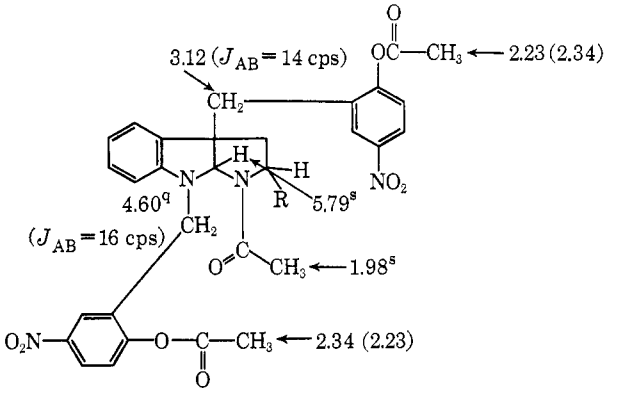
product was nearly homogeneous; **10** and **12** were crystallized directly. **11** was an unstable oily material which resisted crystallization but was smoothly converted to **12** by further acetylation with Ac_2O–NaOAc. Pertinent nmr assignments are indicated on the structures.

Preliminary experiments on the alkylation of N-acetyltryptamine (**4**) with 1 equiv of **1** indicated that the major product contained 2 moles of reagent. Accordingly the alkylation was carried out with 2 equiv of **1**. Purification was effected inadvertently during an acetylation attempt with Ac_2O (room temperature) when the major product crystallized directly from the acetylation mixture as a 1:1 complex with Ac_2O (60% yield). This material dissolved readily in $CHCl_3$ at room temperature and, after 20–30 min, deposited an almost insoluble 1:1 chloroform complex of the composition $C_{26}H_{24}N_4O_7$–$CHCl_3$. An ir spectrum (KBr) indicated associated phenolic stretching vibrations (3000–3400 cm^{-1}) and a hydrogen-bonded (tertiary?) amide carbonyl (1620 cm^{-1}). This material was acetylated with Ac_2O–pyridine (1:1) to give a quantitative yield of the N,O,O-triacetate **13**, $C_{30}H_{28}N_4O_9$, obtained solvent free on crystallization from EtOAc–hexane or as a 1:1 $CHCl_3$ complex from $CHCl_3$–hexane. A high-resolution mass measurement of the parent molecular ion indicated *m/e* 588.178 (calcd 588.183). A low-resolution mass spectrum was consistent with the consecutive loss of two units of *m/e* 194 each from the parent. The molecular extinction of 35,800 at 400 mμ in alkaline ethanol is consistent with a molecular weight of 707 for the chloroform complex of **13**, from which base forms 2 moles of the characteristic chromophore of the *p*-nitrophenoxide ion (ϵ_{410} 18,000). Structure **13**, though awaiting confirmation by X-ray crystallography, is preferred to other alternatives such as the open indolenine tautomer with N_b carrying acyl and benzyl groups.



13, R = H (mp 164–167°; $CHCl_3$ adduct, mp 96–100°)

14, R = COOMe (mp 95–105°)

$\lambda\lambda_{max}$ 252, 270 (sh) mμ

$\lambda\lambda_{max}$ (OH^- then H^+) 246, 315 mμ

Three products resulted when N-acetyl-L-tryptophan methyl ester (**5**) was treated with 2 equiv of the reagent and then acetylated with Ac_2O–pyridine (1:1 room temperature, 3 days). The major component (37% after silica chromatography) had the composition $C_{32}H_{30}N_4O_{11}$ (mp 95–105° after crystallization from ether–ligroin). The near identity of its uv spectrum with **13**, before and after base treatment, and many close similarities in its nmr spectrum (**13**) suggest the analogous structure **14**. Such a dihydroindole system would no longer show the reactivity that bound tryptophan shows toward N-bromosuccinimide.[6]

Acknowledgment. We wish to acknowledge our indebtedness to Dr. G. W. A. Milne for determining the exact mass for compound **13** and to Dr. Takashi Tokuyama for obtaining several of the nmr spectra.

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The Selective Photolysis of Dihydrothymidine

Sir:

Of all the building stones of DNA, thymine most easily undergoes photochemical transformations, such as dimerization[1-3] or possibly reduction,[4] events which are of genetic and mutagenic interest. This report shows that dihydrothymidine, in contrast to dihydrouridine, undergoes a selective "photochemical hydrolysis" of the Ciamician–Silber type[5] which, though well known for homocyclic systems,[6] is here demonstrated for the first time for a heterocyclic representative of biological significance.

In a typical run, a 2×10^{-2} *M* aqueous unbuffered solution of dihydropyrimidine (Ia or Ib) was irradiated with a 250-W high-pressure mercury lamp (Hanovia S654-36, no filter) which was surrounded by a cylindrical water-cooled quartz jacket. Two semicircular quartz vessels which surrounded the cooler and contained the sample were 3 cm from the light source. Irradiation of 1-dihydrothymidine (Ib)[7] for 30 hr led to complete disappearance of the uv absorption at 230 mμ. The photoproduct, a yellow oil, was lyophilized, chromatographed over silica gel, and eluted with chloroform–methanol (9:1). The three major fractions yielded (*S*)-(−)-dihydrothymine, mp 263° (Ia),[7] *n*-propylurea (VIa, 6%), mp 109° (*p*-nitrobenzoate mp 170–171° dec), and N_1-deoxyribosyl-N_1-*n*-propylurea (VIb, 64%), which on acid hydrolysis gave *n*-propylurea, mp 109°, and deoxyribose (diphenylamine test). Dihydrothymine on photolysis gave 75% *n*-propylurea (VIa) and 5% urea. *Under identical conditions the photolysis of dihydrouridine led only to minor cleavage of the ribosyl residue and to the isolation of 5% of dihydrouracil.*

There are two likely reaction mechanisms. Pathway A would begin with homolytic cleavage between the carbonyl group (position 4) and the ureido nitrogen

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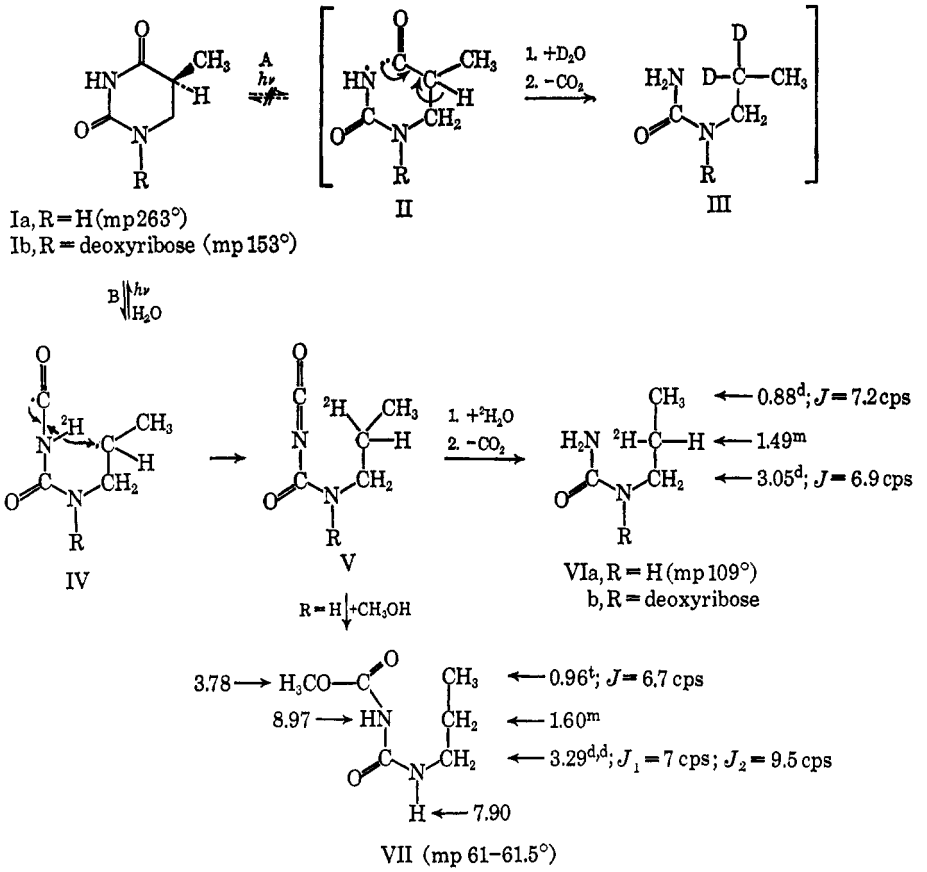
(2) A. Wacker, *Progr. Nucleic Acid Res.*, **1**, 369 (1963).
(3) R. B. Setlow and W. L. Carrier, *J. Mol. Biol.*, **17**, 237 (1966).
(4) T. Yamane, B. J. Wyluda, and R. G. Shulman, *Proc. Natl. Acad. Sci. U. S.*, **58**, 439 (1967).
(5) G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910).
(6) *Cf.* G. Quinkert, *Angew. Chem.*, **77**, 229 (1965).
(7) Y. Kondo and B. Witkop, *J. Am. Chem. Soc.*, **90**, 764 (1968). The chemical evidence for the *S* configuration of the asymmetric center at C-4 of 1-dihydrothymidine has been supplemented and confirmed by a complete X-ray structure analysis (I. L. Karle, Naval Research Laboratory). There is evidence that *exposure to radiation by X-ray leads to partial conversion of dihydrothymidine to thymidine*, and probably of dihydrothymine [*cf.* S. Furberg and L. H. Jensen, *ibid.*, **90**, 470 (1968)] to thymine.



(position 3) to yield, *via* the diradical II, an intermediate ketene, which could add (heavy) water and decarboxylate to III, containing *two atoms of deuterium*. The alternative (pathway B) would start with fission between C-4 and C-5 to give, *via* the diradical IV and intramolecular transfer of $^2H\cdot$, the isocyanate V which would add water with spontaneous decarboxylation to the *monodeuterated n*-propylurea VIa.

When the photolysis of dihydrothymine was carried out in D_2O, the nmr spectrum of *n*-propylurea in D_2O clearly showed the *presence of one deuterium* in support of structure VIa. Undeuterated VIa shows a characteristic triplet at 3.04 ppm for the methylene group adjacent to nitrogen. Additional evidence came from *photolysis of dihydrothymine in methanol* which trapped the isocyanate intermediate V (R = H) by the formation of the crystalline carbamate VII. *n*-Propylurea (VIa) and its deoxyriboside VIb on prolonged irradiation undergo slow dealkylation to deoxyribosylurea and urea (50% yield after 100 hr).

The sequence I → VI assumes intramolecular transfer of hydrogen (deuterium) from NH (position 2).[8] In accordance with this view 1,3-dimethyl-5,6-dihydrothymine (mp 39.5°), which lacks such transferable hydrogen, is stable to photolysis under identical conditions. The stability of dihydrouridine to photolysis supports the assumption of the diradical IV. The corresponding ethyl radical, expected from the photolysis of uridine, would be considerably less stable than the isopropyl radical IV. Recombination to uridine would be faster than hydrogen transfer. That this intramolecular transfer of hydrogen involves the favorable six-membered transition state IV is in agreement with similar cyclic mechanisms postulated for the Hofmann–Löffler–Freytag[9] or Barton[10] reactions. The photolysis of hydantoin derivatives proceeds in an analogous fashion. The isolation of dimers in certain cases lends further support to radical intermediates.[11]

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(9) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

(10) *Cf.* K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964).

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The Conversion of Dewar Hexamethylbenzene to Pentamethylcyclopentadienylrhodium(III) Chloride

Sir:

We wish to communicate some details of a very novel ring-contraction reaction whereby Dewar hexamethylbenzene (hexamethylbicyclo[2.2.0]hexadiene) (1) is converted to a pentamethylcyclopentadienylrhodium(III) complex. This work was undertaken as part of our investigation of the reactions of Dewar benzenes with transition metals. We have already reported the preparation of Dewar hexamethylbenzenepalladium chloride (dichloro(hexamethylbicyclo[2.2.0]hexadiene)palladium);[1] a number of other workers have also prepared other Dewar benzene–metal complexes. These were all obtained from the Dewar benzene and a suitable metal complex.[2–5]

(1) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).