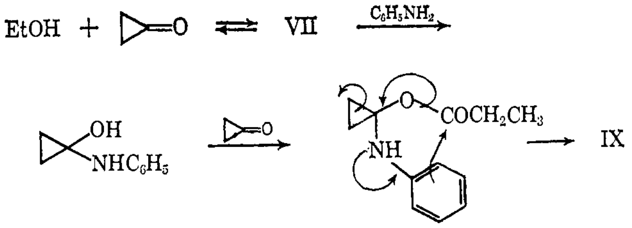
The unusual formation of IX at high temperature may be explained by the following mechanism involving cyclopropanone as an intermediate.[10]



Acknowledgment. This investigation was supported in part by Public Health Service Research Grant GM-07874 from the National Institute of General Medical Sciences.

(10) N,N-Dipropionylaniline or propionanilide failed to give IX under these reaction conditions.

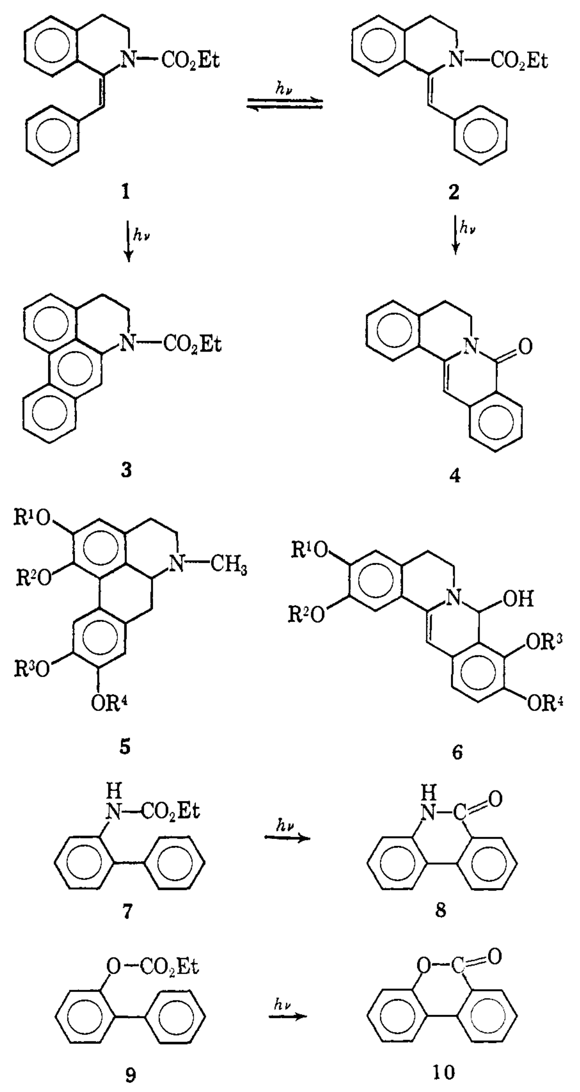
(11) National Institutes of Health Predoctoral Fellow, 1962–1965.

Harry H. Wasserman, Donald C. Clagett[11]
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Received September 20, 1966

Intramolecular Photoacylation of Carbamates and Carbonates[1]

Sir:

In applying photochemical reactions to organic syntheses, we irradiated *cis*-1-benzylidene-2-carbethoxy-1,2,3,4-tetrahydroisoquinoline (**1**). After a rapid *cis–trans* isomerization, the *cis* isomer was converted into a dehydroaporphane (**3**) in 65% yield.[2] Another product was isolated from the reaction mixture by chromatography in 10–21% yield depending on the reaction conditions. The minor product was identified as dehydroprotoberberine (**4**, $C_{17}H_{13}ON$), mp 93–94° (ether–hexane), $\gamma_{\max}$ 6.08, 6.17, 6.26, and 13.05 μ; $\lambda_{\max}$ 233 mμ (log ϵ 4.32), 322 (4.17), 343 (4.08), and 358 (3.90); τ 6.95 (triplet, J = 7 cps, 2 H), 5.62 (triplet, J = 7 cps, 2 H), 3.01 (singlet, 1 H), 2.05–2.83 (multiplet, 7 H), and 1.55 (doublet, J = 9 cps, 1 H). *Anal.* Found: C, 82.47; H, 5.24; N, 5.60; mol wt (mass spectrum), 247.101. It is probable that irradiation of a common intermediate similar to compounds **1** or **2** will give two compounds simultaneously which may be readily converted into an aporphine alkaloid (**5**) and a berberine alkaloid (**6**). The application of this reaction to the synthesis of alkaloids is being investigated.



Dehydroprotoberberine (**4**) may be derived from an intramolecular photoacylation from compound **2**. It has been shown by molecular orbital calculation that there is localization of electron density at the *ortho* positions of stilbene in the excited state.[3] The aromatic system is thus activated in the excited state, and the intramolecular acylation occurs. On the basis of this hypothesis the reaction has been extended to another carbamate and a carbonate. Irradiation of ethyl N-*o*-biphenylylcarbamate (**7**) in methanol with a conventional Hanovia lamp yielded a crystalline residue which exhibited an infrared spectrum virtually identical with that of phenanthridone (**8**).[4] Recrystallization of the residue from ethanol yielded pure phenanthridone in 85% yield, mp 291–292°, and tlc of the mother liquor showed only the presence of phenanthridone contaminated with a small amount of **7**. Under similar conditions, ethyl *o*-biphenylyl carbonate (**9**) was converted into dibenz-α-pyrone (**10**)[5] in 85% yield. The scope and the mechanism of these reactions are being investigated.

---

(1) The authors wish to thank the National Science Foundation and the U. S. Public Health Service for the support of this work. The authors also wish to acknowledge the National Science Foundation and the Louis Block Fund of the University of Chicago for their support in purchasing the MS-9 high-resolution mass spectrometer and the nmr spectrometers used in this work.

(2) N. C. Yang, G. R. Lenz, and A. Shani, *Tetrahedron Letters*, 2941 (1966); see also M. P. Cava, S. C. Havlicek, A. Lindert, and R. J. Spangler, *ibid.*, 2937 (1966).

(3) H. C. Ting, Ph.D. Thesis, University of Chicago, 1965.

(4) Sadtler Standard Spectra, Spectrum No. 21101.

(5) J. D. Brooks, *J. Appl. Chem.*, **5**, 250 (1955).

N. C. Yang, Arnon Shani, G. R. Lenz
Department of Chemistry, University of Chicago
Chicago, Illinois 60637
Received September 30, 1966