0.76 (2 s, 1 total, H_1 or H_8 in nitrogen ring, depending on isomeric form).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.97; N, 6.39. Found: C, 87.76; H, 5.98; N, 6.30.

The picrate after two recrystallizations from 95% ethanol melted at 190–192° (reported[12] for 4-benzylisoquinolinium picrate, 195–196°).

Anal. Calcd for $C_{22}H_{16}N_4O_7$: C, 58.93; H, 3.60; N, 12.50. Found: C, 58.62; H, 3.47; N, 12.17.

Small quantities of two other picrates were also isolated when the crude benzal dihydroisoquinoline was treated with picric acid and the salts were fractionally crystallized. One melted at 229–230° (dec) after recrystallization from ethanol; on admixture with isoquinoline picrate, the melting point was 200–210°.

Anal. Calcd for $C_{22}H_{14}N_4O_7$: C, 59.19; H, 3.16; N, 12.55. Found: C, 59.44; H, 3.22; N, 12.49, 12.47.

A hydrobromide prepared from this picrate decomposed at 308–312° after recrystallization from absolute ethanol; its elemental analyses, like that of the picrate, also suggested a lower hydrogen content than that demanded by a salt of **3** or **4**.

Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; Br, 26.80; N, 4.70. Found: C, 64.57; H, 4.04; Br, 26.63; N, 4.59.

The free base from the bromide partially melted, then resolidified at 157–159°, and finally remelted at 225–230°. The base peak (*m/e*) in the mass spectrum was 217; a small peak at 218 (M + 1) was present but there were no peaks at *m/e* 434–436 (coupled products). Fragments of mass 91 (benzyl) and M − 91 were not present.

The other picrate after recrystallization from acetonitrile decomposed at 266–267°; admixture with the picrate of dibenzal tetrahydrobiisoquinoline, mp 268–269° (see above), depressed the melting point to 245–250°. The ir spectra of these two compounds also differed. Perhaps this compound is the picrate of 4,4′-dibenzyl-1,1′-biisoquinoline, but it was not investigated further.

Anal. Calcd for $C_{44}H_{30}N_8O_{14}$: C, 59.06; H, 3.38; N, 12.52. Found: C, 58.95; H, 3.28; N, 12.49.

5,5′-Dinitro-1,1′-biisoquinolin eand 5-Nitro-1,1′-biisoquinoline. —1,1′-Biisoquinoline (8.7 g; 0.039 mol) was nitrated by the procedure of Le Fèvre and Le Fèvre[13] for making 5-nitroisoquinoline. The dried crude product (12.2 g) was dissolved in 2 l. of boiling xylene, filtered from 1.49 of inorganic salts, and chilled to 0°; 8.6 g (72.9%) of dinitro compound was recovered, decomposing at 265–270° after turning black at 250°. A portion was recrystallized from dimethylformamide as pinkish white, feathery needles, melting at 293–294° dec if plunged into a bath preheated to 290°. If heated from room temperature, the compound turned black at 265°, then decomposed at 270–280°: τ ($CF_3COCF_3 \cdot 1.6D_2O$) 2.37 (d, 2, H_7, H_8), 1.25 (m, 1, H_6), 1.05 (s, 2, H_3, H_4).

Anal. Calcd for $C_{18}H_{10}N_4O_4$: C, 62.43; H, 2.94; N, 16.18. Found: C, 62.76; H, 2.82; N, 15.78, 15.87.

Evaporation of the xylene left 2.2 g (20.6%) of solid which was recrystallized from 95% ethanol, mp 186–187° dec. The analyses and nmr are consistent with those required for **5-nitro-1,1′-biisoquinoline:** τ ($CF_3COCF_3 \cdot 1.6D_2O$) 2.65–1.79 (m, 6, H_7, $H_{7'}$, H_8, $H_{8'}$, $H_{5'}$, $H_{6'}$), 1.68–1.44 (m, 3, H_6, $H_{3'}$, $H_{4'}$), 1.28 (s, 2, H_3, H_4).

Anal. Calcd for $C_{18}H_{11}N_3O_2$: N, 13.95. Found: N, 14.04.

Registry No.—**1a,** 25080-52-8; **1b,** 25055-08-7; **2a,** 35202-34-7; **2b,** 35202-35-8; **3**, 35202-36-9; **3** picrate, 35249-61-7; **4,** 35202-37-0; **4** picrate, 35202-38-1; **5a,** 35202-39-2; **5a** picrate, 35202-40-5; **5b,** 35202-41-6; **5b** dihydrochloride, 35202-42-7; **5b** picrate, 35202-43-8; 4-bromoisoquinoline, 1532-97-4; 4-bromiisoquinolinum nitrate, 35202-45-0; 3,3′-biisoquinoline, 35202-46-1; 4,6-dinitroisoquinoline, 35202-47-2; 5-nitroisoquinoline, 607-32-9; 4,4′-dibenzyl-1,1′-biisoquinoline picrate, 35202-49-4.

Acknowledgment.—The assistance of Dr. R. L. Atkins in elucidating the structure of 4,6-dinitroisoquinoline is appreciated.

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[13] C. G. La Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1470 (1935).

Synthesis and Reactions of 2-Alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-ones

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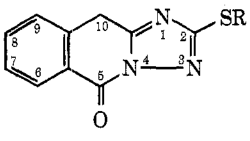
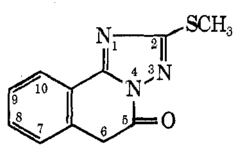
Homophthalic anhydride reacted with *S*-alkylisothiosemicarbazides to give 2-alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-ones (**1**). Compounds **1** coupled with diazonium salts to give the 10-arylhydrazones of 5,10-dihydro-2-alkylthio-*s*-thiazolo[1,5-*b*]isoquinoline-5,10-diones (**6**) and condensed with aromatic aldehydes to form the 10-arylmethylene derivatives **11**. Compounds **1** also condensed with nitroso compounds to yield the 10-arylimino derivatives **17**, which on hydrolysis afforded 5,10-dihydro-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinoline-5,10-diones (**18**). Formylation of **1a** gave 5,10-dihydro-2-methylthio-5-oxo-*s*-triazolo[1,5-*b*]isoquinoline-10-carboxaldehyde (**19**).

During investigation of the condensation reactions of homophthalic anhydride to obtain fused isoquinolines, we found that homophthalic anhydride reacts with *S*-methylisothiosemicarbazide in refluxing dimethylformamide to give a product which can be formulated as either 2-methylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10H)-one (**1a**) or the isomeric compound, 2-methylthio-*s*-triazolo[5,1-*a*]isoquinolin-5(6*H*)-one (**2**). The 2-ethylthio (**1b**) and 2-benzylthio (**1c**) analogs were similarly prepared.



1a, $R = CH_3$
b, $R = C_2H_5$
c, $R = CH_2C_6H_5$



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The available data are compatible with the linear structure **1**, rather than the angular structure **2**. Homophthalic anhydride has been reported to react with hydrazine to yield *N*-aminohomophthalimide,[1] and to condense with *o*-phenylenediamine to give mainly the linear product **3** and not **4**.[2–5]

The ir spectrum of **1a** shows carbonyl absorption at 1720 cm^{-1}. For a comparison between the ir spectra

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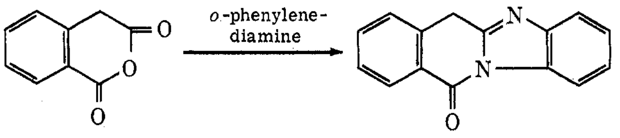
[1] G. Rosen and F. D. Popp, *J. Heterocycl. Chem.*, **6**, 9 (1969).

[2] A. Bistrzycki and K. Fassler, *Helv. Chim. Acta*, **6**, 519 (1923).

[3] M. F. Sartori, A. Oken, and H. E. Schroeder, *J. Org. Chem.*, **31**, 1498 (1966).

[4] E. Schefczik, *Justus Liebigs Ann. Chem.*, **729**, 83 (1969).

[5] A. Mustafa, M. I. Ali, and A. A. El-Sayed, *ibid.*, **739**, 68 (1970).



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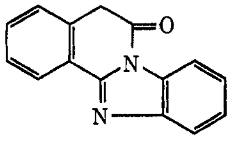
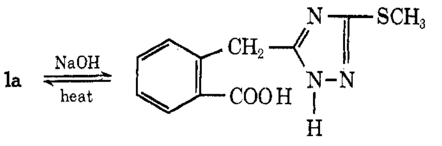


4

of **1a** and those of its coupling product **6a** and its benzylidene derivative **11a**; see below.

The nmr spectrum (TFA) of **1a** shows a methyl group (s) at δ 2.90 ppm and a methylene group (s) at 5.10. Three of the aromatic protons appear as a multiplet centered at δ 7.25 and the fourth appears as a multiplet centered at 8.0. The methylene signal disappeared when the spectrum was taken in DMSO-d_6 plus D_2O.

Compound **1a** undergoes ring opening in aqueous sodium hydroxide to give 3-*o*-carboxybenzyl-5-methylthio-1,2,4-triazole (**5**), which can be isolated on acidification. When **5** is heated above its melting point or in boiling dimethylformamide, it reverts to the original compound **1a**.



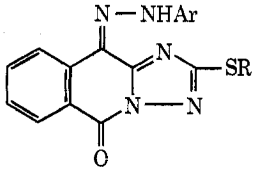
5

Compound **5** also has been obtained when the reaction between homophthalic anhydride and *S*-methylisothiosemicarbazide was carried out in dimethylformamide at room temperature for several days.

The pyridone ring in **1a** also was opened by the action of phenylhydrazine to give the phenylhydrazide of **5**.

Compounds **1** coupled with aryldiazonium salts in pyridine to yield the corresponding 10-arylazo derivatives, more properly represented as 5,10-dihydro-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinoline-5,10-dione 10-arylhydrazones (**6a–l**) (see Table I, Experimental Section). Unlike azo compounds obtained from diazonium salts coupled with aliphatic carbon atoms, which absorb strongly at ~280 nm, the uv spectrum of **6a** shows an absorption maximum at 446 nm; similar hydrazones are known to exhibit strong absorption at wavelengths higher than 320 nm.[6]

The ir spectral data provide further evidence that the starting compound has the linear structure **1a**. Thus the phenylhydrazone **6a** shows carbonyl absorption at 1720 cm^{-1}, almost with no shift from that of the starting compound **1a**. If this phenylhydrazone derivative has formula **7** (derived from the angular structure **2**), it would reveal a large downward shift in the frequency of the CO group, due to the conjugation of the C=O with C=N and the strong chelation that would be expected to occur between the hydrazone H and the CO group.[6] On the other hand, the linear formula **6a** affords structural environment for the CO group which is similar to that of the starting material **1a**. The relation between CO absorption in **1a** and **6a** is substantiated by the absence of any significant shift in the CO absorption in **3** and its phenylhydrazone derivative **8**.[5] On the other hand, the ir spectra of the angular compound **4** and its phenylhydrazone derivative **9**[5] reveal a considerable downward shift in the CO absorption.



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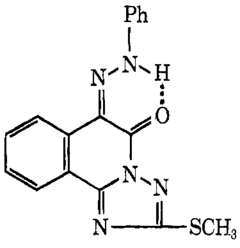

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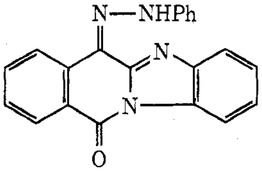

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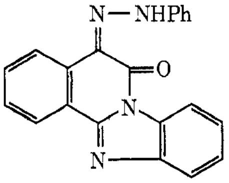

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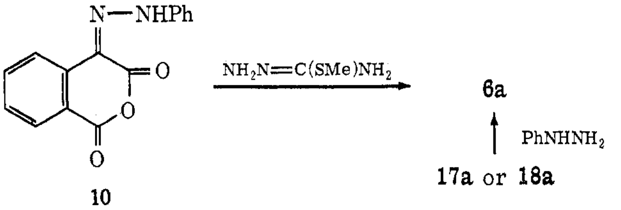
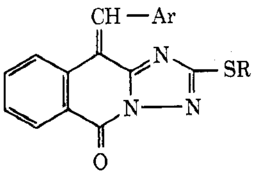
ν_{CO} of **8**, 1693 cm^{-1} ν_{CO} of **9**, 1642 cm^{-1}
ν_{CO} of **3**, 1684 cm^{-1} ν_{CO} of **4**, 1705 cm^{-1}

The phenylhydrazone **6a** also has been prepared by heating the phenylazo derivative, **10**,[7] of homophthalic anhydride with *S*-methylisothiosemicarbazide.



10

Compounds **1** condensed with aromatic aldehydes, in refluxing acetic acid in the presence of anhydrous sodium acetate, to give 10-arylmethylene-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-ones (**11a–j**) (see Table II, Experimental Section). The ir spectrum of the benzylidene derivative **11a** shows carbonyl absorption near 1717 cm^{-1}, similar to that of the starting compound **1a**. Again, if the starting material has the angular structure **2**, the CO group of its benzylidene derivatives **12** will be conjugated with C=C double bond, a combination which is known to lower the stretching frequency of the CO group.[8] The absence



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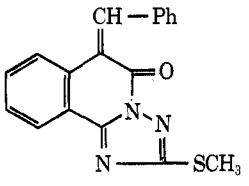
[6] H. C. Yao and P. Resnick, *J. Amer. Chem. Soc.*, **84**, 3514 (1962).

[7] W. Dieckmann and W. Meiser, *Chem. Ber.*, **41**, 3253 (1908).

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen Ltd., London, 1957, p 136.



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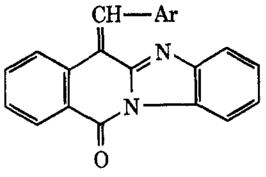
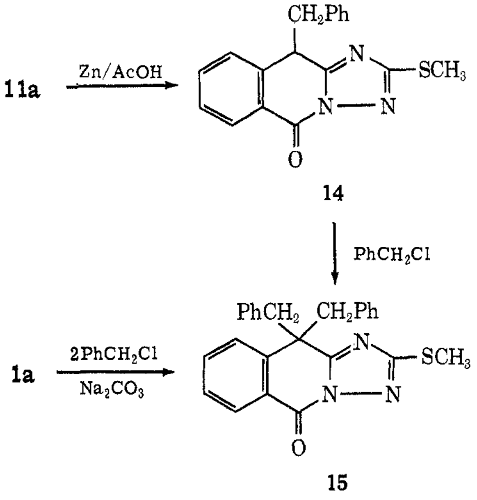
of such a shift in the ir spectrum of **11a** is in favor of the linear structure **1a**.

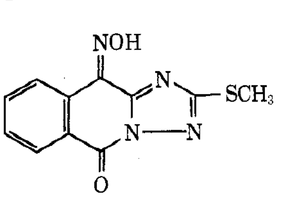
In a similar manner, we have prepared the arylmethylene derivatives **13a** and **13b**, from **3** and *p*-chloro- and *p*-nitrobenzaldehyde, respectively.



13a, Ar = C_6H_4Cl-*p*
b, Ar = $C_6H_4NO_2$-*p*

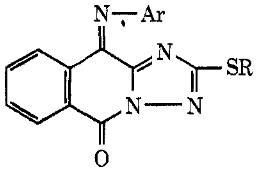
The benzylidene derivative **11a** is reduced by zinc dust and acetic acid (or by thiophenol at 140°) to form 10-benzyl-2-methylthio-*s*-triazolo[1,5-*b*]-isoquinolin-5(10*H*)-one (**14**). Reaction of the latter with benzyl chloride in presence of sodium carbonate yielded the 10,10-dibenzyl derivative **15**. The latter compound was also obtained from the reaction of **1a** with an excess of benzyl chloride. Compound **1a** underwent nitrosation at the methylene group on treatment with nitrous acid to give the oximino derivative **16**.





16

Compounds **1** reacted with nitroso compounds to yield 10-arylimino-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5-(10*H*)-ones (**17a–d**) (see Table III, Experimental Section), which were hydrolyzed by a hydrochloric-acetic mixture to give the diketo compounds 5,10-dihydro-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinoline-5,10-diones (**18**).



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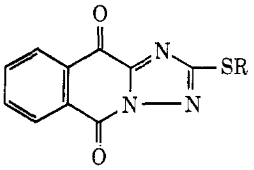
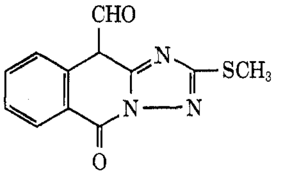


18

Compounds **17a** and **18a** reacted with phenylhydrazine to form the phenylhydrazone derivative **6a**.

The diketo compound **18a** condensed with *o*-phenylenediamine in refluxing acetic acid to give a product formulated as **17e**.

Formylation of **1a** with dimethylformamide and phosphorus oxychloride gave 5,10-dihydro-2-methylthio-5-oxo-*s*-triazolo[1,5-*b*]isoquinoline-10-carboxaldehyde (**19**), which was characterized as its phenylhydrazone and semicarbazone.



19

Experimental Section

Ir spectra (KBr disks, unless otherwise stated) were recorded on a Perkin-Elmer 457 grating ir spectrophotometer. Nmr spectra were recorded on a Varian A-60A spectrophotometer, with TMS as internal reference. The uv spectrum was recorded on a Beckman DK spectrophotometer.

2-Methylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-one (1a).—A mixture of 16.3 g (0.1 mol) of homophthalic anhydride, 27.7 g (0.12 mol) of *S*-methylisothiosemicarbazide hydriodide, and 16.4 g (0.2 mol) of anhydrous fused sodium acetate in 50 ml of dry dimethylformamide was gently heated, with shaking, to boiling. The source of heat was removed, and the reaction mixture, which continued to boil on its own accord, was shaken for 10 min, left to cool somewhat, and then poured into ~200 ml of cold water. The greenish white precipitate that separated was filtered off, washed with little ethanol, and finally crystallized from dimethylformamide to give 17 g (73.5%) of **1a**, mp 255°.

Anal. Calcd for $C_{11}H_9N_3OS$: C, 57.11; H, 3.92; N, 18.18; S, 13.86; mol wt, 231.3. Found: C, 57.40; H, 4.00; N, 17.90; S, 13.80; *m/e* 231.

The 2-ethylthio analog **1b** was similarly prepared using *S*-ethylisothiosemicarbazide hydriodide. A 70% yield of **1b** was obtained, recrystallized from dimethylformamide, mp 224°.

Anal. Calcd for $C_{12}H_{11}N_3OS$: C, 58.75; H, 4.52; S, 13.07. Found: C, 58.87; H, 4.72; S, 12.93.

The 2-benzylthio analog **1c** was similarly obtained using *S*-benzylisothiosemicarbazide hydrochloride, in ~40% yield. It was crystallized from ethanol, mp 195°.

Anal. Calcd for $C_{17}H_{13}N_3OS$: C, 66.41; H, 4.26; S, 10.43. Found: C, 66.14; H, 4.50; S, 10.62.

3-(*o*-Carboxybenzyl)-5-methylthio-*s*-triazole (5). A.—A mixture of 8.1 g (0.05 mol) of homophthalic anhydride, 13.9 g (0.06 mol) of *S*-methylisothiosemicarbazide hydriodide and 8.2 g (0.1 mol) of anhydrous fused sodium acetate in 50 ml of dry dimethylformamide was left at room temperature for several days with occasional shaking (little methanethiol evolved). The reaction mixture was poured into 200 ml of cold water and left for some time. The crystalline white precipitate that separated was filtered off and recrystallized from ethanol to give 4 g (33%) of **5**, mp 195° dec (solidified and then melted again at ~250°), not depressed on admixture with the product prepared as described in B below.

Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 52.99; H, 4.45; S, 12.86. Found: C, 52.85; H, 4.45; S, 13.01.

B.—A solution of 4.6 g of **1a** in 50 ml of 5% NaOH was refluxed until it lost its fluorescence (~3 hr), and the solution was left to cool and was acidified with dilute acetic acid. The white precipitate formed was collected, washed with water, and crystallized from ethanol to give 3 g (61%) of **5**, mp 195°, not depressed on admixture with the previous compound.

Cyclization of 5 to 1a. A.—Two grams of **5** was refluxed in 10 ml of dimethylformamide for 15 min and then poured into 50 ml of cold water. The greenish precipitate formed was filtered off, triturated with a solution of sodium carbonate, and washed with water. It was crystallized from dimethylformamide to give 1 g (53%) of **1a**, mp and mmp 255°.

B.—Two grams of **5** was heated in an oil bath at 200° (bath temperature) for 15 min. The reaction mixture was worked up as above to yield 1.2 g (64%) of **1a**.

Phenylhydrazide of 5.—A suspension of 2 g of **1a** and 1.1 g of phenylhydrazine in 30 ml of ethanol was refluxed for 3 hr and left overnight. The orange crystals that separated were filtered off, washed with a small amount of ethanol, and recrystallized from dilute dioxane to give 1.8 g (60%) of the phenylhydrazide of **5**, mp 240°.

Anal. Calcd for $C_{17}H_{17}N_5OS$: C, 60.15; H, 5.05. Found: C, 60.44; H, 4.91.

5,10-Dihydro-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinoline-5,10-dione 10-Arylhydrazones (6a–l). General Procedure.—About 2 g of **1** was dissolved in 40 ml of pyridine, cooled in an ice bath, and treated with an equimolecular amount of the appropriate diazotized aniline. The mixture was left for 1 hr and then poured into cold water. The precipitate was collected, dried, and crystallized from the proper solvent. See Table I.

TABLE I

5,10-DIHYDRO-2-ALKYLTHIO-*s*-TRIAZOLO[1,5-*b*]ISOQUINOLINE-5,10-DIONE 10-ARYLHYDRAZONES (**6**)

Compd	R	Ar	Solvent of crystn[a]	Mp, °C	Yield, %[b]
6a	CH_3	C_6H_5	A	238	90
6b	CH_3	$C_6H_4CH_3$-*p*	A	258	92
6c	CH_3	$C_6H_4OCH_3$-*p*	B	233	82
6d	CH_3	$C_6H_4OC_2H_5$-*p*	B	205	82
6e	CH_3	C_6H_4Br-*p*	A	245	87
6f	CH_3	$C_6H_4NO_2$-*p*	A	280	79
6g	C_2H_5	C_6H_5	B	205	90
6h	C_2H_5	$C_6H_4OCH_3$-*p*	B	165	84
6i	C_2H_5	C_6H_4Br-*p*	B	197	87
6j	C_2H_5	$C_6H_4NO_2$-*p*	A	258	76
6k	$C_6H_5CH_2$	C_6H_5	A	230	75
6l	$C_6H_5CH_2$	C_6H_4Br-*p*	B	203	75

[a] A, nitrobenzene; B, acetic acid. [b] Satisfactory analytical data (±0.4%) were reported for all compounds: **6a** (C, H, N, S); **6b, 6g, 6h** (C, H, S); **6c** (S, Br); all others, S only.

Reaction of Phenylazohomophthalic Anhydride (10) with *S*-Methylisothiosemicarbazide Hydriodide.—A mixture of 2.6 g of **10**, 2.8 g of *S*-methylisothiosemicarbazide hydriodide, 2 g of fused anhydrous sodium acetate, and 10 ml of dry dimethylformamide was heated gently, with shaking, to boiling. The reaction mixture (heating discontinued) was then shaken occasionally for 10 min and poured into cold water. The precipitate formed was collected, washed with ethanol, and crystallized from nitrobenzene to give 2.8 g (85%) of **6a**, mp and mmp 238°.

10-Arylmethylene-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5-(10*H*)-ones (11). General Procedure.—A mixture of 2 g of **1**, 3 g of anhydrous fused sodium acetate, 20 ml of acetic acid, and an equimolecular amount of the appropriate aldehyde was refluxed for 3 hr. The reaction mixture was cooled and poured into cold water. The precipitate formed was collected, washed with water, and finally crystallized from the proper solvent. See Table II.

12-*p*-Chloro- (13a) and 12-*p*-Nitrobenzylidenebenzimidazo[1,2-*b*]isoquinolin-5(12*H*)-one (13b).—A mixture of 2 g of **4**, 3 g of fused anhydrous sodium acetate, 20 ml of acetic acid, and 0.9 g of *p*-chlorobenzaldehyde was refluxed for 20 min. The reaction mixture was left to cool and the solid **13a** that separated was filtered off, washed with water, and finally crystallized from dioxane, mp 245°, yield 82%.

TABLE II

10-ARYLMETHYLENE-2-ALKYLTHIO-*s*-TRIAZOLO[1,5-*b*]-ISOQUINOLIN-5(10*H*)-ONES (**11**)

Compd	R	Ar	Solvent of crystn[a]	Mp, °C	Yield, %[b]
11a	CH_3	C_6H_5	A	165	87
11b	CH_3	$C_6H_5OCH_3$-*p*	A	145	85
11c	CH_3	C_6H_4Cl-*o*	A	201	85
11d	CH_3	$C_6H_4NO_2$-*p*	B	260	89
11e	C_2H_5	C_6H_5	C	149	84
11f	C_2H_5	$C_6H_5CH{=}CH$	A	177	79
11g	C_2H_5	$C_6H_4NO_2$-*p*	A	211	89
11h	$CH_2C_6H_5$	C_6H_5	A	155	77
11i	$CH_2C_6H_5$	C_6H_4Cl-*p*	A	175–176	90

[a] A, acetic acid; B, dimethylformamide; C, dilute dioxane. [b] Satisfactory analytical data (±0.4%) were reported for all compounds: **11a** (C, H, N, S); **11e, 11g, 11h** (C, H, S); **11i** (S, Cl); all others, S only.

Anal. Calcd for $C_{22}H_{13}ClN_2O$: C, 74.05; H, 3.67. Found: C, 74.40; H, 3.84.

The *p*-nitrobenzylidene derivative **13b** was similarly prepared in 85% yield. It was crystallized from dimethylformamide, mp 280°.

Anal. Calcd for $C_{22}H_{13}N_3O_3$: C, 71.93; H, 3.57. Found: C, 72.26; H, 3.78.

10-Benzyl-2-methylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-one (14). A.—A solution of 1 g of **11a** in 20 ml of acetic acid was gradually treated with 1 g of zinc dust. The mixture was then refluxed till the yellow color of the solution disappeared. The solution was filtered and the filtrate was diluted with water. The product **14** was collected and crystallized from acetic acid as pale yellow crystals, mp 225°, yield 62%. **14** was readily soluble in 5% aqueous sodium hydroxide and gave a green fluorescent solution.

Anal. Calcd for $C_{18}H_{15}N_3OS$: C, 67.26; H, 4.70; *S*, 9.98. Found: C, 67.43; H, 4.77; S, 9.94.

B.—A mixture of 1 g of **11a**, 0.5 g of thiophenol, and 1 drop of piperidine was heated at 140° for 2 hr. The mass was triturated with little ethanol and then crystallized from acetic acid to give pale yellow crystals of **14**, mp 225°, not depressed on admixture with the above product.

10,10-Dibenzyl-2-methylthio-*s*-triazolo[1,5-*b*]isoquinolin-5-(10*H*)-one (15). A.—A suspension of 0.5 g of **14** in 20 ml of 10% sodium carbonate solution and 10 ml of ethanol was treated with 0.3 g of freshly distilled benzyl chloride. The whole was refluxed for 3 hr, diluted with water, and cooled. The solid that separated was filtered off and crystallized from ethanol to give colorless crystals of **15**, mp 160°, not depressed on admixture with a sample prepared as described in B below.

Anal. Calcd for $C_{25}H_{21}N_3OS$: C, 72.96; H, 5.14; S, 7.79. Found: C, 73.01; H, 5.22; S, 7.78.

B.—A mixture of 2.3 g (1 mol) of **1a**, 50 ml of 10% sodium carbonate solution, 20 ml of ethanol, and 2.6 g (2 mol) of benzyl chloride was refluxed for 3 hr. The reaction mixture was cooled and poured into cold water. The precipitate formed **15**, which was collected, washed with water, and finally crystallized from ethanol, mp 160°.

5,10-Dihydro-2-methylthio-*s*-triazolo[1,5-*b*]isoquinoline-5,10-dione 10-Oxime (16).—A suspension of 1 g of **1a** in 5 ml of concentrated hydrochloric acid and 20 ml of water was cooled to 0° and treated with 0.3 g of sodium nitrite in 10 ml of water with stirring. The solid that separated was collected, washed with water, and finally crystallized from acetic acid to give 0.85 g (75%) of **16**, mp 235–236°.

Anal. Calcd for $C_{11}H_8N_4O_2S$: C, 50.75; H, 3.09; S, 12.31. Found: C, 51.10; H, 2.90; S, 12.21.

10-Arylimino-2-alkylthio-*s*-triazolo[1,5-*b*]isoquinolin-5(10*H*)-ones (17).—A cold solution of 3.14 g of *p*-nitrosodimethylaniline hydrochloride in 100 ml of methanol was treated with a cold solution of 0.8 g of sodium hydroxide in 50 ml of methanol. This mixture was added to an equimolecular amount of **1** in 50 ml of dimethylformamide. The reaction mixture was left overnight and then poured into cold water. The blue precipitate formed was collected, washed with water and then with ethanol, and finally crystallized from benzene. See Table III.

TABLE III
10-ARYLIMINO-2-ALKYLTHIO-*s*-TRIAZOLO[1,5-*b*]ISOQUINOLIN-5(10*H*)-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(10*H*)-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.

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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,

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