

Chemical Propulsion Department, Laboratories Division
Aerospace Corporation

The Thermal Decomposition of 3-Azido-4-benzylideneamino-*s*-triazoles

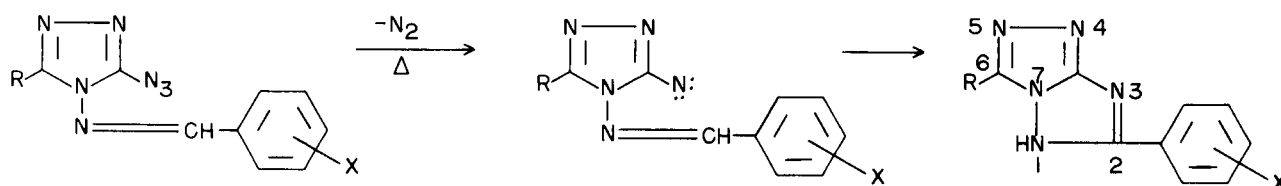
H. H. Takimoto, G. C. Denault and S. Hotta

The synthesis and thermal decomposition of a series of 3-azido-4-benzylideneamino-*s*-triazoles are described. The decompositions resulted in a loss of nitrogen and intramolecular cyclization at the carbon atom of the azomethine linkage to produce 1*H*-2-aryl-*s*-triazolo-[3,2-*c*]-*s*-triazoles.

The thermal decompositions of aryl azides containing α,β -unsaturated substituents at the *ortho* position are known to result in a cyclization (1). In particular, cyclization at the azomethine linkage of univalent, unchanged nitrogen species formed during azide decomposition have been reported. For example, pyrolysis of 2-azidobenzylidenamines (2) resulted in the formation of indazole derivatives, whereas benzylidene-2-azidoanilines (3,4) yielded 2-substituted benzimidazoles. The cyclizations appear to proceed with facility at either the carbon or the nitrogen atom of the azomethine linkage, over those of six members where a choice is available. Similarly the thermolysis of 3-azido-4-benzylideneamino-5-methyl-*s*-triazole has been reported (5) to yield the corresponding triazolo-triazole. The present report is an extension of the above work involving the thermal decompositions of a series of 3-triazolyl azides with a benzylideneamino group on the 4-position to determine the utility of this reaction for the preparation of 6-substituted 2-aryl-*s*-triazolo-[3,2-*c*]-*s*-triazoles.

The synthesis of the 3-azido-4-benzylideneamino-*s*-triazoles was accomplished by the treatment of 5-substituted 4-amino-3-hydrazino-*s*-triazole hydrochlorides with nitrous acid, followed by condensation with substituted benzaldehydes. The 4-amino-3-azido-*s*-triazoles were not isolated during the synthesis except in the case of the phenyl triazole system. In Table I are listed the 3-azido-4-benzylideneamino-*s*-triazoles. These azides in general appear to be sensitive to heat and darken on prolonged standing. When placed on a block pre-heated to approximately 25° above its melting point, each azide undergoes explosive decomposition.

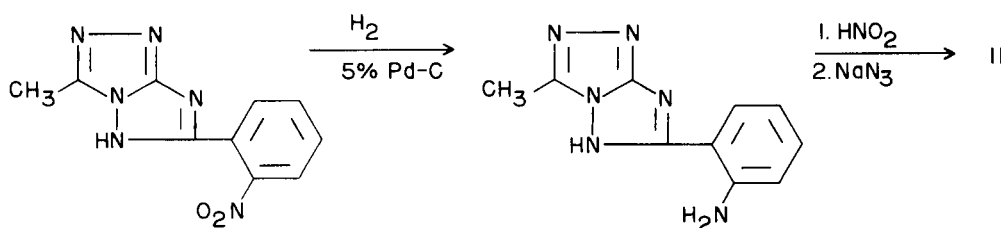
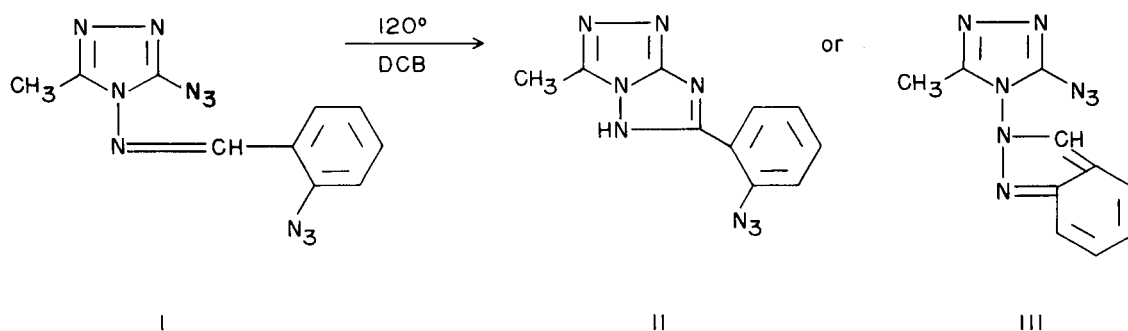
The thermal decomposition of each 3-azido-4-benzylideneamino-*s*-triazole was carried out in chlorobenzene or 1,2-dichlorobenzene at a temperature where a smooth liberation of nitrogen was observed. The results are summarized in Table II. Cyclizations occurred at the carbon atom of the azomethine linkage to yield 6-substituted 2-aryl-*s*-triazolo-[3,2-*c*]-*s*-triazoles. Although the hydrogen



is shown on N-1 in the above equation, other tautomeric forms such as N-3 or C-6 are also possible. In the case of the thermolyses of 5-methyl, 5-ethyl, or 5-phenyl-3-azido-*s*-triazoles, excellent yields of 6-substituted 2-aryl-*s*-triazolo-[3,2-*c*]-*s*-triazoles were obtained, whereas the replacement of the methyl (ethyl or phenyl) with hydrogen in the starting triazolyl azides resulted in a marked decrease in the yields of the decomposition products. Furthermore, the presence of a substituent on the triazole ring stabilizes the electron-deficient nitrogen intermediate so that the evolution of nitrogen is effected at a lower temperature (*ca.* 15°). Thus, not only is the stability of the 3-triazolyl azide increased in the absence of a substituent, but also considerable influence is exerted on the cyclization reaction of the nitrene occurring at the azomethine linkage. Steric factors (7) appear to play a dominant role since conformations of the starting azides favoring cyclizations at the double bond are preferred when a bulky substituent is present on the 5-position. On the other hand, electronic factors exert a lesser effect since the site of cyclization is sufficiently removed from the ring. The substituent on the benzylidene group, in agreement with earlier reports (2,3,4), appears to have relatively little effect on the ease of decomposition of the azide with the exception of one *p*-nitro derivative which required higher temperature.

In order to ascertain the relative stability of an azido group attached to a triazole *vs.* that appended on a phenyl ring, 3-azido-4-(2-azidobenzylidene-amino)-5-methyl-*s*-triazole, (I), was prepared by the condensation of the triazolyl azide with 2-azidobenzaldehyde. Heating this diazide (I) in chlorobenzene at 120° resulted in a loss of one mole of nitrogen to yield a mono-azide. This product may be either 1*H*-6-methyl-2-(2-azidophenyl)-*s*-triazolo-[3,2-*c*]-*s*-triazole (II) formed by the decomposition of the azido group attached to the triazole or 3-azido-4-(2-indazolyl)-5-methyl-*s*-triazole (III) resulting from the thermolysis of the azidobenzylidene group. Compound II was prepared by the reduction of 1*H*-6-methyl-2-(2-nitrophenyl)-*s*-triazolo-[3,2-*c*]-*s*-triazole (see Table II, No. 6) followed by the conversion of the resulting amine to the azide. This azide was identical to the product obtained from the partial decomposition of the diazide (I). These results indicate that the triazolyl azide decomposed completely under conditions where the 2-azidobenzylidene group remained unchanged. Although II decomposed further upon heating at 140° with the liberation of nitrogen, attempts to isolate a crystalline product from the reaction mixture were unsuccessful.

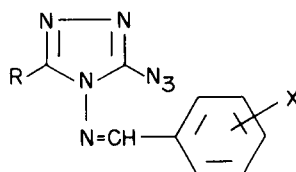
In Table III are listed the ultraviolet data for *s*-triazolo-[3,2-*c*]-*s*-triazoles in ethanol. The similarity of the results obtained here for 2-aryl-*s*-



triazolo-[3,2-*c*]-*s*-triazoles to those reported for 3-aryl-*s*-triazoles (8) indicates the lack of electronic interaction between the two fused triazole rings. In the case of the decomposition products of 3-azido-5-phenyl-*s*-triazoles (the last two compounds in Table III), the ultraviolet spectrum exhibits the resultant effects of the two triazole rings each substituted with an aryl group.

In contrast to the cyclization of triazolyl azides possessing a benzylideneamino group at the 4-position, 4-amino-3-azido-*s*-triazoles undergo an intramolecular rearrangement during decomposition to yield 3-amino-*s*-tetrazines (9). Thus, the course of the pyrolysis reaction is completely altered when a suitably situated substituent for cyclization is lacking. These results will be reported in a later communication.

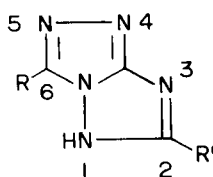
TABLE I

3-Azido-4-Benzylideneamino-*s*-Triazoles

No.	R	X	Yield %	M. P. °C dec. . .	Empirical Formula	Carbon %		Hydrogen %		Nitrogen %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
1	CH ₃	H	47	113-116	C ₁₀ H ₉ N ₇	52.85	52.80	4.00	4.18	43.16	43.14
2	CH ₃	<i>p</i> -CH ₃	48	130-131	C ₁₁ H ₁₁ N ₇	54.76	54.58	4.59	4.65	40.65	40.29
3	CH ₃	<i>p</i> -CH ₃ O	66	122-123	C ₁₁ H ₁₁ N ₇ O	51.35	51.59	4.31	4.36	38.11	37.89
4	CH ₃	<i>p</i> -Cl	62	134-136	C ₁₀ H ₈ N ₇ Cl	45.90	45.72	3.08	3.50	37.47	37.52
5	CH ₃	<i>p</i> -NO ₂	81	152	C ₁₀ H ₈ N ₈ O ₂	44.11	43.99	2.96	3.26	41.17	40.95
6	CH ₃	<i>o</i> -NO ₂	79	140-141	C ₁₀ H ₈ N ₈ O ₂	44.11	44.19	2.96	3.17	41.17	41.08
7	CH ₃	<i>o</i> -N ₃	80	153	C ₁₀ H ₈ N ₁₀	44.77	44.85	3.01	3.54	52.22	52.21
8	H	H	70	149-152	C ₉ H ₇ N ₇	50.70	50.48	3.31	3.45	46.00	46.13
9	H	<i>p</i> -CH ₃	76	158-161	C ₁₀ H ₉ N ₇	52.85	52.63	4.00	4.19	43.16	43.00
10	H	<i>p</i> -CH ₃ O	50	156-157	C ₁₀ H ₉ N ₇ O	49.37	49.26	3.73	3.82	40.31	40.37
11	H	<i>p</i> -Cl	81	159	C ₉ H ₆ N ₇ Cl	43.64	43.73	2.44	2.65	39.60	39.36
12	H	<i>p</i> -NO ₂	90	168-171	C ₉ H ₆ N ₈ O ₂	41.86	42.04	2.34	2.52	43.40	43.20
13	C ₂ H ₅	H	96	68.5-70	C ₁₁ H ₁₁ N ₇	54.76	54.49	4.59	4.70	40.65	40.50
14	C ₂ H ₅	<i>p</i> -CH ₃	97	95-96	C ₁₂ H ₁₃ N ₇	56.46	56.52	5.13	5.24	38.41	38.40
15	C ₂ H ₅	<i>p</i> -CH ₃ O	82	107-108	C ₁₂ H ₁₃ N ₇ O	53.12	52.81	4.84	4.88	36.14	36.23
16	C ₂ H ₅	<i>p</i> -NO ₂	87	160-161	C ₁₁ H ₁₀ N ₈ O ₂	46.15	46.06	3.53	3.68	39.14	39.33
17	C ₆ H ₅	H	95	142	C ₁₅ H ₁₁ N ₇	62.27	62.23	3.83	3.90	33.89	33.67
18	C ₆ H ₅	<i>p</i> -NO ₂	90	168	C ₁₅ H ₁₀ N ₈ O ₂	53.89	54.05	3.02	3.17	33.52	33.44

TABLE II

Decomposition of 3-Azido-4-Benzylideneamino-s-Triazoles

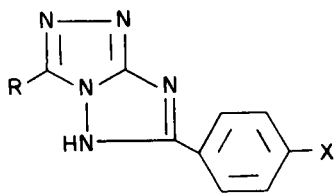


No.	1 <i>H</i> -s-Triazolo- [3,2-c]-s-triazole	Yield %	M. P. °C	Empirical Formula	Carbon %		Carbon %		Nitrogen %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
1	2-phenyl-6-methyl (a)	89.6	226-228 (d)	C ₁₀ H ₉ N ₅	60.29	60.57	4.56	4.63	35.16	35.29
2	2-(4-tolyl)-6-methyl (a)	91.5	238-240	C ₁₁ H ₁₁ N ₅	61.95	61.72	5.20	5.15	32.84	32.88
3	2-(4-anisyl)-6- methyl (a)	95	237-238	C ₁₁ H ₁₁ N ₅ O	57.63	57.44	4.84	4.76	30.55	30.67
4	2-(4-chlorophenyl)- 6-methyl (a)	92	263-264	C ₁₀ H ₈ N ₅ Cl	51.40	51.53	3.45	3.68	29.97	29.75
5	2-(4-nitrophenyl)- 6-methyl (a)	94	335-340	C ₁₀ H ₈ N ₆ O ₂	49.18	49.18	3.30	3.40	34.42	34.23
6	2-(2-nitrophenyl)- 6-methyl (a)	96	188-189.5	C ₁₀ H ₈ N ₆ O ₂	49.18	49.42	3.30	3.43	34.42	34.49
7	2-(2-azidophenyl)- 6-methyl (a)	97	218	C ₁₀ H ₈ N ₈	50.00	50.15	3.36	3.38	46.65	46.78
8	2-phenyl (b)	35	216-218	C ₉ H ₇ N ₅	58.37	58.47	3.81	4.05	37.82	37.99
9	2-(4-tolyl) (b)	57	279-281	C ₁₀ H ₉ N ₅	60.29	60.09	4.56	4.61	35.16	35.21
10	2-(4-anisyl) (b)	36	271-273	C ₁₀ H ₉ N ₅ O	55.80	55.60	4.22	4.49	32.55	32.42
11	2-(4-chlorophenyl) (b)	35	308-311	C ₉ H ₈ N ₅ Cl	49.22	49.07	2.76	2.99	31.90	31.79
12	2-(4-nitrophenyl) (c)	40	340-345	C ₉ H ₈ N ₆ O ₂	46.96	46.77	2.63	2.76	36.51	36.65
13	2-phenyl-6-ethyl (a)	91	200-203	C ₁₁ H ₁₁ N ₅	61.95	61.71	5.20	5.10	32.84	32.62
14	2-(4-tolyl)-6-ethyl (a)	96	198-201	C ₁₂ H ₁₃ N ₅	63.42	63.69	5.77	5.76	30.81	30.52
15	2-(4-anisyl)-6-ethyl (a)	82.5	188-190	C ₁₂ H ₁₃ N ₅ O	59.25	59.20	5.38	5.26	28.79	28.85
16	2-(4-nitrophenyl)- 6-ethyl (a)	95	233-235	C ₁₁ H ₁₀ N ₆ O ₂	51.16	51.00	3.91	4.07	32.55	32.38
17	2-phenyl-6-phenyl (b)	95	262-263	C ₁₅ H ₁₁ N ₅	68.94	68.82	4.24	4.39	26.81	26.80
18	2-(4-nitrophenyl)- 6-phenyl (b)	96.5	315-319	C ₁₅ H ₁₀ N ₆ O ₂	58.81	58.93	3.29	3.45	27.44	27.25

(a) Decomposed in chlorobenzene at 120°. (b) Decomposed in 1,2-dichlorobenzene at 135°. (c) Decomposed in 1,2-dichlorobenzene at 170°. (d) Lit. (6), m.p. 228.5.

TABLE III

Ultraviolet Spectra (a)
of *s*-Triazolo-[3,2-*c*]-*s*-triazoles



R	X	λ max m μ	ϵ
CH ₃	H	248	22,300
CH ₃	CH ₃	253	24,600
CH ₃	CH ₃ O	264	25,400
CH ₃	Cl	257	27,000
CH ₃	NO ₂	300	16,700
H	H	249	22,100
H	CH ₃	253	24,700
H	CH ₃ O	263	25,100
H	Cl	256	26,800
H	NO ₂	298	16,700
C ₂ H ₅	H	248	22,000
C ₂ H ₅	CH ₃	253	24,500
C ₂ H ₅	CH ₃ O	265	25,100
C ₂ H ₅	NO ₂	298	16,800
C ₆ H ₅	H	255	27,600
C ₆ H ₅	NO ₂	300	27,100

(a) Solvent was ethanol.

EXPERIMENTAL

Tribenzoyl Derivative of 4-Amino-3-hydrazino-5-phenyl-*s*-triazole.

A mixture of 14 g. of triaminoguanidine hydrochloride, 70 ml. of benzoyl chloride and 100 ml. of pyridine was refluxed for a total of 18 hours. After approximately 0.5 hour of heating, a violent exothermic reaction was observed and the color of the reddish mixture turned dark amber. The volatile materials were removed under reduced pressure and the viscous residue was poured into 100 ml. of water and allowed to stand for 15 hours. The solidified product was separated and recrystallized from benzene to yield 38.3 g. (76%) of white solid, m.p. 235-237°.

Anal. Calcd. for C₂₃H₂₂N₆O₃: C, 69.31; H, 4.41; N, 16.72. Found: C, 69.06; H, 4.53; N, 16.90.

4-Amino-3-hydrazino-5-phenyl-*s*-triazole Hydrochloride.

A mixture of 30 g. of the tribenzoyl derivative of 4-aminohydrazino-5-phenyl-*s*-triazole was heated for 2 hours in 1000 ml. of 6*N* hydrochloric acid to produce a clear solution. Refluxing was continued for an additional 6 hours. The benzoic acid, which separated upon cooling to room temperature, was discarded and the filtrate evaporated to dryness yielding 13.0 g. (96%) of a beige solid, m.p. 190-195°.

An analytical sample (m.p. 211-212° dec.) was obtained by recrystallization from ethanol.

Anal. Calcd. for C₈H₁₁N₃Cl: C, 42.39; H, 4.89; N, 37.08. Found: C, 42.46; H, 5.09; N, 37.34.

All the triazolyl azides employed in this study were prepared by the treatment of 4-amino-3-hydrazino-*s*-triazole hydrochlorides (5, 10) with nitrous acid and their subsequent condensations with the appropriate benzaldehydes. The azides prepared in this manner are summarized in Table I. A typical example is given below.

3-Azido-5-ethyl-4-(4-methylbenzylideneamino)-*s*-triazole.

A solution of 1.75 g. of sodium nitrite in 10 ml. of water was added dropwise to a cold solution (0-5°) of 3.57 g. of 4-amino-3-

hydrazino-5-ethyl-*s*-triazole hydrochloride in 20 ml. of water and 10 ml. of 2*N* hydrochloric acid. The mixture was stirred in the cold for 25 minutes and then neutralized with 1.15 g. of sodium carbonate to yield a clear amber-colored solution. To this solution was added 3.0 g. of *p*-nitrobenzaldehyde and the mixture was stirred at room temperature for an additional 16 hours. The mixture was then filtered yielding 5.9 g. of crude material from which 5.0 g. (87%) of product was obtained. Recrystallizations from benzene-ethanol gave yellow needles, m.p. 160-161° dec.

In the case of the 5-phenyl-*s*-triazole system, 4-amino-3-azido-5-phenyl-*s*-triazole was isolated prior to treatment with the corresponding benzaldehyde derivatives.

Thermal decompositions of the azides were carried out in either chlorobenzene or 1,2-dichlorobenzene at a temperature where a smooth liberation of nitrogen was obtained. The results are summarized in Table II. Pyrolysis of 3-azido-4-(4-chlorobenzylideneamino)-5-methyl-*s*-triazole is described below as a representative example.

1*H*-2-(4-Chlorophenyl)-6-methyl-*s*-triazolo-[3,2-*c*]-*s*-triazole.

A solution of 1.31 g. of 3-azido-4-(4-chlorobenzylideneamino)-5-methyl-*s*-triazole in 150 ml. of chlorobenzene was heated for 3 hours at 120°. The yellow solution turned orange-red with liberation of nitrogen during this heating period. The reaction mixture was concentrated under reduced pressure and 1.08 g. (92% yield) of white solid (m.p. 255-260°), which separated, was collected. An analytical sample melting at 263-264° was obtained by recrystallizations from benzene containing a few drops of ethanol.

1*H*-2-(2-Aminophenyl)-6-methyl-*s*-triazolo-(3,2-*c*)-*s*-triazole.

A solution of 4.90 g. of 1*H*-6-methyl-2-(2-nitrophenyl)-*s*-triazolo-[3,2-*c*]-*s*-triazole in 200 ml. of ethanol was hydrogenated with 0.5 g. of 5% palladium on charcoal on a Paar shaker for 1.5 hours at 60 psi. The mixture was filtered and the solvent was removed at reduced pressure. The residue was purified by dissolving in tetrahydrofuran and reprecipitating by the addition of petroleum ether (b.p. 60-90°) to yield 4.0 g. (92%). Several recrystallizations resulted in an analytical sample melting at 215-218°.

Anal. Calcd. for C₁₀H₁₀N₆: C, 56.05; H, 4.71; N, 39.23. Found: C, 55.82; H, 4.68; N, 39.45.

1*H*-2-(2-Azidophenyl)-6-methyl-*s*-triazolo-[3,2-*c*]-*s*-triazole.

A solution of 0.35 g. of sodium nitrite in 5 ml. of water was added dropwise to 1.0 g. of 1*H*-2-(2-aminophenyl)-6-methyl-*s*-triazolo-[3,2-*c*]-*s*-triazole in 75 ml. of acetic acid and 25 ml. of concentrated hydrochloric acid. The mixture was kept at 0-5° using an ice-salt bath. After stirring in the cold for 15 minutes, 50 ml. of cold water was added followed by a solution of 2.0 g. of sodium azide in 10 ml. of water. The mixture was diluted further with 200 ml. of water after 0.5 hour. Attempted extraction with ether caused copious solid to precipitate. This solid (0.73 g., 65% yield) was separated by filtration and recrystallized from *p*-dioxane as white needles. On a melting point block, it turned golden at about 200° and black at 220°. When placed on a block preheated to 250°, it exploded with a puff of smoke. The infrared spectrum of this product taken on a potassium bromide wafer exhibited an azido absorption band at 2130 cm⁻¹ and was identical to that obtained on a mono-azide resulting from the partial decomposition of 1*H*-3-azido-4-(2-azidobenzylideneamino)-5-methyl-*s*-triazole.

Acknowledgment.

The authors are indebted to Dr. L. Schieler for his helpful interest in this work.

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Received December 4, 1965

El Segundo, California 90245