

The Preparation of 3-Phenyl[1,2,4]triazolo[4,3-*a*]pyridines and Their Benzologs from *N*-(Phenylsulfonyl)benzohydrazonoyl Chloride and Pyridines¹⁾

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3-Phenyl[1,2,4]triazolo[4,3-*a*]pyridines were obtained in good yields from *N'*-[α -(1-pyridinio)benzylidene]benzenesulfonohydrazidates, generated from 2-unsubstituted pyridines and *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**2**), by oxidation with chloranil. The reaction of quinoline and isoquinoline with **2** gave 1-phenyl-3-phenylsulfonyl-3,3a-dihydro[1,2,4]triazolo[4,3-*a*]quinoline and 3-phenyl-1-phenylsulfonyl-1,10b-dihydro[1,2,4]triazolo[3,4-*a*]isoquinoline respectively, both in good yields; they aromatized to the corresponding triazoles by the 1,2-elimination of benzenesulfonic acid on heating.

[1,2,4]Triazolo[4,3-*a*]pyridines, -quinolines, and [1,2,4]triazolo[3,4-*a*]isoquinolines²⁾ are generally prepared by the ring closure of 2-hydrazinopyridines, -quinolines, or 1-hydrazinoisoquinolines with acidic-type cyclodehydration agents.³⁾ A variation of this method involving the oxidative cyclization of 2-pyridylhydrazones and their homologs is also available.⁴⁾

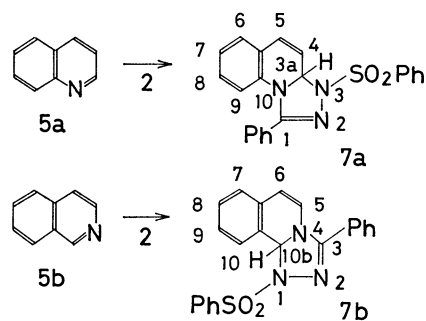
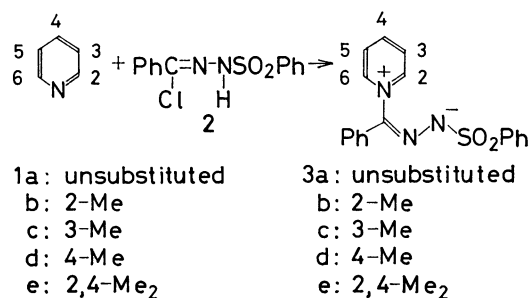
In the present paper, we wish to describe an alternative route for preparing the title triazolopyridines (**4**) *via* the oxidative cyclization of *N'*-[α -(1-pyridinio)benzylidene]benzenesulfonohydrazidates (**3**), obtained from *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**2**) and pyridines (**1**), and also a simple method for obtaining [1,2,4]triazoloquinoline (**8a**) and -isoquinoline (**8b**) from quinoline (**5a**) and isoquinoline (**5b**) by the reaction with **2** *via* dihydrotriazoloquinoline (**7a**) and -isoquinoline (**7b**) respectively as the intermediates. A specific feature of **2** lies in the electrophilicity of the imidoyl carbon and the acidity of the amino proton (and hence the stability of the resulting anion), which are enhanced by the phenylsulfonyl group. The sulfonyl group serves not only as the activating group in **2**, but also as the leaving group in a cationic or an anionic mode in the elimination step, leading to the triazoles, **4** and **8**.

Results and Discussion

Reaction of Hydrazonoyl Chloride (2) with Pyridines (1), Quinoline (5a), and Isoquinoline (5b).

The reaction of *N*-(2,4-dichlorophenyl)pyruvohydrazonoyl chloride with excess pyridine (**1a**) under refluxing gave *N'*-[α -(1-pyridinio)acetonylidene]-2,4-dichlorophenylhydrazidate.⁵⁾ Analogously, *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**2**) reacted with **1a** and alkyl-substituted pyridines (**1b—e**) at room temperature to afford the corresponding, bright-yellow colored pyridinium betaines, *N'*-[α -(1-pyridinio)benzylidene]benzenesulfonohydrazidates (**3**). However, the reaction of **2** with quinoline (**5a**) and isoquinoline (**5b**) yielded 1-phenyl-3-phenylsulfonyl-3,3a-dihydro[1,2,4]triazolo[4,3-*a*]quinoline (**7a**) and 3-phenyl-1-phenylsulfonyl-1,10b-dihydro[1,2,4]triazolo[3,4-*a*]isoquinoline (**7b**) respectively, both in good yields (Scheme 1, Table 1).

In the reaction of **1** with **2**, the use of a solvent such as dichloromethane and THF resulted in the formation of 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine as a by-product; such a by-product may be formed *via* the mutual nucleophilic process



Scheme 1.

of **3** generated: compounds **3a—e** changed into the dihydrotetrazine when dissolved in such solvents.

The IR and NMR spectral data for these compounds are summarized in Table 2. The sulfonyl absorptions near 1275 and near 1135 cm⁻¹ in the IR spectra were diagnostic for the characterization of **3a—e** and were consistent with those observed at lower frequencies (1270—1285 and 1130—1140 cm⁻¹) with *N*-(1-pyridinio)benzenesulfonamides.^{6,7)} Furthermore, a gross similarity can be seen in the NMR patterns of the pyridine ring between **3a—e** and the *N*-(1-pyridinio)benzenesulfonamides. The normal sulfonyl-absorption frequencies and the chemical shifts at δ 5.90—6.61 ppm with compounds **7a, b** support the cyclized structures.

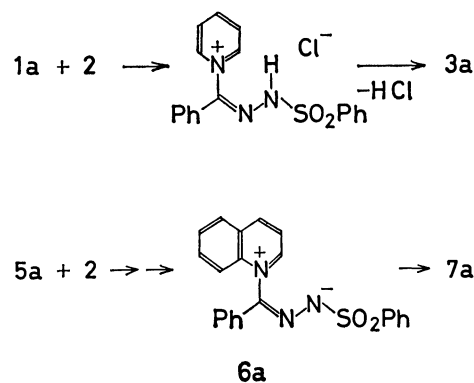
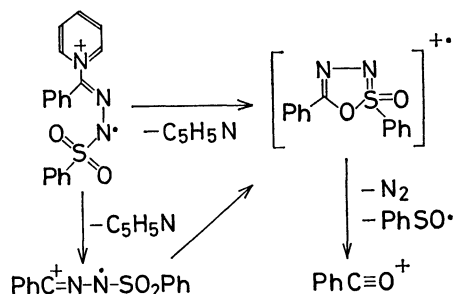
The mass spectra of **3** (ionizing energy: 75 eV) did not exhibit the M⁺ ions: the main fragment ions with the betaine **3a**, for example, are *m/e* 250 (15%), 141 (10%, PhSO₂⁺), 125 (21%, PhSO⁺), 105 (23%, PhC≡O⁺), 79 (100%, C₅H₅N⁺), 77 (35%, Ph⁺), 52 (60%, [C₅H₅N-HCN]⁺), and 51 (34%, [Ph-C₂H₂]⁺). The signal at *m/e* 250 is compatible with the [PhSO₂-SPh]⁺ ion, probably arising from thermal processes.⁸⁾ The occurrence of the PhC≡O⁺ ion can be explained as is illustrated below:

TABLE 1. PYRIDINIUM BETAINES, DIHYDROTRIAZOLOQUINOLINE, AND -ISOQUINOLINE

Compound	Yield/% ^{a)}	Mp/°C	Formula	Calcd (%)			Found (%)		
				C	H	N	C	H	N
3a	89	153—155 (dec)	C ₁₈ H ₁₅ N ₃ O ₂ S	64.08	4.48	12.45	63.87	4.45	12.57
3b	58	116—120	C ₁₉ H ₁₇ N ₃ O ₂ S	64.94	4.88	11.96	64.45	5.01	11.76
3c	83	150—153 (dec)	C ₁₉ H ₁₇ N ₃ O ₂ S	64.94	4.88	11.96	64.81	4.86	11.87
3d	82	153—156 (dec)	C ₁₉ H ₁₇ N ₃ O ₂ S	64.94	4.88	11.96	65.12	4.92	11.85
3e	26	107—109	C ₂₀ H ₁₉ N ₃ O ₂ S	65.73	5.24	11.50	65.33	5.29	11.16
7a	91	114—116 (dec)	C ₂₂ H ₁₇ N ₃ O ₂ S	68.20	4.42	10.85	68.05	4.40	10.84
7b	96	128—130 (dec)	C ₂₂ H ₁₇ N ₃ O ₂ S	68.20	4.42	10.85	68.00	4.47	10.79

a) Yield (isolated) as mole per cent based on **2**.TABLE 2. SPECTRAL DATA OF COMPOUNDS **3** AND **7**

Compound	IR (ν SO ₂ , cm ⁻¹ , KBr)	¹ H-NMR (δ , ppm, CDCl ₃)
3a	1274 1138	7.07—8.03 (m, 13H; 2 Ph, 3,4,5-H), 8.62 (dd, 2H; $J=5$ Hz, $J=1$ Hz; 2,6-H)
3b	1279 1139	2.55 (s, 3H; 2-Me), 6.91—7.99 (m, 13H; 2 Ph, 3,4,5-H), 8.49 (dd, 1H; $J=5$ Hz, $J=1.5$ Hz; 6-H)
3c	1274 1135	2.33 (s, 3H; 3-Me), 7.03—8.00 (m, 12H; 2 Ph, 4,5-H), 8.43 (br s, 2H; 2,6-H)
3d	1273 1132	2.35 (s, 3H; 4-Me), 7.02—7.99 (m, 12H; 2 Ph, 3,5-H), 8.47 (dd, 2H; $J=5$ Hz, $J=2$ Hz; 2,6-H)
3e	1276 1134	2.26 (s, 3H; 4-Me), 2.45 (s, 3H; 2-Me), 6.80—8.07 (m, 12H; 2 Ph, 3,5-H), 8.33 (d, 1H; $J=5$ Hz; 6-H)
7a	1364 1176	6.07 (s, 1H; 3a-H), 6.12 (d, 1H; $J=8.8$ Hz; 4-H), 6.61 (d, 1H; $J=8.8$ Hz; 5-H), 6.76—8.17 (m, 14H; 2 Ph, 6,7,8,9-H)
7b	1359 1170	5.90 (d, 1H; $J=7.5$ Hz; 5-H), 6.29 (d, 1H; $J=7.5$ Hz; 6-H), 6.42 (s, 1H; 10b-H), 6.93—8.17 (m, 14H; 2 Ph, 7,8,9,10-H)



Scheme 2.

As has previously been reported,⁹⁾ **2** does not afford *N*-(phenylsulfonyl)benzonitrilimine, a 1,3-dipole, on treatment with triethylamine, but is subjected to nucleophilic attack on the imidoyl carbon by the hydrazonoyl chloride *N*-anion generated from another molecule of **2** via deprotonation, which results in the formation of 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine. Thus, the formation of **3** and **7** probably proceeds via the step-by-step mechanism given in Scheme 2. Compound **7a** (and **7b**) should be formed by the 1,5-dipolar cyclization of the betaine intermediate.

The behavior in quinoline and isoquinoline systems different from that in the pyridine series can be explained in terms of the mesomeric effect of the fused benzene ring; that is, the electron deficiency attributable to this effect at the α -carbon (2-C of quinoline, and 1-C of isoquinoline skeleton) in the betaine structure (**6a**, **b**) and that at the amino nitrogen (10-N in **7a** and 4-N in **7b**) may contribute to the ready

cyclization of **6a**, **b** and the stabilization of **7a**, **b** respectively. On the other hand, the corresponding pyridine derivatives are lacking in such an effect, and so the aromatic stabilization of the pyridine ring is lost when **3** cyclize to dihydrotriazolopyridines. Consequently, the products from **1** prefer the betaine structure.

Oxidation of Pyridinium Betaines (3) and Dihydrotriazoles (7) with Chloranil. When the betaine **3a** was treated with chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone) in benzene or dioxane at room temperature, 3-phenyl[1,2,4]triazolo[4,3-*a*]pyridine (**4a**) was obtained in a comparable yield, together with a small amount of 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine. 2,3-Dichloro-5,6-dicyano-

TABLE 3. OXIDATION OF THE BETAINES **3a**

Oxidizing agent	Solvent	Reaction time/h ^a	Yield/% ^b of 4a ^c
Chloranil	Benzene	3	61
DDQ	Benzene	2	38
Chloranil	Dioxane	2	51
DDQ	Dioxane	1	37
HgO	Dioxane	6	5

a) The progress of reaction was checked by means of TLC. b) Isolated yield. c) Mp 173–175 °C (lit,^{3b}) mp 173–174 °C).

TABLE 4. TRIAZOLOPYRIDINES, -QUINOLINE, AND -ISOQUINOLINE OBTAINED BY THE OXIDATION OF **3** and **7**

Reactant ^a	Reaction time/h	Product (Yield ^b)/%
3b	2	4b (0)
3c	2.5	4c + 4c' (25 + 2) ^{c, d}
3d	2	4d (39) ^e
3e	2	4e (0)
7a	1	8a (94) ^f
7b	9	8b (35) ^g

a) Oxidizing agent and solvent: chloranil-benzene. The progress of reaction was checked by means of TLC. b) Isolated yield. c) **4c** and **4c'** were obtained as a mixture; the ratio was determined by means of NMR. d) Recrystallization gave no uncontaminated **4c** or **4c'**, and further purification was not attempted. Mp of the mixture: 156–160 °C (**4c**: lit,^{3a}) mp 187–188 °C; **4c'**: lit,^{3a}) mp 115 °C). e) Mp 128–130 °C (lit,^{3a}) mp 127–128 °C). f) Mp 114–115 °C (lit,^{4b}) mp 89 °C; lit,^{4e}) mp 136–137 °C). g) Mp 186–188 °C (lit,^{4d}) mp 186–187 °C; lit,^{4e}) 182 °C).

p-benzoquinone (DDQ) or mercury(II) oxide (yellow) also gave **4a** in a diminished yield. The results are summarized in Table 3. 2,3-Dichloro-5,6-dicyano-4-hydroxyphenyl benzenesulfonate generated from DDQ could be isolated. In the case of chloranil, 2,3,5,6-tetrachloro-1,4-phenylene bis(benzenesulfonate) and 2,3,5,6-tetrachlorohydroquinone, disproportionated products of the 2,3,5,6-tetrachloro-4-hydroxyphenyl benzenesulfonate which should be primarily formed, were obtained.

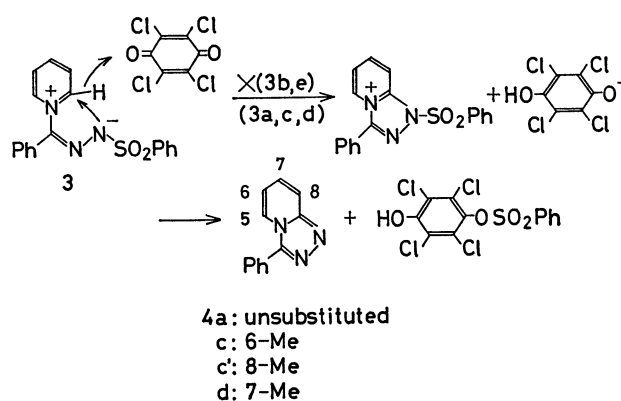
On the same treatment (chloranil-benzene), the betaines **3c**, **d** and the dihydrotriazoles **7a**, **b** afforded the corresponding triazolo compounds, **4c**, **4d**, **8a**, and **8b**, and also **4c'** which was detected by means of NMR as a minor component in the production of **4c** (Table 4). However, the betaines **4b**, **e** yielded no triazolopyridines; this may be the result of spatial interference between the *C*-phenyl and the α -methyl group of the pyridine ring. UV and NMR spectroscopic studies¹⁰ have revealed the steric interaction between 3-phenyl and 5-methyl group in the 3-phenyl-[1,2,4]triazolo[4,3-*a*]pyridine systems and have led to the conclusion that the 3-phenyl group is coplanar with the bicyclic nucleus in the 5-unsubstituted derivatives, but with a 5-methyl substituent the steric requirement can only be satisfied by the phenyl group adopting a conformation skew to the nucleus. Thus, in the betaines **3b**, **e**, the coplanarity of the *C*-phenyl group with the hydrazidate moiety, if conserved, should

TABLE 5. AROMATIZATION OF DIHYDROTRIAZOLOQUINOLINE AND -ISOQUINOLINE BY THE ELIMINATION OF BENZENESULFINIC ACID

Method ^a	Solvent	Refluxing time/h	Yield/% of 8
A	CCl ₄	3	67
A	Dioxane	5	82
B	CCl ₄	5	64
B	Dioxane	5	24
A	CCl ₄	2	68
A	Dioxane	6	60
B	CCl ₄	8	48
B	Dioxane	5	10

a) A: Thermolysis of **7** isolated. B: Direct method from **2** and **5**.

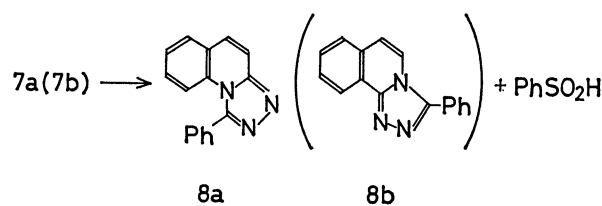
prevent the formation of **4b**, **e**.



Scheme 3.

Aromatization of Dihydrotriazoloquinoline (7a) and -isoquinoline (7b) by the Thermally Induced Elimination of Benzenesulfonic Acid.

The dihydrotriazolo compounds **7a**, **b** gave aromatized compounds, **8a**, **b** respectively, in good yields, along with *S*-phenyl benzenethiosulfonate (**9**), when refluxed in dioxane or carbon tetrachloride. Compound **9** is probably generated from benzenesulfonic acid¹¹ (Scheme 4).



Scheme 4.

A direct method in which **2** was treated with **5** in a boiling solvent also gave **8** in a diminished yield. Table 5 summarizes these results. The good leaving ability of the arenesulfonato group has been revealed in aromatization reactions¹² and other reactions, such as a cyclization reaction,¹³ and it is probably the driving force for the present reaction.

Experimental

The melting points were determined with a Yanagimoto micromelting point apparatus, Model MP-S3, and are

uncorrected. The microanalysis was performed on a Perkin-Elmer elemental analyzer, Model, 240. The IR, NMR, and mass spectra were recorded with a Hitachi 260, a Varian EM-360A, and a JEOL JMS-013G-2 spectrometer respectively. *N*-(Phenylsulfonyl)benzohydrazonoyl chloride (**2**) was prepared by the method previously reported.^{13a)}

Preparation of 3. *General Procedure:* A ground 2.95-g (10 mmol) portion of **2** was dissolved in pyridine (15 ml) at room temperature with stirring. A few minutes after dissolution, the product was separated by adding water, collected by filtration, and then washed with water, followed by small amounts of dilute ethanol. Further purification was achieved by repeated washings with ethanol. The results are summarized in Table 1.

Reaction of 5 with 2. A solution of **5a** (1.42 g, 11 mmol) in dichloromethane (3 ml) was added, drop by drop, to a solution of **2** (1.47 g, 5 mmol) in dichloromethane (5 ml) at room temperature. The reaction mixture was allowed to stand for 10 min. After the subsequent removal of the solvent *in vacuo*, a small portion of water was added to the oily residue. Crystallization was induced by scratching the flask, and the resulting precipitates were filtered. 1-Phenyl-3-phenylsulfonyl-3,3a-dihydro[1,2,4]triazolo[4,3-*a*]quinoline (**7a**; 1.87 g; 92%) was obtained in a fairly pure state by washing the precipitates with water and then with small amounts of cold ethanol. A further purified specimen could be prepared by repeated washings with ethanol. 3-Phenyl-1-phenylsulfonyl-1,10b-dihydro[1,2,4]triazolo[3,4-*a*]isoquinoline (**7b**; 1.84 g; 95%) was also obtained from **5b** and **2** in a similar manner. For the preparation of **7**, the procedure for **3** described above can also be used, but the present method may be more convenient. Table 1 shows the results obtained by the former procedure.

Oxidation of 3 and 7. (A) *With Chloranil or DDQ.* *General Procedure:* A mixture of 2 mmol of **3** (or **7**) and 2 mmol of chloranil (or DDQ) in a 15-ml portion of a solvent (benzene or dioxane) was stirred at room temperature for the period given in Tables 3 and 4. After the removal of the solvent *in vacuo*, the residue was chromatographed on a silica-gel column (100–200 mesh, 2.0 × 15 cm). Elution with benzene gave traces of 3,6-diphenyl-1,2,4,5-tetrazine and 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine (mp 151–156 °C(dec), 6–30%).¹⁴⁾ Elution with benzene-ether (19:1, and then 9:1, v/v) gave 2,3,5,6-tetrasubstituted 4-hydroxyphenyl benzenesulfonate (from DDQ) or its disproportionated products (from chloranil),¹⁵⁾ 1,4-phenylene bis(benzenesulfonate), and free hydroquinone (total yield in one run: 13–65%).

2,3-Dichloro-5,6-dicyano-4-hydroxyphenyl Benzenesulfonate. Mp 202–204 °C, IR (KBr, cm⁻¹): 1384, 1186 (νSO₂). Found: C, 45.38; H, 1.65; N, 7.17%. Calcd for C₁₄H₆Cl₂N₂O₄S: C, 45.55; H, 1.64; N, 7.59%.

2,3,5,6-Tetrachloro-1,4-phenylene Bis(benzenesulfonate). Mp 237–238 °C, IR (KBr, cm⁻¹): 1385, 1191 (νSO₂). Found: C, 40.88; H, 1.73%. Calcd for C₁₈H₁₀Cl₄O₆S₂: C, 40.93; H, 1.91%.

2,3,5,6-Tetrachlorohydroquinone. Mp 228–230 °C (lit.,¹⁶⁾ mp 230–231 °C). Found: C, 28.96; H, 0.71%.

Elution with benzene-ethanol (19:1, v/v) gave the corresponding triazolo compound, which was then purified by crystallization from benzene or carbon tetrachloride. The results are summarized in Tables 3 and 4. Each triazolo compound gave satisfactory C, H, and N analyses (±0.4%), and all were found to be spectroscopically identical with authentic specimens.

(B) *With Mercury(II) Oxide (Yellow).* A mixture of **3a** (1.685 g, 5 mmol), HgO (1.62 g, 7.5 mmol), K₂CO₃

(2 g, 15 mmol), CaSO₄ (2 g, 15 mmol), and dioxane (50 ml) was stirred for 6 h at room temperature. The reaction mixture was then filtered and washed with dioxane. The filtrate combined with washings was concentrated and then chromatographed to give **4a** (51 mg, 5%). Table 1 shows the results.

Thermolysis of 7. A 775-mg (2 mmol) portion of **7a** (or **7b**) was refluxed in a 30-ml portion of a solvent (CCl₄ or dioxane) for a period required. After the removal of the solvent, the reaction mixture was chromatographed (silica gel, benzene-ethanol), giving the corresponding triazoloquinoline, **8a** (or -isoquinoline, **8b**), along with *S*-phenyl benzenethiosulfonate, **9** (mp 42–43 °C, lit.,¹⁷⁾ mp 45 °C, yield: 20–25%) (Table 5: Method A).

One-flask Preparation of 8 from 2 and 5. A mixture of **2** (590 mg, 2 mmol) and **5a** or **5b** (775 mg, 6 mmol) in a solvent (30 ml) was refluxed. The reaction mixture was extracted with chloroform and washed with dilute hydrochloric acid, followed by water. The subsequent chromatographic treatment of the chloroform extract gave **8a** or **8b** (Table 5: Method B).

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14) In general, the yield of dihydrotetrazine was low when the triazolo compound was formed in a high yield.

15) Chromatographic treatment and recrystallization induced the disproportionation: no undisproportionated compound could be isolated in a pure state from the chloranil-oxidation reaction.

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