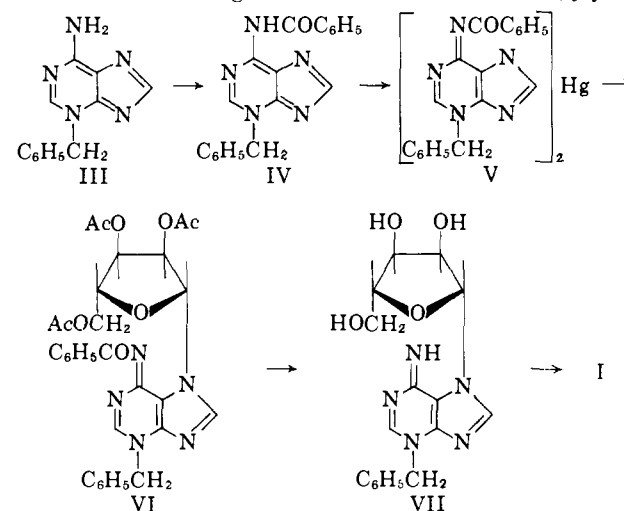
Sir:

The final identification of the nucleoside moiety of vitamin B<sub>12</sub> as 1- $\alpha$ -D-ribofuranosyl-5,6-dimethylbenzimidazole was achieved by comparing its picrate with a synthetic specimen.<sup>2</sup> Later a nucleoside was isolated from pseudovitamin B<sub>12</sub> and identified as 7-D-ribofuranosyladenine.<sup>3</sup> Although the configuration of the glycosyl linkage of this nucleoside was thought to be  $\alpha$ ,<sup>4</sup> this point has not been established by chemical means in the years since the isolation of the nucleoside.

Using a recently developed method<sup>5</sup> for the synthesis of 7-glycosylpurines, we have now synthesized both 7- $\beta$ -D-ribofuranosyladenine (I) and 7- $\alpha$ -D-ribofuranosyladenine (II) and established the identity of the nucleoside from pseudovitamin B<sub>12</sub> and II.



3-Benzyladenine (III), prepared by the benzylation of adenine in *N,N*-dimethylacetamide in the absence of base,<sup>7</sup> was allowed to react with benzoic anhydride to give *N*<sup>6</sup>-benzoyl-3-benzyladenine (IV), which was converted to its mercury derivative (V) in the usual manner.<sup>8</sup> The mercury derivative V was coupled with tri-*O*-acetyl-D-ribofuranosyl chloride by refluxing a xylene suspension of the two materials for 1 hr. Removal of the acyl groups from the blocked nucleoside VI was accomplished by refluxing for 30 min. a methanol solution of it containing sodium methoxide. A 51% yield



(1) This work was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institutes, National Institutes of Health, Contract No. SA-43-ph-1740.

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