fied by vpc and vacuum distillation) contained in 10 mm × 300 mm Pyrex glass irradiation tubes having a neck-down at 150 mm. The tubes were attached to an all-metal vacuum system by means of greaseless O-ring seals. An oil diffusion pump, separated from the manifold by a liquid nitrogen trap, was used to degas the solutions by four freeze–pump–thaw cycles. The tubes were sealed at the neck-down and irradiated in a merry-go-round[7] device. The 366-mμ band from a Hanovia Type A, 550-W, medium-pressure mercury arc was isolated with Corning filters 7380 and 5840. Three irradiation tubes containing potassium ferrioxalate actinometer solutions[8] were irradiated concurrently with the stilbene solutions. The slope of the optical density *vs.* ferrous ion concentration was checked and found to be $1.11 \times 10^4 M^{-1}$. The irradiated stilbene solutions were evaporated to near dryness on a rotary evaporator and redissolved in carbon disulfide for gas chromatographic analysis on a 10 ft × 0.25 in. stainless steel column packed with 10% OV 17 on 60–80 mesh Chromosorb WAWDMCS at 230° using a Varian 1700 flame ionization chromatograph.[9]

The quantum yields are reported in Table I. The discrepancy between our results and those of Hammond and Lamola may lie in a large part in their neglect of the back-reaction,[10] but it is not possible to determine if this is so from their published data. We found ϕ_t to be constant at 0.55 ± 0.02 for *trans*-stilbene concentrations of 10^{-2} *M* or greater and for seven sensitizers with phosphorescence energies greater than 57 kcal.[11] The lack of a concentration effect demonstrates the absence of any self-quenching by *trans*-stilbene which leads preferentially to one isomer. Saltiel[12] also reached the same conclusion based on the lack of concentration dependence of the photostationary state. The value of ϕ_c was found to be 0.42 ± 0.03 for all sensitizers for which it was measured. Thus, the sum of these quantum yields is unity within experimental error and the ratios, ϕ_t/ϕ_c, are in excellent agreement with the photostationary state predictions[4] for high-energy sensitizers.

Table I. Quantum Yields for Sensitized Photoisomerization of *cis*- and *trans*-Stilbene at 25°

Sensitizer	Stilbene, *M*	$\phi_t{}^a$	$\phi_c{}^a$	$\phi_t + \phi_c$	ϕ_t/ϕ_c
Benzophenone[b]	0.2	0.56, 0.55			
4-Methylbenzophenone[b]	0.05	0.57, 0.56			
	0.09		0.41, 0.42	0.98	1.36
α-(4-Ethylbenzoyl)naphthalene[c]	0.05	0.56			
α-(2,4,6-Triethylbenzoyl)naphthalene[c]	0.04	0.57, 0.53 0.56, 0.59	0.39, 0.42		
	0.05	0.56		0.98	1.38
	0.06	0.54			
β-Benzoylnaphthalene[b]	0.02	0.56, 0.55			
	0.09	0.56, 0.54			
	0.05	0.56, 0.56			
	0.008	0.54			
	0.005	0.51			
	0.003	0.53, 0.53			
β-(4-Ethylbenzoyl)naphthalene[c]	0.05	0.58, 0.48 0.52			
	0.04	0.54, 0.49			
β-(2,4,6-Triethylbenzoyl)naphthalene[c]	0.05	0.48			
	0.04	0.55, 0.64 0.59	0.43, 0.45 0.41	1.0	1.31

[a] Quantum yields have been corrected for back-reaction according to ref 10. [b] Eastman Organic Chemicals, recrystallized from ethanol and checked for purity by flame-ionization vpc analysis. [c] Synthesis will be reported in a full paper now in preparation.

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(7) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(8) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

(9) The linearity of the detector response for the sample sizes used was demonstrated by analyzing a sample containing 3.5% *cis*-stilbene and 96.5% *trans*-stilbene over the whole range of sample sizes. Integration of peak areas was performed with the aid of a disk integrator.

(10) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(11) From 77°K emission spectra to be reported in a future paper, and from W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(12) J. Saltiel, *ibid.*, **90**, 6394 (1968).

Howell A. Hammond, D. E. DeMeyer, J. L. R. Williams
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

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Photochemical Addition of Alcohols to an Amidine C=N Bond

Sir:

We wish to report the first examples of photoreduction by alcohols of and photoaddition of alcohols to an amidine C=N bond. We also report the photochemical addition of a methyl group of *t*-butyl alcohol to the same system to form a β-hydroxyalkyl derivative; we believe that this is the first such photoaddition to be observed.

5-Phenyl-7-acetamidofurazano[3,4-*d*]pyrimidine[1] (I) was irradiated (Rayonet reactor, 350-mμ lamps, Pyrex tube, continuous N_2 flow) for 24 hr in anhydrous ethanol. The solution was evaporated to *ca.* 25 ml and chromatographed on Florisil. Elution with chloroform, evaporation of the initial eluate to a small volume, and chilling gave 5-phenyl-7-acetamido-6,7-dihydrofurazano[3,4-*d*]pyrimidine (III; 5% yield, mp 265° dec), identical with an authentic sample prepared by sodium borohydride reduction of I[2] (ir (Nujol) 3300 (N*H*), 1660 cm^{-1} (NHC*O*CH$_3$); nmr (DMSO-d_6) δ 1.77 (3 H, C*H*$_3$CONH), 6.70 (1 H, J_1 = 2 Hz, J_2 = 8 Hz, C$_7$-*H*), 7.44 (3 H, aromatic multiplet), 7.90 (2 H, aromatic multiplet), 9.20 (2 H, broad, two N*H*); uv $\lambda_{\max}^{C_2H_5OH}$ (mμ (log ε)) 242 (4.08), 292 (3.95)). Further elution of the Florisil column with chloroform gave a second colorless crystalline solid which was shown by microanalytical and spectral data to be the 1:1 adduct II (R = CH_3; R′ = H) with one molecule of ethanol of crystallization (85% yield, mp 220–221° dec; nmr (DMSO-d_6) δ 1.17 (3 H, doublet, *J* = 7 Hz, C*H*$_3$CH), 1.79 (3 H, singlet, C*H*$_3$CONH), 4.06 (1 H, diffuse quartet, *J* = 7 Hz, CH$_3$C*H*), 5.35 (2 H, O*H*, deuterium exchangeable), 7.45 (3 H, aromatic multiplet), 7.90 (2 H, aromatic multiplet), 8.47 and 8.63 (each 1 H, broad, CH$_3$CON*H* and N*H*, deuterium exchangeable), 0.9 (3 H, triplet, *J* = 7 Hz), and 4.1 (2 H, multiplet, C*H*$_3$C*H*$_2$OH); ir 3400–3600 (sh, broad), 3150–3400 (broad), 1660 cm^{-1}). The mass spectrum showed a parent peak at *m/e* 301, cor-

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(1) E. C. Taylor, Y. Maki, and G. P. Beardsley, in press.

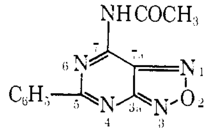
(2) Satisfactory microanalytical results were obtained for all compounds reported.

responding to the molecular weight of the 1:1 adduct. Drying of this "2:1 adduct" for 5 days at 110° *in vacuo* over P_2O_5 resulted in complete loss of one molecule of ethanol to give the 1:1 adduct II ($R = CH_3$; $R' = H$); its nmr spectrum (DMSO-d_6) was identical with that of the "2:1 adduct" except for loss of one of the two OH signals and the ethyl signals at δ 0.9 and 4.1. The uv spectra of the 1:1 adduct and its ethanolate were identical ($\lambda_{\max}^{C_2H_5OH}$ (mμ (log ϵ)) 239 (4.07), 288 (3.94)) and almost superimposable with the spectrum of the 6,7-dihydro compound III.[3]

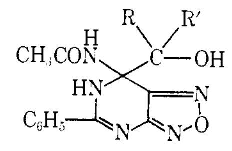
Irradiation of I under similar conditions in 2-propanol gave III (6% yield) and the 1:1 adduct II ($R = R' = CH_3$) (64% yield, mp 190° dec; ir (KBr) 3380 (sh), 3260 (NH and OH), 1655 cm^{-1} (NH*CO*CH$_3$); nmr (DMSO-d_6) δ 1.08, 1.35 (each 3 H, $C(CH_3)_2$),[4] 1.80 (3 H, CH_3CONH), 5.23 (1 H, OH), 7.55 (3 H, aromatic multiplet), 7.94 (2 H, aromatic multiplet), 8.42 and 8.60 (each 1 H, broad, CH_3CONH and NH); uv $\lambda_{\max}^{C_2H_5OH}$ (mμ (log ϵ)) 239 (4.11), 292 (3.96)). Analogously, the 1:1 adduct II ($R = R' = H$) was obtained by irradiation of I under similar conditions in methanol (61% yield, mp 224–225° dec; ir (Nujol) 3460, 3350, 3270 (OH, NH), 1665 cm^{-1} (CH_3CONH); nmr (DMSO-d_6) δ 1.75 (3 H, CH_3CONH), 3.86 (2 H, diffuse doublet, J = 7 Hz, CH_2OH), 5.41 (1 H, OH), 7.58 (3 H, aromatic multiplet), 8.05 (2 H, aromatic multiplet), 8.85 and 9.05 (each 1 H, broad, NH and CH_3CONH).

Finally, prolonged (72 hr) irradiation of I in *t*-butyl alcohol surprisingly gave the 1:1 adduct IV (35% yield, mp 192–193.5° dec; ir (KBr) 3525, 3515, 3420 (sh), 3300 (NH and OH), 1660 cm^{-1} (CH_3CONH); uv $\lambda_{\max}^{C_2H_5OH}$ (mμ (log ϵ)) 239 (4.12), 290 (3.98); nmr (DMSO-d_6) δ 0.95 (6 H, singlet, $C(CH_3)_2$), 2.35 (2 H, multiplet, $CH_2C(OH)(CH_3)_2$), 1.70 (3 H, singlet, CH_3CONH), 4.35 (1 H, broad singlet, OH, deuterium exchangeable), 7.5–7.9 (5 H, aromatic multiplet), 8.6 and 8.9 (each 1 H, broad, CH_3CONH and NH, deuterium exchangeable), in which a methyl group has added across the 6,7-amidine C=N bond.

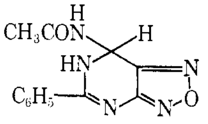
Using as input the precise bond lengths found for 7-aminofurazano[3,4-*d*]pyrimidine,[5] MO calculations were carried out on this system.[6] Of particular interest to the present results are the localization indices, L_r, obtained in this way for the carbon atoms at positions 3a, 5, 7, and 7a (see structure I). The calculated values were found to be 4.07, 3.19, 2.17, and 4.36 β, respectively (*cf.* benzene (2.5) and anthracene (2.0),[7a] styrene (terminal position) (1.7),[7b] and purine, which undergoes photoaddition of alcohols to the 6-position[3] (2.329)[8]). The L_r difference between positions 7 and 5 (1.02 β) represents a relative reactivity difference[7c] to $\cdot CCl_3$ in the neighborhood of 10^{12}; while the 5-phenyl and 7-acetamido groups of I would undoubtedly affect these values to some extent, this overwhelming propensity toward radical reaction at the 7 position correlates extremely well with our observed quantitative attack at position 7 both in photoreduction and photoaddition reactions.



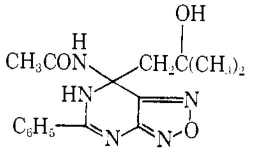
I



II



III



IV

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(3) It has previously been reported that alcohols may be added photochemically to an azomethine (C=N) bond in purine (H. Linschitz and J. S. Connolly, *J. Am. Chem. Soc.*, **90**, 2979 (1968)), quinolines and isoquinolines (F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968); F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968)), pyrimidines and pyrazolo[3,4-*d*]pyrimidines (M. Ochiai and K. Morita, *Tetrahedron Letters*, 2349 (1967); M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968)), and 9,4a-dialkyl-1,2,3,4-tetrahydrocarbazolenium salts (P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **45**, 1992 (1962)) to give α-hydroxyalkyl derivatives, which in some cases are isolable and in others dehydrate to the C-alkyl heterocycle. Addition to an *amidine* C=N bond, however, is unprecedented and unexpected.

(4) Nonequivalence of the two methyl groups is ascribed to restricted rotation about the C_7–C bond; an analogous nonequivalence has been observed in the photoadduct of 2-propanol to purine (Linschitz and Connolly[3]).

(5) We are indebted to Professor Eli Shefter, Department of Pharmaceutics, School of Pharmacy, State University of New York at Buffalo, for the X-ray analysis, details of which will be the subject of a separate paper.

(6) β proportional to S (R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949)), variation of α (A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 135); complete inclusion of overlap (P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950)).

(7) *Cf.* Streitwieser:[6] (a) p 399; (b) p 408; (c) p 399 ff.

(8) B. Pullman, *J. Chem. Soc.*, 1621 (1959).

(9) On leave from the Gifu College of Pharmacy, Gifu, Japan.

(10) National Science Foundation Predoctoral Fellow, 1967–1969.

Edward C. Taylor, Yoshifumi Maki,[9] Ben E. Evans[10]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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The pK_a of Triphenylcyclopropene. Electrochemical Determination of an Inaccessible Equilibrium Constant

Sir:

We have earlier reported[1] kinetic evidence that triphenylcyclopropene is considerably less acidic than is triphenylmethane; no conditions were found in which triphenylcyclopropenyl anion (I) could be demonstrated to be even a transient intermediate. The situation is related to the low kinetic acidities of other cyclopropene derivatives.[2] However, with electrophilic carbonyl, sulfone, and cyano groups[2] the hybrid structure of the anion leaves less of the charge on the three-membered ring; antiaromatic destabilization of the cyclopropenyl anion system should manifest itself even more strongly with only the three electron-accepting phenyl substituents in I. Thus, the pK_a of triphenyl-

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(1) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963).

(2) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967); R. Breslow and M. Douek, *ibid.*, **90**, 2698 (1968); R. Breslow, *Angew. Chem. Intern. Ed. Engl.*, **7**, 565 (1968).