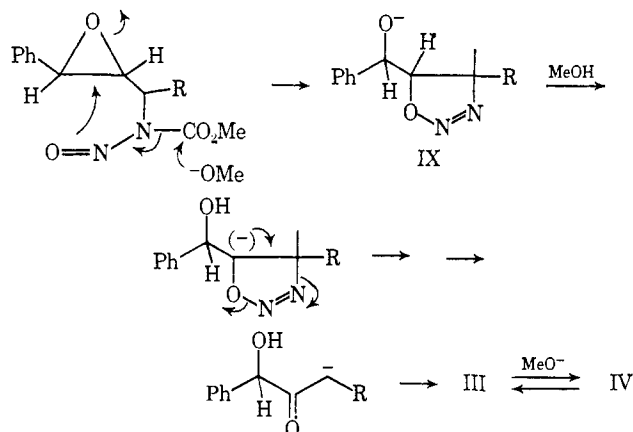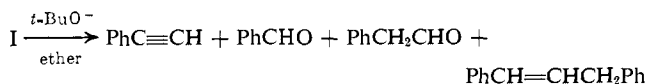philic attack of the diazotate ion on the epoxide ring. Alternatively, the opening of the three-membered ring may be synchronous with attack of the base on the carbonyl carbon. Proton exchange of intermediate IX followed by collapse of the resultant anion and loss of nitrogen could give the enolate anion of ketone III.

Ketone III could then rearrange to give IV. This conversion would depend on the reaction conditions and the manner in which the products were separated from the reaction mixture. Although we have not been successful in obtaining direct evidence for this mechanism,[19] it appears attractive for several reasons. First, it readily accounts for the presence of the hydroxy ketones in an anhydrous methanolic solution. Secondly, it accounts for the negligible quantities of IV when sodium carbonate was used as the base. This is readily attributed to the low rate of enolization of III with a weak base. A third factor that makes this mechanism intuitively attractive is our finding that the reaction follows a different course in an aprotic medium. Thus, treatment of I with potassium t-butoxide in ether resulted in the formation of phenylacetylene, benzaldehyde, phenylacetaldehyde, 1,3-diphenyl-1-propene, and 80% of a carbonate mixture consisting mainly of di-t-

butyl carbonate and methyl t-butyl carbonate. In this case, intermediate IX cannot undergo proton exchange readily and instead fragments to benzaldehyde and phenylacetaldehyde. The latter undergoes self-condensation to give 1,3-diphenyl-1-propene.[20]
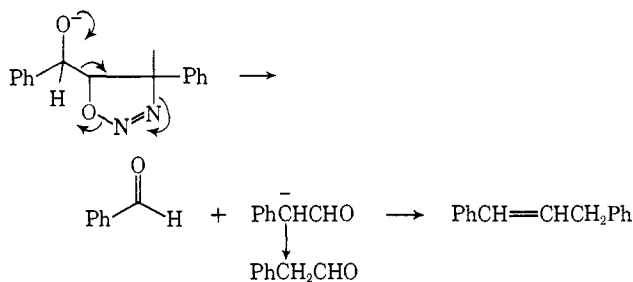
(19) The mechanisms we have presented here prove useful in explaining the products observed and in pointing the way toward new experiments. In no case do we consider these mechanisms as firmly established.

(20) E. K. Raunio and W. A. Bonner, J. Org. Chem., 31, 396 (1966).

Further work on the mechanism of the base- and thermal-induced transformations of epoxy-N-nitrosocarbamates is currently under way and will be the subject of future reports.

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Quantum Yields for the Sensitized Photoisomerization of cis- and trans-Stilbene

Sir:

In continuing our study[1] of photosensitization by polymeric sensitizers, we obtained quantum yields for the sensitized isomerization of cis- and trans-stilbene that were different from those reported by Malkin and Fischer[2] and by Hammond, et al.[3] In his thesis,[4] Valentine has also reported values different from those of the above authors. These numbers are pertinent to the discussion of the mechanism for photoisomerization of the stilbenes in particular and therefore of olefins in general.[2–5] Further, the sensitized isomerization of trans-stilbene has been used as an actinometer for other photochemical studies.[4,6]

Malkin and Fischer[2] reported that at 25° the *trans* to *cis* quantum yield, ϕ_t, and the *cis* to *trans* quantum yield, ϕ_c, for 10^{-4} M methylcyclohexane solutions of stilbene were 0.50 and 0.30, respectively. According to Hammond,[3] ϕ_t and ϕ_c for 0.05 M stilbene sensitized by a high-energy sensitizer, such as benzophenone or 4-methylbenzophenone, were 0.44 ± 0.01 and 0.39 ± 0.01, respectively. The fact that the sum, $\phi_t + \phi_c$, was less than unity was interpreted as an inefficiency in the stilbene photoisomerization. Furthermore, it was reported that as the concentration of trans-stilbene was decreased, ϕ_t increased, becoming about 0.5 at 10^{-4} M. This was taken as evidence that self-quenching by trans-stilbene was the source of some of this inefficiency. On the other hand Valentine[4] reported a quantum yield of 0.55 for the benzophenone-sensitized isomerization of a 0.05 M solution of trans-stilbene. We therefore undertook to measure carefully the quantum yields ϕ_t and ϕ_c for several sensitizers over a wide range of stilbene concentrations, and we report here data that verify the value of ϕ_t obtained by Valentine. Our data also demonstrate the lack of self-quenching by trans-stilbene.

Solutions for irradiation were made by adding 6 ml of Eastman Spectro Grade benzene to weighed amounts of a sensitizer and either Eastman Scintillation Grade trans-stilbene or Aldrich Research Grade cis-stilbene (puri-

(1) R. Searle, J. L. R. Williams, J. C. Doty, D. E. DeMeyer, S. H. Merrill, and T. M. Laakso, *Makromol. Chem.*, 107, 246 (1967).
(2) S. Malkin and E. Fischer, *J. Phys. Chem.*, 68, 1153 (1964).
(3) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964).
(4) D. Valentine, Ph.D. Thesis, California Institute of Technology, 1966.
(5) A. Bylina and Z. Grabowski, *Trans. Faraday Soc.*, 65, 458 (1969).
(6) C. DeBoer, *J. Am. Chem. Soc.*, 91, 1855 (1969).

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

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-Methylbenzo-phenone[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-Triethyl-benzoyl)naphthalene[c]	0.04	0.57, 0.53	0.39, 0.42		
		0.56, 0.59			
	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-Triethyl-benzoyl)naphthalene[c]	0.05	0.48			
	0.04	0.55, 0.64	0.43, 0.45	1.0	1.31
		0.59	0.41		

^{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.

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

(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).

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.

(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).

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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 (NH), 1660 cm^{-1} (NHCOCH₃); nmr (DMSO-d_6) δ 1.77 (3 H, CH_3CONH), 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 NH); 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, CH_3CH), 1.79 (3 H, singlet, CH_3CONH), 4.06 (1 H, diffuse quartet, $J = 7$ Hz, CH_3CH), 5.35 (2 H, OH, deuterium exchangeable), 7.45 (3 H, aromatic multiplet), 7.90 (2 H, aromatic multiplet), 8.47 and 8.63 (each 1 H, broad, CH₃CONH and NH, deuterium exchangeable), 0.9 (3 H, triplet, $J = 7$ Hz), and 4.1 (2 H, multiplet, CH_3CH_2OH); ir 3400–3600 (sh, broad), 3150–3400 (broad), 1660 cm^{-1}). The mass spectrum showed a parent peak at m/e 301, cor-

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

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