TABLE III

10-ARYLIMINO-2-ALKYLTHIO-s-TRIAZOLO[1,5-b]ISOQUINOLIN-5(10H)-ONES (17) AND 5,10-DIHYDRO-2-ALKYLTHIO-s-TRIAZOLO-[1,5-b]ISOQUINOLINE-5,10-DIONES (18)

Compd	R	Ar	Solvent of crystn[a]	Mp, °C	Yield, %[b]
17a	CH_3	$C_6H_4N(CH_3)_2$-p	A	218	62
17b	C_2H_5	C_6H_5	A	175	67
17c	C_2H_5	$C_6H_4N(CH_3)_2$-p	A	205	64
17d	$CH_2C_6H_5$	$C_6H_4N(CH_3)_2$-p	A	162	59
18a	CH_3		B	255	72
18b	C_2H_5		B	188	68
18c	$CH_2C_6H_5$		B	194	61

[a] A, benzene; B, acetic acid. [b] Satisfactory analytical data (±0.4%) were reported for all compounds: **17a**, **17c**, **18a** (C, H, S); all others, S only.

Reaction of 1b with Nitrosobenzene.—A mixture of 1 g of **1b**, 0.5 g of nitrosobenzene, and 20 ml of ethanol was refluxed for 1 hr. The reaction mixture was left to cool whereas a bluish white precipitate was formed. The precipitate was collected and crystallized from benzene to give 1 g of **17b**, mp 175°.

Reaction of 17a with Phenylhydrazine.—A suspension of 1.2 g of **17a** and 0.4 g of phenylhydrazine was refluxed in 30 ml of ethanol for 3 hr. The orange crystals formed were collected, washed with little ethanol, and recrystallized from nitrobenzene to give 0.7 g (63%) of **6a**, mp and mmp 238°.

5,10-Dihydro-2-alkylthio-s-triazolo[1,5-b]isoquinoline-5,10-diones (18).—A solution of 2 g of **17** in 20 ml of acetic acid was treated with 5 ml of concentrated hydrochloric acid (the blue color of the solution turned brown). The solution was poured into cold water and the precipitate formed was collected, washed with water, and crystallized from the proper solvent to give **18** (see Table III): ir of **18a**, 1735 (CO), 1720 cm^{-1} (CO amide).

Reaction of 18a with Phenylhydrazine.—A suspension of 1.2 g of **18a** and 0.6 g of phenylhydrazine was refluxed in 30 ml of ethanol for 3 hr. The product obtained was collected, washed with little ethanol, and crystallized from nitrobenzene to give 1.2 g (72%) of **6a**, mp and mmp 238°.

10-o-Aminophenylimino-2-methylthio-s-triazolo[1,5-b]isoquinolin-5(10H)-one (17e).—A mixture of 0.6 g of **18a** and 0.3 g of o-phenylenediamine was refluxed in 20 ml of acetic acid for 15 min. The product was collected and crystallized from dimethylformamide to give 0.7 g (85%) of **17e**, mp 275°.

Anal. Calcd for $C_{17}H_{13}N_5OS$: C, 60.87; H, 3.91; S, 9.56. Found: C, 60.90; H, 4.20; S, 9.45.

5,10-Dihydro-2-methylthio-5-oxo-s-triazolo[1,5-b]isoquinoline-10-carboxaldehyde (19).—To a solution of 3 ml of phosphorus oxychloride in 10 ml of dimethylformamide was added 4 g of finely powdered **1a**. The reaction mixture was heated on a water bath for 6 hr, left to cool, and treated with ~50 ml of cold 10% NaOH solution. The solid that separated was filtered off, washed with water, and crystallized from ethanol to give 3.1 g (70%) of yellow crystals of **19**, mp 280°. When this compound was left for some time, its yellow color turned to green; thus it was identified as its derivatives.

The phenylhydrazone of **19** was prepared by heating **19** with phenylhydrazine in boiling ethanol for 10 min. The yellow solid that separated was filtered off and crystallized from acetic acid, mp 245°.

Anal. Calcd for $C_{18}H_{15}N_5OS$: C, 61.87; H, 4.32; N, 20.05. Found: C, 61.59; H, 4.48; N, 20.37.

The semicarbazone was similarly prepared. It was crystallized from dimethylformamide, mp 260°.

Anal. Calcd for $C_{13}H_{12}N_6O_2S$; C, 49.36; H, 3.83; S, 10.14. Found: C, 49.60; H, 4.10; S, 10.20.

Registry No.—**1a**, 35146-79-3; **1b**, 35146-80-6; **1c**, 35146-81-7; **5**, 35146-82-8; **5** phenylhydrazide, 35146-83-9; **6a**, 35146-84-0; **6b**, 35146-85-1; **6c**, 35146-86-2; **6d**, 35146-87-3; **6e**, 35146-88-4; **6f**, 35146-89-5; **6g**, 35146-90-8; **6h**, 35146-91-9; **6i**, 35146-92-0; **6j**, 35146-93-1; **6k**, 35146-94-2; **6l**, 35146-95-3; **11a**, 35191-68-5; **11b**, 35191-69-6; **11c**, 35191-70-9; **11d**, 35191-71-0; **11e**, 35211-91-7; **11f**, 35191-72-1; **11g**, 35191-73-2; **11h**, 35191-74-3; **11i**, 35191-75-4; **13a**, 35146-96-4; **13b**, 35146-97-5; **14**, 35146-98-6; **15**, 35146-99-7; **16**, 35147-00-3; **17a**, 35147-01-4; **17b**, 35147-02-5; **17c**, 35147-03-6; **17d**, 35147-04-7; **17e**, 35147-05-8; **18a**, 35147-06-9; **18b**, 35147-07-0; **18c**, 35147-08-1; **19**, 35147-09-2; **19** phenylhydrazone, 35147-10-5; **19** semicarbazone, 35147-11-6.

Acknowledgment.—The authors wish to thank Dr. A. S. Shawali of the same department for his help with the spectral data.

Reactions of Vinyl Azides with α-Keto Phosphorus Ylides. Synthesis of N^1-Vinyltriazoles

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The reaction of vinyl azides (**1**) with α-ketophosphoranes (**2**) provides a convenient synthesis of 1-vinyl-1,2,3-triazoles (**3**). No reaction of the ylide with the C=C and/or C=O function occurred at room temperature, as was inferred by nmr analysis of the crude reaction products. An nmr criterion is described to eluciate the stereochemistry of the trisubstituted olefinic N-1 substituents of the adducts. This criterion is further used to determine unambiguously the stereochemistry of the first bis(vinyl azide), **6**, prepared from dibenzalacetone (**4**).

Recently, two methods have been developed for the synthesis of N^1-vinyltriazoles. The first method involves the condensation of active methylene compounds with vinyl azides under basic conditions.[1] This method is applicable to simple vinyl azides,[2] but fails when α-azidovinyl ketones are used as substrates. Only tarry materials are then produced. The second method consists of reacting vinyl azides with acetylenic compounds[3] by the well-known 1,3-dipolar cycloaddition process.[4] In most cases, however, the method suffers from the disadvantage of producing the two possible regioisomeric[5] triazoles. In the present paper,

(1) G. L'abbé and A. Hassner, *J. Heterocycl. Chem.*, **7**, 361 (1970); G. L'abbé, *Ind. Chim. Belge*, **36**, 3 (1971).

(2) G. L'abbé and A. Hassner, *Angew. Chem.*, **83**, 103 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 98 (1971).

(3) G. L'abbé, J. E. Galle, and A. Hassner, *Tetrahedron Lett.*, 303 (1970); G. L'abbé and A. Hassner, *Bull. Soc. Chim. Belg.*, **80**, 209 (1971).

(4) R. Huisgen, *Angew. Chem.*, **75**, 741 (1963); *Angew. Chem. Int. Ed. Engl.*, **2**, 633 (1963); *J. Org. Chem.*, **33**, 2291 (1968); G. L'abbé, *Chem. Rev.*, **69**, 345 (1969).

(5) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

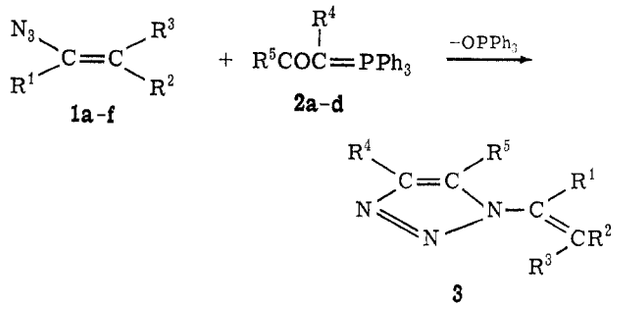
TABLE I

SYNTHESIS OF N^1-VINYLTRIAZOLES

Ylide 2	Vinyl azide 1	Reaction time at room temperature	Vinyltriazole 3 R¹	R²	R³	R⁴	R⁵	No.	Isolated yield, %	Mp, °C
2a	1a	1 month	Ph	H	H	Me	Me	3a	54	76–77
2b	1a	3 weeks	Ph	H	H	H	Me	3b	*a*	Orange liquid
2b	1b	0.5 hr	H	PhCO	H	H	Me	3c	98	142–142.5
2b	1c	4.5 months	PhCO	H	Me	H	Me	3d	20	109–110
2b	1d	1 month	PhCO	H	Ph	H	Me	3e	*a*	Red oil
2b	1e	30 days	PhCO	H	*m*-$NO_2C_6H_4$	H	Me	3f	75	162–163
2c	1a	3.5 months	Ph	H	H	H	Ph	3g	*a*	Orange oil
2c	1b	1.5 hr	H	PhCO	H	H	Ph	3h	95	132–133
2c	1c	4.5 months	PhCO	H	Me	H	Ph	3i	15	103.5–104.5
2c	1d	2 months	PhCO	H	Ph	H	Ph	3j	44	109–111
2c	1f	8 days	PhCO	H	*p*-$NO_2C_6H_4$	H	Ph	3k	63	161–162
2d	1b	1 day	H	PhCO	H	H	*p*-$NO_2C_6H_4$	3l	96	174.5–175.5
2d	1d	7.5 months	PhCO	H	Ph	H	*p*-$NO_2C_6H_4$	3m	60	78–79
2d	1f	8 days	PhCO	H	*p*-$NO_2C_6H_4$	H	*p*-$NO_2C_6H_4$	3n	64	89–90
2d	1e	47 days	PhCO	H	*m*-$NO_2C_6H_4$	H	*m*-$NO_2C_6H_4$	3o	64	62–65, 158–160[b]

[a] A sample of the pure triazole has been isolated by column chromatography on silica gel (EtOAc). [b] This triazole seems to exist in two different crystalline forms with different melting points and different ir (KBr) spectra. The ir spectra in DMSO solution, as well as the nmr spectra, are the same.

a third and regiospecific method is described for the synthesis of N^1-vinyltriazoles (**3**), based on the reactions of vinyl azides (**1**) with α-ketophosphoranes (**2**).



1a-f + **2a-d** $\xrightarrow{-OPPh_3}$ **3**

1a, R^1 = Ph; $R^2 = R^3$ = H
b, $R^1 = R^3$ = H; R^2 = PhCO
c, R^1 = PhCO; R^2 = H; R^3 = Me
d, R^1 = PhCO; R^2 = H; R^3 = Ph
e, R^1 = PhCO; R^2 = H; R^3 = *m*-$NO_2C_6H_4$
f, R^1 = PhCO; R^2 = H; R^3 = *p*-$NO_2C_6H_4$

2a, $R^4 = R^5$ = Me
b, R^4 = H; R^5 = Me
c, R^4 = H; R^5 = Ph
d, R^4 = H; R^5 = *p*-$NO_2C_6H_4$

In the formal sense, four different pathways can be envisaged for the reactions of α-ketophosphoranes with the vinyl azides studied in this work: *i.e.*, reaction of the ylide with (1) the azide function,[6] (2) the C=C bond,[7] (3) the β-carbon atom of β-azidovinyl ketones (β-ketovinylation[8] followed by transylidation[7]), and (4) the C=O bond of azidovinyl ketones (Wittig reaction[9]).

To determine the reaction course, equimolar amounts of the two reagents were allowed to react in dichloromethane at room temperature to completion. The mixtures were then analyzed by nmr. In all but two cases (namely with vinyl azide **1c**) the nmr spectra indicated the formation of vinyltriazoles (**3**) exclusively. With α-azidoethylideneacetophenone (**1c**), decomposition of the azide to untractable tars (*ca.* 15%) under the basic conditions competed with triazole formation. The results are summarized in Table I (optimalization of the yields was not attempted).

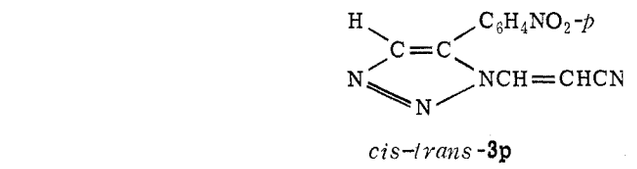
All isolated products exhibited analytical and spectral data in accordance with the assigned structures. The regiochemistry of this reaction has been well established[6] and is further substantiated in this work by the isolation of the known triazoles **3b** and **3g**.

The stereochemistry about the olefinic C=C bond, however, was considered in more detail, since cis–trans isomerization might have occurred under the basic reaction conditions.[10] That this is not the case was evident from the nmr spectra. The 100-MHz spectra of compounds **3c** (C_6D_6) and **3l** ($CDCl_3$) showed two doublets in the aromatic region ($\tau \sim 2$), characteristic of an AB system with a coupling constant of 14 Hz (*trans*-vinyl hydrogens, ir 950 cm^{-1}). We were also able to elucidate by nmr ($CDCl_3$) the configuration of the other disubstituted vinyltriazoles (trisubstituted olefins). Indeed, the methyl protons of the R^3 substituent in compounds **3d** (τ 8.18) and **3i** (τ 8.12) were shielded by ~0.15 ppm relative to the parent olefin (τ 8.00). This effect is attributed to the ring current of the triazole group in cis position to the methyl substituent. An even more pronounced effect was observed for the *o*-phenyl protons of R^3 in compounds **3e**, **3j**, and **3m**, which absorbed in the region τ 3.0–3.4 (multiplet). The corresponding ortho protons in *trans*-chalcone resonated at τ 2.4–2.8. The absorption patterns of the other examples in Table I were much more complex, but detailed analysis with a 100-MHz instrument pointed to the same conclusion.

The absence of isomerization was also indicated by the reaction of β-azidoacrylonitrile (**1g**) with *p*-nitrobenzoylmethylenetriphenylphosphorane (**2d**). The synthetic method used to prepare **1g** furnished a cis–

(6) G. R. Harvey, *J. Org. Chem.*, **31**, 1587 (1966); P. Ykman, G. L'abbé, and G. Smets, *Tetrahedron*, **27**, 845, 5623 (1971).
(7) H. J. Bestmann and R. Zimmerman, *Fortschr. Chem. Forsch.*, **20**, 1 (1971).
(8) M. I. Rybinskaya, A. N. Nesmeyanov, and N. K. Kochetkov, *Usp. Khim.*, **38**, 961 (1969); *Russ. Chem. Rev.*, **38**, 433 (1969).
(9) A. W. Johnson, "Ylid Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1966, p 132.
(10) A. Hassner, G. L'abbé, and M. J. Miller, *J. Amer. Chem. Soc.*, **93**, 981 (1971).

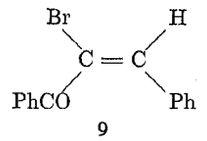
trans mixture in a ratio of 37:63 (see Experimental Section). When this mixture was allowed to react to completion with the ylide, the two geometrical vinyltriazoles (**3p**) were obtained in the same cis–trans ratio (quantitative yield). Structure assignment of the isomeric vinyltriazoles **3p** was based on the coupling constants of the olefinic protons, being 9.5 (cis) and 14 Hz (trans).



cis-trans-**3p**

The nmr criterion described above can now be used to determine the stereochemistry of the first bis(vinyl azide), **6**, prepared in this laboratory. The synthetic method consists of treating **5** (the bromine adduct of **4**) with 4 equiv of sodium azide in dimethylformamide at room temperature (Scheme I). The mechanism of step **5** → **6** is described elsewhere for mono-α-azidovinyl ketones,[10] and the stereochemistry of **6** is deduced from the nmr spectra ($CDCl_3$) of the triazole adducts **7** and **8**. The latter were obtained by reaction of **6** with 1 equiv of benzoylmethylenetriphenylphosphorane (**2c**) at room temperature. Compounds **7** and **8** exhibited an upfield shift for the *o*-phenyl protons in β position with respect to the triazole group, thus indicating their stereochemistry. Similarly, when **6** was treated with 2 equiv of *p*-nitrobenzoylmethylenetriphenylphosphorane (**2d**) to completion (2 months at room temperature), the corresponding yellow bistriazole (70%, mp 265–267°) showed an upfield multiplet absorption at τ 2.85–3.00 (DMSO-d_6 at 80°) for the ortho hydrogen atoms under discussion.

A comparison of the phenyl absorption patterns of compounds **4** and **6** showed a downfield shift of the ortho hydrogen atoms in the case of **6**. This has been attributed by Hemetsberger, Knittel, and Weidmann[11] to the anisotropic effect of the vinylic azide function in the cis position. As noticed elsewhere,[10] this criterion should be used with caution since the same effect has been found for olefin **9** which has the phenyl group in cis position to the C=O function. However, it is worthwhile to note here that the deshielding effect

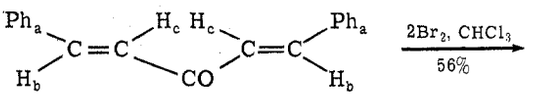


9

seems to be a general phenomenon of cis-β-arylvinyl azides, whereas it only occurs in exceptional cases with *cis*-β-arylvinyl ketones, depending on the spacial position of the C=O group.

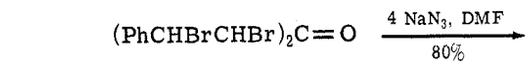
(11) H. Hemetsberger, D. Knittel, and H. Weidmann, *Monatsh. Chem.*, **100**, 1599 (1969).

SCHEME I



4

τ_a = 2.3–2.8 (m, 10 H)
τ_b = 2.25 (br d, 2 H, J = 16 Hz)
τ_c = 2.9 (d, 2 H, J = 16 Hz)



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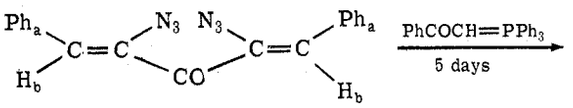
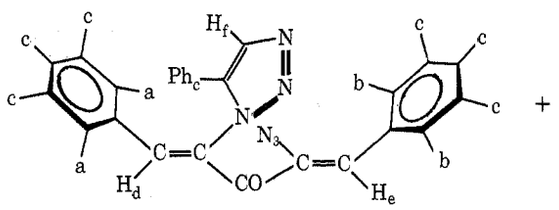


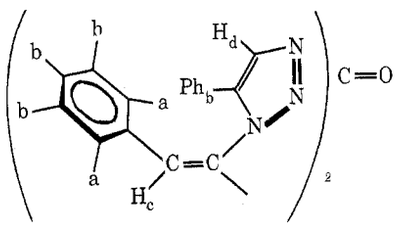
6

τ_a = 2.05–2.35 (m, 4 ortho H), 2.5–2.75 (m, 6 meta and para H)
τ_b = 3.38 (s, 2 H)



7 (49%, yellow, mp 138° dec)

τ_a = 2.9–3.1 (m, 2 H)
τ_b = 2.1–2.4 (m, 2 H)
τ_c = 2.5–2.9 (m, 11 H)
τ_d = 2.20 (br s, 1 H)
τ_e = 3.63 (s, 1 H)
τ_f = 2.10 (s, 1 H)



8 (10%, white, mp 103–105°)

τ_a = 3.15–3.45 (m, 4 H)
τ_b = 2.6–3.0 (m, 16 H)
τ_c = 2.32 (br s, 2 H)
τ_d = 2.15 (s, 2 H)

Experimental Section

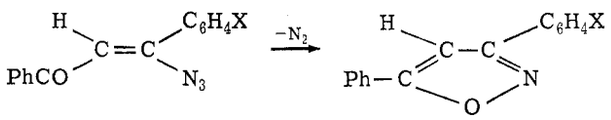
α-Styryl azide (**1a**),[12] *trans*-phenyl β-azidovinyl ketone (**1b**),[13] α-azidoethylideneacetophenone (**1c**),[10] and α-azidochalcone (**1d**),[10] were prepared as reported.

α-Azido-(*m*-nitrobenzylidene)acetophenone (**1e**) was prepared by reaction of the dibromide of *m*-nitrobenzylideneacetophenone (0.1 mol) with 2 equiv of sodium azide in dry DMF (200 ml) at room temperature for 5 hr. The solution was then poured into a mixture of water–chloroform, and the chloroform layer washed several times with water and dried ($MgSO_4$). After the solvent was removed *in vacuo*, a yellow residue was obtained, composed of **1e** and **11** (25% by nmr). Fractional crystalliza-

(12) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

(13) A. N. Nesmeyanov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, **170**, 600 (1966); *Proc. Acad Sci. USSR*, **170**, 916 (1966).

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.

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

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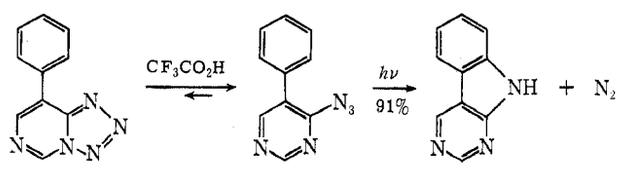
The photolysis of 8-(phenyl)-, 8-(*p*-toluyl)-, 8-(*p*-methoxyphenyl)-, and 8-(*p*-chlorophenyl)tetrazolo[1,5-*c*]-pyrimidines in trifluoroacetic acid produces in high yield the corresponding 7-substituted 9*H*-pyrimido[4,5-*b*]-indoles. Evidence suggests that the reaction arises from acid-catalyzed 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-

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