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Reactions of *N*-Sulfinylarylamines with Carbonyl Compounds and a Nitrile in the Presence of Copper

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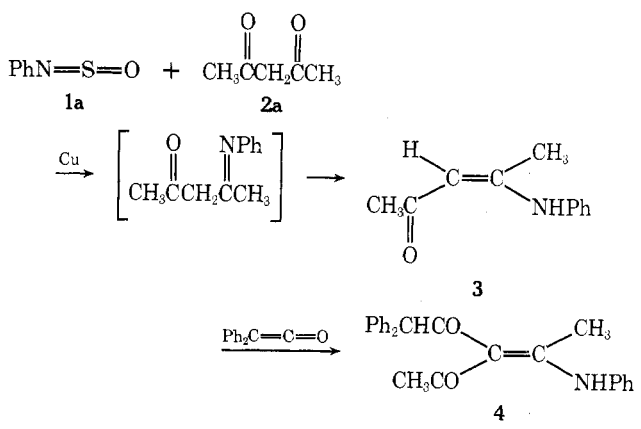
The copper-catalyzed reactions of *N*-sulfinylarylamines **1a,b** with activated carbonyl **2a–d,f** and nitrile compounds **12** were studied. Each carbonyl compound gave amino ketones **3, 5, 8, 9,** and **11** and sulfides **6** and **7.** Phenylacetonitrile (**12**) yielded *trans*-α,β-dicyanostilbene (**13**). The formation mechanism of these products was discussed.

Reactions of *N*-sulfinyl-*p*-toluenesulfonamides with various aldehydes and ketones can lead to *N*-sulfonylimines,[1,2] oxathioles,[3,4] and α-sulfonamido ketones.[5] In this paper we report on the reactions of the less reactive *N*-sulfinylanilines and the effect of copper[6] in these reactions.

A mixture of *N*-sulfinylaniline (**1a**), acetylacetone (**2a**), and copper shavings in mesitylene was refluxed for 6 h to give 4-anilino-3-penten-2-one (**3**)[10] in 46% yield; gas was evolved. Without copper, however, only starting **1a** and **2a** were recovered. Thus, copper catalyzes the formation of the enamino ketone **3** from **1a** and **2a.**

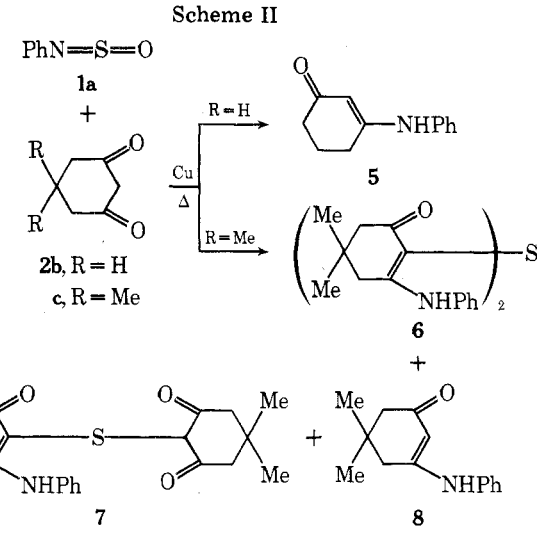
Scheme I



The reaction of **3** with diphenylketene gave **4,** analogous to the products from enamino ketones and isothiocyanates.[7]

The reaction between **1a** and 1,3-cyclohexanedione (**2b**) similarly took place to provide 3-anilino-2-cyclohexen-1-one (**5**) in quantitative yield.

Scheme II



In contrast to **2b,** use of 5,5-dimethyl-1,3-cyclohexanedione (**2c**) gave rise to the formation of unexpected sulfide **6** in 67% yield along with two minor products, the sulfide **7** (16%) and the anilino ketone **8** (12%).

In a separate reaction, treatment of **8** with sulfur under the same conditions gave the sulfide **6** in good yield. Similar treatment of an equimolar mixture of **8** and **2c** with sulfur afforded a mixture of **6** (40%) and the unsymmetrical sulfide **7** (43%). These results suggest that the sulfides, **6** and **7,** were formed in the reaction by oxidative coupling between **8** and either a second molecule of **8** or **2c** in the presence of elemental sulfur. The latter could be produced by reduction of sulfur dioxide or sulfur monoxide on copper in the reaction system.

The difference of reactivities between **2b** and **2c** with **1a** is presumably due to the steric effect of the substituent on the 1,3-cyclohexanedione derivative.

A similar reaction of diethyl malonate (**2d**) with **1a** in refluxing xylene for 6 h gave malonanilic acid ethyl ester (**9**) in 43% yield together with diethyl sulfite but not tetracarboethoxyethylene as reported in the reaction with *N*-sulfinyl-*p*-toluenesulfonamide.[3] A reaction of *N*-sulfinylaniline (**1a**) with 2,5-hexanedione (**2e**) under similar conditions produced only 1-phenyl-2,5-dimethylpyrrole (**10**) in 65% yield. The formation of **10** is explicable by intramolecular dehydration of intermediate 2-anilino-2-hexen-5-one corresponding to the enamino ketones as shown above.

With benzalacetophenone as the carbonyl reagent, (β-anilino-β-phenyl)ethyl phenyl ketone (**11**) was obtained in 58% yield. For the formation mechanism of the product **11**, reduction and hydrolysis of the 1,4 cycloadduct of **1a** to **2f** are conceivable, but attempts to isolate the cycloadduct were unsuccessful.

In the reaction using phenylacetonitrile (**12**), in place of 1,3-diketones, as the active methylene compound, copper metal also catalyzed the formation of *trans*-α,β-dicyanostilbene (**13**) in 26% yield. Its formation may analogously proceed via a sequence of sulfinylation of **12** to phenyl cyanosulfine, dimerization, decomposition to 2,3-dicyano-2,3-diphenylthiirane, and successively reductive desulfurization of the thiirane by copper metal or heat, as proposed by previous workers.[3,4,8,9]

However, copper salts such as cuprous or cupric chlorides showed no catalytic effect in any of the above reactions.

Experimental Section

All melting points were determined with a Yanagimoto micromelting apparatus and are uncorrected. The NMR spectra were obtained on a Joellmm 3H-60 spectrometer with tetramethylsilane as an internal standard. The ir spectra were recorded with a Jasco IR-E spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer.

Materials. *N*-Sulfinylaniline (**1a**) and *N*-sulfinyl-*p*-toluidine (**1b**) were prepared from the corresponding amines and thionyl chloride. Copper shavings (Wako Chemicals) were dried in vacuo before use.

General Procedure. In a dried, three-necked, 100-ml, round-bottomed flask, fitted with a reflux condenser and stirrer, were placed *N*-sulfinylamines (0.03 mol), ketones (0.03 mol), copper shavings (3 g) and mesitylene (or *m*-xylene, 30 ml). The reactions were carried out at refluxing temperature under dry N_2.

Reaction of *N*-Sulfinylaniline (1a) with Acetylacetone (2a). A solution containing **1a** (4.20 g, 0.03 mol), **2a** (3.0 g, 0.03 mol), and copper shavings (3 g) in 30 ml of dry mesitylene was allowed to stir under reflux for 6 h. The organic layer was separated and concentrated in vacuo. The residue was chromatographed on silica gel using hexane as eluent to give 2.40 g (46%) of **4-anilino-3-penten-2-one** (**3**), which was recrystallized from benzene–hexane affording a pure sample: mp 49–51 °C (lit.[10] mp 47–48 °C); ir (Nujol) 1590 (C=O) and 1560 cm^{-1} (C=C); NMR (C_6D_6) δ 1.55 (s, 3 H, CH_3C=C), 2.05 (s, 3 H, $COCH_3$), 4.95 (s, 1 H, C=CH), 6.50–7.15 (m, 5 H, phenyl protons), and 12.90–13.10 [broad, 1 H, PhN**H**C=CCOCH$_3$ (cis)].

Reaction of 3 with Diphenylketene. Diphenylketene (0.58 g, 3 mmol) dissolved in 5 ml of dry benzene was added dropwise to a stirred solution of **3** (0.53 g, 3 mmol) in 10 ml of benzene. The reaction took place immediately to give 1.10 g of white crystals. The crude white crystals were recrystallized from methylene chloride–benzene to give pure **1,1-diphenyl-3-acetyl-4-anilino-3-penten-2-one** (**4**): mp 174–176 °C; ir (Nujol) 1645 (C=O), 1580 (C=O), and 1545 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.70–2.05 [broad, 3 H, **C**H$_3$C=CCOCHPh$_2$ (cis)], 2.10 (s, 3 H, $COCH_3$), 5.50 (s, 1 H, methine proton), 6.95–7.55 (m, 15 H, phenyl protons), and 18.50–18.75 [broad, 1 H, PhN**H**C=CCOCH$_3$ (cis)]; mass spectrum (70 eV) *m/e* 369 (M^+) and 194 $(Ph_2CCO)^+$.

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.26; H, 6.28; N, 3.79. Found: C, 81.25; H, 6.22; N, 3.58.

Reaction of *N*-Sulfinylaniline (1a) with 1,3-Cyclohexanedione (2b). The reaction was carried out as described above using **1a** (4.2 g, 0.03 mol), **2b** (3.4 g, 0.03 mol), and copper shavings (3 g). After similar treatment, **3-anilino-2-cyclohexen-1-one** (**5**) was obtained in a yield of 5.55 g (99%): mp 186–186.5 °C (from chloroform–benzene); ir (Nujol) 3240 (NH), 1590 (C=O), and 1570 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.65–2.65 [m, 6 H, $-(CH_2)_3-$], 5.50 (s, 1 H, HC=C), 6.90–7.45 (m, 5 H, phenyl protons), and 8.25–8.35 (broad, 1 H, NH); mass spectrum (70 eV) *m/e* 187 (M^+).

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.18; H, 6.92; N, 7.36.

Reaction of *N*-Sulfinylaniline (1a) with 5,5-Dimethyl-1,3-cyclohexanedione (2c). The reaction of **1a** (4.2 g, 0.03 mol) with **2c** (4.2 g, 0.03 mol) in the presence of copper shavings (3 g) was carried out in a similar manner as described above. After similar treatment, the residue was chromatographed on silica gel using hexane–benzene and benzene as eluent. The first fraction gave a mixture of **bis(1-oxo-3-anilino-5,5-dimethyl-2-cyclohexen-2-yl) sulfide** (**6**) and **(1-oxo-3-anilino-5,5-dimethyl-2-cyclohexen-2-yl) (1,3-dioxo-5,5-dimethylcyclohexan-2-yl) sulfide** (**7**). Pure samples of individual **6** (4.61 g, 67%) and **7** (0.90 g, 16%) were isolated by repeated recrystallization of the mixture from benzene–hexane.

6 had mp 265–266 °C; ir (Nujol) 1585 (C=O) and 1550 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.00 (s, 12 H, methyl protons), 2.38 (s, 4 H, C=CCH_2–) 2.50 (broad s, 4 H, $COCH_2$–), 7.20–7.40 (m, 10 H, phenyl protons), and 11.10–11.25 (broad, 2 H, NH); mass spectrum (70 eV) *m/e* 460 (M^+), 246, and 216.

Anal. Calcd for $C_{28}H_{32}N_2O_2S$: C, 73.02; H, 7.00; N, 6.08. Found: C, 72.85; H, 6.87; N, 6.05.

7 had mp 208–210 °C; ir (Nujol) 1620 (C=O), 1585 (C=O), and 1550 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.00 (s, 6 H, methyl protons), 1.06 (s, 6 H, methyl protons), 2.25–2.50 (broad, 8 H, methylene protons), 7.15–7.35 [m, 6 H, phenyl protons (5 H) and methine proton (1 H)],

and 10.50–10.65 (broad, 1 H, NH); mass spectrum (70 eV) *m/e* 385 (M^+), 246, 215, and 172.

Anal. Calcd for $C_{22}H_{27}NO_3S$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.58; H, 6.69; N, 3.52.

The second fraction afforded 0.82 g (12%) of **3-anilino-5,5-dimethyl-2-cyclohexen-1-one** (**8**), mp 184–185 °C (benzene–hexane), as yellowish needles: ir (Nujol) 3200 (NH), 1590 (C=O), and 1560 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.00 (s, 6 H, methyl protons), 2.05 (s, 2 H, $-CH_2C=C$), 2.35 (s, 2 H, $COCH_2-$), 5.30 (s, 1 H, CH=C<), 7.05–7.40 (m, 5 H, phenyl protons), and 8.70–8.80 (broad, 1 H, NH); mass spectrum (70 eV) *m/e* 215 (M^+).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.76; H, 7.82; N, 6.28.

Reaction of 3-Anilino-5,5-dimethyl-2-cyclohexen-1-one (8) with Sulfur. A solution of 1.08 g (5 mmol) of **8** and 0.32 g (10 mmol) of sulfur in 15 ml of mesitylene containing copper shavings (1.0 g) was refluxed for 3 h. After the reaction mixture was allowed to stand at ambient temperature overnight, the resulting solid was filtered and recrystallized from benzene to give 0.85 g (74%) of **bis(1-oxo-3-anilino-5,5-dimethyl-2-cyclohexen-2-yl) sulfide,** mp 265–266 °C, which was consistent with **6** obtained in the above reaction.

Reaction of a Mixture of 3-Anilino-5,5-dimethyl-2-cyclohexen-1-one and 5,5-Dimethyl-1,3-cyclohexanedione with Sulfur. The reaction was similarly carried out as described above using **8** (1.08 g, 5 mmol), **2c** (0.70 g, 5 mmol), sulfur (0.64 g, 20 mmol), and copper shavings (1.0 g). After removal of the resulting 0.45 g (40%) of the sulfide **6**, the filtrate was concentrated in vacuo and the residue was chromatographed on silica gel to give 0.82 g (43%) of **(1-oxo-3-anilino-5,5-dimethyl-2-cyclohexen-2-yl)(1,3-dioxo-5,5-dimethylcyclohexan-2-yl) sulfide,** mp 208–210 °C, which was consistent with **7** obtained in the above reaction.

Reaction of *N*-Sulfinylaniline (1a) with Diethyl Malonate (2d). The reaction was carried out at 140 °C for 6 h using the procedure described above with **1a** (4.20 g, 0.03 mol), **2d** (4.80 g, 0.03 mol), and copper shavings (3 g) in *m*-xylene (30 ml). After removal of solvent containing formed diethyl sulfite, of which structure was determined by comparison of the retention time with that of an authentic sample, the residue was similarly treated to give 2.65 g (43%) of **malonanilic acid ethyl ester** (**9**): mp 38–40 °C (lit.[11] mp 38–39 °C); ir (Nujol) 3300 (NH), 1730 (C=O), and 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.85 (t, 3 H, CH_2CH_3), 3.20 (s, 2 H, $COCH_2CO$), 3.85 (q, 2 H, CH_2CH_3), 6.85–7.75 (m, 5 H, phenyl protons), and 9.10–9.30 (broad, 1 H, NH).

Reactions of *N*-Sulfinylaniline (1a) with Ketones 2e,f. The reactions were carried out in a similar manner. After similar workup, **1-phenyl-2,5-dimethylpyrrole** (**10**) and **(β-anilino-β-phenyl)ethyl phenyl ketone** (**11**) were obtained in 65 and 58% yields, respectively.

10 had mp 50–51 °C (lit.[12] mp 49–51 °C); white plates; ir (Nujol) 1590 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.05 (s, 6 H, methyl protons), 5.90 (s, 2 H, CH=C), and 7.00–7.50 (m, 5 H, phenyl protons); mass spectrum (70 eV) *m/e* 171 (M^+).

11 had mp 171–172 °C; pale yellow needles; ir (Nujol) 3350 (NH) and 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.40 (d, J = 7 Hz, 2 H, $COCH_2-$), 3.85–4.15 (broad, 1 H, NH), 4.98 (t, J = 7 Hz, 1 H, CH_2-**CH**<), and 6.40–7.15 (m, 15 H, phenyl protons); mass spectrum (70 eV) *m/e* 301 (M^+) and 209 ($M^+ - NHPh$).

Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.52; H, 6.14; N, 4.69.

Reaction of *N*-Sulfinyl-*p*-toluidine (1b) with Phenylacetonitrile (12). The reaction was carried out at 140 °C for 6 h using the procedure described above with **1b** (3.06 g, 0.02 ml), **12** (4.68 g, 0.04 mol), and copper shavings (2 g) in 20 ml of *m*-xylene. After similar treatment, the residue was chromatographed on silica gel to give 0.60 g (26%) of ***trans*-α,β-dicyanostilbene** (**13**): mp 161–162 °C (lit.[13] mp 161 °C); ir (Nujol) 2250 cm^{-1} (CN); NMR ($CDCl_3$) δ 7.10–7.95 (m, phenyl protons).

Registry No.—**1a,** 1122-83-4; **1b,** 15795-42-3; **2a,** 123-54-6; **2b,** 504-02-9; **2c,** 126-81-8; **2d,** 105-53-3; **2e,** 110-13-4; **2f,** 94-41-7; **3,** 26567-78-2; **4,** 60224-19-3; **5,** 24706-50-1; **6,** 60224-20-6; **7,** 60224-21-7; **8,** 18940-21-1; **9,** 53341-66-5; **10,** 83-24-9; **11,** 742-43-8; **12,** 140-29-4; **13,** 2450-55-7; copper, 7440-50-8; diphenylketene, 525-06-4.

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Intramolecular Diels–Alder Reactions. 12. Competitive [4 + 2] and [2 + 2] Cycloadditions of *N*-(Phenylpropargyl)-*cis*-cinnamamide[1a]

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Refluxing *N*-(phenylpropargyl)-*cis*-cinnamamide in Ac_2O gave competitive [4 + 2] and [2 + 2] intramolecular cycloadditions in mode 2 to form (a) a mixture of benz[*f*]isoindole (**2b**) and its dihydro derivative **2a** and (b) substituted 3-pyrrolin-2-one **12** (following spontaneous cycloreversion), respectively. Structural studies on **12** and its bromo and dideuterio derivatives are reported. Modal selectivity in the cyclizations is interpreted in terms of relative frontier molecular orbital energy levels, while regiospecificity is interpreted in terms of stereochemical relationships. Action of the C≡C in an electron acceptor role in these cycloadditions is discussed.

In a preceding paper in this series[2] we described the syntheses of the nine possible unsaturated amides of the type $Ph(C_2)CH_2NHC(=O)(C_2)'Ph$, where (C_2) and $(C_2)'$ are variously *cis*-CH=CH–, *trans*-CH=CH–, and –C≡C– units. Six of these amides were investigated for possible intramolecular cyclization in refluxing acetic anhydride. Of these six, one [$(C_2) = (C_2)' =$ *trans*-CH=CH–] failed to undergo cyclization, while the other five underwent [4 + 2] cycloadditions either in mode 1 ("normal" Diels–Alder reaction) or mode 2 "abnormal" Diels–Alder reaction), or in a combination of both modes.[2] In particular, *N*-(phenylpropargyl)-*trans*-cinnamamide (**1**) cyclized in mode 2 to yield an unresolved mixture (**2**) (ca. 4:1) of *N*-acetyl lactams **2a** and **2b** in 75% yield (eq 1). The present paper concerns the cyclization of a seventh one of these am-