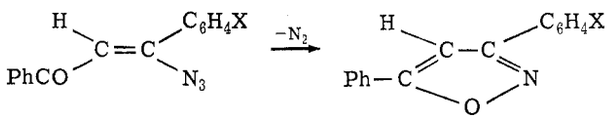
tion from ethyl acetate yielded the isoxazole **11** (mp 169–170°) and the pure azide **1e** (48%, mp 82–84°). The origin of the isoxazole **11** is supposed to be the vinyl azide **10**, which can be deduced from the complex mechanistic scheme of the reaction.[10]



10, X = *m*-NO_2 **11**, X = *m*-NO_2
12, X = *p*-NO_2 **13**, X = *p*-NO_2

α-Azido(p-nitrobenzylidene)acetophenone (**1f**) was similarly prepared from the dibromide of *p*-nitrobenzylideneacetophenone and 2 equiv of sodium azide in DMF at room temperature for 2 hr. After work-up, the azide residue was contaminated with the isoxazole **13** (20% by nmr). The mixture was treated with $CHCl_3$ and cooled to yield **13** (mp 225°). The residual orange oil was finally crystallized from methanol and furnished the pure azide **1f** in 43–55% yield (mp 108°, lit.[11] 112.5°).

β-Azidoacrylonitrile (**1g**).—Acrylonitrile was treated with IN_3 by the method of Hassner, *et al.*,[12] to yield the IN_3 adduct in 68% yield. The product was purified by column chromatography on silica gel ($CHCl_3$) and treated with 2 equiv of sodium azide in DMF at room temperature for 3 days. After work-up in the usual manner, a brown liquid was obtained, composed of *cis*-**1g** (37%, doublets at τ 2.95 and 5.25, J = 7.5 Hz) and *trans*-**1g** (63%, doublets at τ 2.90 and 4.90, J = 14 Hz).

α,α-Bis(azidodibenzal)acetone (**6**).—Compound **5**, prepared from dibenzalacetone (**4**) and bromine in 56% yield, was treated with 4 equiv of sodium azide in dry DMF at 10° for 6 hr. The reaction mixture was worked up in the usual manner and yielded a yellow-brown residue. Recrystallization from MeOH–$CHCl_3$ furnished a yellow, crystalline product (**6**) in 70–80% yield (dec pt 93°), ir (KBr) 2120 and 1625 cm^{-1}. *Anal.* Calcd for $C_{17}H_{12}N_6O$ (316): C, 64.55; H, 3.79; N, 26.58. Found: C, 64.65; H, 3.75; N, 26.40.

General Procedure for the Synthesis of 1-Vinyl-1,2,3-triazoles (**3, 7, and 8**).—Equimolar amounts (0.01 mol) of ylide **2** and azide **1** were treated in 50 ml of CH_2Cl_2 at room temperature to completion (checked by ir). Triazole **3p** precipitated completely and triazole **3o** partially from the solution. To isolate the other triazoles, the solvent was removed and the residue crystallized from methanol (**3c, 3f, 3h, 3k, 3l, 3m, 3n, 3o**) or fractionally crystallized from ether (**3a, 3d, 3i, 3j**) and/or $CHCl_3$–pentane (**7** and **8**). Triazoles **3b, 3e,** and **3g** together with triphenylphosphine oxide were isolated in nearly quantitative yield and a sample of each was purified by column chromatography on silica gel (EtOAc as the eluent). The solid triazoles were recrystallized from the appropriate solvents and analyzed. Their C, H, and N analyses were within 0.3%.

Registry No.—**1e**, 35213-03-7; **1f**, 26087-02-5; *cis*-**1g**, 35213-05-9; *trans*-**1g**, 35213-06-0; **3a**, 35213-07-1; **3b**, 27643-29-4; **3c**, 35225-67-3; **3d**, 35225-68-4; **3e**, 35261-89-3; **3f**, 35225-69-5; **3g**, 27643-30-7; **3h**, 35225-71-9; **3i**, 35261-90-6; **3j**, 35225-72-0; **3k**, 35225-73-1; **3l**, 35225-74-2; **3m**, 35225-75-3; **3n**, 35225-76-4; **3o**, 35225-77-5; **4**, 35225-79-7; **6**, 35225-80-0; **7**, 35225-81-1; **8**, 35261-91-7; **11**, 31609-82-2; **13**, 31108-56-2.

Acknowledgments.—The authors are indebted to Dr. S. Toppet for her advice in the interpretation of the nmr spectra. Thanks are due to the NFWO and to the IWONL for postdoctoral (G. L'a.) and doctoral (P. Y. and G. M.) fellowships.

Photochemistry in the Tetrazole–Azidoazomethine System. A Facile Synthesis of 9*H*-Pyrimido[4,5-*b*]indoles

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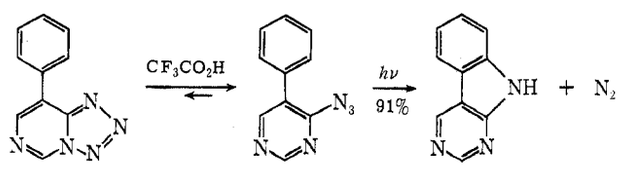
The photolysis of 8-(phenyl)-, 8-(*p*-toluyl)-, 8-(*p*-methoxyphenyl)-, and 8-(*p*-chlorophenyl)tetrazolo[1,5-*c*]-pyrimidines in trifluoroacetic acid produces in high yield the corresponding 7-substituted 9*H*-pyrimido[4,5-*b*]-indoles. Evidence suggests that the reaction arises from acid-catalyzed conversion of the tetrazole to the isomeric azide which subsequently photolyzes to produce the indole derivative. In contrast to the high yield photolyses of the 8-phenyl derivatives in trifluoroacetic acid, photolysis or thermolysis in nonpolar media proceeded slowly and in poorer yield. The quantum yield for photolysis of the 8-phenyl derivative at 300 nm is 0.45, indicative of a reaction of high efficiency.

For several years we have been interested in both the photophysical and photochemical properties associated with 2-substituted biaryl derivatives.[2] The high yield cyclizations of 2-substituted groups to the adjacent aryl ring in biphenyls suggested such processes might be of synthetic utility in heterocyclic biaryl systems. Recently, we noted in a preliminary report that photolysis of 8-phenyltetrazolo[1,5-*c*]pyrimidine, **1a**, in trifluoroacetic acid produced the 9*H*-pyrimido-[4,5-*b*]indole, **3a**, in high yield.[3] In view of the synthetic potential of this method in yielding this heretofore neglected ring system[4] in high yield, we have explored the generality of this method by studying several substituted derivatives. We wish to report here the synthetic expedient of the acid-catalyzed control of the tetrazole–azidoazomethine equilibrium and a general high yield synthesis of 9*H*-pyrimido-[4,5-*b*]indoles.



1a **2a** **3a**

Synthesis.—Limitations in preparative photochemi-

(1) (a) Ohio State University Fellow, 1970–1971; (b) Alfred P. Sloan Foundation Fellow (1970–1972), Camille and Henry Dreyfus Teacher-Scholar Awardee, 1971.

(2) (a) J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967); (b) *ibid.*, 3421 (1968); (c) J. S. Swenton, T. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, **92**, 3103 (1970); (d) J. S. Swenton, T. J. Ikeler, and B. H. Williams, "Excited State Chemistry," J. N. Pitts, Ed., Gordon and Breach, New York, N. Y., 1970, pp 93–106; (e) G. Smyser, M. S. Thesis, The Ohio State University, 1971.

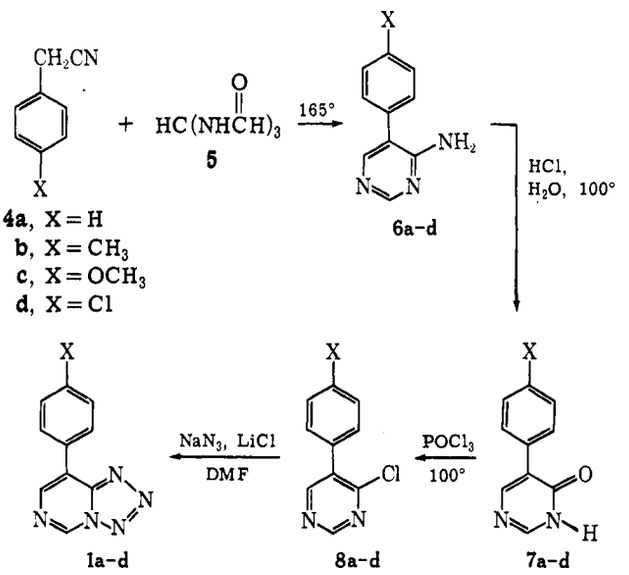
(3) J. A. Hyatt and J. S. Swenton, *J. Heterocycl. Chem.*, **9**, 409 (1972).

(4) Two examples of this ring system have been reported: (a) K. E. Schulte, J. Reisch, and U. Stoess, *Angew. Chem., Int. Ed. Engl.*, **4**, 1081 (1965); (b) R. Gluchkov, V. Volokova, and O. Y. Magidson, *Khim. Farm. Zh.*, **1**, 25 (1967).

cal methods for substituted derivatives of a parent system often arise from two sources. First, the electronic nature of the group can effect the excited state electron distribution and thus markedly alter the reactive properties of the excited state.[2d] Second, the substituent itself may be photochemically labile under the reaction conditions. Thus, a possibility limiting the usefulness of this photolytic method was that, in the highly acidic trifluoroacetic acid, aromatic rings bearing electron-donating groups would be subject to photochemical change.[5] A particular instance is that of a halogen substituent which, while a useful handle for further synthetic manipulation, is often cleaved under photochemical conditions.[6] With these considerations and those of preparative convenience in mind, we selected the *p*-toluyl, *p*-methoxyphenyl, and *p*-chlorophenyl derivatives as models to test the generality of the preparative process.

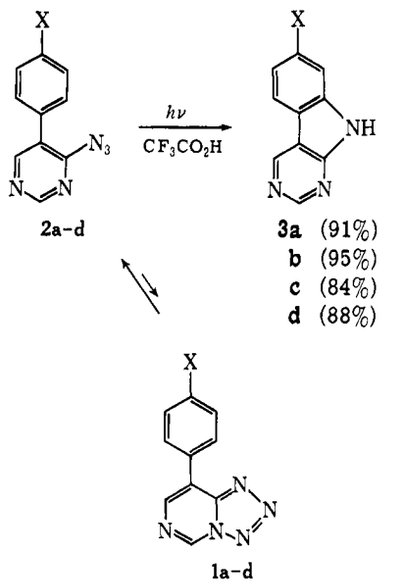
The synthesis of these compounds is outlined in Scheme I. The reaction of tris(formylamino)methane[7] with the substituted phenylacetonitriles according to the procedure of Tsatsaronis and coworkers[8] readily afforded the 4-amino-5-(para-substituted phenyl)-pyrimidines (**6a–d**). Hydrolysis of the aminopyrimidines in concentrated hydrochloric acid[9] gave the 4-pyrimidones (**7a–d**) which were treated with phosphorus oxychloride[9] to yield the 4-chloro derivatives **8a–d**. The reaction of these 4-chloropyrimidines with sodium azide–lithium chloride in *N*,*N*-dimethylformamide gave high yields of products exhibiting the characteristic tetrazole absorption in the ir at *ca.* 9.4 μ.[10] None of the products (**1a–d**) exhibited the characteristic azide absorption at *ca.* 4.7 μ in KBr or neutral solution phase spectra. Thus, spectroscopic data established that compounds **1a–d** exist nearly exclusively in neutral media as the tetrazole tautomer.

SCHEME I



Preparative Photolyses.—While photolyses of the tetrazole **1a** in benzene proceeded slowly to produce the indole **3a** in low yield, photolysis of **1a** in trifluoroacetic acid produced the indole in 91% yield. Likewise, photolyses of **1b–d** in trifluoroacetic acid afforded one product in high yield and purity. The structures of the photoproducts **3a–d** were assigned as the respective 7-substituted 9*H*-pyrimido[4,5-*b*]indoles **10a–d** on the basis of their elemental analyses, ir, nmr, uv, and mass spectral properties. Under our photolysis conditions, products derived from modification of either the methoxy or halogen linkage of **3c** or **3d** were not detected.

To compare the efficiency of the tetrazole photolysis in trifluoroacetic acid with that of the 2-azidobiphenyls, the quantum yield for the parent system was measured at 300 nm. The observed quantum yields for disappearance of **2a** and appearance of **3a** were measured as 0.42 and 0.49, being quite analogous to those recorded for 2-azidobiphenyl itself (Φ = 0.42).[2c] In contrast to the 2-azidobiphenyls which produce from 3 to 16% yields of azo compounds upon direct irradiation, no analogous products were detected in the photolysis of azides **2a–d**.



Thermolyses.—The thermolysis of 2-azidobiaryls is also known to produce carbazoles in high yield from the classic studies of Smith and coworkers.[11] Furthermore, Wentrup and Crow[12] have described the facile formation of 1-cyanoimidazoles **11** upon pyrolysis of certain tetrazolo[1,5-*c*]pyrimidines **9**. To check if the thermal route possessed synthetic advantage over the photochemical process, the thermolysis of **1a** was briefly explored. While **1a** did decompose in refluxing *o*-dichlorobenzene, the indole, **3a** was produced in only

(5) Aromatic photosubstitution is quite facile in numerous systems. For leading references see (a) E. Havinga and M. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); (b) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969).

(6) (a) J. P. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.*, 1267 (1969); (b) L. R. Hamilton and P. J. Kropp, *ibid.*, 1625 (1971); (c) R. A. F. Deeleman, H. C. van der Plas, A. Koudijs, and P. S. Darwinkel-Resseeuw, *ibid.*, 4159 (1971).

(7) H. Bredereck, R. Gompper, H. Rempfer, K. Klemm, and H. Keck, *Chem. Ber.*, **92**, 329 (1959).

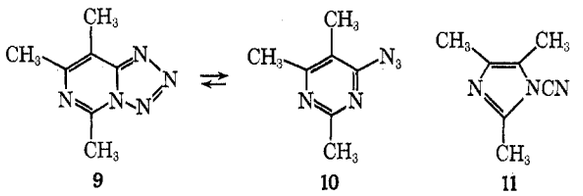
(8) (a) G. Tsatsaronis and F. E. Effenberger, *ibid.*, **94**, 2876 (1961); (b) G. Tsatsaronis and A. Kehayoglow, *J. Org. Chem.*, **35**, 438 (1970).

(9) W. Davies and H. Piggot, *J. Chem. Soc.*, 347 (1945).

(10) E. Lieber, D. Levering, and C. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(11) (a) P. Smith and J. Boyer, *J. Amer. Chem. Soc.*, **73**, 2626 (1951); (b) P. Smith, B. Brown, R. Putney, and P. Reinick, *ibid.*, **75**, 6335 (1953); (c) P. Smith and B. Brown, *ibid.*, **73**, 2438 (1951); (d) P. Smith, J. Clegg, and J. Hall, *J. Org. Chem.*, **23**, 524 (1958).

(12) C. Wentrup and W. Crow, *Tetrahedron*, **26**, 4915 (1970).



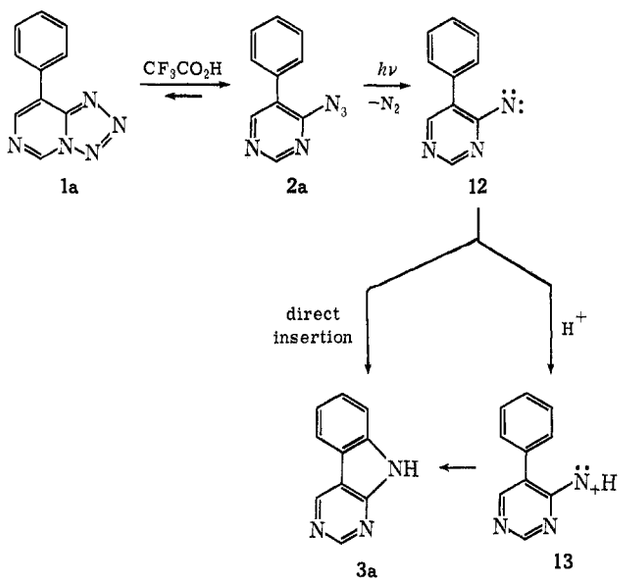
9 10 11

50% yield in addition to an equal quantity of uncharacterized tarry residue. When the tetrazole **1a** was refluxed in trifluoroacetic acid (bp 72°) for 3 hr in the dark only a trace of **11a** was noted by tlc in addition to unreacted starting material. Since thermolysis did not appear synthetically more advantageous than the photochemical route, our studies were terminated at this point.

Discussion

The present study has demonstrated the photolysis of biaryltetrazoles in acid media is a high yield route to the 9*H*-pyrimido[4,5-*b*]indole ring system. The reaction is conveniently viewed as involving a shift of the tetrazole–azidoazomethine equilibrium in the acid media to the azide tautomer and its subsequent photolysis (Scheme II). Such an effect of acid on the

SCHEME II



position of the tetrazole–azidoazomethine equilibrium has been noted previously in several systems.[13] This point was confirmed in our work by noting that the ir spectra of tetrazoles **1a–d** in trifluoroacetic acid showed strong azide absorption at *ca.* 4.5 μ and nearly complete absence of the characteristic tetrazole absorption at 9.4 μ. The identity within experimental error of the quantum yield of **1a** photolysis and that of 2-azidobiphenyl itself (0.48 *vs.* 0.42) strongly suggests that the initial photochemical reaction is loss of nitrogen to produce the corresponding nitrene **12**. This step can be followed by nitrene insertion to produce **3a**. However, in the high acidic trifluoroacetic acid, protonation would result in formation of the nitrenium ion[14] **13**, which would be most reasonably followed by cyclization and proton loss to yield **3a**.[15] While evidence is not available to distinguish between these two possibilities, the total absence of azo compounds from direct photolysis of these pyrimidine systems contrasts with the 3 to 16% yield of azo compounds produced by 2-azidobiphenyls. The latter bimolecular products, which were attributed to the reactions of a triplet nitrene in the biphenyl system, are either not characteristic processes in the heterocyclic series or else not produced due to the highly acidic media. In view of the high yield results obtained in our model systems, the photolysis of related tetrazoles in trifluoroacetic acid promises to be not only of synthetic utility but also a convenient method of studying the reactions of heteroaromatic nitrenes and/or nitrenium ions.

Experimental Section

Melting points were determined in a Thomas-Hoover apparatus and are corrected. Infrared spectra were taken as Nujol mulls on a Perkin-Elmer Model 137 spectrophotometer; only prominent bands are reported. Nmr spectra were obtained on a Varian A-60A instrument in the specified solvent with tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS-9 instrument at an ionizing potential of 70 eV. Ultraviolet spectra were determined in 95% ethanol solution with a Cary Model 14 recording spectrophotometer. All elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, on sublimed samples. All photolyses were performed with a bank of 16 RPR-3000-Å lamps.

8-Phenyltetrazolo[1,5-*c*]pyrimidine, 1a, and 9*H*-pyrimido[4,5-*b*]indole, 3a, have been previously reported.[3]

4-Amino-5-(*p*-toluyl)pyrimidine (6b).—A mixture of 25.0 g (0.18 mol) of *p*-methylbenzyl cyanide, 53.0 g (0.36 mol) of tris(formamino)methane, 3.0 g of *p*-toluenesulfonic acid, and 35 ml of formamide was heated at 170–180° for 10 hr. The cooled reaction mixture was acidified with 10% hydrochloric acid, diluted with 50 ml of water, and treated with decolorizing charcoal. The clarified solution was basified with 10% sodium hydroxide solution and the precipitated product chromatographed on 300 g of Florisil (5% methanol in chloroform as eluent). Recrystallization of this material from benzene yielded 13.0 g (39%) of white crystalline product: mp 166.5–167.0°; ir 2.97, 3.12, and 6.12 μ; nmr ($CDCl_3$) δ 8.50 (s, 1 H), 8.10 (s, 1 H), 7.25 (s, 4 H), 5.42 (br s, 2 H), and 2.38 (s, 3 H).

Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.18; H, 5.92; N, 22.82.

5-(*p*-Toluyl)pyrimidone-4 (7b).—A solution of 10.0 g (0.054 m) of 4-amino-5-(*p*-toluyl)pyrimidine, **6b**, in 35 ml of concentrated hydrochloric acid was heated at 70–90° for 10 hr in a rapid stream of hydrogen chloride. The precipitated hydrochloride salt of product was filtered off, the filtrate yielding 3.0 g of unreacted starting amine. The crude hydrochloride was slurried in 35 ml of water, 30% aqueous sodium hydroxide added until solution was effected, and the solution diluted with 50 ml of water. Saturation of this solution with carbon dioxide yielded the crude product which was recrystallized from methanol to yield 6.0 g (86%) of **7b**: mp 191.5–192.5°; ir 6.05 μ; nmr ($CDCl_3$) δ 11.1 (br s, 1 H), 8.16 (s, 1 H), 8.09 (s, 1 H), 7.4 (center of AB quartet, J = 8.5 Hz, 4 H), and 2.42 (s, 3 H).

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.02; H, 5.53; N, 15.06.

4-Chloro-5-(*p*-toluyl)pyrimidine (8b).—A mixture of 5.0 g (0.026 mol) of **7b** and 15 ml of freshly distilled phosphorus oxychloride was refluxed for 0.75 hr. After removal of excess phosphorus oxychloride *in vacuo*, the resulting oily residue was treated with 200 ml of ice water. The precipitated solid was collected and recrystallized from *n*-hexane to yield 3.75 g (71%) of white crystalline material: mp 78.5–79.5°; ir 6.55, 12.32, 13.03, 13.18,

(13) (a) C. Temple, R. McKee, and J. Montgomery, *J. Org. Chem.*, **30**, 829 (1965); (b) N. Smirnova, I. Postovskii, N. Vereshchagina, and I. Ludina, *Chem. Heterocycl. Compounds (USSR)*, **4**, 130 (1971) (English translation); (c) C. Wentrup, *Tetrahedron*, **26**, 4969 (1970).

(14) For a review see P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(15) A similar proposal has been advanced to account for the products involving nucleophilic aromatic substitution from deoxygenation of nitrosobenzene in triethyl phosphite containing acetic acid: R. J. Sundberg, R. H. Smith, and J. E. Bloor, *J. Amer. Chem. Soc.*, **91**, 3392 (1969).

14.00, and 14.60 μ; nmr ($CDCl_3$) δ 8.94 (s, 1 H), 8.64 (s, 1 H), 7.32 (s, 4 H), and 2.42 (s, 3 H).

Anal. Calcd for $C_{11}H_9N_2Cl$: C, 64.56; H, 4.48; N, 13.60; Cl, 17.32. Found: C, 64.85; H, 4.85; N, 13.20; Cl, 17.38.

8-(*p*-Toluyl)tetrazolo[1,5-*c*]pyrimidine (1b).—A solution of 3.50 g (0.017 mol) of **8b**, 1.10 g (0.017 mol) of sodium azide, and 0.71 g (0.017 mol) of lithium chloride in 25 ml of *N*,*N*-dimethylformamide was stirred for 8 hr at RT. The reaction mixture was then poured into 300 ml of ice water and the resulting light yellow solid recrystallized from ethanol to afford 3.53 g (98%) of pure product: mp 125–126.5°; ir 6.24 and 9.35 μ; nmr ($CDCl_3$) δ 9.59 (s, 1 H), 8.50 (s, 1 H), 7.76 (center of AB quartet, J = 7.5 Hz, 4 H), and 2.43, (s, 3 H).

Anal. Calcd for $C_{11}H_9N_5$: C, 62.53 H, 4.30; N, 33.18. Found: C, 62.47; H, 4.26; N, 33.37.

7-Methyl-9*H*-pyrimido[4,5-*b*]indole (3b).—A solution of 0.50 g (0.024 mol) of **1b** in 50 ml of trifluoroacetic acid was irradiated through Pyrex for 2 hr and the trifluoroacetic acid removed *in vacuo*. The residue was diluted with 50 ml of water and made basic with 10% sodium hydroxide, and the aqueous layer extracted with ether (6 × 30 ml). Removal of the ether from the sodium sulfate dried organic phase yielded a solid product which was recrystallized from benzene–ethanol to yield 0.42 g (95%) of white solid: mp 228.5–230.5°; ir 6.18, 6.24, 10.12, 12.41, and 13.35 μ; nmr (DMSO-d_6) δ 12.1 (br s, 1 H), 9.36 (s, 1 H), 8.90 (s, 1 H), 8.11 (d, J = 8 Hz, 1 H), 7.23 (m, 2 H), and 2.47 (s, 3 H).

Anal. Calcd for $C_{11}H_9N_3$: C, 72.10; H, 4.95; N, 22.95. Found: 72.02; H, 4.97; N, 22.72.

4-Amino-5-(*p*-methoxyphenyl)pyrimidine (6c).—A mixture of 30 g (0.20 mol) of *p*-methoxyphenylacetonitrile, 58 g (0.40 mol) of tris(formamino)methane, 3 g of *p*-toluenesulfonic acid, and 35 ml of formamide was reacted in a manner analogous to that of **6b**. Recrystallization of the crude material from benzene yielded 20.2 g (51%) of **6c**: mp 165.5–167.5°; ir 2.98, 3.10, and 6.12 μ; nmr ($CDCl_3$) δ 8.46 (s, 1 H), 8.07 (s, 1 H), 7.12 (center of AB quartet, J = 9 Hz, 4 H), 5.39 (br s, 2 H), and 3.78 (s, 3 H).

Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.74; H, 5.27; N, 20.71.

5-(*p*-Methoxyphenyl)pyrimidone-4 (7c). In a manner analogous to that of **7b** a solution of 9.0 g (0.045 mol) of **6c** in 35 ml of concentrated hydrochloric acid was treated with dry hydrogen chloride at 80–90° for 12 hr. Work-up of the reaction yielded 2.1 g of recovered starting material in addition to the pyrimidone. Recrystallization of the product from methanol yielded 5.82 g (83%) of **7c**: mp 205.5–206.5°; ir 6.02, 8.05, and 9.75 μ; nmr (DMSO d_6) δ 12.5 (br s, 1 H), 8.11 (br s, 2 H), 7.43 (center of AB quartet, J = 8.5 Hz, 4 H), and 3.79 (s, 3 H).

Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34 H, 4.98; N, 13.85. Found: C, 65.21; H, 4.96; N, 13.83.

4-Chloro-5-(*p*-methoxyphenyl)pyrimidine (8c).—A mixture of 9.0 g (0.045 mol) of **7c** and 20 ml of phosphorus oxychloride was refluxed for 1 hr and the excess phosphorus oxychloride removed *in vacuo*. Treatment of the residual oil with ice water yielded a crude yellow solid which was recrystallized from *n*-hexane to give 5.62 g (57%) of product: mp 95.5–96.5°; ir 6.21, 8.05, and 13.10 μ; nmr ($CDCl_3$) δ 8.86 (s, 1 H), 8.56 (s, 1 H), 7.16 (center of AB quartet, J = 8.5 Hz, 4 H), and 3.78 (s, 3 H).

Anal. Calcd for $C_{11}H_9N_2OCl$: C, 59.88; H, 4.11; N, 12.69; Cl, 16.07. Found: C, 60.03; H, 4.22; N, 12.68; Cl, 16.25.

8-*p*-(Methoxyphenyl)tetrazolo[1,5-*c*]pyrimidine (1c).—A solution of 4.50 g (0.020 mol) of **8c**, 1.70 g (0.025 mol) of sodium azide, and 1.10 g (0.025 mol) of lithium chloride in 35 ml of *N*,*N*-dimethylformamide was stirred for 8.5 hr at room temperature. Work-up as previously described followed by recrystallization of the crude product from ethanol yielded 4.35 g (95%) of **1c**: mp 146.5–147.5°; ir 6.23, 8.05, and 9.31 μ; nmr ($CDCl_3$) δ 9.56 (s, 1 H), 8.48 (s, 1 H), 7.60 (center of AB quartet, J = 8.5 Hz, 4 H), and 3.85 (s, 3 H).

Anal. Calcd for $C_{11}H_9N_5O$: C, 58.14; H, 3.99; N, 30.82. Found: C, 57.84; H, 4.02; N, 30.48.

7-Methoxy-9*H*-pyrimido[4,5-*b*]indole (3c).—Photolysis of 0.50 g (0.0023 mol) of **1c** in 50 ml of trifluoroacetic acid for 1.75 hr followed by work-up as usual yielded **3c** as a yellow crystalline product. Sublimation of this material *in vacuo* followed by recrystallization from benzene yielded 0.36 g (84%) of white crystalline **3c**: mp 238.5–239.5°; ir 6.16 and 7.92 μ; nmr (DMSO-d_6) δ 12.15 (br s, 1 H), 9.32 (s, 1 H), 8.90 (s, 1 H), 8.12 (d, J = 8.0 Hz, 1 H), 7.04 (m, 2 H), and 3.88 (s, 3 H).

Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.14; H, 4.68; N, 20.91.

4-Amino-5-(*p*-chlorophenyl)pyrimidine (6d).—A mixture of 30.4 g (0.20 mol) of *p*-chlorophenylacetonitrile, 57.0 g (0.40 mol) of tris(formamino)methane, 3.5 g of *p*-toluenesulfonic acid, and 35 ml of formamide was stirred at 155–160° for 11 hr. Work-up of the reaction as for **6b**, followed by recrystallization of the crude material from ethanol, yielded 28.2 g (68%) of the pyrimidine as light tan product, mp 205.5–206.5°. Sublimation followed by recrystallization from ethanol yielded the analytical sample: mp 207.5–208.5°; ir 2.95, 3.10, and 6.04 μ; nmr (DMSO-d_6) δ 8.31 (s, 1 H), 7.96 (s, 1 H), 7.43 (s, 4 H), and 6.67 (br s, 2 H).

Anal. Calcd for $C_{10}H_8N_3Cl$: C, 58.41; H, 3.92; N, 20.43; Cl, 17.24. Found: C, 58.39; H, 3.88; N, 20.80; Cl, 17.58.

5-(*p*-Chlorophenyl)pyrimidone-4 (7d).—A solution of 15.0 g of **6d** in 50 ml of concentrated hydrochloric acid was heated at 80–90° for 12 hr in a stream of hydrogen chloride gas. After work-up in the usual manner there was obtained 4.2 g of unreacted amine in addition to product. Recrystallization of the crude product from methanol yielded 10.2 g (94%) of white crystalline material: mp 254.5–256.5°; ir 6.03, 7.30, and 8.02 μ; nmr (DMSO-d_6) δ 8.61 (br s, 1 H), 8.20 (d, J = 2 Hz, 2 H), 7.63 (center of AB quartet, and J = 9 Hz, 4 H).

Anal. Calcd for $C_{10}H_7N_2OCl$: C, 58.13; H, 3.42; N, 13.55. Found: C, 57.73; H, 3.73; N, 13.46.

4-Chloro-5-(*p*-chlorophenyl)pyrimidine (8d).—A mixture of 5.0 g (0.024 mol) of **7d** and 20 ml of phosphorus oxychloride was refluxed for 0.75 hr. Work-up as for **8b** gave after recrystallization from hexane 5.10 g (94%) of faintly yellow crystalline product: mp 111.5–113.5°; ir 6.57, 9.20, 10.08, and 13.92 μ; nmr ($CDCl_3$) δ 9.0 (s, 1 H), 8.67 (s, 1 H), 7.45 (s, 4 H).

While colorless material could be obtained by sublimation which was homogeneous by tlc under several sets of conditions, acceptable combustion analytical data (±0.3%) could not be obtained. Even column chromatographed material did not yield acceptable analyses. The data given below comprise the average of three determinations.

Anal. Calcd for $C_{10}H_6N_2Cl_2$: C, 53.37; H, 2.69; N, 12.45; exact mass, 223.9908. Found: C, 53.95; H, 2.86; N, 12.12; exact mass, 223.9905.

8-(*p*-Chlorophenyl)tetrazolo[1,5-*c*]pyrimidine (1d).—A solution of 4.50 g (0.020 mol) of **8d**, 1.60 g (0.025 mol) of sodium azide, and 1.05 g (0.025 mol) of lithium chloride in 75 ml of *N*,*N*-dimethylformamide was stirred at room temperature for 14 hr. The usual work-up followed by recrystallization of the crude product from ethanol gave 4.12 g (89%) of yellow crystalline material: mp 149.5–151.5°; ir 6.22, 9.32, 11.31, and 12.03 μ; nmr ($CDCl_3$) δ 9.64 (s, 1 H), 8.56 (s, 1 H), and 7.83 (center of AB quartet, J = 9 Hz, 4 H).

Anal. Calcd for $C_{10}H_6N_5Cl$: C, 51.85; H, 2.61; N, 30.23; Cl, 15.30. Found: C, 51.87; H, 2.80; N, 30.44; Cl, 15.60.

7-Chloro-9*H*-pyrimido[4,5-*b*]indole (3d).—Photolysis of 0.50 g (0.002 mol) of **1d** in 50 ml of trifluoroacetic acid for 3.0 hr followed by the usual work-up, continuous ether extraction of the basic aqueous suspension, and recrystallization of the crude product from methanol gave 0.39 g (88%) of white crystalline product: mp 287.5–289.5°; ir 8.02, 8.25, 10.09, 11.00, 11.51, and 12.42 μ; nmr (DMSO-d_6) δ 9.39 (s, 1 H), 8.90 (s, 1 H), 8.20 (d, J = 8.0 Hz, 1 H), and 7.33 (m, 2 H).

Anal. Calcd for $C_{10}H_6N_3Cl$: C, 58.98; H, 2.97; N, 20.64; Cl, 17.41. Found: C, 58.80; H, 3.02; N, 20.76; Cl, 17.43.

Thermolysis of 8-Phenyltetrazolo[1,5-*c*]pyrimidine (1a).—A solution of 0.5 g of **1a** in 50 ml of *o*-dichlorobenzene was refluxed until all the tetrazole had disappeared (8.0 hr). Removal of the solvent from the orange colored reaction mixture followed by recrystallization of the residue from benzene yielded 0.22 g (50%) of 9*H*-pyrimido[4,5-*b*]indole as identified by mp and ir comparison with known material. Thermolysis of the tetrazole in refluxing trifluoroacetic acid for 3 hr in the dark yielded recovered starting material.

Quantum Yield Determination for the Photolysis of 8-Phenyltetrazolo[1,5-*c*]pyrimidine (1a).—The quantum yield determinations for the photolysis of **1a** were measured using a cylindrical photolysis cell containing two compartments, each 2 cm in diameter and having a 5-cm optical path. The cell was constructed from 2-cm Pyrex tubing and had quartz faces and a quartz divider separating the two compartments. The light source was a Bausch and Lomb high intensity grating monochromator set at 3000 Å. Quantum yield measurements were performed as pre-

viously described on 5×10^{-3} *M* solutions of **1a** in trifluoroacetic acid. Typical light intensities were on the order of 2.4×10^{-6} einsteins/15 ml min.[16] The product analysis was by uv at 261.5 nm while that for loss of starting material was measured at 295.0 nm; an isosbestic point was observed at 280.0 nm. The quantum yield measurements were independent of conversion between 0.25 and 7.0% giving average quantum yields of $\Phi_{2a} = 0.42 \pm 0.10$ and $\Phi_{3a} = 0.49 \pm 0.05$.

(16) Potassium ferrioxolate actinometry was employed: C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., London*, **235**, 518 (1956).

Registry No.—**1a**, 35202-17-6; **1b**, 35202-18-7; **1c**, 35202-19-8; **1d**, 35202-20-1; **3b**, 35202-21-2; **3c**, 35340-32-0; **3d**, 35202-22-3; **6b**, 35202-23-4; **6c**, 35202-24-5; **6d**, 35202-25-6; **7b**, 35202-26-7; **7c**, 35202-27-8; **7d**, 35202-28-9; **8b**, 35202-29-0; **8c**, 35202-30-3; **8d**, 33258-76-3.

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Alkali-Induced Reactions of *N*-Nitrosooxazolidones and *N*-Nitrosoacetylamino Alcohols Containing Cyclopropyl Groups[1]

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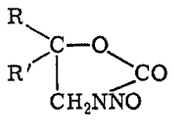
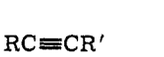
The reactions of 5-cyclopropyl-5-phenyl-3-nitrosooxazolidone (**6**), 5,5-dicyclopropyl-3-nitrosooxazolidone (**7**), and 5-cyclopropyl-5-methyl-3-nitrosooxazolidone (**8**) under alkaline conditions are described. When methanolic solutions of **6** are treated with aqueous hydroxide, about 90% yields of cyclopropylphenylacetylene (**9a**) are obtained. On similar treatment, **7** yields about 52% dicyclopropylacetylene (**9b**) together with about 21% 2,2-dicyclopropylvinyl methyl ether (**10b**), and **8** yields only 16% cyclopropylmethylacetylene (**9c**) together with about 64% a nearly 1:1 mixture of the *Z* and *E* forms of 2-cyclopropyl-1-propenyl methyl ether (**10c**). When a cyclohexene solution of **6** is added to a suspension of lithium ethoxide in cyclohexene, an 84% yield of **9a** is obtained. On similar treatment, **7** yields 64% **9b** and about 13% 7-(dicyclopropylmethylene)bicyclo[4.1.0]-heptane (**5b**), while **8** yields about 26% **9c** and 44% 7-(2-cyclopropylpropylidene)bicyclo[4.1.0]heptane (**5c**). Mechanisms which involve unsaturated carbonium ions and unsaturated carbenes are advanced to explain the results. Treatment of a cyclohexene–pentane solution (containing a small amount of Aliquat, a long chain quaternary ammonium chloride) of 2-(*N*-nitrosoacetylamino)-1,1-dicyclopropylethanol (**17**) with 50% sodium hydroxide afforded a 64% yield of **5b**. Similar treatments of 1-(*N*-nitrosoacetylamino)-2-cyclopropyl-2-propanol (**18**) yielded 52% **5c**.

The reactions of 5,5-disubstituted-3-nitrosooxazolidones (**1**) with bases in polar media have been studied.[3a] When one or both R groups are phenyl, acetylenes (**2**) are formed. When alkyl groups are involved, disubstituted aldehydes (**3**) and/or rearranged ketones (**4**) are formed. If the reactions are carried out in cyclohexene with lithium ethoxide, substituted ethylidenecyclopropanes (**5**) are produced.[3b]



1



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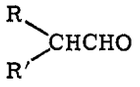

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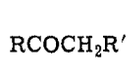

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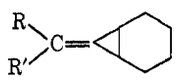
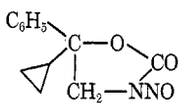


5b, R = R′ = Δ
c, R = Δ; R′ = CH_3

The present work was undertaken to find out how compounds such as **1** with cyclopropyl groups would behave under similar conditions. Cyclopropyl groups were chosen because they are between aryl groups and alkyl groups[4] in their tendency to participate in reactions involving cationic intermediates. Accordingly, 5-cyclopropyl-5-phenyl-3-nitrosooxazolidone (**6**), 5,5-dicyclopropyl-3-nitrosooxazolidone (**7**), and 5-cyclopropyl-5-methyl-3-nitrosooxazolidine (**8**) were prepared by procedures similar to those described,[3] and were treated with bases under the two different sets of reaction conditions discussed below.



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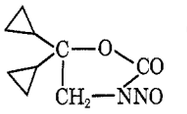
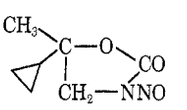
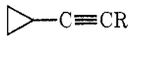


7

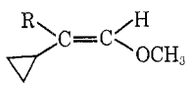


8

I. Treatment with Methanolic Potassium Hydroxide.—When methanolic solutions of the nitrosooxazolidones at room temperature were treated with methanolic potassium hydroxide, vigorous reactions occurred to yield mainly cyclopropylphenylacetylene (**9a**) from **6**, dicyclopropylacetylene (**9b**), and 2,2-dicyclopropylvinyl methyl ether (**10b**) from **7**, and cyclopropylmethylacetylene (**9c**) and both isomers of 2-cyclopropyl-1-propenyl methyl ether (**10c**) from **8**. The results are listed in Table I.



9a, R = C_6H_5
b, R = Δ
c, R = CH_3



10b, R = Δ
c, R = CH_3

These results seem best explained by assuming that the intermediate (A), similar to one previously postulated,[3b] undergoes a trans elimination *via* rotamers B and C to yield the isomeric intermediates D and E as shown in Scheme I. Each of these can give rise to

(1) This work was supported largely by Grant G-12445X from the National Science Foundation.

(2) This work was taken from the Ph.D. thesis presented by S. Gromelski to The Ohio State University, 1971.

(3) (a) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951); (b) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969).

(4) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **92**, 5270 (1970).