

Table II. Exact Masses of Selected Ions in the Mass Spectrum of TNT

observed mass, amu	empirical formula	calcd mass, amu	deviation, mmu
210.0149	C ₇ H ₅ N ₃ O ₅	210.0151	-0.2
209.0076	C ₇ H ₅ N ₃ O ₅	209.0073	+0.3
193.0121	C ₇ H ₅ N ₃ O ₄	193.0124	-0.3
180.0171	C ₇ H ₅ N ₃ O ₄	180.0171	0
179.0088	C ₇ H ₅ N ₃ O ₄	179.0092	-0.4
166.0017	C ₆ H ₅ N ₃ O ₄	166.0015	+0.2
164.0222	C ₇ H ₄ N ₃ O ₃	164.0222	0
163.0144	C ₇ H ₅ N ₃ O ₃	163.0144	0
151.0148	C ₆ H ₅ N ₃ O ₃	151.0143	+0.5
149.0113	C ₇ H ₅ N ₃ O ₃	149.0113	0
134.0241	C ₇ H ₄ N ₃ O ₂	134.0242	-0.1
120.0088	C ₆ H ₅ N ₃ O ₂	120.0086	+0.2
117.0215	C ₇ H ₃ N ₃ O	117.0215	0
105.0218	C ₆ H ₅ N ₃ O	105.0215	+0.3
104.0262	C ₇ H ₄ N ₃ O	104.0263	-0.1
103.0185	C ₇ H ₃ N ₃ O	103.0184	+0.1
89.0392	C ₇ H ₅	89.0392	0
88.0313	C ₇ H ₄	88.0313	0
87.0236	C ₇ H ₃	87.0235	+0.1
77.0265	C ₅ H ₅ N	77.0266	-0.1
76.0316	C ₆ H ₄	76.0313	+0.3
74.0161	C ₆ H ₃	74.0156	+0.5
63.0246	C ₅ H ₃	63.0235	+1.1
62.0169	C ₅ H ₂	62.0156	+1.3

(2,4,6-¹⁵NO₂)-TNT, as shown in Table I. Other mechanisms, including the total scrambling of hydrogen and deuterium, produce generally lower ratios of [C₅H₂D]⁺ to [C₅H₂D₂]⁺ and [C₅H₂D]⁺ to [C₅D₃]⁺ than is found experimentally. It is likely that other scrambling does occur in the [C₇H₂D₃]⁺ ion in addition to that which we have considered. However, the exact solution undoubtedly includes a major contribution from the proposed pathway.

Finally, there is the question of ring fragmentation in TNT. We have verified by metastable analysis a limited number of

ring degradation reactions where a ring carbon atom is involved. These are summarized in Figure 3.

Registry No. TNT, 118-96-7; α -d₃-TNT, 52886-05-2; (4-¹⁵NO₂)-TNT, 83858-97-3; (2,6-¹⁵NO₂)-TNT, 86456-41-9; (2,4,6-¹⁵NO₂)-TNT, 86456-42-0; α -d₃-(2,4,6-¹⁵NO₂)-TNT, 86456-43-1; 2,4-dinitrotoluene, 121-14-2; 4-nitrotoluene, 99-99-0; toluene, 108-88-3.

Literature Cited

- (1) Shackelford, S. A.; Beckmann, J. W.; Wilkes, J. S. *J. Org. Chem.* **1977**, *42*, 4201.
- (2) Beckmann, J. W.; Wilkes, J. S.; McGuire, R. R. *Thermochim. Acta* **1977**, *19*, 11.
- (3) Guldry, R. M.; Davis, L. P. *Thermochim. Acta* **1979**, *32*, 1.
- (4) Carper, W. R.; Davis, L. P.; Extine, M. W. *J. Phys. Chem.* **1982**, *86*, 459.
- (5) Dennis, W. H.; Rosenblatt, D. H.; Blucher, W. G.; Coon, C. L. *J. Chem. Eng. Data* **1975**, *20*, 202.
- (6) Bulusu, S.; Axenrod, T. *Org. Mass Spectrom.* **1979**, *14*, 585.
- (7) Myerson, S.; Puskas, I.; Fields, E. K. *J. Am. Chem. Soc.* **1966**, *88*, 4974.
- (8) Myerson, S.; Vanderhaar, R. W.; Fields, E. K. *J. Org. Chem.* **1972**, *37*, 4114.
- (9) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, CA, 1967.
- (10) Collin, J. *Bull. Soc. R. Sci. Liege* **1954**, *23*, 194.
- (11) Larkins, J. T.; Saalfeld, F. E.; Kaplan, L. *Org. Mass Spectrom.* **1969**, *2*, 213.
- (12) Rinehart, K. L.; Buchholz, A. C.; Van Lear, G. E.; Cantrill, H. L. *J. Am. Chem. Soc.* **1968**, *90*, 2983.
- (13) Rylander, P. N.; Myerson, S.; Grubb, H. M. *J. Am. Chem. Soc.* **1957**, *79*, 842.
- (14) Myerson, S. *J. Am. Chem. Soc.* **1963**, *85*, 3340.
- (15) Meyer, F.; Harrison, A. G. *J. Am. Chem. Soc.* **1964**, *86*, 4757.
- (16) Siegel, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5277.
- (17) Howe, I.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 99.

Received for review August 20, 1982. Revised manuscript received December 13, 1982. Accepted May 16, 1983. Financial support was provided W.R.C. by fellowships from AFOSR and the National Research Council. The high-resolution mass-spectral and MIKES measurements at the University of Nebraska were supported by the National Science Foundation Regional Instrumentation facilities program.

Preparation of 2-Amino-2,3-dihydrobenzimidazole and Its Derivatives

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New compounds, derivatives of 2-amino-2,3-dihydrobenzimidazole, were prepared by modified Gabriel reaction of 2-chloro-2,3-dihydrobenzimidazole with potassium phthalimide. Their mass spectra are presented.

The well-known methods of synthesis of 2,3-dihydrobenzimidazole derivatives are the reactions of aldehydes or ketones with *o*-phenylenediamine. The products of the reactions are often a mixture of compounds that are difficult to separate (1-3). Recent publications describe the synthesis of derivatives of 2-thioxo-2,3-dihydrobenzimidazole in the reaction of *o*-phenylene diisocyanate with amines (4), and of derivatives of 2-oxo-2,3-dihydrobenzimidazole which were obtained in the Curtius rearrangement (5).

2-Amino-2,3-dihydrobenzimidazole and its derivatives are new compounds.

In ref 6 was described a method of preparation of 2-chloro-2,3-dihydrobenzimidazole from chloroform and *o*-phenylenediamine.

Table I. Melting Points, NMR Data, and Yields of 2-Amino-2,3-dihydrobenzimidazole and Its Derivatives

compd	mp, °C	¹ H NMR δ	yield, %
1	210	7 (d, J = 11 Hz, 1 H, 2-H, CH), 6.6 (NH), 6.8-7.4 (ArH)	94
5'	102	6.5 (d, J = 5 Hz, 1 H, 2-H, CH), 4.4 (NH), 6.2-6.8 (ArH)	23
2	166		90
3	sub 340		59
4	sub 320, romb cryst		95
5	136		11
5'''	98		98
6	211		8.7

The methods of preparation of 2-amino-2,3-dihydrobenzimidazole and its derivatives are presented in Scheme I. Melting points, NMR data, and yields of these compounds are presented in Table I.

Table II. Mass Spectra of 1, 5, and 5'

<i>m/e</i>	rel intensity		
	1	5	5'
254 ^a			0.04
119		0.02	
118	0.08	0.24	
109	7.65	7.68	7.35
108	100	100	100
107	21.54	9.26	9.43
91	4.2	1.2	1.15
90	1.16	0.03	
81	19.89	7.5	7.59
80	54.16	8.3	8.4

^a *m/e* 254, C₆H₄(NH)₂CHN⁺H₂CH(NH)₂C₆H₄.Table III. Mass Spectrum of 5'''^a

<i>m/e</i>	rel intensity	<i>m/e</i>	rel intensity
296	0.9	148	13.22
225	10.63	147	12.52
224	84.27	133	15.83
193	17.92	119	6.43
192	100	59	9.36
160	20.31	45	9.29

^a 15 eV.Table IV. Mass Spectrum of 3^a

<i>m/e</i>	rel intensity	<i>m/e</i>	rel intensity
237	1.83	132	12.13
220	2.42	108	2.58
163	10.19	105	3.61
162	100	104	29.01
133	1.88	32	12.13

^a 15 eV.Table V. Mass Spectrum of 6^a

<i>m/e</i>	rel intensity	<i>m/e</i>	rel intensity
268	22.53	167	10.78
228	16.23	136	14.41
221	24.96	135	69.13
220	100	119	3.4
192	5.8	93	69.47

^a 15 eV.

The new compounds gave satisfactory elemental analyses, mass spectra, and ¹H NMR data. The mass spectra of 1, 5, and 5' were similar (Table II). In these spectra ions appeared at *m/e* 118 (benzimidazole), 108 (*o*-phenylenediamine), 91 (C₆H₄NH), 80 (C₆H₄NH). The mass spectrum of 5' contained an M + 1 ion at *m/e* 254.

In Table III are presented the mass spectral data of 5''': *m/e* 296 (M⁺), 224 (*o*-C₆H₄(NH(CO)OCH₃)₂), 192 (*o*-C₆H₄NH((CO)OCH₃)NCO), 160 (*o*-C₆H₄(NCO)₂), 119 (*o*-C₆H₄(NH)₂CH), 59 (COCH₃). In Table IV are presented the mass spectral data of 3: *m/e* 162 (*o*-C₆H₄(NH₂)NHCHNCO), 132 (C₆H₄(CO)₂), 104 (C₆H₄CO), 108 (C₆H₄(NH₂)₂). In Table V are presented the mass spectral data of 6: *m/e* 268 (*o*-C₆H₄(NH)NCNHCSNHC₆H₅), 228 (C₆H₅NHCSNHC₆H₅), 220 (*o*-C₆H₄(NCS)NHCHNCS), 135 (C₆H₅-NCS), 119 (*o*-C₆H₄(NH)₂CH), 192 (*o*-C₆H₄(NCS)₂).

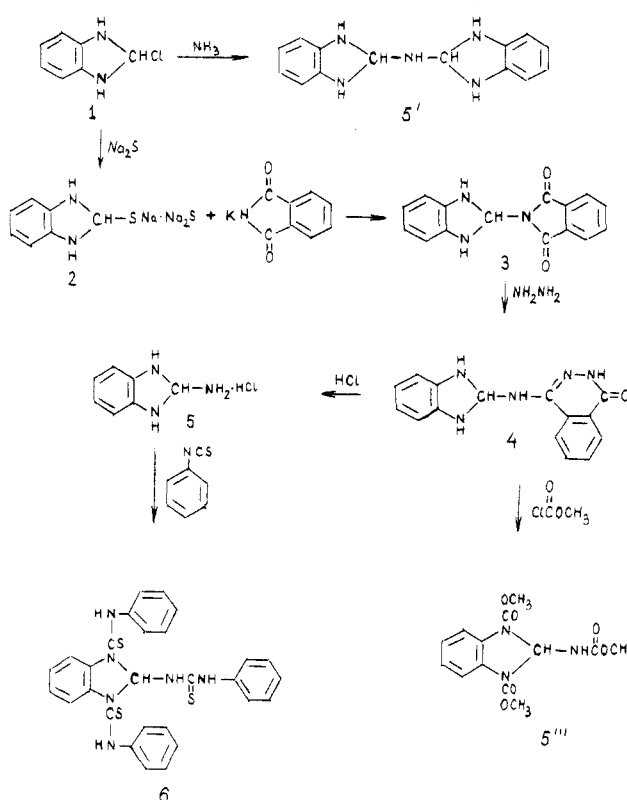
Experimental Section

Mass spectra were measured with a LKB-2091 instrument working at an ionizing electron energy of 15 and 70 eV. A direct insertion probe was used in either case. For some compounds two probe temperatures were used.

NMR spectra were recorded with a 60-MHz Tesla instrument in CD₃COCD₃ (Me₄Si standard).

Syntheses. **2-Chloro-2,3-dihydrobenzimidazole (1).** A 42.1-g sample of *o*-phenylenediamine, 0.65 g of cuprous

Scheme I



bromide, and 4 g of stannous chloride were dissolved in 900 cm³ of methanol; 0.936 mol of hydrogen chloride and 32.1 cm³ of chloroform were added and the reagents were heated at 60 °C for 0.5 h. The methanol was evaporated and 57.35 g of crude product was obtained. The product was purified by sublimation.

2,2'-Iminobis(2,3-dihydrobenzimidazole) (5'). A 28-g sample of 1 was boiled with concentrated hydrochloric acid with 2X mole excess. The reagents were evaporated to 1/3 volume, 100 cm³ of ethanol was added, and the crystalline product was filtered and treated with NH₃. A brown-violet precipitate was obtained (24.5 g). The product was purified by sublimation.

Sodium 2,3-Dihydrobenzimidazole-2-thiolate Disodium Sulfide (2). A 17.1-g sample of *o*-phenylenediamine dihydrochloride and 10.4 g of *o*-phenylenediamine were mixed and 2.5 g of stannous chloride was added. All reagents were dissolved in 500 cm³ of methanol, 30 cm³ of chloroform was added, and the reagents were heated at 60 °C for 4 h. The methanol was evaporated and the dry residue was dissolved in 150 cm³ of water; at 90 °C disodium sulfide was added. At this temperature stannous sulfide was filtered, and the filtrate was cooled, yielding a crystalline silver-violet product (26.65 g).

2-Phthalimidyldi-2,3-dihydrobenzimidazole (3). A 26.65-g sample of 2 and 48.0 g of potassium phthalimide were mixed and melted at 160 °C for 1 h. After being cooled, the product was ground in a porcelain mortar and washed with warm water; 26.9 g of product was obtained.

4-(2,3-Dihydrobenzimidazol-2-yl-amino)-1-oxo-1,2-dihydrophthalazine (4). A 26.9-g sample of 3 was dissolved in 500 cm³ of methanol and 29 cm³ of 80% aqueous hydrazine was added. The reagents were stirred at 60 °C for 1.5 h. After the solution was cooled, a pink precipitate was obtained.

2-Amino-2,3-dihydrobenzimidazole Hydrochloride (5). A 16.9-g sample of 4 was treated with 10 cm³ of concentrated hydrochloric acid and 100 cm³ of water. The reagents were boiled for 10 min. The blue precipitate was filtered. The filtrate was neutralized with KOH and a pink-red precipitate was filtered. The filtrate was concentrated to 50 cm³, cooled, and

extracted with a mixture of ether-benzene. The extract was evaporated and a red residue was crystallized; 1.1 g of product was obtained.

Dimethyl 2-[(Methoxycarbonyl)amino]-2,3-dihydrobenzimidazole-1,3-dicarboxylate (5'''). A 5-g sample of 4 was added to 50 cm³ of methyl chloroformate. The reagents were boiled at 69 °C for 5 h. A brown precipitate was filtered, the methyl chloroformate was evaporated, and 5.4 g of a dry residue was obtained.

2-[(Phenylthiocarbamoyl)amino]-2,3-dihydrobenzimidazole-1,3-dicarbothioamide (6). A 8.35-g sample of 1 and 15 g of potassium phthalimide were mixed in a porcelain mortar. The reagents were heated at 200 °C for 2 h. The product was cooled and dissolved in 100 cm³ of methanol, and 10 cm³ of 80% aqueous hydrazine was added. The reagents were stirred under reflux for 3 h. The precipitate was filtered and the filtrate was neutralized with KOH. The filtrate was extracted with a mixture of ether-benzene and reextracted with water. The water solution was treated with 10 g of phenyl

thioisocyanate and heated and intensively stirred. After 2 h a few drops of emulsion were transferred into green solid product.

Registry No. 1, 85354-90-1; 2, 85355-01-7; 3, 85354-91-2; 4, 85354-92-3; 5, 85354-93-4; 5', 86834-46-0; 5''', 85354-94-5; 6, 85354-95-6; NH₃, 7664-41-7; *o*-phenylenediamine, 95-54-5; chloroform, 67-66-3; *o*-phenylenediamine dihydrochloride, 615-28-1; potassium phthalimide, 1074-82-4; hydrazine, 302-01-2; methyl chloroformate, 79-22-1; phenyl isothiocyanate, 103-72-0.

Literature Cited

- (1) Nemeth, S.; Simaudi, L. *J. Mol. Catal.* **1982**, *14*, 87.
- (2) Craig, I. C.; Ekwuribe Nuochiri, N.; Fu Cherug, C.; Walker, K. A. M. *Synthesis* **1981**, *4*, 303.
- (3) Smith, D. M. *Chem. Heterocycl. Compd.* **1981**, *40*, 331.
- (4) Griffith, D.; Hull, R.; Seden, T. P. *J. Chem. Soc., Perkin Trans. 1* **1980**, *16*, 1240.
- (5) Faluny, A. F. M.; Ali Nawal, F.; Essawy, S. A. *Egypt. J. Chem.* **1977**, *20*, 1.
- (6) Studnicki, M. *Ind. Eng. Chem. Prod. Res. Dev.*, in press.

Received for review February 28, 1983. Accepted June 1, 1983.

Reaction of 4,6-Diarylhexahydro-1,3,5-triazine-2-thiones with α -Haloketones. 3

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4,6-Diarylhexahydro-*s*-triazine-2-thiones reacted with α -haloketones to give the *S*-substituted derivatives, which were cyclized to substituted thiazolo[3,2-*a*]-*s*-triazines. 7-(3-Aryl-2-propenoyl)-6-methyl-2,4-diphenyl-2,3,4-trihydro-thiazolo[3,2-*a*]-*s*-triazines were prepared and their behavior toward amine derivatives and benzamidine was investigated.

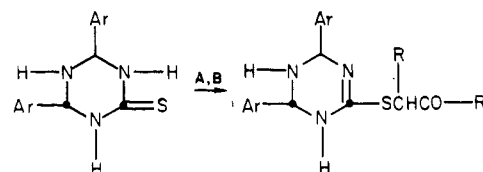
In continuation of my previous work on the reaction of triazinethiones (1, 2), I report here on the reaction of triazine-thiones with α -haloketones.

Experimental Section

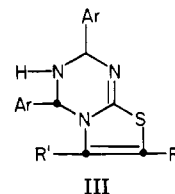
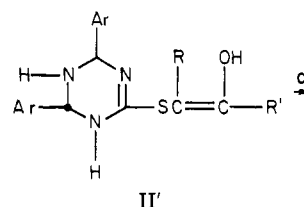
Satisfactory elemental analyses were found.

4,6-Diaryl-3,4,5,6-tetrahydro-2-(phenacylthio)-1,3,5-triazines (IIa,b,d,e,g,h). A solution of about 1 g of Ia-c in 25 mL of ethanol, to which 3 mL of 10% sodium hydroxide solution had been added, was treated with an equimolecular quantity of the phenacyl bromide, refluxed for 2 h, and left overnight. The precipitate was collected and crystallized (see Table I).

4,6-Diaryl-3,4,5,6-tetrahydro-2-(2,4-dioxopent-3-ylthio)-1,3,5-triazines (IIc,f,i). A mixture of 0.1 mol of I in 200 mL of ethanol and 5.6 g (0.1 mol) of 85% potassium hydroxide was heated at 70–80 °C for 10 min. After the resulting solution was cooled to 30 °C, 13.45 g (0.1 mol) of α -chloroacetylacetone was added in one portion. An exothermic reaction set in causing a temperature rise from 30 to 40 °C. The reaction mixture was stirred at room temperature for 18 h and added to 200 g of ice water. The precipitates which formed by stirring were collected by filtration, washed with water, and crystallized (see Table I). The IR spectrum of IIc shows an absorption band at 1705 cm⁻¹ (CO) and a broad band at 3100 cm⁻¹ (NH and OH) while the IR spectrum of IIa shows only a broad band at 3050 cm⁻¹ (NH and OH). Compounds II



Ia, Ar = C₆H₅
b, Ar = C₆H₄OCH₃-*p*
c, Ar = C₆H₄Cl-*p*



II, IIIa, Ar = C₆H₅; R = H; R' = C₆H₅
b, Ar = C₆H₅; R = H; R' = C₆H₄CH₃-*p*
c, Ar = C₆H₅; R = COCH₃; R' = CH₃
d, Ar = C₆H₄OCH₃-*p*; R = H; R' = C₆H₅
e, Ar = C₆H₄OCH₃-*p*; R = H; R' = C₆H₄CH₃-*p*
f, Ar = C₆H₄OCH₃-*p*; R = COCH₃; R' = CH₃
g, Ar = C₆H₄Cl-*p*; R = H; R' = C₆H₅
h, Ar = C₆H₄Cl-*p*; R = H; R' = C₆H₄CH₃-*p*
i, Ar = C₆H₄Cl-*p*; R = COCH₃; R' = CH₃

A = phenacyl bromides

B = α -chloroacetylacetone

C = polyphosphoric acid

give a deep color with ferric chloride solution. Compounds II exist in the enolic form II'.