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Reactions of Acyl-aminoquinone Tosylhydrazones. II.[1] A Simple Synthesis of 5-Substituted Indazoloquinones

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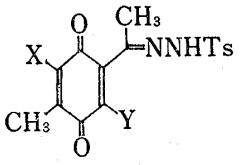
Indazoloquinone (**4**) or 5-substituted indazoloquinones (**5a—c**) were obtained with an acid-catalyzed substitution reaction of mono- (**2a—c**) or diaminoquinone tosylhydrazones (**3a—c**) in high yields. The reaction mechanism and rate were investigated.

In a previous communication,[1] it was shown that thermolysis of acetyl-monoaminoquinone tosylhydrazones (**2a—c**) gave indazoloquinone (**4**) and the reduced product of **4** together with 1,2-disubstituted indoloquinones (**10a—c**). Reported here is an investigation on an acid-catalyzed substitution reaction of acetyl-mono-or diaminoquinone tosylhydrazones. This reaction provides a simple, convenient synthesis of 5-substituted indazoloquinones which possess the same chromophores as those of mitomycins and rifamycin derivatives[3] and seem



1: X = Y = H

2a : X = H, Y = 

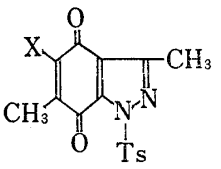
2b : X = H, Y = 

2c : X = H, Y = 

3a : X = Y =

3b : X = Y = 

3c : X = Y = 

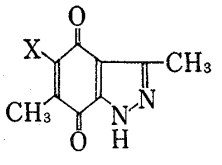


4: X = H

5a : X = 

5b : X = 

5c : X = 

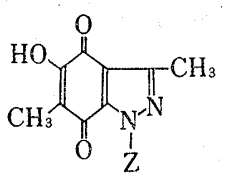


6: X = H

7a : X = 

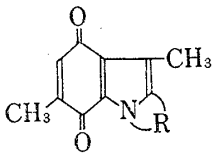
7b : X = 

7c : X = 



8 : Z = Ts

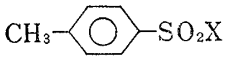
9 : Z = H



10a : R = -$(CH_2)_3$-

10b : R = -$(CH_2)_4$-

10c : R = -$(CH_2)_2OCH_2$-



11a : X = 

11b : X = 

11c : X = 

Chart 1

1) Part I: T. Takada, Y. Kosugi, and M. Akiba, *Tetrahedron Letters*, **1974**, 3283.
2) Location: *1432-1, Horinouchi, Hachiôji-shi, Tokyo, 192-03, Japan.*
3) A.N. Tischler, F.M. Thompson, L.J. Libertini, and M. Calvin, *J. Med. Chem.*, **17**, 948 (1974).

to have similar biological activities.

Acetyl-diaminoquinone tosylhydrazones (**3a**—**c**) prepared by the reaction of the corresponding acetyl-monoaminoquinone tosylhydrazones with the large excess of secondary amines (pyrrolidine, piperidine, and morpholine) were unstable to acid. On treatment with 10% hydrochloric acid, **3a**—**c** afforded an unexpected product in high yields. Its molecular formula, $C_9H_8O_3N_2$ was confirmed by mass spectrum (M^+, *m/e* 192) and microanalysis; nuclear magnetic resonance (NMR) (pyridine-d_5): 9.82 (2H, broad, –OH and –NH–), 2.64 (3H, s, $-CH_3$), 2.29 (3H, s, $-CH_3$). Based upon these spectroscopic data and the following chemical methods, the product was assigned to 5-hydroxyindazoloquinone (**9**). Treated with 1% hydrochloric acid, **3a** gave 1-tosyl-5-pyrrolidinoindazoloquinone (**5a**) (mp 154—156°, 63%) and 1-tosyl-5-hydroxyindazoloquinone (**8**) (mp>300°, 20%). Dipiperidino- or dimorpholinoquinone tosylhydrazone (**3b** or **3c**) similarly gave only 1-tosyl-5-piperidinoindazoloquinone (**5b**) (mp 125—128°, 70%) or 1-tosyl-5-morpholinoindazoloquinone (**5c**) (mp 118—120°, 65%). On the other hand, the reaction of **5a**—**c** with the corresponding amines afforded 5-aminoindazoloquinones (**7a**—**c**) and sulfonamides (**11a**—**c**). **7a**—**c** and **11a**—**c** were also synthesized by reactions of **4** with pyrrolidine, piperidine, and morpholine. **9** was also obtained by the hydrolysis of **5a**—**c**, **7a**—**c**, and **8** with 10% hydrochloric acid. In the case of monoaminoquinones **2a**—**c**, **4** and indazoloquinone (**6**) were also obtained by the similar reaction.

From the above results, a reasonable reaction mechanism for the formation of 5-hydroxyindazoloquinone was explained by the process shown in Chart 2.

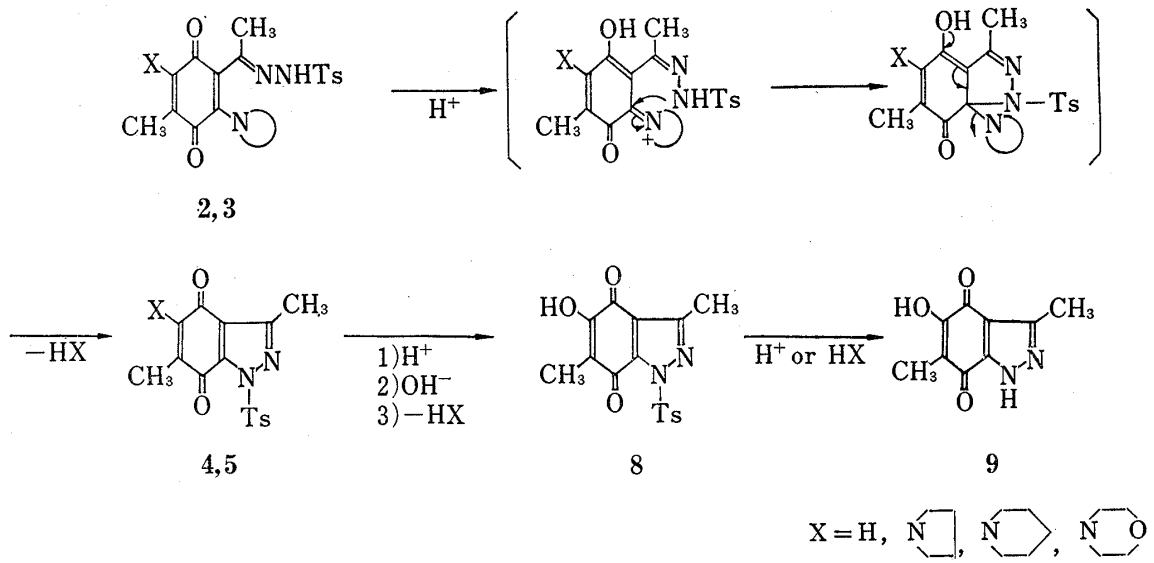


Chart 2

In the case of the preparation of acetyl-aminoquinone tosylhydrazones (**2**) from quinone (**1**) and thermolysis of **2**, as reported previously,[1] the formation of **4** and **11** may be rationally explained by considering the intramolecular nucleophilic substitution and elimination of amines. It was also found from thin-layer chromatography (TLC) and ultraviolet (UV) spectrum that the relative rates of intramolecular cyclization reaction of **2a**—**c** or **3a**—**c** with acid to **4** or **5a**—**c** and those of intermolecular nucleophilic substitution reaction of **7a**—**c** to **9** followed the order: pyrrolidino>piperidino>morpholino (Table I).

3a or **7a** displays UV absorptions at 352 nm (log ε_{max} 4.04), 392 nm (log ε_{max} 3.98) and 535 nm (log ε_{max} 3.00) or at 494 nm (log ε_{max} 3.65) and on the other hand, **5a** at 540 nm (log ε_{max} 3.63) or **9** at 390 nm (log ε_{max} 3.12) in the visible region. Fig. 1 and 2 show UV spectral change as a function of time upon treating **3a** and **7a** with 3 mmol/liter hydrochloric acid in ethanol at 25°.

The rates of reaction were determined by measuring the decrease of the absorbance at 352 nm, 392 nm, and 535 nm in **3a**, at 494 nm in **7a** and the increase of absorbance at 540 nm in **5a**, at 390 nm in **9**. The first order rate constant (K) was calculated from multiplying slope of a plot of log $a/a-x$ versus time by 2.303, where $a-x$ is concentration at time t (Fig. 3 and 4). The results of UV spectra and rate constants for **2a—c**, **3a—c**, and **7a—c** are summarized in Table I.

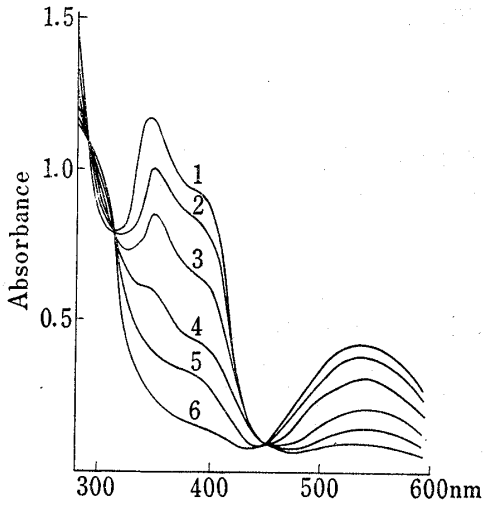


Fig. 1. UV Spectral Change with the Lapse of Time for Dipyrrolidinoquinone Tosylhydrazone (**3a**) in 3×10^{-3} M Ethanolic HCl at 25°

1, 3 min; 2, 18 min; 3, 30 min; 4, 1 hr; 5, 3 hr; 6, 4 hr

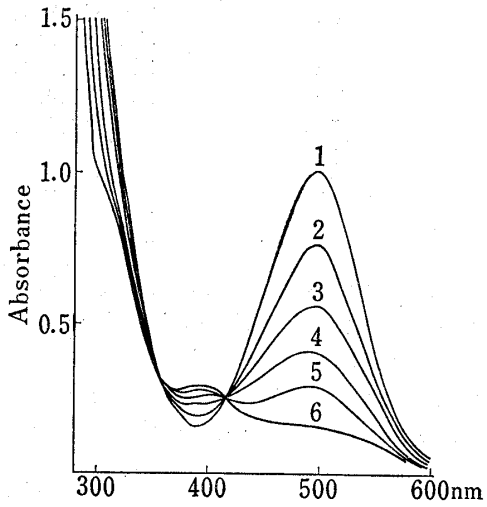


Fig. 2. UV Spectral Change with the Lapse of Time for 5-Pyrrolidinoindazoloquinone (**7a**) in 3×10^{-3} M Ethanolic HCl at 25°

1, 10 min; 2, 30 min; 3, 1 hr; 4, 1.5 hr; 5, 2 hr; 6, 6 hr

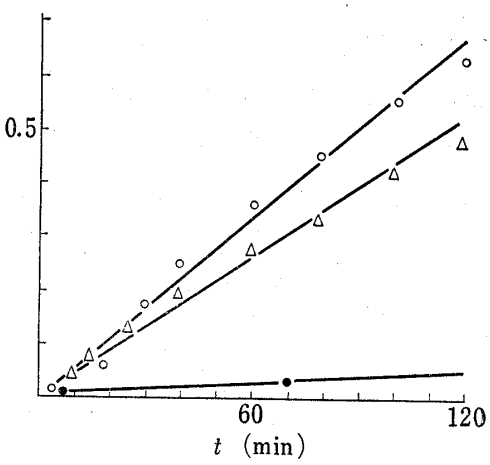


Fig. 3. First-order Rate Plots for log $(a/a-x)$ *vs.* Time of the Acid-Catalyzed Diaminoquinone Tosylhydrazone (**3a—c**)

○: X=Y=-N⟨ ⟩

△: X=Y=-N⟨ ⟩

●: X=Y=-N⟨ O⟩

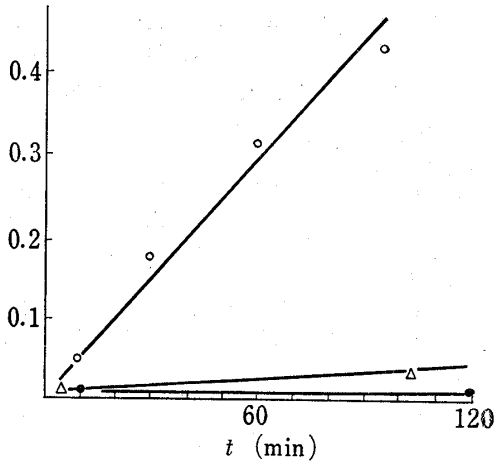


Fig. 4. First-order Rate Plots for log $(a/a-x)$ *vs.* Time of the Acid-Catalyzed 5-Aminoindazoloquinone (**7a—c**)

○: X=Y=-N⟨ ⟩

△: X=Y=-N⟨ ⟩

●: X=Y=-N⟨ O⟩

Table I. UV Spectra and Rate Constant for Acetylaminoquinone Tosylhydrazones and 5-Aminoindazoloquinones

Compounds	UV spectra λ_{max}^{EtOH} nm (log ε)	Rate constant $K \times 10^4$ sec^{-1}
2a	234.5(4.45), 275(4.00), 515(3.46)	79
2b	230.5(4.43), 521(3.37)	24
2c	230 (4.43), 508(3.41)	2.3
3a	228.5(4.31), 273(4.30), 352(4.04), 392 (3.98), 535(3.00)	140
3b	233 (4.51), 435(3.93)	110
3c	230 (4.42), 423(3.76)	15
7a	224 (4.11), 274(4.15), 494(3.65)	120
7b	267(4.00), 504(3.49)	4.6
7c	220.5(4.22), 265(4.06), 320(3.71), 491 (3.55)	0.3

The approximate order of the relative rates of acid catalyzed substitution reaction was similar to that of hydrolysis of pyrrolidino-, piperidino-, and morpholino-enamine.[4]

Further study on the intermolecular nucleophilic substitution which suggests possibility of mitomycins to interchange one another *in vivo* and its implications in the thermal decomposition reaction of diaminoquinone (**3a**—**c**) are being carried out.

Experimental

All melting points were determined by a micro hot-stage apparatus (Yanagimoto) and are uncorrected. IR spectra and UV spectra were recorded on a Hitachi Model 215 and a Hitachi Model 323 spectrometer, respectively. NMR spectra were obtained by a NEVA T-60 at 60 MHz or by a JEOL PS-100 at 100 MHz using tetramethylsilane as an internal standard. Mass spectra were measured by a Hitachi Model RMU-7L.

Acetyl-diaminoquinone Tosylhydrazones. 2-Acetyl-5-methyl-3,6-dipyrrolidino-1,4-benzoquinone Tosylhydrazone (3a)——To a solution of 2-acetyl-5-methyl-3-pyrrolidino-1,4-benzoquinone tosylhydrazone (**2a**, 500 mg) in $CHCl_3$ (30 ml) was added 1 g of pyrrolidine at 0°. After leaving for 2 days at 0°, the solvent was removed off *in vacuo*. The residue was purified by column chromatography (Al_2O_3, $CHCl_3$: ethylacetate=1: 1) to give 249 mg (43%) of dark red crystals, mp 125—130° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3100—3200 (broad, >NH), 1615, 1520 (>N–C=C–C=O). 1160 (–SO_2–). UV λ_{max}^{EtOH} nm (log ε): 228.5 (4.31), 273 (4.30), 352 (4.04), 392 (3.98), 535 (3.00). NMR ($CDCl_3$) δ: 7.75 (2H, d, J=8 Hz, aromatic proton), 7.20 (2H, d, J=8 Hz, aromatic proton), 3.10—3.80 (8H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.38 (3H, s, $-CH_3$), 1.99 (3H, s, $-CH_3$), 1.97 (3H, s, $-CH_3$), 1.55—2.04 (8H, m, $-CH_2-CH_2-$). Reliable combustion analysis could not be obtained owing to the instability of the title compound.

2-Acetyl-5-methyl-3,6-dipiperidino-1,4-benzoquinone Tosylhydrazone (3b)——To a solution of 2-acetyl-5-methyl-3-piperidino-1,4-benzoquinone tosylhydrazone (**2b**, 500 mg) in $CHCl_3$ (30 ml) was added 1.5 g of piperidine. After standing overnight at room temperature, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (SiO_2, $CHCl_3$) to give 260 mg (35%) of dark green crystals, mp 185° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3200 (>NH), 1628, 1550 (>N–C=C–C=O), 1160 (–SO_2–). UV λ_{max}^{EtOH} nm (log ε) 233 (4.51), 435 (3.93). NMR ($CDCl_3$) δ: 7.90 (2H, d, J=8 Hz, aromatic proton), 7.35 (2H, d, J=8 Hz, aromatic proton), 3.20 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.70 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.42 (3H, s, $-CH_3$), 2.02 (3H, s, $-CH_3$), 1.90 (3H, s, $-CH_3$), 1.61—1.45 (12H, m, $-(CH_2)_3-\times 2$). Reliable combustion analysis could not be obtained owing to the instability of the title compound.

2-Acetyl-5-methyl-3,6-dimorpholino-1,4-benzoquinone Tosylhydrazone (3c)——To a solution of 2-acetyl-5-methyl-3-morpholino-1,4-benzoquinone tosylhydrazone (**2c**, 500 mg) in $CHCl_3$ (50 ml) was added 2 g of morpholine. After standing overnight at room temperature, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (SiO_2, $CHCl_3$: ethylacetate=4: 1) to yield 487.6 mg (81%) of dark green crystals, mp 198—200° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3180 (>NH), 1620, 1560 (–N–C=C–C=O), 1160 (–SO_2–). UV λ_{max}^{EtOH} nm (log ε): 230 (4.42), 423 (3.76). NMR ($CDCl_3$) δ: 7.85 (2H, d, J=8 Hz, aromatic proton), 7.30 (2H, d, J=8 Hz, aromatic proton), 3.85—3.55 (8H, m, morpholino-H), 3.42—3.13 (4H, m, mor-

4) *a*) P.Y. Sollenberger and R.B. Martin, *J. Am. Chem. Soc.*, 92, 4261 (1970); *b*) W. Maas, M.J. Janssen, E.J. Stamhuis, and H. Wynberg, *J. Org. Chem.*, 32, 1111 (1967).

pholino-H), 2.90—2.71 (4H, m, morpholino-H), 2.44 (3H, s, $-CH_3$), 2.02 (3H, s, $-CH_3$), 1.92 (3H, s, $-CH_3$). Reliable combusion analysis could not be obtained owing to the instability of the title compound.

Reaction of 3a, 3b, and 3c with 10% Hydrochloric Acid. Formation of 5-Hydroxy-3,6-dimethyl-1H-indazole-3,7-dione (9)——To a solution of **3a** (100 mg) in $CHCl_3$ (5 ml) was added 2 ml of 10% aq. HCl. After adding 5 ml of EtOH, the solution was stirred for 5 min at room temperature, and then warmed at 40° for 30 min. The solution was poured into water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried and evaporated. The residue was recrystallized from EtOH to yield yellow crystals (36.0 mg, 88%), mp 300°. IR ν_{max}^{KBr} cm^{-1}: 3340 (–OH), 3180 (>NH), 1630 (>C=O), 1460, 1380, 1340, 1130, 1075, 840, 760, 740, 710. UV λ_{max}^{EtOH} nm (log ε): 236 (4.10), 270 (4.15), 390 (3.12). NMR (pyridine-d_5) δ: 9.82 (2H, broad, –OH and –NH–), 2.64 (3H, s, $-CH_3$), 2.29 (3H, s, $-CH_3$). Mass Spectrum *m/e*: 192 (M^+). *Anal.* Calcd. for $C_9H_8O_3N_2$: C, 56.25; H, 4.20; N, 14.58. Found: C, 55.84; H, 4.21; N, 13.99. This compound (**9**) was also obtained from **3b** or **3c** by the same method discribed above.

Reaction of Acetyl-diaminoquinone Tosylhydrazones with 1% Hydrochloric Acid. Formation of 3,6-Dimethyl-5-pyrrolidino-1-tosyl-1H-indazole-4,7-dione (5a)——A solution of **3a** (100 mg) in $CHCl_3$ (2 ml) and EtOH (2 ml) containing 1% aq. HCl (2 ml) was stirred for 3 min at room temperature. After pouring into water, the mixture was extracted with $CHCl_3$ and then the $CHCl_3$ solution was dried and evaporated. The residue was purified by column chromatography to give 50 mg (63%) of **5a** as dark blue crystals, mp 154—156° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1680 (>C=O), 1620 (>C=O), 1520 (>N–C=C–C=O), 1390, 1280, 1200, 1180 ($-SO_2-$), 920, 660. UV λ_{max}^{EtOH} nm (log ε): 236 (4.38), 540 (3.63). NMR ($CDCl_3$) δ: 8.21 (2H, d, $J=8$ Hz, aromatic proton), 7.27 (2H, d, $J=8$ Hz, aromatic proton), 3.73 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.53 (3H, s, $-CH_3$), 2.45 (3H, s, $-CH_3$), 2.02 (3H, s, $-CH_3$), 1.93 (4H, m, $-CH_2-CH_2-$). 14 mg (20%) of the colorless product in soluble to all solvents was obtained from second fraction. mp>300°, IR ν_{max}^{KBr} cm^{-1}: 3770 (–OH), 1655 (>C=O), 1340, 1195, 1180 ($-SO_2-$), 915, 807, 735. Mass Spectrum *m/e*: 191 ($M^+-C_7H_7O_2S$). On treatment with 10% HCl, this product gave 5-hydroxy-3,6-dimethyl-1H-indazole-3,7-dione **9** in high yields. Base upon these data, this compound was considered as 5-hydroxy-3,6-dimethyl-1-tosyl-1H-indazole-4,7-dione (**8**).

Formation of 3,6-Dimethyl-5-piperidino-1-tosyl-1H-indazole-4,7-dione (5b)——To a solution of **3b** (50 mg) in $CHCl_3$ (10 ml) and EtOH (2 ml) was added 1% aq. HCl (2 ml) at room temperature. After stirring for 15 min, the solution was poured into water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried and evaporated. The residue was purified by column chromatography (SiO_2, C_6H_6) to give 29 mg (70%) of **5b** as dark blue crystals, mp 125—128° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1665 (>C=O), 1640 (>C=O), 1540 (>N–C=C–C=O), 1398, 1198 ($-SO_2-$), 925, 660. UV λ_{max}^{EtOH} nm (log ε): 236 (4.42), 318 (3.83), 550 (3.56). NMR ($CDCl_3$) δ: 8.15 (2H, d, $J=8$ Hz, aromatic proton), 7.35 (2H, d, $J=8$ Hz, aromatic proton), 3.30 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.75 (3H, s, $-CH_3$), 2.43 (3H, s, $-CH_3$), 1.99 (3H, s, $-CH_3$), 1.68 (6H, m, $-(CH_2)_3-$).

Formation of 3,6-Dimethyl-5-morpholino-1-tosyl-1H-indazole-4,7-dione (5c)——To a solution of **5c** (35 mg) in $CHCl_3$ (10 ml) and EtOH (3 ml) was added 1% aq. HCl (2 ml) at room temperature. After stirring for 2.5 hr, the mixture was poured into water and extracted with $CHCl_3$. The $CHCl_3$ layer was dried and evaporated. The residue was purified by column chromatography (SiO_2, C_6H_6–$CHCl_3$) to give 19.0 mg (65%) of **5c** as dark blue crystals, mp 118—120° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 1670 (>C=O), 1640 (>C=O), 1540 (>N–C=C–C=O), 1198 ($-SO_2-$), 660. UV λ_{max}^{EtOH} nm (log ε): 235 (4.35), 318 (3.79), 537 (3.47). NMR ($CDCl_3$) δ: 8.18 (2H, d, $J=8$ Hz, aromatic proton), 7.35 (2H, d, $J=8$ Hz, aromatic proton), 3.80 (4H, t, $J=5$ Hz, morpholino–H), 3.35 (4H, t, $J=5$ Hz, morpholino–H), 2.55 (3H, s, $-CH_3$), 2.44 (3H, s, $-CH_3$), 2.00 (3H, s, $-CH_3$). Since these title compounds were quite thermally and photolytically unstable, satisfactory combustion analyses could not be obtained.

Reaction of 5a with Amine (Formation of 3,6-Dimethyl-5-pyrrolidino-1H-indazole-4,7-dione (7a))——To a solution of **5a** (20 mg) in $CHCl_3$ (3 ml) was added a drop of pyrrolidine. After refluxing for 20 min, the solvent was evaporated to dryness. The residue was chromatographed (SiO_2, $CHCl_3$: ethylacetate=4: 1) to separate indazoloquinone (**7a**) and sulfonamide (**11a**). **11a** was recrystallized from *n*-hexane to give 10.9 mg (99%) of colorless needles, mp 122—123°, which was identified with those obtained by the usual method by comparing their melting points and infrared (IR) spectra. **7a** was twice purified by column chromatography to give 10.5 mg (87%) of red crystals, mp 185—190°. IR ν_{max}^{KBr} cm^{-1}: 3100 (–NH), 1665 (>C=O), 1580 (>N–C=C–C=O), 1480, 1435, 1365, 1280, 1260, 1060, 860. UV λ_{max}^{EtOH} nm (log ε): 224 (4.11), 274 (4.15), 494 (3.65). NMR ($CDCl_3$) δ: 3.80 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.62 (3H, s, $-CH_3$), 2.10 (3H, s, $-CH_3$), 1.92 (4H, m, $-CH_2-CH_2-$). Mass Spectrum *m/e*: 245 (M^+).

3,6-Dimethyl-5-piperidino-1H-indazole-4,7-dione (**7b**) and 3,6-dimethyl-5-morpholino-1H-indazole-4,7-dione (**7c**) are also preparable from (**5b**) and (**5c**) according to the same procedure as described for (**7a**), respectively.

3,6-Dimethyl-5-piperidino-1H-indazole-4,7-dione (7b)——To a solution of **3b** (100 mg) in $CHCl_3$ (30 ml) and EtOH (10 ml) was added 1% aq. HCl (5 ml). After stirring for 20 min at room temperature, 200 mg of piperidine was added and then the mixture was warmed at 50° for 3 hr. After cooling, the mixture was poured into water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried and evaporated. The residue was

chromatographed (SiO_2, $CHCl_3$: ethylacetate=1:1) to give 13 mg (24%) of **7b** which was recrystallized from C_6H_6 to reddish brown crystals, mp 155—160°. IR ν_{max}^{KBr} cm^{-1}: 3100—3200 (broad, >NH), 1660 (>C=O), 1635 (>C=O), 1545 (>N–C=C–C=O), 1290, 1080, 945 UV λ_{max}^{EtOH} nm (log ε): 267 (4.00), 504 (3.49). NMR ($CDCl_3$) δ: 10.60 (1H, broad, >NH), 3.36 (4H, m, $-N\langle^{CH_2-}_{CH_2-}$), 2.67 (3H, s, $-CH_3$), 2.02 (3H, s, $-CH_3$), 1.70 (6H, m, $-(CH_2)_3-$). Mass Spectrum *m/e*: 259 (M^+).

3,6-Dimethyl-5-morpholino-1H-indazole-4,7-dione (7c)——**7c** was also prepared from **3c** according to the similar method as used for (**7b**), in 25% yield. **7c** was recrystallized from C_6H_6 to dark red crystals, mp 215—220°. IR ν_{max}^{KBr} cm^{-1}: 3200 (>NH), 1663 (>C=O), 1620 (>C=O), 1550 (>N–C=C–C=O), 1450, 1233, 1110, 955, 750. UV λ_{max}^{EtOH} nm (log ε): 220.5 (4.22), 265 ((4.06), 320 (3.71), 491 (3.55). NMR ($CDCl_3$) δ: 3.85 (4H, t, J=5 Hz, morpholino–H), 3.42 (4H, t, J=5 Hz, morpholino–H), 2.68 (3H, s, $-CH_3$), 2.07 (3H, s, $-CH_3$). Mass Spectrum *m/e*: 261 (M^+).

3,6-Dimethyl-1-tosyl-1H-indazole-4,7-dione (4)——To a solution of **2a** (100 mg) in $CHCl_3$ (20 ml) and EtOH (10 ml) was added 1% aq. HCl (5 ml). After stirring for 4 hr at room temperature, the mixture was poured into water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried and evaporated. The residue was chromatographed (SiO_2, $CHCl_3$) to give 49.8 mg of **4** as a crude product. Recrystallization from EtOH gave yellow needles (34.2 mg, 42%), mp 172—174°. IR ν_{max}^{KBr} cm^{-1}: 1680 (>C=O), 1660 (>C=O), 1395, 1195 ($-SO_2-$), 1180, 1135, 910, 810. UV λ_{max}^{EtOH} nm (log ε): 236 (4.28), 259 (4.16), 319 (3.59). NMR ($CDCl_3$) δ: 8.18 (2H, d, J=8 Hz, aromatic proton), 7.40 (2H, d, J=8 Hz, aromatic proton), 6.54 (1H, q, J=1.5 Hz, >C=C–H), 2.58 (3H, s, $-CH_3$), 2.45 (3H, s, $-CH_3$), 2.10 (3H, d, J=1.5 Hz, $-CH_3$). *Anal.* Calcd. for $C_{16}H_{14}O_4N_2S$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.64; Y, 4.13; N, 9.14.

3,6-Dimethyl-1H-indazole-4,7-dione (6)——To a solution of **2a** (100 mg) in $CHCl_3$ (20 ml) and EtOH (10 ml) was added 1% aq. HCl (10 ml) and the mixture was heated for 1 hr on a water bath. The mixture was extracted with $CHCl_3$ and the extract was dried and evaporated. The residue was recrystallized from C_6H_6 to give 14.6 mg (33%) of **6** as yellow crystals, mp 230° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3225 (>N–H), 1660 (>C=O), 1585, 1555, 1215, 900. UV λ_{max}^{EtOH} nm (log ε): 225 (4.10), 254 (4.22), 328 (3.36). NMR (pyridine-d_5) δ: 9.95 (1H, broad, >NH), 6.62 (1H, q, J=2 Hz, >C=C–H), 2.63 (3H, s, $-CH_3$), 2.06 (3H, d, J=2 Hz, $-CH_3$). Mass Spectrum *m/e*: 176 (M^+).

Kinetic Study——The rates of reaction were measured by following the change in absorbance at a wavelength between 340—600 nm. The reactions were carried out at 25° in quartz-cells, where the initial concentration of reactants was 1×10^{-4} M, and the solution employed was 3×10^{-3} M ethanolic HCl. First-order rate constants were estimated graphically from the plots of absorbance *vs* time (min).

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