1600 (CO) $cm^{-1}$; $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 323 (4.15), 255 (4.23), 242 (sh, 4.13); NMR ($CDCl_3$) $\delta$ 8.90 (m, 1, $C_6$ H), 7.2–7.7 (m, 8, aromatic), 3.80 (s, 3, $NCH_3$); mass spectrum, *m/e* (relative intensity) 308 (9, $M^+$·).

Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.21; H, 3.92; N, 9.09. Found: C, 65.98; H, 3.92; N, 9.08.

**1-Methyl-3-[(phenylmethyl)carbonyl]-2(3*H*)-benzimidazolethione (28).** The betaine **26** (X = $NCH_3$; 1.0 g, 3.24 mmol) was stirred in aqueous $Me_2SO$ (4 mL of 10% solution) at room temperature for 12 h. The separated product was collected and recrystallized from THF, forming colorless plates: 0.8 g (88%); mp 180–181 °C; IR (KBr) 1700 (CO) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 8.15 (m, 1, $C_4$ H), 7.0–7.5 (m, 8, aromatic), 5.1 (s, 2, $CH_2$), 3.75 (s, 3, $NCH_3$); mass spectrum, *m/e* (relative intensity) 282 (25, $M^+$·).

Anal. Calcd for $C_{16}H_{14}N_2OS$: C, 68.07; H, 5.00; N, 9.93. Found: C, 68.04; H, 4.98; N, 9.96.

**2-Hydroxy-4-oxo-3-phenylbenzo[*f*]-4*H*-imidazo[2,1-*b*][1,3]thiazine (32).** 2(3*H*)-Benzimidazolethione[25] (6.9 g, 46 mmol) was added with stirring to (chlorocarbonyl)phenylketene (8.3 g, 46 mmol) in dry dioxane (100 mL). Triethylamine (4.65 g, 46 mmol) was added dropwise and the reaction mixture refluxed for 4 h. The solvent was removed under reduced pressure and the remaining solid washed with water (200 mL) and recrystallized from ethanol, forming colorless prisms: 14.2 g (91%); mp 293 °C dec; IR (KBr) 2500–3200 (br, OH), 1690 (CO) $cm^{-1}$; $\lambda_{max}$ ($CH_3OH$) nm (log $\epsilon$) 305 (4.33), 295 (sh, 4.26), 278 (4.18), 245 (4.29), 210 (4.43); NMR ($Me_2SO$-$d_6$) $\delta$ 12.9 (s, 1, OH), 8.70 (m, 1, $C_6$ H), 7.1–8.0 (m, 8, aromatic); mass spectrum, *m/e* (relative intensity) 294 (95, $M^+$·).

Anal. Calcd for $C_{16}H_{10}N_2O_2S$: C, 65.29; H, 3.42; N, 9.52. Found: C, 64.99; H, 3.48; N, 9.60.

**Methylation of 2-Hydroxy-4-oxo-3-phenylbenzo[*f*]-4*H*-imidazo[2,1-*b*][1,3]thiazine (32).** The hydroxy compound **32** (2.94 g, 10 mmol) in ethanol (50 mL) was added with stirring to an ethereal solution of diazomethane (ca. 1.5 g, 36 mmol) at 0 °C. The solution was allowed to warm to room temperature with stirring over 24 h. Removal of the solvent and recrystallization of the remaining solid product from acetone gave colorless prisms, 2.3 g. TLC in benzene–acetone (1:1) showed this to be a two-component mixture, and on fractional crystallization from THF the less soluble 4-methoxy-2-oxo-3-phenylbenzo[*f*]-4*H*-imidazo-[2,1-*b*][1,3]thiazine (**34**) was obtained as colorless prisms: 0.8 g (25%); mp 211–212 °C; IR (KBr) 1670 (CO) $cm^{-1}$; $\lambda_{max}$ ($CH_3OH$) nm (log $\epsilon$) 305 (3.67), 264 (4.57), 218 (sh, 4.22); NMR ($CDCl_3$) $\delta$ 8.60 (m, 1, $C_6$ H), 7.45 (br s, 8, Ph and aromatic), 3.96 (s, 3, $OCH_3$); mass spectrum, *m/e* (relative intensity) 308 (100, $M^+$·).

Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.21; H, 3.92; N, 9.09. Found: C, 66.44; H, 3.93; N, 9.04.

***anhydro*-2-Hydroxy-1-methyl-4-oxo-3-phenylbenzo[*b*]-4*H*-thiazolo[3,2-*a*]pyrimidinium Hydroxide (35).** 2-(Methylamino)benzothiazole[26] (1.42 g, 8.65 mmol) was added with stirring to (chlorocarbonyl)phenylketene (1.73 g, 9.6 mmol) in dry THF (50 mL). After the mixture was stirred at room temperature for 6 h, the separated material was collected and recrystallized from acetone, forming bright yellow prisms: 2.5 g (86%); mp 205 °C; IR (KBr) 1625 (CO) $cm^{-1}$; $\lambda_{max}$ ($CH_3OH$) nm (log $\epsilon$) 330 (3.65), 255 (4.39), 213 (4.50); NMR ($CDCl_3$) $\delta$ 9.23 (m, 1, $C_6$ H), 7.2–7.9 (m, 8, aromatic), 3.68 (s, 3, $NCH_3$); mass spectrum, *m/e* (relative intensity) 308 (100, $M^+$·).

Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.21; H, 3.92; N, 9.09. Found: C, 66.17; H, 3.89; N, 9.32.

**Registry No.** **1**, 60-56-0; **2**, 17118-70-6; **3**, 73395-65-0; **5**, 73384-43-7; **6**, 73384-44-8; **7**, 872-35-5; **8**, 73384-45-9; **9**, 25433-13-0; **10**, 73384-46-0; **11**, 13431-10-2; **12**, 73384-47-1; **13**, 96-45-7; **14**, 73384-48-2; **15**, 38942-51-7; **16**, 73384-49-3; **17**, 13183-79-4; **18**, 73384-50-6; **19**, 6142-06-9; **20**, 73384-51-7; **21**, 149-30-4; **22**, 73384-52-8; **24a**, 66085-23-2; **24b**, 73384-53-9; **25** (X = O), 2382-96-9; **25** (X = $NCH_3$), 2360-22-7; **26** (X = O), 73384-54-0; **26** (X = $NCH_3$), 73384-55-1; **28**, 21541-38-8; **32**, 73384-56-2; **34**, 73384-57-3; **35**, 73384-58-4; diazomethane, 334-88-3; dimethyl acetylenedicarboxylate, 762-42-5; ethyl propiolate, 623-47-2; 2(3*H*)-benzimidazolethione, 583-39-1; 2-(methylamino)benzothiazole, 16954-69-1.

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# 7*H*-[1,2,4]Triazolo[5,1-*b*][1,3]thiazin-7-ones by Deamination Cyclization of *S*-Acrylates of 4-Amino-3(3*H*)-1,2,4-triazolethiones

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Condensation of 4-amino-3(3*H*)-1,2,4-triazolethiones with methyl propiolate gave *S*-acrylic esters. *S*-Acrylic acids prepared from these esters underwent a deamination cyclization of 7*H*-[1,2,4]triazolo[5,1-*b*][1,3]thiazin-7-ones with the loss of the elements of hydroxylamine.

The vicinal amino and mercapto functions in the tautomeric form of 4-amino-3(4*H*)-1,2,4-triazolethiones (**1**) offer nucleophilic loci for heterocyclic syntheses involving potential bridging reactings with alkynyl esters. Our earlier studies, which make these triazoles available in quantity,[1] and our continuing interest in synthetic applications of acetylene esters[2,3] prompted our investigation of the condensation of **1** and methyl propiolate.

Combination of equimolar quantities of **1a–c** and methyl propiolate (Scheme I) in refluxing anhydrous methanol resulted in 53–83% yields of 1:1 adducts identified as S-substituted acrylic esters (**2a–c**). Infrared spectra retained the characteristic primary amine bands at 3630 to 3550 $cm^{-1}$, and $^1H$ NMR spectra displayed a singlet, $D_2O$ exchangeable and integrating for 2 protons, between $\delta$ 5.9 and 6.3, which excludes adduct formation involving the primary amino group and the alkyne.

Exclusion of the tautomeric ring nitrogen of the thiolactam as a site of Michael addition rests on both literature precedent and Raney nickel treatment of **2b**. Kovalev has

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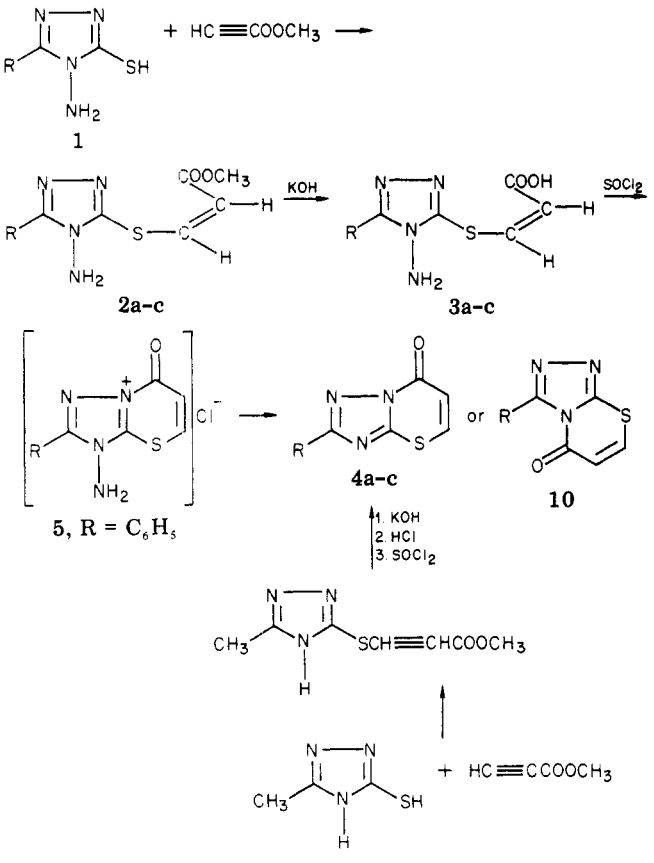
0022-3263/80/1945-2479$01.00/0 

Scheme I



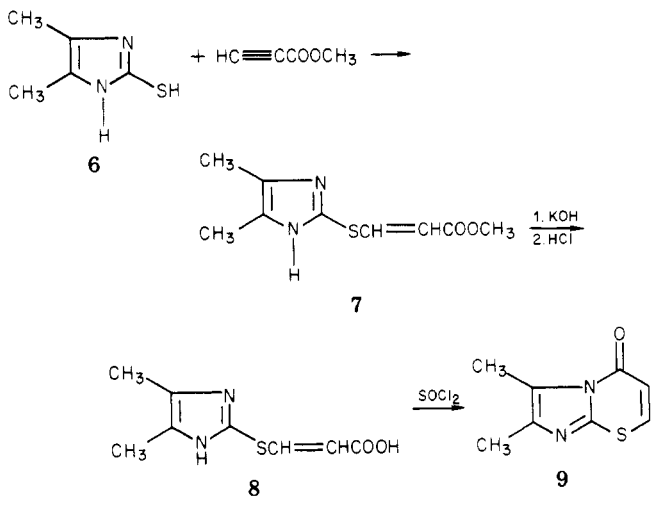
a, R = $CH_3$; b, R = $C_6H_5$; c, R = $(CH_3)_3C$

reported that the 3-thiol/thione of 3(3*H*)-1,2,4-triazolethiones adds to acrylonitrile in preference to the potentially tautomeric ring NH.[4] Further support was found when the propiolate adduct of the aminotriazolethione characterized structurally as **2b** was refluxed with Raney nickel and the gases were swept by a nitrogen stream into a solution of bromine in $CCl_4$. Methyl 1,2-dibromopropionate, identified by spectral comparison with authentic material, was isolated from the trapping solution. For control purposes it was possible to show that the 1:1 adduct of pyrrolidine and methyl propiolate did not suffer acryloyl scission on similar treatment.

The acrylic adducts **2a–c** were of cis configuration, reflecting a trans addition to the acetylenic linkage. The two olefinic protons displayed coupling constants of $J$ = 9–10 Hz as reported for similar cis adducts of methyl propiolate and thioamides. Lown and Ma report that in such additions the cis adducts ($J$ = 10.0 Hz) predominate over the trans adducts ($J$ = 15.5 Hz).[5] Characterization of **2a–c** as being of cis geometry would appear to favor the anticipated cyclization pathway of the pendant primary amino group to the methyl ester carbonyl.

Closure to the amine, however, was not observed under numerous reaction conditions selected for evaluation: reflux in xylene, treatment with sodium methylate in methanol or in xylene, neat fusion, fusion with zinc chloride, thermolysis in refluxing diphenyl ether, or condensation with sodium hydride in xylene. In all cases, either the unreacted *S*-acrylate esters were recovered or, under the more drastic reaction conditions probed, colored tarry multicomponent (TLC) oils were obtained from which

Scheme II



nothing identifiable could be isolated.

Caustic hydrolysis of the ester adducts **2a–c** gave after acidification the corresponding acrylic acids in 50–89% yields. In anticipation of a ring closure via the acid chlorides, these carboxylic derivatives (**3a–c**) were refluxed with thionyl chloride. From **3a** and **3c**, non-chlorine-containing products analyzing for the loss of the elements of hydroxylamine were isolated directly. From **3b** a thermally labile water-soluble chlorine-containing compound with an analysis in agreement with that expected for the acryloyl chloride was obtained. The compound **5** was not, in fact, the acid chloride, for it was recovered unchanged with no evidence of ester formation after prolonged reflux in alcohol and possessed a carbonyl absorption at 1745 $cm^{-1}$ but no charged NH bands in the infrared spectrum. Heating or subliming the material caused the loss of the elements of chloramine and generated **4b**, the molecular and spectral counterpart of the compounds **4a** and **4c** obtained directly from **3a** and **3c**, respectively. The products **4a–c** displayed no NH bands in their infrared spectra, no $D_2O$ exchangeable resonances in the $^1H$ NMR spectra, a distinctive pair of cis-coupled ($J$ = 10 Hz) vinyls centered at 6.93 ± 0.02 and 7.37 ± 0.02 ppm, and a carbonyl absorption at 1690 $cm^{-1}$. Options **4** and **10** appear to be in accord with these data.

An independent synthesis which does not distinguish between **4** and **10** but which does confirm that one of these is the correct product structure was undertaken from 5-methyl-3(2*H*)-1,2,4-triazolethione. Addition of this tautomeric thione–mercaptan to methyl propiolate followed by saponification, acyl chlorination, and in situ cyclization gave a material identical in all respects with **4a** or **10** (Scheme I).

Cyclization of the acrylic acid side chain onto the ring nitrogen adjacent to the substituent at C-5 of the triazole yields a carbonyl in the peri position to that attachment (see alternative **4e**). Where the C-5 substituent is a methyl, considerable anisotropic deshielding should occur. The $^1H$ NMR spectra of **2a**, **3a**, and **4a** display the ring methyl at 2.36, 2.35, and 2.42 ppm, respectively, indicating virtually no downfield shift postcyclization. The methyl propiolate adduct of 4,5-dimethyl-1,3-dihydro-2(2*H*)-imidazolethione (**6**) was prepared to demonstrate that a flanking carbonyl would indeed shift a methyl by a detectable magnitude. This adduct (**7**) was saponified, chlorinated, and cyclized to 2,3-dimethyl-5*H*-imidazolo[2,1-*b*][1,3]thiazin-5-one (**9**). The methyl resonances in **7** and **8** were identical and were detected at 2.10 ppm. Cyclization produced two nonequivalent methyls at 2.15 and

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(5) J. Lown and J. Ma, *Can. J. Chem.*, 45, 953 (1967).

2.55 ppm, clearly indicating that the deshielding effect of the peri carbonyl would have been evident, if present, and confirming structure **4** as the cyclization product of **3** (Scheme II).

Retrospectively, **5** appears as an attractive structural option for the salt-like transient isolated in the phenyl-containing system. Presumably, cationic character in the triazole ring is stabilized by the aryl attachment and permits isolation of the intermediate in this case. Nucleophilic attack on the 3-amino nitrogen of **5** would effect deamination and lead to **4b**. An additional reflection of the diminished nucleophilicity of the *N*-amino group of these tautomeric aminotriazolethiones, which thwarted its closure to the acryloyl carboxyl and facilitated the deamination pathway, was its resistance to anil formation. Reactive aromatic aldehydes reacted only sluggishly at the *N*-amino group and indeed one of the more reactive analogues, 4-amino-5-(*o*-methoxyphenyl)-2,4-dihydro-3-(3*H*)-1,2,4-triazolethione[1] gave only a 19% yield of the anil upon 24-h condensation with *p*-nitrobenzaldehyde.

## Experimental Section

Infrared spectra were obtained as 1–2% KBr disks on a Perkin-Elmer 257 spectrophotometer. $^1$H NMR spectra were obtained in $Me_2SO$-$d_6$ on a Hitachi Perkin-Elmer R20A spectrometer. Melting points, determined in capillaries on a Thomas-Hoover apparatus, are uncorrected. The combustion analyses were provided by Dr. George I. Robertson, Florham Park, NJ.

**5-Substituted-4-amino-3(3*H*)-1,2,4-triazolethiones (1a–c).** Triazoles **1a**[6] and **1b**[7] were known compounds and were prepared by literature methods. **1c** was prepared by the condensation of potassium 3-pivaloyldithiocarbazinate (0.12 mol) with anhydrous hydrazide (0.30 mol) in 20 mL of water according to method A in our previously published procedures.[1] The potassium 3-pivaloyldithiocarbazinate was generated in situ from a reaction of 0.15 mol each of pivalic acid hydrazide and KOH in 200 mL of ethanol and 25 mL of carbon disulfide. Refluxing (6 h) followed by chilling in ice produced 27.4 g (81%) of the dithiocarbazinate as a fine white powder which was used directly in the synthesis of **1c**. **1c** was obtained as white platelets from 4:1 water–ethanol in 69% yield: mp 193–194 °C; IR (KBr) 3290, 3200, 2980, 1605, 1550, 1465, 1255, 920 cm$^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 1.42 (s, 9, *t*-Bu), 5.55 (s, 2, $NH_2$), 13.49 (s, 1, NHC=S). Anal. Calcd for $C_6H_{12}N_4S$: C, 41.84; H, 7.02; N, 32.50. Found: C, 41.57; H, 7.08; N, 32.31.

**3-[(4-Amino-5-substituted-1,2,4-triazol-3-yl)thio]acrylate Methyl Esters (2a–c).** A suspension of 12.0 mmol each of methyl propiolate and the requisite 4-amino-3(4*H*)-1,2,4-triazolethiones (**1a–c**) in 40 mL of MeOH was stirred at room temperature for 1 h, refluxed for 20 h, and evaporated to virtual dryness in vacuo. Filtration and recrystallization from the indicated solvents gave the title compounds in 53–83% yields.

**2a**: 53% yield; mp 166–169 °C (from ethyl acetate). Anal. Calcd for $C_7H_{10}N_4SO_2$: C, 39.25; H, 4.69; N, 26.15. Found: C, 39.24; H, 4.82; N, 25.55.

**2b**: 76% yield; mp 204–206 °C (from 1:1 methanol–water). Anal. Calcd for $C_{12}H_{12}N_4SO_2$: C, 52.30; H, 4.35; N, 20.21. Found: C, 52.35; H, 4.32; N, 19.81.

**2c**: 83% yield, mp 170–172 °C (from 1:1 chloroform–hexane). Anal. Calcd for $C_{10}H_{16}N_4SO_2$: C, 46.86; H, 6.29; N, 21.86. Found: C, 46.73; H, 6.28; N, 22.04.

**3-[(4-Amino-5-substituted-1,2,4-triazol-3-yl)thio]acrylic Acids (3a–c).** A mixture prepared from 10 mmol of a thioacrylate (**2a**, **2b**, or **2c**) and 30 mL of 15% aqueous KOH was refluxed for 15 min, cooled, and carefully neutralized with concentrated HCl. The precipitated acid was filtered, washed well with cold water, redissolved in a minimum of saturated aqueous $NaHCO_3$, filtered, and reacidified with concentrated HCl to give the target acids in 50–89% yields.

**3a**: 50% yield; mp 218–220 °C dec. Anal. Calcd for $C_6H_8N_4SO_2$: C, 36.00; H, 4.03; N, 27.98. Found: C, 36.18; H, 4.19; N, 28.24.

**3b**: 89%; mp 204–205 °C dec. Anal. Calcd for $C_{11}H_{10}N_4SO_2$: C, 50.38; H, 3.84. Found: C, 50.35; H, 3.97.

**3c**: 53%; mp 213–215 °C dec. Anal. Calcd for $C_9H_{14}N_4SO_2$·0.25$H_2O$: C, 43.80; H, 5.92. Found: C, 43.52; H, 5.86.

**2-Substituted-7*H*-[1,2,4]triazolo[5,1-*b*][1,3]thiazin-7-ones (4a and 4c).** A well-agitated solution of 15 mmol of *S*-acrylic acid **3a** or **3c** in 50 mL of anhydrous chloroform was treated with the dropwise addition of 40 mmol of thionyl chloride over a 10-min interval. The mixture was stirred at reflux for 24 h, the chloroform and thionyl chloride were removed under vacuum, and the crude product **4a** or **4c** was washed with saturated aqueous sodium bicarbonate, mulled in hot ethanol, filtered, and dried. Pure product could be obtained by recrystallization from cyclohexane, or, more conveniently, by sublimation in vacuo at 175 °C (0.1 mmHg).

**4a**: 80%; mp 193–195 °C. Anal. Calcd for $C_6H_5N_3SO$: C, 43.11; H, 3.01; N, 25.13. Found: C, 43.34; H, 3.18; N, 25.40.

**4c**: 66%; mp 191–192 °C. Anal. Calcd for $C_9H_{11}N_3SO$: C, 51.66; H, 5.30; N, 20.08. Found: C, 51.61; H, 5.35; N, 20.28.

**2-Phenyl-3-amino-[1,2,4]triazolium[5,1-*b*][1,3]thiazin-7-one Chloride (5).** Combination of 15 mmol of **3b** and 40 mmol of thionyl chloride in 50 mL of dry chloroform precipitated a white-yellow solid upon brief heating (less than 10 min). Reflux was continued for 24 h, solvents were removed in vacuo, and the resulting solid was triturated with ethanol and filtered. The product (**5**), a white solid, was obtained in 98% yield after repeated triturations with ethanol, mp 242–249 °C. The compound precipitated silver chloride from aqueous silver nitrate and gave a single spot on TLC (Bakerflex IBF with 4:1 methanol–water eluant): IR (KBr) 3130, 3000, 2950, 1745, 1530, 1445, 1345, 1280, 1170, 1110, 820, 780, 705 cm$^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 6.26 (d, 1, =CH, $J$ = 9 Hz), 7.40–8.40 (m, 7, Ar H and $NH_2$), 8.67 (d, 1, =CH, $J$ = 9 Hz). Anal. Calcd for $C_{11}H_9ClN_4SO$: C, 47.20; H, 3.22. Found: C, 47.15; H, 3.51.

**2-Phenyl-7*H*-[1,2,4]triazolo[5,1-*b*][1,3]thiazin-7-one (4b).** Sublimation of 3.00 g (12.0 mmol) of **5** at 175 °C (0.1 mmHg) gave 1.48 g (54%) of **4b**: mp 264–266 °C; IR (KBr) 3020, 1690, 1605, 1555, 1480, 1445, 1330, 1295, 1280, 1190, 1060, 965, 800, 720 cm$^{-1}$. Anal. Calcd for $C_{11}H_7N_3SO$: C, 57.62; H, 3.08; N, 18.33. Found: C, 57.18; H, 3.27; N, 18.59.

**2-Methyl-7*H*-[1,2,4]triazolo[5,1-*b*][1,3]thiazin-7-one (4a). Alternative Synthesis.** A solution of 0.10 mol each of 5-methyl-3(2*H*)-1,2,4-triazolethione[8] and methyl propiolate and 200 mL of anhydrous methanol was refluxed for 1 h and evaporated to dryness in vacuo, and the residue was refluxed with 8% aqueous potassium hydroxide (100 mL) until solution resulted. The cooled solution was carefully neutralized with concentrated hydrochloric acid to precipitate the *S*-acrylic acid as a white powder (41%) which was dried and used directly in the cyclization without further purification: IR (KBr) 3140–2350 (br), 1660, 1560, 1420, 1230, 1160, 1055, 890, 780 cm$^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 2.41 (s, 3, $CH_3$), 6.10 (d, 1, =CH, $J$ = 10 Hz), 7.99 (d, 1, =CH, $J$ = 10 Hz), 11.40–13.80 (br s, 2, COOH + NH). A solution of the crude dried acid (30 mmol), thionyl chloride (40 mmol), and anhydrous chloroform (50 mL) was refluxed with stirring for 24 h and evaporated in vacuo, and the residue was washed with saturated aqueous sodium bicarbonate and cold water, dried, and sublimed at 175 °C (0.1 mmHg) to give **4a** (82%), mp 196–197 °C. Melting point and mixture melting point with previous material described above were undepressed.

**2,3-Dimethyl-5*H*-imidazolo[2,1-*b*][1,3]thiazin-5-one (9).** A solution of 0.20 mol each of 4,5-dimethyl-2(2*H*)-imidazolinethione[9] (**6**) and methyl propiolate and 200 mL of anhydrous methanol containing 0.10 g of sodium methylate was refluxed for 2 h and evaporated to dryness in vacuo, and the crude *S*-acrylate ester (**7**), mp 148–152 °C, obtained: NMR ($Me_2SO$-$d_6$) 2.10 (s, 6, 2 $CH_3$), 3.70 (s, 3, $CH_3O$), 6.04 (d, 1, =CH, $J$ = 9 Hz), 7.72 (d, 1, =CH, $J$ = 9 Hz), 12.18 (s, 1, NH). The crude **7** was refluxed with 8% aqueous potassium hydroxide (100 mL) until solution resulted, cooled, and carefully neutralized with concentrated hydrochloric acid to precipitate the crude *S*-acrylic acid **8** as tan

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(9) H. Anschutz and H. Gekdermann, *Justus Liebigs Ann. Chem.*, **261**, 129 (1890); **284**, 9 (1894).

crystals: mp >300 °C; 76%; IR (KBr) 3300–2360 (br), 1640, 1580, 1395, 1290, 1170, 1035, 825, 800 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) 2.10 (s, 6, 2 $CH_3$), 5.99 (d, 1, =CH, $J$ = 9 Hz), 7.51 (m, 3, COOH, NH, and =CH). The crude acid **8** (12 mmol), thionyl chloride (35 mmol), and 30 mL of anhydrous chloroform were refluxed for 6 h and evaporated to dryness in vacuo, and the crude **9** was purified by sublimation at 100 °C (0.1 mmHg) to give white crystals: 55%; mp 120–121 °C; IR (KBr) 3015, 2910, 1680, 1600, 1450, 1365, 1295, 1120, 1040, 795, 755 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) 2.15 (s, 3, $CH_3$), 2.55 (s, 3, $CH_3$), 6.57 (d, 1, =CH, $J$ = 9 Hz), 8.20 (d, 1, =CH, $J$ = 9 Hz). Anal. Calcd for $C_8H_8N_2SO$: C, 53.31; H, 4.47; N, 15.54. Found: C, 53.08; H, 4.52; N, 15.27.

**4-Amino-5-(*o*-methoxyphenyl)-2,4-dihydro-3(3*H*)-1,2,4-triazolethione *p*-Nitrobenzaldehyde Anil.** A solution of 4.0 mmol of 4-amino-5-(*o*-methoxyphenyl)-3(4*H*)-1,2,4-triazolethione[1] and 20 mmol of *p*-nitrobenzaldehyde in 100 mL of anhydrous methanol was refluxed for 1 h and allowed to stand for 24 h. Evaporation in vacuo and chilling at ice-bath temperature gave 0.30 g (19%) of orange crystals of the title compound, mp 209–211 °C. Anal. Calcd for $C_{16}H_{13}N_5SO_3$: N, 19.71. Found: N, 19.73.

**Registry No. 1a**, 20939-15-5; **1b**, 22706-11-2; **1c**, 73396-58-4; (*Z*)-**2a**, 73396-59-5; (*Z*)-**2b**, 73396-60-8; (*Z*)-**2c**, 73396-61-9; (*Z*)-**3a**, 73396-62-0; (*Z*)-**3b**, 73396-63-1; (*Z*)-**3c**, 73396-64-2; **4a**, 73396-65-3; **4b**, 73396-66-4; **4c**, 73396-67-5; **5**, 73396-68-6; **6**, 1192-72-9; (*Z*)-**7**, 73396-69-7; (*Z*)-**8**, 73396-70-0; **9**, 73396-71-1; potassium 3-pivaloyldithiocarbazinate, 73396-72-2; hydrazine, 302-01-2; pivalic acid hydrazide, 42826-42-6; carbon disulfide, 75-15-0; methyl propiolate, 922-67-8; 4-amino-5-(*o*-methoxyphenyl)-2,4-dihydro-3(3*H*)-1,2,4-triazolethione *p*-nitrobenzaldehyde anil, 73396-73-3; *p*-nitrobenzaldehyde, 555-16-8.

# Steric Inhibition to Cyclization of β-Keto Amides to Indeno[1,2,3-*de*]quinolinones and Related Compounds

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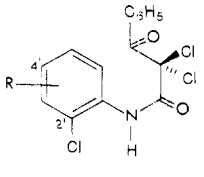
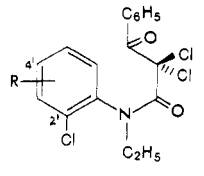
The preferred conformation of *N*-ethyl-2,2,2′-trichlorobenzoylacetanilide (**1f**) was deduced from $^1H$ NMR data and served to account for the failure of **1f** to cyclize in $H_2SO_4$ in terms of a steric hindrance to attainment of the requisite conformation for ring closure. Consistent with this view was the observation that pentachlorodihydroquinolinone **7a** with $H_2SO_4$ underwent ring opening to give as chief product alkene **8**, and only a minor amount of indenoquinolinone **2**. Substrate **7a** was formed, in preference to amide **11**, from difluorooxyborane **6a** and $SO_2Cl_2$, on allowing HCl to escape from the reaction mixture.

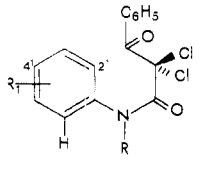
In the course of the conversion of β-keto amides **1** to indeno[1,2,3-*de*]quinolinones **2** by using concentrated sulfuric acid,[1] substrates **1d** and **11** each yielded a yellow,



**1a**, R = H
**b**, R = 3′,4′—diCH$_3$
**c**, R = 4′—Br—3′,5′—diCH$_3$
**d**, R = 4′—Cl—3′,5′—diCH$_3$



**1e**, R = H
**f**, R = 4′—Br—3′,5′—diCH$_3$
**g**, R = 4′—Cl—3′,5′—diCH$_3$



**1h**, R = H; R$_1$ = 2′,4′—diCH$_3$
**i**, R = H; R$_1$ = 4′—Cl—2′,3′—diCH$_3$
**j**, R = H; R$_1$ = 4′—Cl—3′,5′—diCH$_3$

**1k**, R = C$_2$H$_5$; R$_1$ = 2′,5′—diCH$_3$
**l**, R = C$_2$H$_5$; R$_1$ = 4′—Cl—3′,5′—diCH$_3$
**m**, R = i—C$_3$H$_7$; R$_1$ = 3′,5′—diCH$_3$

high-melting product which we suspect[2] to be indenoquinolinones **2a** and **2c**, respectively. The related 4′-bromo amide **1c** likewise underwent cyclization to an indenoquinolinone product, but in contrast, the corresponding *N*-ethyl derivatives, **1f** and **1g**, under similar conditions, gave neither **2** nor quinolinone **3** and were recovered largely unchanged.[3] The difficulties with **1f** and **1g** seemingly stem from steric factors, for which there appear to be few relevant precedents in the literature.

Koelsch and Britain[4] cyclized *N*-alkylbenzoylacetanilides to *N*-alkylquinolinones with sulfuric acid when the alkyl group was primary but not when it was secondary, as in **4a**. Failure in the latter instance, in their view, probably resulted from steric inhibition of N–Ar conjugation, an interpretation supported by UV properties of related *N*-alkyl-*p*-nitroacetanilides. In strong acid media, however, the aforementioned N-lone-pair participation may be of little importance,[2] and we prefer to rationalize the behavior of substrates such as **1f**, **1g**, **4a**, and **4b**, primarily in terms of steric hindrance to attainment of the conformation requisite for ring closure.[2] With a view to substantiating this suggestion, amide **1f** was selected for a conformational analysis, utilizing the results of $^1H$ NMR spectral studies with a variety of aniline derivatives[5,6] and our findings[3] with representative β-keto amides **1**. Some general conclusions concerning the steric preferences of the latter compounds were drawn from the following results.

Amides **1h** (δ 7.4), **1i** (δ 7.2), and **1j** (δ 7.2) each showed an "acylation shift" ($CDCl_3$) of the ortho proton comparable to that in the corresponding acetanilide, supporting

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